THE SYNTHESIS AND STRUCTURE-ACTIVITY RELATIONSHIPS OF DIALKYL 2,6-DIMETHYL-3,5-DICARBOXYLATE-4-(3-NITRO-PHENYL)-1,4-DIHYDROPYRIDINES USING SINGLE CRYSTAL X-RAY DIFFRACTION AND MOLECULAR MODELING METHODS

By

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CHAPTER I

INTRODUCTION AND BACKGROUND

Scope of Thesis Study

Numerous structure-activity relationships (SAR's) for 1,4-dihydropyridine (DHP) derivatives are available in the literature. However, the influence of the alkoxy groups at the C3 and C5 ester positions on the conformation of the rest of the molecule and, thus, on the activity is still somewhat unclear. A further understanding of 1) the effect of increasing the length and bulk of the ester alkyl groups on the overall conformation of 1,4-DHP compounds and 2) the conformational changes associated with DHP decomposition to the nitro-pyridine form and the potential effects on the calcium antagonistic activity of these changes was the focus of this study. The nine new compounds prepared and the four prepared using literature preparations have C3 and C5 ester alkyl groups that range from a two carbon to an eight carbon chain (compounds V, VII, VIV, XIII, XVII, XVIV, and XX). In order to observe the conformational dependence upon increased bulk of these side chains; isopropyl, isobutyl, tertiary butyl, isopentyl, and benzyl groups were also included (compounds VIII, X, XII, XIV, and XXII). The decomposition products studied were those of nifedipine (I and II), dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (IV), 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (III), diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VI), di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XI), di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XV), di-neopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-

pyridine-3,5-dicarboxylate(XVI), dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XVIII), and nitrendipine(XXIII). To investigate the effect of inserting an oxygen in the side chain di-2-methoxyethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XXI) was synthesized. These compounds are tabulated in TABLE 4. Compounds V, VII, VIII, and XXI, which had been prepared previously, but had not been examined by single crystal studies.

Calcium in biological processes

Calcium is the most abundant metal ion in the body. Over 90% is in the form of hydroxyapatite, which occurs in the bones and teeth. The rest is in the form of the soluble calcium ion, Ca^{2+}[1]. This ion is involved in numerous functions in the cell acting as a intercellular messenger and also as a trigger for cell death.

Cells normally maintain a very low concentration of Ca^{2+} (~ 10^{-8} M), but this value can rise transiently during cell excitation. Calcium is involved in the regulation of excitation-contraction and stimulus-secretion coupling. The cellular mechanism that links surface membrane excitation with an increase in intracellular calcium, and thus with the initiation of contraction, is termed excitation-contraction coupling. In smooth, cardiac, and skeletal muscle cytoplasmic calcium ions regulate contractile protein activation and the generation of tension of the cell[1]. The sarcoplasmic reticulum (S. R.) is an intracellular organelle that acts as a reservoir for calcium ions within muscle cells. Following membrane excitation, calcium is released from the S.R. which activates the contractile proteins[2]. Ca^{2+} can thus be regarded as a cellular trigger which interacts with calcium-binding proteins such as troponin C and calmodulin[2]. This interaction, in turn, initiates the stimulus-response coupling of

the cell. A constant elevation of the calcium ion concentration within the cell may also serve as a lethal cell signal, the rise being caused by excessive cell stimulation, cell damage, or disease[3].

Events mediated by Ca^{2+} actions at extracellular sites, including blood clotting, cell adhesion, and membrane stabilization, are low affinity processes operating at the millimolar concentrations of Ca^{2+} found in the serum[3]. The intracellular Ca^{2+} mediated processes, such as the major categories of excitation-contraction and stimulus-secretion coupling, are high affinity processes occurring at the micromolar concentrations of ionized Ca^{2+} achieved in excitable cells[3].

Ion Channels

Cells normally maintain an asymmetric distribution of ions across the cell membrane, maintained by the selective permeability of the cell membrane itself and by the operation of metabolically driven pumps. Since the cell membrane is made up of a lipid bilayer, impermeable to ions, ion channels are used to transport ions from the intracellular space to the extracellular space (Figure 1). These channels are proteins that span the membrane and form aqueous pores through which ions can travel[4]. The movement of ions, subsequent to cell stimulation, serves to carry current and allows certain ions to act as cellular messengers[3]. The possible functions of a channel may be defined by the location on the cell, the voltage range over which a given type of channel opens, and the duration of that opening.

Ion channels are a regulated species and can be considered as allosteric enzymes. As part of the membrane, ion channels respond to chemical and electrical signals (hence regulation) and allow ion flow and membrane potential change. Ion channels are regulated by a variety of receptor initiated stimuli and

by various organic and inorganic ligands. They possess specific drug binding sites and are regulated by various drugs. They may also possess a multitude of ligand binding sites, for example, the voltage-gated Na^+ channel possesses at least five[5].

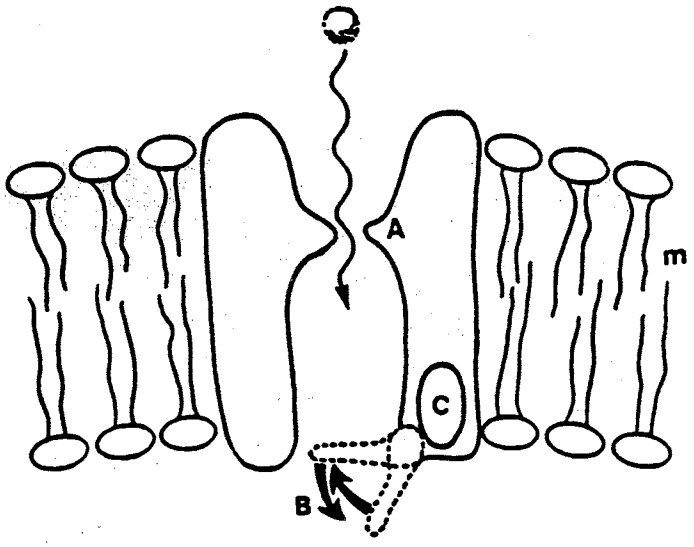


Figure 1: A generic ion channel, shown as a protein molecule that spans the lipid bilayer (m). (A) Selectivity filter determining which ions may pass; (B) Channel gate(s); (C) Sensor that determines the position of the gate.[4]

Ion channels can be classified according to many different criteria, such as ion selectivity, voltage sensitivity, and pharmacological sensitivities[3,5]. There are two basic classes of ion channels that are involved in the generation of electrical signals: ligand gated and voltage sensitive. Voltage sensitive channels mediate rapid, voltage-gated changes in membrane ion permeability during action potentials (the change of electrical conductance of the cell) in excitable cells and

also modulate membrane potential[6]. Ligand gated channels play a role more akin to a receptor. These ligand gated ion channels include the nicotinic acetylcholine receptor, γ-aminobutyric acid (GABA) receptor, and the glycine receptor. These channels also mediate local increases in ion conductance at chemical synapses[6].

Ion channels exist in different states of activation, which may alter their affinity for various ligands. Therefore, different points of view must be considered in the analysis of these channels as sites for drug regulation. For example, different states may have different affinities for certain drug molecules, certain ligands may stabilize different channel states, and the structure-activity relationships of a class of compounds may change depending upon which state of the channel with which they are interacting.

Ion channels also have certain gating characteristics. Normally there are three gating processes, a) activation, b) deactivation, and c) inactivation[4]. These gating characteristics dictate the availability of an ion channel to regulation by the binding of ligands.

Calcium Channels

The type, location, density and function of calcium channels varies with different kinds of cells[7]. The calcium channel is highly selective for calcium, as opposed to Na^+ or Mg^{2+}, which may arise from high affinity Ca^{2+} binding sites in the ion conducting pore[7].

The physiology of these channels include a wide variety of functions such as excitation-contraction coupling, control of secretion, excitability, conduction and pacemaker activity[8]. It has also been shown that three different modes of channel gating exist for the calcium channel[9].

Voltage-sensitive Ca^{2+} channels play many essential roles in the cell. They are an important part of all excitable cells in that they convert electrical

signals into biochemical events[10]. They constitute the link between transient changes in membrane potential and are involved in a variety of cellular responses such as secretion of neurotransmitters and hormones, initiation of contraction in cardiac and smooth muscle, and activation of second messenger responses in many types of cells[11]. In cardiac and smooth muscle, voltage-dependent calcium channels are important in controlling the supply of calcium that is directly or indirectly used in the contractile process[2,12].

Calcium channels are usually classified as receptor operated (ROC) or potential dependent channels (PDC). Receptor operated channels are far less well characterized than the potential dependent channels, and less is known about their function.

The potential dependent channels have been much more susceptible to pharmacologic and electrophysiological definition, thus, a variety of subclasses have emerged. At least 3 classes of voltage sensitive calcium channels that require a large amount of depolarization before they are activated (high-threshold), have been observed, and one class of the low-threshold type[3,8,13].

1) L channels ---- This type plays a key role in excitation-contraction coupling in smooth and cardiac muscle. They may also be involved in modulating membrane excitability and the release of some hormones and neurotransmitters. They are sensitive to the class of compounds known as the 1,4-dihydropyridines (DHP). The highest concentration of DHP sensitive L channels is in skeletal muscle, where they mediate slowly activated, long lasting Ca^{2+} currents. The evidence of the essential role of these channels in the heart is the observation that channel blockade with DHP's or phenylalkylamines results in decreased force of cardiac contraction and can result in total suppression of cardiac activity[2].

2) N channels ---- These are found mainly in neuronal cells and play a major role in neurotransmitter release[2]. They are DHP insensitive.

3) P channels ---- These are insensitive to DHP's, but sensitive to certain spider toxins[2].

4) T channels (transient) ---- These are low threshold, that is they are activated with small amounts of depolarization and inactivate rapidly[2]. They are most abundant in sinoatrial and purkinje cells, the pacemaker cells of the atria and ventricles, respectively, and are insensitive to DHP's.

Subtypes of the above channels also exist in different cell and tissue types.

The greatest advances in elucidation of the structure and composition of a calcium channel has been made for the L-type calcium channel of skeletal muscle[2]. This is a result of the abundance in skeletal muscle t-tubules of L-type calcium channels with high-affinity binding sites for the dihydropyridine class of compounds and of the availability of a variety of DHP ligands to which these channels are sensitive.

The primary amino acid (AA) sequence for the DHP receptor from rabbit skeletal and cardiac muscle has been deduced[7,14]. There is a 66% degree of AA sequence homology between the cardiac and the skeletal muscle DHP receptor (calcium channel). The skeletal muscle DHP receptor AA sequence is homologous to that of the sodium channel. The general similarity in biochemical properties of Na^+ channel subunits and Ca^{2+} channel subunits has its basis in this substantial similarity of AA sequence.

Sodium and calcium channels consist of a principal transmembrane subunit, which forms the ion-conducting pore (Figure 1)[15]. The subunits of K^+, Ca^{2+}, and Na^+ channels are members of an homologous gene family, therefore they are all formed from a similar encoded gene and hence show similar

structure. It is now generally believed that the Ca^{2+} channel of skeletal muscle is composed of several subunits, termed α1, α2, β, γ and δ[6]. The overall structure of Ca^{2+} channels consists of a single principal subunit expressed in association with a variable number of other polypeptides. Only the α1-subunit, which is the central component of the protein complex, binds calcium channel antagonist compounds (DHP's)[16]. Hofmann et al illustrated this by radiolabeling a DHP molecule, letting it bind to its receptor in the channel, and then isolating the portion that was labeled (Figure 2)[10].

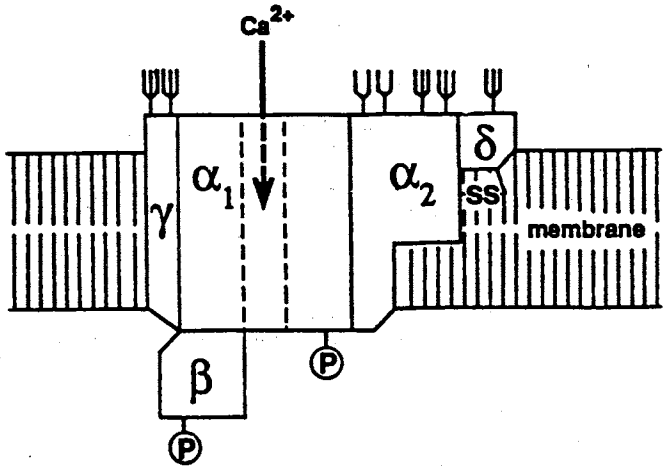


Figure 2: The Subunit Organization of the Calcium Channel.[15]

Since the α1-subunit is the observed receptor in these channels, its membrane organization is important. Different models have been proposed for the transmembrane organization of the α1-subunit[7,14,15]. Given the homology between the Na and Ca channels, there will obviously be a similarity in secondary structure.

The sodium channel consists of four homologous domains[14]. It has been proposed that each of these domains contains six regions of probable α-helical structure long enough to span the membrane, which are designated S1-S6. It

was suggested that S1 and S2, which are hydrophobic with occasional hydrophilic residues, and the S5 and S6 segments, which are uniformly hydrophobic, formed the transmembrane structure of the protein, whereas segments S3 which has more numerous charged residues, and S4, which are both hydrophobic and positively charged, project from the cytoplasmic surface of the protein [15,17](Figure 3). This initial description of the S4 segments as probable α-helices with both hydrophobic and positively charged characteristics led to specific models of the voltage dependent gating in which these segments had a transmembrane organization.

The substantial AA sequence similarity of the calcium channel to the sodium channel led to a proposal of an analogous transmembrane structure. The proposed model by Tanabe et al indicates the presence of four internal repeats that exhibit sequence homology as stated above[7]. Each of the four repeats consists of six membrane spanning α-helical sequences. The S4 regions of each repeat, which consists of alternating charged and uncharged residues, likely characterizes the voltage sensor region of the channel (Figure 3).

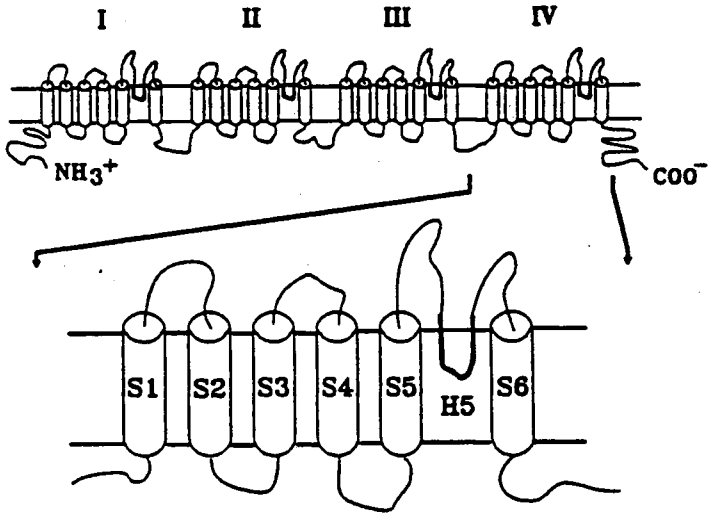
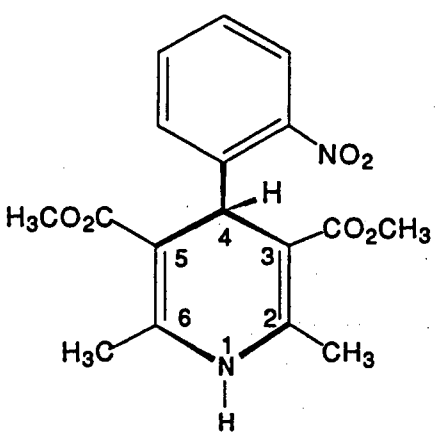
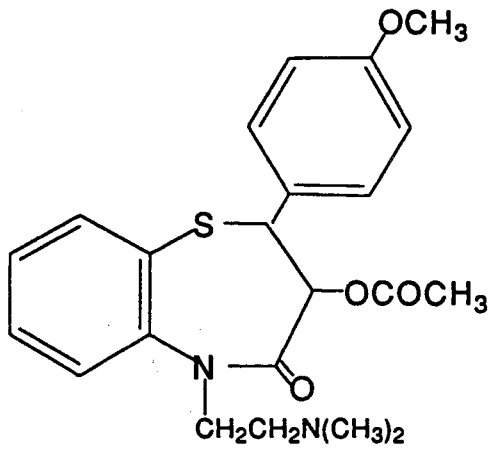


Figure 3: Schematic representation of the predicted structural organization of the voltage-dependent calcium channel α1-subunit.[18]

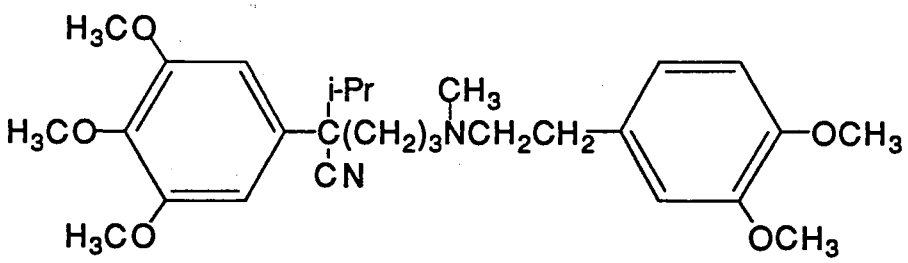
The pharmacology of calcium channels differs depending on where the channel is located and its function. The major ligand classes active in the L-type voltage-dependent Ca^{2+} channel, which has been the best characterized, are the phenylalkylamines (Verapamil), 1,4-Dihydropyridine's (Nifedipine), and the benzothiazepines (Diltiazem) (Figure 4). There is substantial evidence that these three classes define three allosterically linked sites on a component of the protein channel. However, the binding sites of these compounds are not specifically known.



Nifedipine



Diltiazem



Verapamil

Figure 4: General structure of the DHPs, Phenylalkylamines and Benzothiazepines.

Calcium Antagonists -- The 1,4-Dihydropyridines

A wide variety of chemical compounds exhibit calcium antagonistic properties. These range from simple metal ions to highly complex organic molecules[8,19].

Calcium channel antagonists inhibit the flow of calcium into the cell by blockage of certain membrane channels. Therefore, they mimic the effect of Ca^{2+} withdrawal on the heart and hence block contraction. These compounds produce a negative inotropic effect in heart muscle, a marked relaxation of smooth muscle, decreased vasoconstriction, and a decrease in cardiac arrhythmias. Calcium antagonists reduce the flow of calcium across the sarcolemma during the twitch of the heart muscle. Evidence implies that they do this by blocking calcium flow through slow calcium channels or by affecting the kinetics of the gating process[20]. These agents are clinically used for the treatment of angina, hypertension, peripheral vascular disorders, and some types of cardiac arrhythmias[8,21]. Calcium activators, or agonists, display the opposite effect. They promote the transport of Ca^{2+} through the calcium channels.

The 1,4-dihydropyridine (DHP) class of calcium antagonists has been very useful therapeutically, and also as a biochemical tool with which to analyze and probe the structure and function of the DHP sensitive type L calcium channel (Figure 5). This has been facilitated by the availability of large numbers of DHP derivatives (TABLE 1) and the existence of DHP compounds of similar structure possessing activator properties.

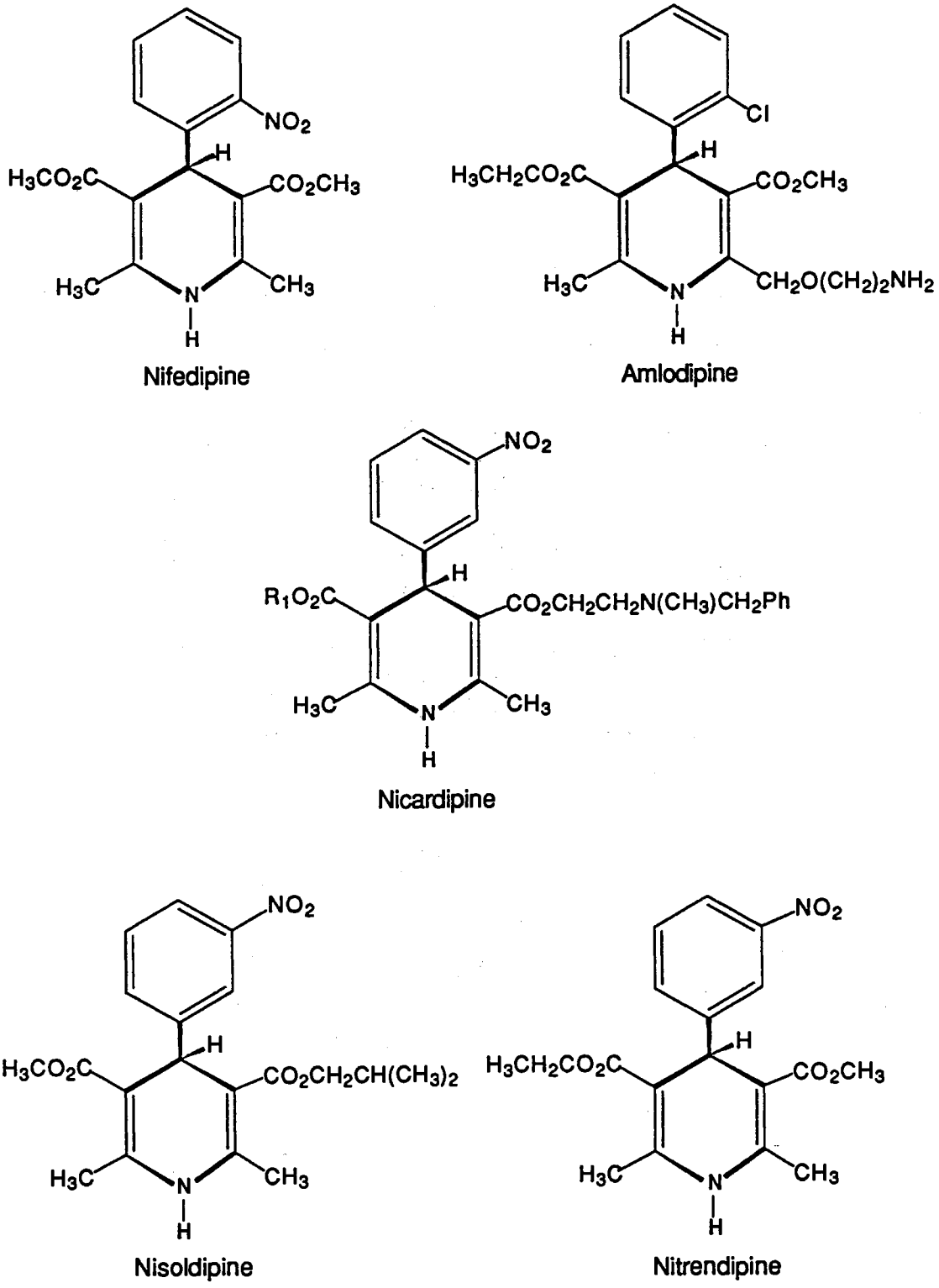
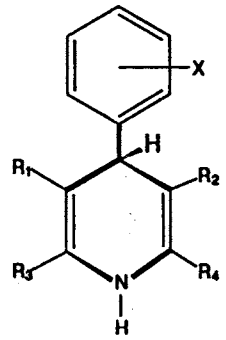


Figure 5: Structural Formula of Nifedipine Analogs.

TABLE 1
1,4-Dihydropyridine Derivatives



X	R1	R2	R3	R4	R5	Reference
2-Br	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29,37
3-Br	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29,79
4-Br	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
2-Cl	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
2-Cl	$CO_2C(CH_3)_3$	$CO_2C(CH_3)_3$	CH_3	CH_3	H	22
2,6-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
2-Cl	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,29,37,38,55
3-Cl	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,29,38
4-Cl	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,29,38
2-Cl	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2N(CH_3)_2$	H	39
2-Cl	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2N(CH_3)CH_2C_6H_5$	H	39
2-Cl	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2NHCH_3$	H	39

2-Cl	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2NH_2$	H	39
2-Cl	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_3N(CH_3)_2$	H	39
2-CF_3	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2N(CH_3)_2$	H	39
2-Cl, 6-F	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2NHCH_3$	H	39
3-Cl	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2NH_2$	H	39
2,3-Cl_2	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2NH_2$	H	39
4-Cl	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2NH_2$	H	39
2-Cl	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2N_3$	H	39
2,3-Cl_2	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2N_3$	H	39
2,3-Cl_2	$CO_2CH_2CH_3$	CO_2CH_3	CH_3	CH_3	H (Felodipine)	35,50
2,6-Cl_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
2,3-Cl_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
3,5-Cl_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
2,4-Cl_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
4-Cl	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NH_2$	H	35
2,4-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NH_2$	H	35
2,6-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NH_2$	H	35
3,4-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	CO_2CH_3	CO_2CH_3	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	CO_2CH_3	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH(CH_3)_2$	CO_2CH_3	CH_3	$CH_2OC(O)NH_2$	H	35

2,3-Cl_2	$CO_2CH(CH_3)_2$	CO_2CH_3	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH_2CH(CH_3)_2$	CO_2CH_3	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH(CH_3)_2$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH_2CH(CH_3)_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	CO_2CH_3	$CO_2CH_2CH_2CH_3$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	CO_2CH_3	$CO_2CH(CH_3)_2$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH(CH_3)_2$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH(CH_3)_2$	$CO_2CH(CH_3)_2$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH_2CH(CH_3)_2$	$CO_2CH(CH_3)_2$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	CO_2CH_3	$CO_2CH_2CH_2CH_2CH_3$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH(CH_3)_2$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH(CH_3)_2$	$CO_2CH_2CH(CH_3)_2$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO2CH_2CH(CH_3)_2$	$CO_2CH_2CH(CH_3)_2$	CH_3	$CH_2OC(O)NH_2$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NHCH_3$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NH\ (CH_2)_2CH_3$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)(CH_2)_3CH_3$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NHCH_2CH(CH_3)_2$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)NHC(CH_3)_3$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)N(CH_3)_2$	H	35

2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)N(CH_3)(CH_2)_3CH_3$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)N(CH_3)CH_2C_6H_5$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)N(CH_2CH_2CH_2CH_3)_2$	H	35
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	$CH_2OC(O)N(CH_2CH(CH_3)_2$	H	35
2,3-Cl_2	$CO_2CH(CH_3)_2$	CO_2CH_3	CH_3	CH_3	H	35
2,4-Cl_2	$C(O)N(CH_2CH_2)_2$	$C(O)N(CH_2CH_2)_2$	CH_3	CH_3	H	46
2-Cl, 4-OH	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
4-Cl, 5-H_2NSO_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
2,4-Cl_2, 5-H_2NSO_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
2-NO_2, 4-Cl	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	24
3-NO_2, 6-Cl	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	24
3-NO_2, 4Cl	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	24
3-NO_2, 6-Cl	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	24
3-NO_2, 6-Cl	$CO_2CH_2CH{=}CH_2$	$CO_2CH_2CH{=}CH_2$	CH_3	CH_3	H	24
2-F, 6-Cl	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29,38
2-Cl, 3-CF_3	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	NH_2	H	39
2-Cl, 5-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
2-CF_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	22,29,42,43,79,80
2-CF_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
2-CF_3	$CO_2C(CH_3)_3$	$CO_2C(CH_3)_3$	CH_3	CH_3	H	22
3-CF_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
4-CF_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22

2-CF_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	CH_3	22
2-CF_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	$CO_2CH_2CH_3$	22
2-CF_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	C_6H_5	22
2-CF_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	H	H	H	22
2-CF_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_2CH_3	CH_2CH_3	H	22
2-CF_3	$C(O)CH_3$	$C(O)CH_3$	CH_3	CH_3	H	22
2-CF_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	Aromatic	22
2-CF_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23
3-CF_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,29
2-CF_3	NO_2	CO_2CH_3	CH_3	CH_3	H	43,80,81
2-CF_3	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
3-CF_3	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
2-CN	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,29,38
3-CN	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	25,29,38
4-CN	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
3-CN	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
2-CO_2CH_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
4-CO_2H	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
2-$CH=CH_2$	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29,79
2-$CH=CHCO_2$-$C(CH_3)_3$	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	82
2-CH_2CH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
2-F	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29,37,38

2-F	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2N_3$	H	39
2-F	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2NH_2$	H	39
2,3,4,5,6-F_5	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	25,29,38,43,79
3-F	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29,38
4-F	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29,38
4-F	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
H	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2NH_2$	H	39
H	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2N_3$	H	39
H	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	29
H	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22,58
H	$CO_2C(CH_3)_3$	$CO_2C(CH_3)_3$	CH_3	CH_3	H	22
H	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	CH_3	22
H	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	$CO_2CH_2CH_3$	22
H	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	C_6H_5	22
H	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	H	H	H	22
H	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	H	22
H	CN	CN	CH_3	CH_3	H	22
H	$C(O)CH_3$	$C(O)CH_3$	CH_3	CH_3	H	22
H	C(O)NHPh	C(O)NHPh	CH_3	CH_3	H	22
H	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	Aromatic	22
H	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21,23,29,38
2-I	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29,37

3-I	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
4-I	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
2-CH_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
2-CH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,29
2-CH_3	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2NHCH_3$	H	39
2,5-$(CH_3)_2$	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
2,4, 6-$(CH_3)_3$	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
3-CH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21
3-CH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29,38
4-CH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,38
4-CH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21,29
2-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	22-24,83
2-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H Nifedipine	24,25,38,43,83
2-NO_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	24
2-NO_2	$CO_2CH(CH_3)_2$	$CO_2CH(CH_3)_2$	CH_3	CH_3	H	24
2-NO_2	$CO_2C(CH_3)_3$	$CO_2C(CH_3)_3$	CH_3	CH_3	H	24
2-NO_2	$CO_2CH_2CH_2OCH_3$	$CO_2CH_2CH_2OCH_3$	CH_3	CH_3	H	24
2-NO_2	$CO_2(CH_2)_2$-OCH_2CH_3	$CO_2(CH_2)_2$-OCH_2CH_3	CH_3	CH_3	H	24
2-NO_2	CH_2CH_2OH	CH_2CH_2OH	CH_3	CH_3	H	24
2-NO_2	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$	CH_3	CH_3	H	24
2-NO_2	CH_2CH CH	CH_2CH CH	CH_3	CH_3	H	24
2-NO_2, 4-OCH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	24

2-NO_2, 4-OCH_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	24
2-NO_2, 5-OCH_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	24
2-NO_2, 5-OH	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	24
2,4-$(NO_2)_2$	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21
2-NO_2	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H Nisoldipine	27,38
2-NO_2	CO_2CH_3	CO_2CH_2-2-Furyl	CH_3	CH_3	H Furnidipine	84
3-NO_2	$CO_2(CH_2)_2$ $N(CH_3)CH_2C_6H_5$	CO_2CH_3	CH_3	CH_3	H Nicardipine	35
3-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21,23,24,38,83
3-NO_2	$CO_2CH_2CH_2OCH_2CH_2CH_3$	$CO_2(CH_2)_2O(CH_2)_2CH_3$	CH_3	CH_3	H Niludipine	23,24,26
3-NO_2	$CO_2CH_2CH_3$	$CO_2CH(CH_3)_2$	CH_3	CH_3	H	23
3-NO_2	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	CH_3	H Nitrendipine	23,26,38,43,80
3-NO_2	$CO_2CH(CH_3)_2$	$CO_2CH_2CH_2OCH_3$	CH_3	CH_3	H Nimodipine	23,26,38,44
3-NO_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	24,26
3-NO_2	$CO_2CH(CH_3)_2$	$CO_2CH(CH_3)_2$	CH_3	CH_3	H	24,26
3-NO_2	$CO_2CH_2CH_2OCH_3$	$CO_2CH_2CH_2OCH_3$	CH_3	CH_3	H	24,26
3-NO_2	$CO_2(CH_2)_2OCH_2CH_3$	$CO_2(CH_2)_2OCH_2CH_3$	CH_3	CH_3	H	24,26
3-NO_2	CH_2-2-Pryidiyl	CH_2-2-Pryidiyl	CH_3	CH_3	H	24
3-NO_2	CH_2-2-Pryidiyl	CH_2-2-Pryidiyl	CH_3	CH_3	H	24
3-NO_2	$CH_2CH=CH_2$	$CH_2CH=CH_2$	CH_3	CH_3	H	24,26
3-NO_2, 4-OCH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	24
3-NO_2, 4-$N(CH_3)_2$	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	24
3-NO_2, 6-SCH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	24

3-NO_2, 4-OH	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	24
3-NO_2, 6-SO_3H	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	24
3-NO_2, 4-$N(CH_3)_2$	$CO_2CH_2CH_2OCH_3$	$CO_2CH_2CH_2OCH_3$	CH_3	CH_3	H	24
3-NO_2	$CO_2C(CH_3)_3$	CO_2CH_3	CH_3	CH_3	H	83
3-NO_2	$CO_2C(CH_3)_3$	CO_2CH_3	CH_3	CH_3	H	83
3-NO_2	$CO_2C(CH_3)_3$	CO_2CH_3	CH_3	CH_3	H	83
3-NO_2	$CO_2C(CH_3)_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	83
3-NO_2	$CO_2C(CH_3)_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	83
3-NO_2	$CO_2C(CH_3)_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	83
3-NO_2	CO_2CH_3	$CO_2CH(CH_3)_2$	CH_3	CH_3	H	26,38,51
3-NO_2	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	CH_2-O-(CH_2)2-NCH_3	H	39
3-NO_2	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
3-NO_2	$CO_2CH_2CH_2OCH_3$	$CO_2CH_2CH_2ONO_2$	CH_3	CH_3	H	47,56
3-NO_2	CO_2CH_3	$CO_2CH_2CH_2ONO_2$	CH_3	CH_3	H	56,85
3-NO_2	CO_2CH_3	$CO_2CH_2CH_2Br$	CH_3	CH_3	H	56
3-NO_2	CO_2CH_3	$CO_2CH_2CH_2NHCH_3$	CH_3	CH_3	H	67
3-NO_2	CO_2CH_3	$CO_2CH_2CH_2N(Bz)CH_3$	CH_3	CH_3	Aromatic	67
3-NO_2	$CO_2CH_2CH_2CH_3$	$CO_2CH_2CH_2CH_3$	CH_3	CH_3	H	26
3-NO_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_2CH_3$	CH_3	CH_3	H	26
3-NO_2	$CO_2CH_2CH(CH_3)_2$	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	26
3-NO_2	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	26
3-NO_2	$CO_2CH_2CH_3$	$CO_2CH_2CH=CH_2$	CH_3	CH_3	H	26

3-NO_2	$CO_2CH_2C(CH_3)_3$	$CO_2CH_2C(CH_3)_3$	CH_3	CH_3	H	41
3-NO_2	$CO_2(CH_2)_2OCH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	26
4-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,38
4-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	24
4-NO_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	24
4-NO_2	$CO_2CH(CH_3)_2$	$CO_2CH(CH_3)_2$	CH_3	CH_3	H	24
4-NO_2	$CO_2C(CH_3)_3$	$CO_2C(CH_3)_3$	CH_3	CH_3	H	24
4-NO_2	$CO_2(CH_2)_3OCH_3$	$CO_2(CH_2)_3OCH_3$	CH_3	CH_3	H	24
4-NO_2	$CO_2(CH_2)_3OH$	$CO_2(CH_2)_3OH$	CH_3	CH_3	H	24
4-NO_2	$CO_2(CH_2)_2CH=CH_2$	$CO_2(CH_2)_2CH=CH_2$	CH_3	CH_3	H	24
4-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21,29
2-OH, 5-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
4-$N(CH_3)_2$	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
3-N_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,38
3-$N(CH_3)_3^+$	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29,38
2-NH_2	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	CH_3	H	49
3-$N(CH_3)_2$	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
3-NH_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
4-$N(CH_3)_2$	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
3-N_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
3-NH_2	CO_2CH_3	$CO_2(CH_2)_2N(Bz)CH_3$	CH_3	CH_3	H	67
3-NH_2	CO_2CH_3	$CO_2(CH_2)_2NHCH_3$	CH_3	CH_3	H	67

3-NH_2	CO_2CH_3	$CO_2(CH_2)_2NHCH_3$	CH_3	CH_3	Aromatic	67
2-OCH_3	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
4-OH	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	22
2-OCH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,29,38
3-OCH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23,29,38
4-OCH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23
2-OCH_3	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	$CH_2O(CH_2)_2NHCH_3$	H	39
2-OCH_2CH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
3-OH	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
2,4,5-$(OCH_3)_3$	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	29
3-OCH_3	CO_2CH_3	$CO_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
2-SCH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	23

The structure activity relationships (SAR's) of the 1,4-DHP's have been the most studied, because of the ease of synthesis of this class of compounds and also because of the therapeutic interest in similar chemical structure with both antagonist and activator properties. Numerous structure-activity studies are available for the DHP antagonists, but few SAR studies have been performed on the DHP activators[21-36]. Calcium antagonistic activity of the 1,4-dihydropyridine family is influenced by a number of factors. The active conformation of these compounds normally includes the presence of the 1,4-dihydropyridine moiety with the DHP ring in a flattened boat configuration and the 4-phenyl substituent in a pseudoaxial conformation. Early SAR studies revealed some basic structural requirements for activity[22] . The activity of these compounds is defined as the compounds ability to block calcium entry into the cell.

i) Antagonist activity increases according to the C4 substituent on the DHP ring in the order: H < CH_3 < cycloalkyl < heterocyclic < phenyl and substituted phenyl.

ii) The position of the substituent on the 4-phenyl ring has an effect. Activity increases as the substituent is moved from *para* << *meta* < *ortho*. The presence of an electron withdrawing group in the ortho position is optimum.

iii) The DHP ring is essential, oxidation to pyridine greatly diminishes activity.

iv) The presence of an N1 hydrogen atom is essential, alkyl substitution at this position decreases activity.

v) Ester groups at C3 and C5 of the DHP ring are optimum, replacement by other electron withdrawing groups such as CN and $C(=O)CH_3$ reduces activity.

These original structural parameters have been largely confirmed in a variety of SAR studies using *in vitro* methods[8]. Subsequent SAR studies, summarized below, have led to further conclusions concerning the structural requirements of this class of compounds.

As stated previously, variation of the phenyl substituent led to the conclusion that ortho substituted derivatives are most active, meta being less active, and para being very inactive. The activity appears to be generally independent of the electronegativity of the phenyl substituent since those with electron withdrawing groups and electron-donating groups possess activity[22]. It has also been observed that the ortho NO_2 group present in the parent compound nifedipine is not essential and that an ortho CF_3 group is more effective[23].

The size of the phenyl substituent appears to have an influence[21,23]. In a series of halogen substituted *ortho*--phenyl derivatives, as the size of the halogen increased, activity also increased[37].

Analysis of a series of nisoldipine derivatives (Figure 5) led to the conclusion that the effects of the ester groups and the phenyl ring substituent are expressed independently[27]. Therefore, in all SAR studies performed, the rank order of activity for the phenyl ring substituents always is the same, o > m >> p, despite the changes in the ester R group[1].

Variation of the C3 and C5 ester substituents has led to conflicting evidence. In an early investigation, it was concluded that an increase in the bulk

of the ester side chain led to an increase in activity[22,38]. However, in a series of *meta*-nitro phenyl derivatives, activity appeared to decrease with an increase in the bulk of the ester side chains[23,35]. To complicate things further, another investigation reported that for *ortho* substituted phenyl derivatives, activity decreased as ester bulk increased; for *meta*-phenyl derivatives, activity increased as bulk increased; and for *para*-phenyl derivatives, activity was always observed to be low[24].

In all the above mentioned derivatives, the C3 and C5 ester groups were the same, therefore, they were symmetrical. However, when the ester groups are different from each other, the C4 carbon becomes chiral. It has been shown that unsymmetrically substituted derivatives tend to show higher activity[26] and stereoselectivity, one enantiomer being much more potent than the other[28,39,40]. Also, it appears that unsymmetrical derivatives tend to exhibit higher activity overall[28].

Although the C3, C5 ester substituents and the phenyl ring substitution have been frequently studied with respect to structure-activity relationships, the effects of the 2, 6 substitution pattern have not been ignored[1]. An amino substituent has been substituted in the 2-position[26] leading to maintenance of antihypertensive activity. Furthermore, it was shown that 2-dialkylamino-3,4-DHP's (hydrogens at C3 and C4 instead of N1 and C4) also exhibited antihypertensive activity comparable to that of the 2-amino derivatives. Therefore, it appears that the N1-H may not be as important as was originally thought.

From a series of 6-methyl 3-carbomethoxy-5-carboethoxy-4-(2-chlorophenyl)-1,4-DHP's containing 2-aminoalkoxy-methyl substituents, it was observed that the derivative bearing a 2-dimethylaminoethoxymethyl substituent (amlodipine) (Figure 5) possessed activity comparable to that of nifedipine, the

parent compound of the 1,4-DHP calcium antagonists[39]. Of considerable interest was the fact that the S-(--) - enantiomer of amlodipine was approximately 1000x more potent than the R-(+) enantiomer[40], suggesting an unsymmetrical binding site for the 2,6-substituents. These structural requirements are summarized in Figure 6.

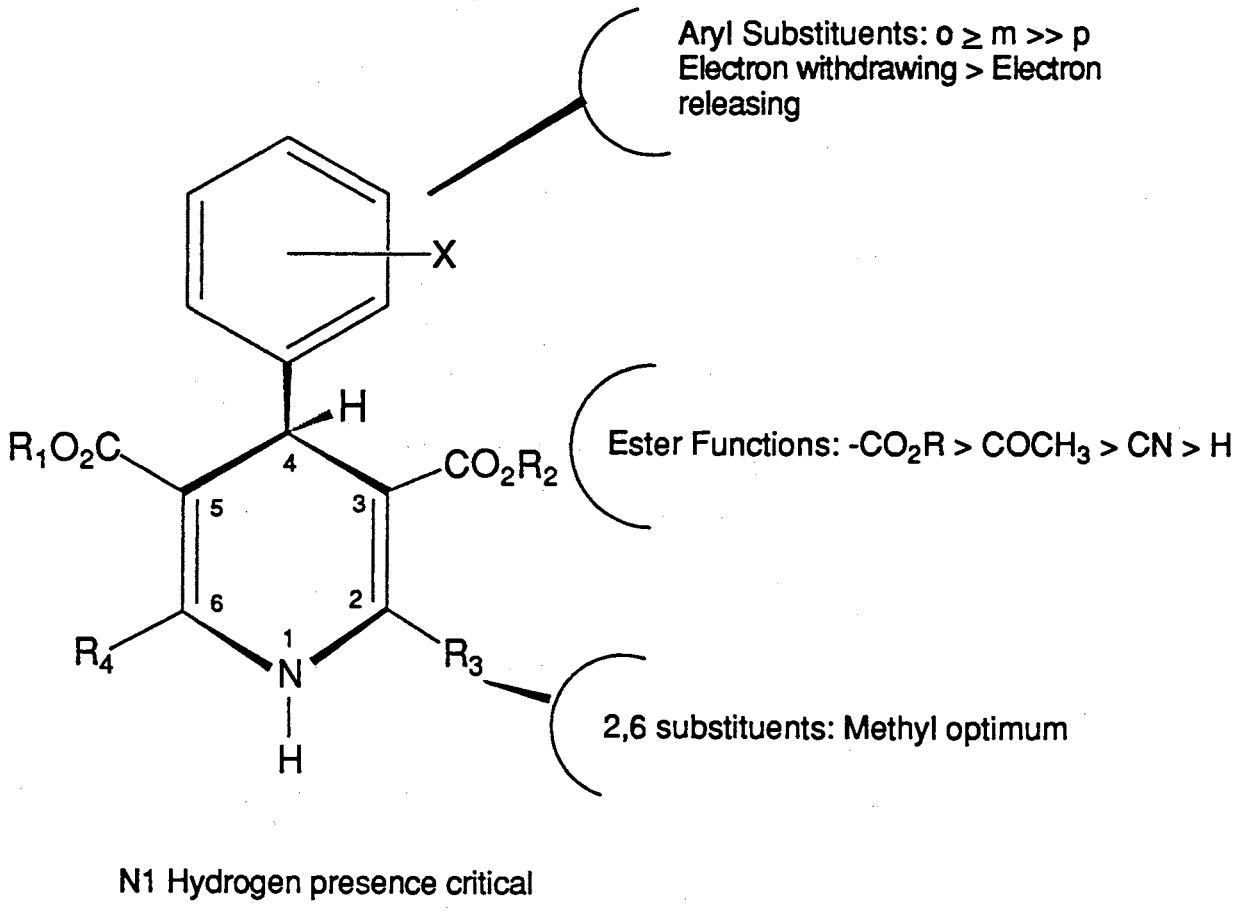


Figure 6: The General Structural Requirements of the 1,4-DHP's for Antagonistic Activity.

Conformational Requirements

The conformational requirements for calcium channel activity of the 1,4-DHP's have been studied by solid-state and solution studies, the synthesis of rigid and semi-rigid analogs, and using theoretical calculations[21,25,27,28,37,39-59]. Numerous DHP compounds have been studied in the solid-state by X-ray diffraction (TABLE 2). These diffraction studies show that the two rings of these compounds (phenyl and DHP) are not oriented coplanar with respect to each other. The 1,4-DHP ring exists as a boat-shaped structure with the C4 phenyl ring in a pseudoaxial position (Figure 7), oriented perpendicular to the plane of the base of the DHP boat.

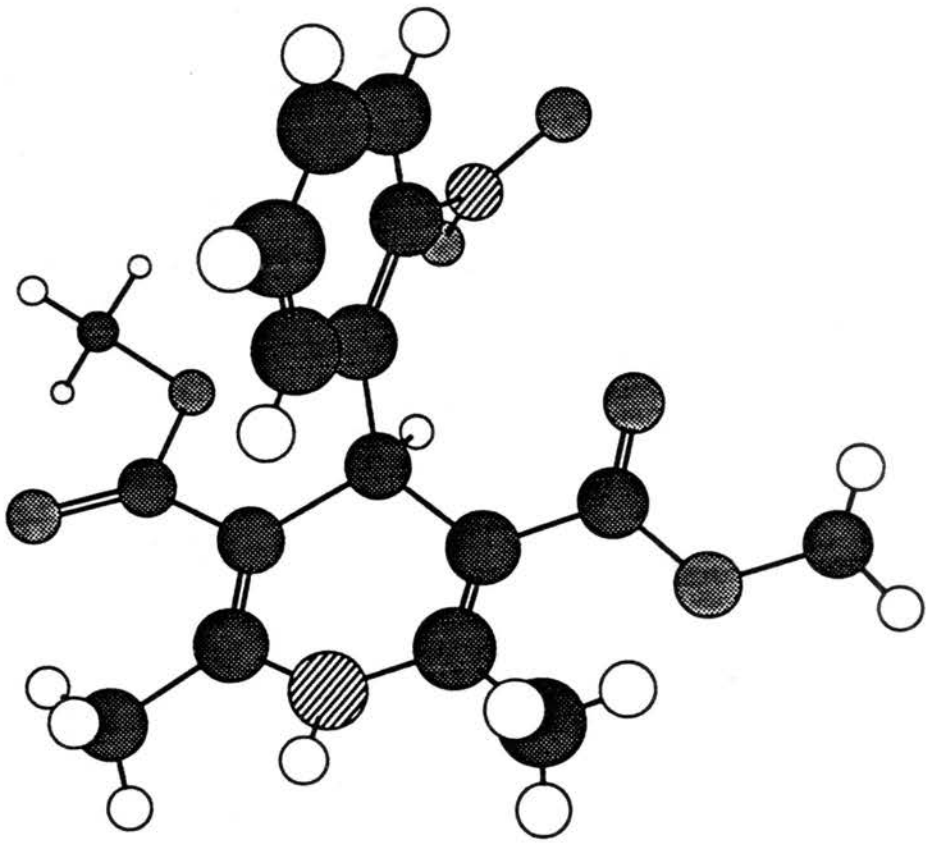
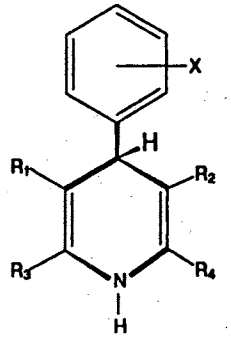


Figure 7: X-Ray Structure of Nifedipine Illustrating General Conformation

TABLE 2

1,4-Dihydropyridine Derivatives Studied by X-Ray Crystallography



X	R1	R2	R3	R4	R5	Reference
H	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	CH_3	CH_3	H	58
2-CF_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	42
2-Cl	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	55
H	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21
3-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21
3-NO_2	$CO_2CH(CH_3)_2$	$CO_2CH_2CH_2OCH_3$	CH_3	CH_3	H Nimodipine	28,44
2-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H Nifedipine	25
3-CH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21

4-CH_3	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21
4-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21
3-CN	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	25
2,4-$(NO_2)_2$	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	21
2,3,4,5,6-F_5	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	25
2-NO_2	CO_2CH_3	$CO_2CH_2CH_2CH(CH_3)_2$	CH_3	CH_3	H Nisoldipine	27
2-CF_3	NO_2	CO_2CH_3	CH_3	CH_3	H	43
3-NO_2	CO_2CH_3	$CO_2(C_5H_7N)$-$CH_2C_6H_5$	CH_3	CH_3	H	52
2-NH_2	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	CH_3	H	49
2,3-Cl_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_2CH(CH_3)_2$	CH_3	CH_3	H Felodipine	50
H	CO_2CH_3	$CO_2CH_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
3-NO_2	CO_2CH_3	$CO_2CH_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
3-CN	CO_2CH_3	$CO_2CH_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
3-OCH_3	CO_2CH_3	$CO_2CH_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
4-F	CO_2CH_3	$CO_2CH_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
2-CF_3	CO_2CH_3	$CO_2CH_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
2,4-Cl_2	$C(O)N(CH_2CH_3)_2$	$C(O)N(CH_2CH_3)_2$	CH_3	CH_3	H	46

3-NO_2	$CO_2CH_2CH_2OCH_3$	$CO_2CH_2CH_2ONO_2$	CH_3	CH_3	H	85
3-NO_2	CO_2CH_3	$CO_2CH_2CH_2ONO_2$	CH_3	CH_3	H	47
3-NO_2	CO_2CH_3	$CO_2CH_2CH_3$	CH_3	CH_3	H Nitrendipine	28
4-Cl	CO_2CH_3	$CO_2CH_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
3-CF_3	CO_2CH_3	$CO_2CH_2CH_2CH(CH_3)_2$	CH_3	CH_3	H	27
4-$N(CH_3)_2$	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	25
3-NO_2	$CO_2CH_2C(CH_3)_3$	$CO_2CH_2C(CH_3)_3$	CH_3	CH_3	H	41
3-NO_2	$CO_2CH(CH_3)_2$	CO_2CH_3	CN	CH_3	H Nilvadipine	51
2-Cl, 3-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	55
2-Cl, 4-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	55
2-Cl, 5-NO_2	CO_2CH_3	CO_2CH_3	CH_3	CH_3	H	55

In this conformation, rotation of the phenyl ring is sterically hindered and the ring is therefore forced to lie close to the vertical plane passing through N1 and C4 and perpendicular to the base of the DHP boat[3]. As the phenyl ring approaches a perfect orthogonal position, activity increases. Synthesis and testing of rigid analogs also support this theory[60].

The conformation of the ortho or meta substituents on the phenyl may be oriented in the *sp* (away from the DHP) or *ap* (toward the DHP) conformation (Figure 8). In the solid state, the *sp* conformation appears to be the preferred orientation, two exceptions being the 3-CN (*ap*) and the 2-Cl, which adopts both the *sp* and *ap* conformations[21,55]. Theoretical calculations support the favored stability of the *sp* conformation. Where some solution studies have indicated a bias toward the *sp* conformation, others indicate the opposite[3,55,61]. This would be consistent with the observation that meta,meta'-disubstituted phenyl derivatives are also potent antagonists[1,29]. Hence, the evidence seems to indicate a lack of bias towards the *sp* or *ap* conformation at the receptor site. However, Rovnyak et al suggest there is a preferred conformation because rigid analogs in which the phenyl substituent is held in the *sp* conformation have higher activities than those in which the phenyl substituent is held in the *ap* conformation[55].

The receptor apparently distinguishes between ortho, meta-disubstituted and ortho, meta'-disubstituted derivatives[55]. Hence, it is suggested that there is an asymmetric preference in the binding site for the phenyl substituents and is indicative of a preferred *sp* conformation for both substituents in the ortho, meta-disubstituted derivative (Figure 8).

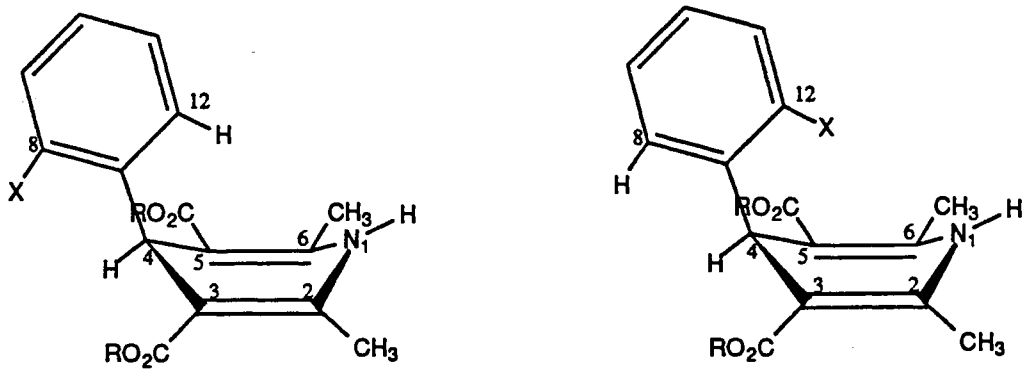


Figure 8: Illustration of the *s,p* and *a,p* Conformations of the Phenyl Substituents.

The DHP ring adopts a flattened boat conformation in all compounds studied thus far. It has been proposed that a direct correlation exists between the flatness of this ring and activity. Flatness is not a sufficient condition for activity, because many inactive compounds have very flat DHP rings. However, it may be the corresponding change in the position of the phenyl ring that alters the activity (Figure 9).

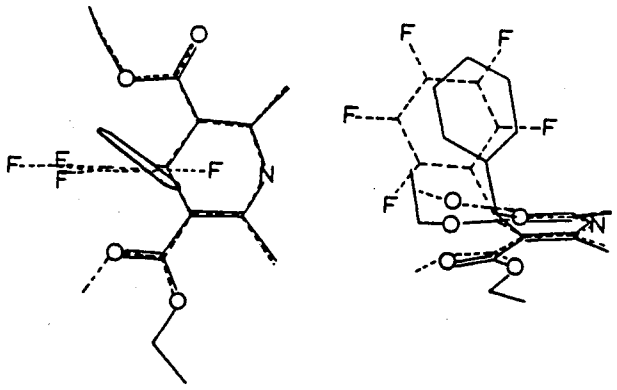


Figure 9: Illustration of the Change in Conformation of the Phenyl Ring as the DHP Ring Becomes Flatter in the Active Pentafluorophenyl Derivative.[3]

Compounds with different ester substituents appear to have the same degree of ring flattening. Hence, the identity of the ester substituent does not appear to affect this parameter.

The ester substituents can adopt one of three different conformations. sp, sp {cis, cis}, ap, ap {trans, trans}, or sp, ap {cis, trans} (Figure 10). The ester carbonyl groups are always found to be nearly coplanar with the nearest double bond in the DHP ring, with the carbonyl group oriented either cis {sp} or trans {ap} to the neighboring carbon carbon double bond of the DHP ring.

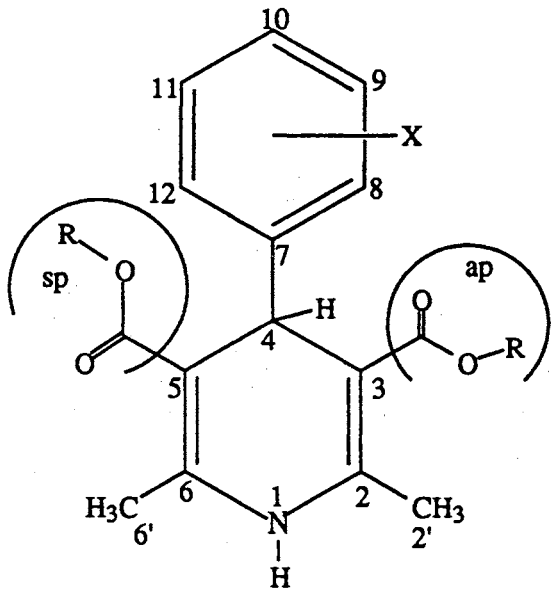


Figure 1

Figure 10: Illustration of the s,p and a,p Conformation of the Ester Substituents.

It appears that in the solid state, ortho-substituted derivatives have a preference for sp, sp geometry, whereas the non-ortho-substituted derivatives prefer sp, ap geometry. These ratios are consistent with the thesis of non-equivalent environments adjacent to the DHP binding site, and the probability of the ester groups being oppositely oriented at the receptor site is high.

The preference for coplanar groups at the receptor is supported by the greater activity of rigid DHP analogs which favor this conformation. These conformational characteristics are summarized in Figure 11.

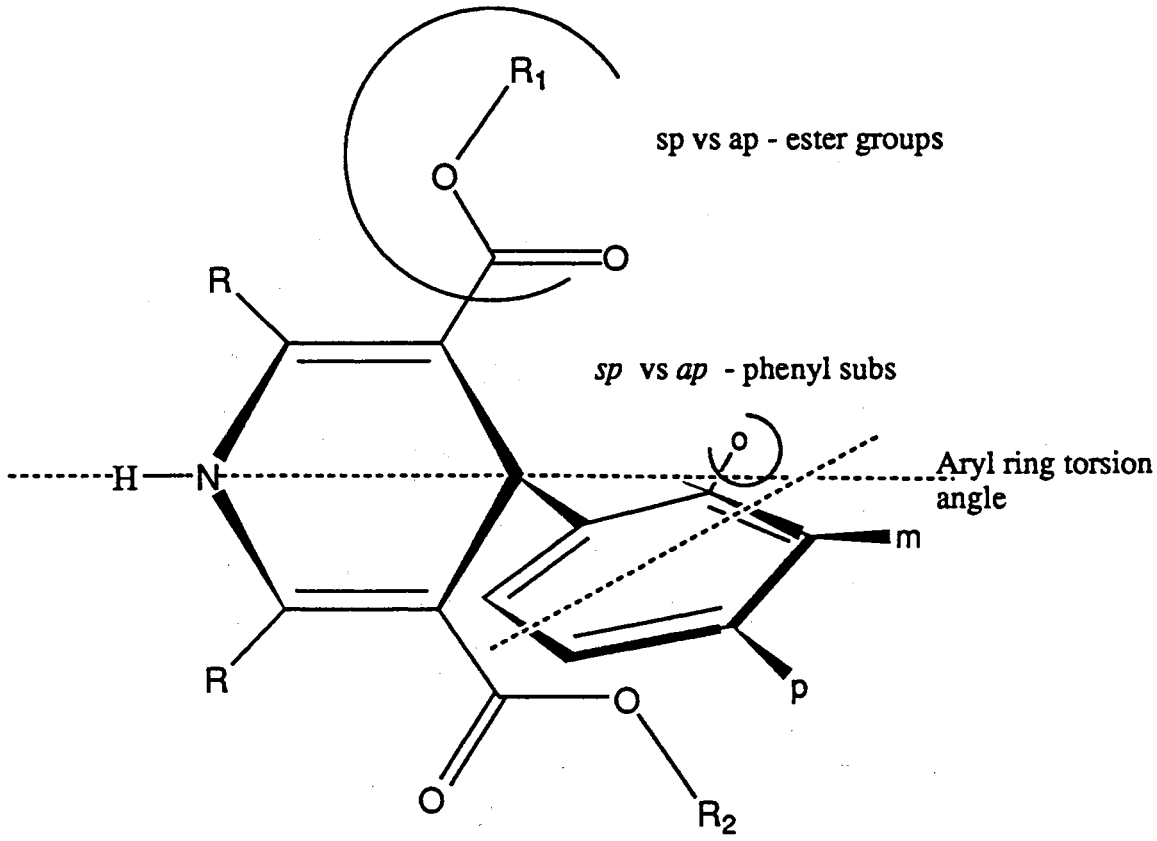


Figure 11: General Conformational Details Consistent with High Activity of the 1,4-Dihydropyridine Derivatives.

DHP Receptor Characteristics

The actual receptor that the 1,4-DHP's bind to is unknown. However, based on the amino acid sequence(AA) of the α1-subunit of the voltage dependent calcium channel isolated from rabbit skeletal muscle transverse tubule

membranes, a receptor model has been proposed[28]. This isolated AA sequence (receptor) has been shown to restore excitation-contraction coupling and restore slow calcium current when reconstituted into membrane bilayers[14].

Characteristics of the voltage-sensing unit[28]

Based on the AA sequences of the channel forming α-subunits of voltage-gated channels, several models have been proposed to describe how the α-subunits (α-helical segments) are arranged in the lipid bilayer[15,17,62]. These ion channel sequences are characterized by four homologous repeating domains which are organized around an ion selective channel. Each of the four domains of the protein sequence contain eight α-helices, and the fourth helix in each domain, termed the S4 helix, has a regular pattern of five or six positively charged arginine (Arg) or lysine (Lys) residues spaced every third AA apart[28].

In an α-helix, each residue is displaced by a 100° right hand rotation from its preceding N-terminal residue. Therefore, there will be 300° right hand, or a 60° left hand helical displacement for each three residue separation. A pattern of five or six Arg and Lys residues, spaced three apart, would form a left handed spiral staircase of positive charges on the outside of the S4 helix. This staircase of charged Lys and Arg side chains has been proposed to H-bond the S4 helix to a matching helical pattern of H-bond accepting groups provided by the outer surrounding collar of α-helices in each voltage sensing bundle. It has also been proposed that the S4 helix is able to slide up or down in this semi-rigid collar of the sensing unit in response to changes in the membrane potential[15,28].

Calcium channel blocking drugs are thought to interfere with the voltage-induced movements of the S4 subunit[28]. The DHP amine function should interact with proton accepting functional side chains of such AA's as aspartic acid (Asp), asparigine (Asn), glutamic acid (Glu), glutamine (Gln), serine (Ser), and

threonine (Thr), while the ester carbonyl oxygens should form H-bonds with such proton donor as Arg, Lys, and histidine (His). Since Lys, Arg, and His residues were scarce on other transmembrane helices, it appeared logical to investigate whether or not a 1,4-DHP molecule could satisfy its H-bonding requirements by interacting with the S4 α-helix. The optimum docking site is proposed to be in between the side chains of two arginine residues lying parallel to each other on successive turns of the helix[28]. While there are a number of these sequences present, modeling studies show that the peptide sequence Arg-Leu-Leu-Arg-Leu-Phe-Lys-Ile, offers the best fit of highly active members of the 1,4-DHP class. Therefore, this portion of the sequence has been used to explore docking efficiency. This was modeled by Langs et al, docking the drug molecule with the phenyl ring between two Arg side chains on the S4 helix (Figure 12)[28].

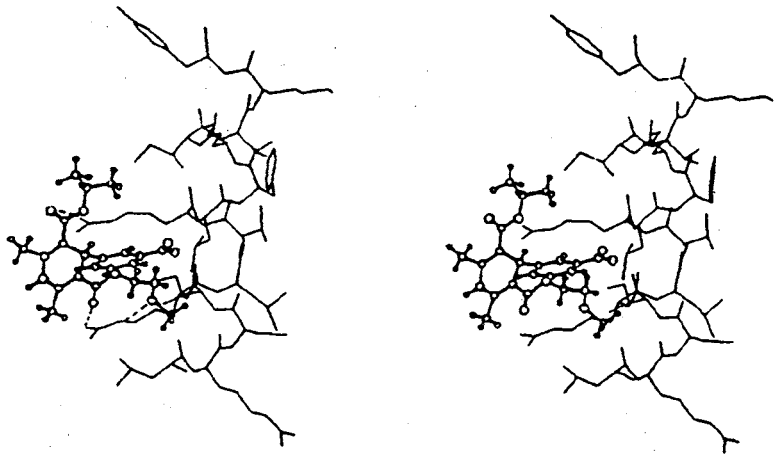


Figure 12: Stereodiagram of nimodipine bound to the proposed receptor surface[28]

The unsubstituted para position of the phenyl ring is seen to have tight van der Waals interactions with the S4 helix core. Thus, this may explain why para substituted derivatives are much less active. The two Arg side chains flank opposite sides of the phenyl ring and also form H-bonds with the carbonyl oxygen

atoms of the drug molecule. When the drug molecule is positioned as shown in Figure 12, the N1-H bond is approximately perpendicular to and directed away from the axis of the S4 helix, supposedly towards a H-bond acceptor, presumably located on an adjacent helical strand in the voltage sensing bundle [28]. The amount of ring pucker affects the projection of the N1-H bond, hence affecting the H-bonding capacity. Those with large ring puckers may not be able to form these H-bonds as well.

Based on the modeling results of Langs et al, it appears that the major recognition surfaces of the receptor lie in helical grooves on the S4 strand, or voltage-sensing α-helix that is positioned in the center of the bundle of transmembrane helices that define each of the four calcium channel domains. Multiple binding clefts defined by Arg-X-X-Arg reading frames exist on the S4 strand.

The tissue selectivity of certain derivatives may also be the result of the differences in lipophilic character, shape and volume of the ester groups. In this model, the ester groups slide under the aliphatic connecting arms of the Arg side chains and rest against the side chain residues of amino acids exposed in the next turn of the helix.

The above model given by Langs et al is merely an hypothesis. The cleft used is only one of many where the DHP may bind. However, it may be a starting point. The degree to which this model may be correct has not yet been established.

Decomposition of the 1,4-Dihydropyridines

1,4-Dihydropyridine derivatives undergo a photodecomposition sequence forming nitroso-pyridine derivatives and finally nitro-pyridine derivatives[63-65]. Nifedipine decomposition has been reported to be extremely wavelength

sensitive. The two decomposition products have been identified by spectroscopic methods (Figure 13). Exposure to UV radiation appears to cause the aromatization of the dihydropyridine ring and reduction of the nitro group to a nitroso moiety (Figure 13b). Daylight and air oxidation lead to reoxidation of the nitroso group to a nitro function. (Figure 13c). The existence of these decomposition products has led to concern about shelf life, packaging and potency of the pharmaceutical[65,66].

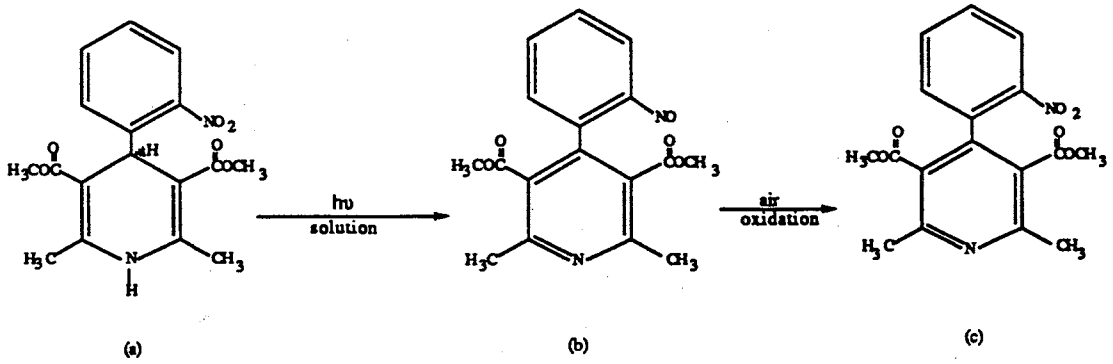


Figure 13: Decomposition Scheme for 1,4-Dihydropyridine Compounds

Oxidation of the 1,4-dihydropyridine ring to pyridine is reported to diminish activity significantly in some cases[22]. The nitro-pyridine decomposition product has been identified as one of the major metabolites of the parent 1,4-dihydropyridine compound[67] and has been reported to be as much as 1000x less active[68]. However, some of the oxidized derivatives do display some activity[22].

Even though the SAR's of the dihydropyridine type compounds seemed highly developed, there appeared to be a lack of understanding concerning the effect of the C3, C5 ester alkyl groups on the activity. For example, there was really no systematic study of increasing the chain length of the ester alkyl groups and how this affected the overall conformation of the compounds. Also, the

effect of decomposition on the conformation of the parent 1,4-DHP's was barely investigated at all.

Therefore, this thesis study set out to accomplish a further understanding of 1) the effect of increasing the length (bulk) of the ester alkyl groups on the overall conformation of these compounds and 2) the conformational changes associated upon decomposition to the nitro-pyridine derivatives and the potential effects of this on the calcium antagonistic activity of these compounds. Furthermore, a study of the calcium blocking efficiency of the parent compounds and their oxidized derivatives can lead to an understanding of the activity factors associated with the relative conformations of the two ring system and the ester alkyl groups.

CHAPTER II

X - RAY CRYSTALLOGRAPHY

The main objective of X-Ray crystallography is the acquisition of a detailed model of the three-dimensional contents of a crystal at the molecular level. A wealth of information is available from the positions of the individual atoms; bond lengths and angles, intermolecular interactions, molecular packing, conformation, and hydrogen bonding. Although this method can only be applied to crystalline materials, it can be adapted to a wide range of different temperatures, pressures and environments.

In the crystalline state, there exists a very high degree of internal order and symmetry. The molecules, atoms, or ions in the crystal are arranged in a precise regular way, a motif which is repeated over and over in all directions. It is this property of crystals that allows the diffraction of X-rays and the subsequent solution of a crystal structure. Most crystals are very regular in shape with sharp faces and edges, but this characteristic is not sufficient to define a crystal. They must have a repeating pattern in three dimensions, which defines the crystal lattice.

The basic "building block" in a crystal is the unit cell. The unit cell is characterized by its cell edges (a, b, and c) and angles (α, β, and γ). The crystal system to which a unit cell belongs is defined by the relationship between these edges and angles. There are seven possible crystal systems (TABLE 3).

TABLE 3

THE SEVEN CRYSTAL CLASSES

Crystal system	Unit cell shape
Triclinic	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$
Monoclinic	$a \neq b \neq c$, $\alpha = \gamma = 90°, \beta \neq 90°$
Orthorhombic	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c$, $\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$, $\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a = b \neq c$, $\alpha = \beta = 90°, \gamma = 120°$
Cubic	$a = b = c$, $\alpha = \beta = \gamma = 90°$

The unit cell of a crystal also may contain a variety of symmetry elements relating atoms or molecules to each other. These can include:

Mirror Plane: A plane of reflection which must be perpendicular to an axis and parallel to one of the crystal faces.

Rotation Axis: An n-fold rotation axis in which the rotation through $2\pi/n$ (n=1, 2, 3 or 4) leaves the appearance of the motif unchanged.

Glide Plane: The combination of a mirror reflection and a translation.

Screw axis: The combination of a rotation and a translation.

Inversion axes: The combination of a rotation axis with a center of symmetry.

The crystal lattice can be classified as primitive, P, or face centered (A, B, or F) or body centered, I. Fourteen Bravais lattices result when the crystal system is combined with these lattice types. The combination of the fourteen Bravais lattices with the space symmetry elements gives rise to a total of 230 possible space groups. Each crystal crystallizes in a specific space group that characterizes that crystalline structure[69].

Since crystals have the highly ordered structure described above, they are capable of diffracting radiation similar to an optical grating. The diffraction pattern of a crystal is much more complicated because a crystal exhibits three-dimensional periodicity and gives rise to diffraction in all directions of space[70]. When crystals diffract X-rays, it is the core electrons that possess the diffracting power. The core electrons act as secondary point sources and diffract the X-ray beam. The diffraction of an X-ray by a crystal obeys a mathematical relationship called Bragg's Law:

$$n\lambda = 2d\sin\theta \qquad (1)$$

where λ is the incident radiation wavelength, d is the interplanar spacing or distance between the regularly oriented layers of a set of (hkl)-planes, θ is the angle of incidence and the angle of diffraction of the X-ray beam. Bragg's law, thus, describes the relationship between the wavelength of the incident radiation, the distance between the parallel planes of the crystal, and the angles at which specific diffracted beams will be observed. Bragg's law must be satisfied in order for diffraction to occur.

The diffraction pattern of a crystal is characteristic of the unit cell and the distribution of the atoms present. The intensities of the diffracted reflections are determined by the types of atoms present and the relative positions of these

atoms within the unit cell. Different types of elements have different abilities to scatter X-rays, which is dependent on the number of core electrons of that specific element. The "heavier" the atom, the greater the ability it possess to scatter the X-ray beam. Each crystal has its own diffraction pattern characteristic of its structure.

The intensity data collected from a crystal supplies all the information necessary to solve the molecular structure of that crystal. However, the intensities of these reflections are influenced by numerous other factors which must be taken into account. The raw intensity data (I_{meas}) must be corrected for these various effects before it can be used to solve the structure. This is termed *data reduction*. These corrections include i) background, ii) polarization, iii) Lorentz effect, iv) absorption factor, and v) decomposition.

i) *Background* — When a reflection intensity is measured, it is usually accompanied by a certain amount of scattered (background) radiation which must be eliminated to obtain the true intensity of a reflection[71]. The correction for the left and right background is calculated as follows:

$$I_{int} = (I_{meas}-L_{bg}-R_{bg}) \times \text{Scan speed} \qquad (2)$$

where:

I_{int} -- Integrated Intensity

I_{meas} -- Measured Intensity

The error in this intensity measurement is given by:

$$\sigma I_{int} = (I_{meas} + L_{bg} - R_{bg})^{1/2} \times \text{Scan speed} \qquad (3)$$

where:

σI_{int} -- The standard deviation of I_{int}

ii) *Polarization factor* — The polarization factor is a function of 2θ. As the data is collected, θ is varied. In so doing, the nature of the X-ray beam and the efficiency in which diffraction occurs also varies. A normal X-ray beam is unpolarized and contains two limiting components, one parallel to the reflecting plane ($I_{||}$) and one perpendicular to the reflecting plane ($I_{\perp}$), These components of the X-ray beam are diffracted by the crystal monochromator with different efficiencies and the ratio of these differences changes with the 2θ angle. At lower 2θ, the $I_{||}$ and $I_{\perp}$ components are diffracted with approximately equal efficiency. At higher 2θ the efficiency of diffraction of the $I_{\perp}$ component decreases dramatically, causing the diffracted beam to become partially polarized. Thus, diffraction measured at high 2θ appears to be less.

The polarization factor, P, is a function of 2θ and is independent of the geometry of data collection. It is calculated by the following expression.

$$P = (1 + \cos^2 2\theta)/2 \qquad (5)$$

iii) *Lorentz factor* — The Lorentz correction (L) is necessary because when the crystal is rotated at a constant speed, some reflections pass through the Bragg position at a faster rate than others. Reflections with low 2θ are positioned in optimum diffraction geometry for a longer period than those with high 2θ. The Lorentz factor corrects for this effect and is given by:

$$L = (\sin 2\theta)^{-1} \qquad (6)$$

The combination of the Lorentz and polarization factors results in what is known as the Lorentz-polarization factor (LP):

$$LP = (1 + \cos^2 2\theta)/2\sin 2\theta \qquad (7)$$

iv) *Absorption factor* — As the data is collected, some of the intensity of the radiation is absorbed by the crystal. This absorption is dependent on the nature of the elements present in the compound being studied, the path length of the beam through the crystal, and the wavelength of the incident X-ray beam. Inorganic crystals containing heavy atoms absorb more strongly than purely organic molecules containing only C, H, N, O, or S. The absorption factor (A) is defined by the following mathematical expression:

$$A = (1 / V) \int e^{-\mu L} dv \qquad (8)$$

where μ is the linear absorption coefficient which is defined as absorption per mm of material passed through, L is the path length through the crystal, and V is the volume of the crystal.

v) *Decomposition* — Many crystals exhibit a steady decrease in diffraction intensity during the process of data collection. This effect appears to be a result of radiation damage to the crystal from the incident X-ray beam and can be observed by the remeasurement of certain high-intensity standard reflections at regular intervals. The correction for this effect is given by:

$$D = I_{orig} / I_{ave} \qquad (9)$$

where:

I_{orig} -- starting intensity of a standard reflection

I_{ave} -- average current intensity of the standard reflection

Once all of the above corrections have been taken into account (data reduced), the total corrected intensity may be calculated by:

$$I_{corr} = I_{int} \times (LP)^{-1} \times A^{-1} \times D \qquad (10)$$

where:

I_{int} -- the integrated intensity (from background corrections)

I_{corr} -- the overall corrected intensity

The reflection is considered to be observed if $I_{int} \geq 2\sigma(I_{int})$ and is used in the solution of the crystal structure.

I_{int} is related to the structure factor (F) by:

$$| F_{hkl} | = (KI_{hkl} / Lp)^{1/2} \qquad (4)$$

where:

p -- polarization factor

L -- Lorentz factor

K -- constant, based on crystal size, beam intensity and machine constants

The structure factor can be calculated, theoretically, once the positions of the atoms are known. Also, this factor is used in the calculation of electron density maps from which the position of the atoms can be determined. The relationship between F and I depends on the corrections listed above and must be taken into account in order to convert |F| into $|F_{obs}|$ which is used in the subsequent structure solution.

The X-rays scattered by a single unit cell of a structure in any direction in which there is a diffraction maximum has a particular combination of amplitude and phase which is termed the structure factor (F). The structure factor may be calculated from the positions of the atoms in the cell, their ability to scatter X-rays, and the phase angle, α_{hkl} (i.e. the difference in period, expressed as an angle, between the wave resulting from a specific set of planes and a wave resulting from scattering at the origin).

where:

$$| F_{hkl} | = \{ (A_{hkl})^2 + (B_{hkl})^2 \}^{1/2}$$

$$A_{hkl} = \Sigma f_j \cos 2\pi (hx_j + ky_j + lz_j)$$

$$B_{hkl} = \Sigma f_j \sin 2\pi (hx_j + ky_j + lz_j)$$

$$\alpha_{hkl} = \tan^{-1} (B_{hkl} / A_{hkl})$$

where f_j is the individual atomic scattering factors and x_j, y_j, z_j are the positional parameters in the unit cell of atom j.

In order to acquire a three dimensional picture of the scattering matter (the electron distribution), a three dimensional Fourier synthesis must be performed. The number of electrons per unit volume or the electron density at any point X, Y, Z, represented by $\rho(XYZ)$ is given by:

$$\rho(XYZ) = (1/V_c) \sum_{h,k,l} \Sigma\Sigma | F_{hkl} | \cos \{2\pi (hX + kY + lZ) - \alpha\} \qquad (13)$$

where:

V_c -- the volume of the unit cell

F_{hkl} -- structure factor for the particular set of indices h,k,l

α -- phase angle

Therefore, if $| F |$ and α were known, ρ could be computed for all values of X, Y, and Z and these values could be plotted to obtain a three-dimensional electron density map. However, only the structure factor can be obtained experimentally, not the phase angle. This value must be derived from the values of A and B from previously known structures or by purely analytical methods. This is what is known as the "phase problem" in X-ray crystallography. In order to solve a structure, a certain number of the phase angles must be determined approximately in order to compute an initial model from which to complete the

structure. This problem has been solved mainly by two mathematical approaches: The Patterson method and direct methods.

The Patterson method is based on the idea that the phase angle is dominated by the presence of the heavy atoms. This method is only successful for structures containing elements with a higher molecular weight than sulfur. This method is based on the following equation

$$P(u, v, w) = (1 / Vc) \Sigma\Sigma\Sigma \mid F \mid^2 \cos 2\pi (hu + kv + lw) \qquad (14)$$

where only the indices and the $\mid F \mid^2$ value of each diffracted beam are needed and which are derivable from the primary experimental quantities. No phase information is required because no origin for the unit cell is implied, only the relative positions of the atoms. The peaks in this map occur at points whose distances from the origin correspond in magnitude and direction to distances between atoms in the crystal.

The Patterson function (P(u, v, w)) is always centrosymmetric (has a center of symmetry at the origin), therefore interatomic distances can be plotted assuming one atom is at the origin. A peak in the Patterson map, called a vector at (u,v,w) implies that there are two atoms in a crystal structure at (x_1, y_1, z_1) and (x_2, y_2, z_2) such that $(x_2-x_1=u, y_2-y_1=v, z_2-z_1=w)$. Thus, the Patterson map gives the orientation and length of every interatomic vector. Depending on the space group in effect, certain spatial relationships can be used to help locate atoms. For example, if a space group contains a mirror plane perpendicular to the b axis, for every atom with coordinates x, y, z, there is another atom with coordinates x , -y, z. Thus the vectors between these atoms all have the coordinates 0, y, 0. This represents what is known as a Harker line[71]. If only one value is fixed, a Harker plane results (eg. 0, v, w from a rotation axis parallel to a).

The heights of the peaks in the Patterson map are proportional to the values of Z_iZ_j, where Z_i is the atomic number of the atom at one end of the vector and Z_j is the atomic number of the atom at the other end of the vector. The vectors formed between those atoms of high atomic number are much more visible than those formed between lighter atoms. Thus, the positions of the heavy atoms are determined from the map by analysis of the stronger Patterson vectors, Harker lines and planes and the use of the general equivalent positions of the space group of that crystal. In this way a starting trial model is obtained.

The second approach most commonly used to obtain the positional parameters of a structure is called direct methods and is applicable to both light and heavy atom structures. Direct methods is a way of determining the phase(s) based on relationships among the intensities of the reflections themselves. The practical objective of direct methods is to phase enough reflections to provide an identifiable representation of the molecule. The first step in this solution requires the conversion of the observed intensities into normalized structure factors by the following equation:

$$| E_{hkl} |^2 = | F_{hkl} |^2 / \Sigma f_i^2 \qquad (15)$$

where:

$|E_{hkl}|$ = normalized structure factor

f_i = the scattering factor of the ith atom

This equation is applied in shells of $10°\theta$. Once the structure factors are normalized, the effects of the decline in atomic scattering power with increasing 2θ are eliminated.

The phases of a subset may be derived directly from the magnitudes of E_{hkl}. This value will allow the calculation of an electron density map from which one can derive a suitable structure.

In defining the electron density it will be recalled that the following equation holds:

$$\rho(XYZ) = (1/V_C) \sum_{h,k,l}\sum\sum | F_{hkl} | \cos \{2\pi (hX + kY + lZ) - \alpha\} \qquad (16)$$

where:

Vc -- the volume of the unit cell

Fhkl -- structure factor for the particular set of indices h,k,l

α -- phase angle

In a centrosymmetric cell, this equation simplifies to:

$$\rho(XYZ) = (1/V_C) \sum_{h,k,l}\sum\sum \pm | F_{hkl} | \cos 2\pi (hX + kY + lZ) \qquad (17)$$

The phase angle has simplified because in a centrosymmetric cell, with each atom at x, y, z, there is an equivalent atom at -x, -y, -z, therefore the phase angle can only be 0 ° or 180 ° (hence the ± sign in front of the structure factor). Thus, the electron density map can be constructed from equation (17), if the signs of a significant number of structure factors are known.

Phases can be initially assigned by the use of what is known as Harker-Kasper inequalities. These inequalities provided the first method of determining the phase of one reflection in terms of its magnitude and those of others. The inequalities that were derived are given below:

$$u^2_{hkl} \leq 1/2 + 1/2\, u_{2h,2k,2l} \qquad (18)$$

$$u^2_{hkl} \leq 1/2\, (\pm 1/2 | u_{2h,2k,2l} |) \qquad (19)$$

where:

u - unitary structure factor

These equations are significant because the only unknown is the phase (or sign) of $u_{2h,2k,2l}$. The quantity u^2_{hkl} must be positive. For example, if u^2_{hkl} is equal to 0.60 and $| u_{2h,2k,2l} |$ is equal to 0.20, then it follows that the sign of $u_{2h,2k,2l}$ must be positive. Only then will equation (19) be satisfied.

Once a few initial phases are determined, it is possible to define relations among the them. These relationships are based on the fact that the electron density can never be negative and that electron density consists of discrete spherically symmetric atoms. For centrosymmetric structures, it can be shown that for any structure factor F_{hkl}, the phase is determined by the products of all of the phases of the pairs of structure factors whose indices add to give (hkl). Thus F_{213} depends on the products of the phases of F_{322} and F_{-1-11}, F_{604} and F_{-41-1}, and so on. This relationship is described in the following equation introduced by Sayre:

$$s(F_{h1k1l1}) \cdot s(F_{h2k2l2}) \approx s(F_{h1 + h2,\ k1 + k2,\ l1 + l2}) \qquad (20)$$

This is known as the triplet product sign relationship, where s means " sign of" and $\approx$ means "is probably equal to". s(h, k, l) may be considered as ± 1, and $(h_1k_1l_1)$, $(h_2k_2l_2)$ and $(h_1 + h_2\ k_1 + k_2\ l_1 + l_2)$ are strong reflections with high $| E |$ values. The triplet product sign relationship is used to expand the number of known phases. Therefore, if two of the signs in the equation are known, the third can be deduced. However, only a limited number of phases can be determined from the triplet relationship. A method termed symbolic addition is used to expand the number of phases known.

In symbolic addition, one starts with a limited number of phases and uses them in connection with equation (20) to build a large enough set of known phases in order to produce a recognizable electron density representation of the structure. The preliminary step in symbolic addition is the calculation of the E

values for the entire data set as given in equation (15). For all the E values that are greater than a chosen minimum, a list is compiled of all the triples of reflections belonging to this set for which the indices sum to zero. The list of strongest relationships is used to select those reflections that are most often and most reliably interconnected, and appropriate ones of these are chosen for origin determination. In the centrosymmetric case, the origin is placed on one of the centers of symmetry in the unit cell. In any primitive, centrosymmetric space group in the triclinic, monoclinic, or orthorhombic systems, arbitrary signs can be allocated to three reflections in order to specify the origin. These form a basic set from which more phases can be defined by using the triplet product relationships. For example, if the signs of 601 and 133 are +1, then 734 is generated by the combination of these and its sign will be positive:

$$s(734) \approx s(601) \cdot s(133) = +1 \cdot +1 = +1$$

Many times these starting reflections will combine to relate to two new ones and imply their phases by equation (20). The next step then involves the assignment of a new, strong reflection as a variable, a, b, or c. This variable stands for a general phase in the non-centrosymmetric case or a sign in the centrosymmetric case. These variables are then used to determine other phases exactly or in terms of one or more variables. This series is continued until a sufficient number of reflections have been phased to provide an initial structural model.

When enough phases have been determined, an electron density map (E-map) is calculated with the | E | values instead of the | F | values.

$$\rho(XYZ) = (1/V_C) \sum_{h,k,l}\sum\sum \pm |E_{hkl}| \cos 2\pi (hX + kY + lZ) \qquad (21)$$

A trial model is derived from the E-map.

When the initial model is defined, the phased structure factors (Fcalc) can be calculated and their magnitudes compared with those that have been measured (Fobs). This is performed by a least squares refinement method (refinement). Least-squares refinement modifies the atomic positional parameters of the calculated structure to improve the least-squares fit. This procedure then identifies any missing atoms (using the difference Fourier | (|Fobs|) - (|Fcalc|) |). The correctness of the model is given by the 'Residual Factor', R_f, defined as:

$$R_f = (\Sigma | (|F_{obs}|) - (|F_{calc}|) |) / (\Sigma | F_{obs} |) \qquad (22)$$

Once this initial R factor is determined, refinement of the total set of atom positions in the crystal structure is performed using the least-squares method. As the model approaches completion, the difference between F_{obs} and F_{calc} is reflected in a lower R_f value.

The atom positions are first refined using isotropic temperature parameters. Each atom has an associated temperature parameter. This value, a measure of the thermal vibration of the atom, effectively spreads the electron cloud over a larger volume. This factor reflects the decrease in the atomic scattering factors as 2θ increases. The scattering factor for an atom at rest is given by the following equation:

$$\exp \{ -B_{iso} (\sin^2\theta) / \lambda^2 \} \qquad (23)$$

where B_{iso} is the isotropic thermal parameter, which is equal to $8\pi^2 \langle u^2 \rangle$, where $\langle u^2 \rangle$ is the mean square displacement of the atom from its equilibrium position. However, the atomic scattering behavior is more accurately defined by an anisotropic thermal parameter given by:

$$\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl) \qquad (24)$$

where bij is the individual anisotropic thermal parameter of the atom. The refinement is continued using the anisotropic form of the temperature parameter which provides more accurate positional parameters and hence a better R_f for the structure. These anisotropic thermal parameters describe an ellipsoidal electron distribution of the electron density.

Hydrogen atom positions are normally calculated using idealized geometry, unless the intensity data is sufficiently good to allow them to be located from the difference Fourier map. When all atoms have been located, an appropriate weighting scheme and extinction correction can be applied. The structural refinement is considered complete when the R_f factor reaches a value of between 3 - 6% and all atom bond lengths and angles are reasonable.

Tables of crystal information (cell dimensions), data collection conditions, anisotropic thermal parameters, positional parameters and bond distances and angles are now prepared. A table of final F_{obs} and F_{calc} structure factors is printed. Three dimensional drawings of the molecule and/or the unit cell are prepared to show the atoms as ellipsoids of 50% probability. From these data, structural characteristics can be interpreted such as bond type, H-bonding parameters, and structural conformation.

CHAPTER III

MOLECULAR MODELING

Introduction to Molecular Modeling

Molecular modeling (MM) is a computer-based method of predicting three dimensional details (bond lengths, bond angles, conformation, torsion angles, etc.) of a chemical structure from minimum energy evaluations. The results obtained can be compared to experimental values or used to predict the properties or reactivity of a molecule. Use of this method in biological research areas has grown extensively during the past decades due to advances in computer hardware and software, which has in turn brought high-performance computing and graphics within the capacity of many industrial and academic laboratories.

Molecular modeling (MM) systems supply the tools necessary to visualize, build, analyze, and store models of complex molecules without the necessity of synthesis. Most MM systems work in approximately the same fashion; the two-dimensional structure of the molecule is entered and a corresponding 3-D model is calculated. Using an empirical, parameterized force field, the computer calculates a total energy value for the model. Subsequently, the model is subjected to small perturbations to reduce its energy until a local minimum is achieved (minimization). This conformation is then considered to be a stable conformer relative to other conformations which may have higher energy values in the gas phase (one molecule only). Conclusions may then be drawn about

structure-activity relationships, binding-site conformations, and reactivity of this conformer. MM can also be used to design new structures with specific biological properties (QSAR). This capacity has made MM an important tool for design of novel drugs because it can eliminate or speed up many processes that are normally very time consuming, i. e., the trial and error method of synthesizing and testing the new compounds. MM helps make this process more efficient by "testing" various 3-D characteristics of the new molecule to ascertain if synthesis and testing are warranted.

The two most common approaches used in drug design are the "direct" and "indirect" methods. Direct drug design utilizes the 3-D features of a known receptor site. The new drug is then designed to conform to this model. For example, if the 3-D structure of a certain protease or enzyme is known, the actual dimensions of the receptor site can be visualized and a molecule can be designed that will act as a key to fit the receptor site and which will inhibit or alter the function of the substrate. The indirect method is based on a known structure, with the desired biological activity, termed a lead compound. Analogs of this compound are designed and MM is used analyze the ability of the analog to mimic the 3-D structure of the lead compound. This is normally a good indication of the biological activity of the analog. Frequently, a number of derivatives have already been synthesized and tested, therefore these structure-activity relationships can be kept in mind during the design process. Direct and indirect methods can also be used together. For example, the indirect method may be used to assess the 3-D properties of various active and inactive molecules. The information gathered from the indirect method can be used to construct a "blueprint" of the receptor site. The selection of new molecules for MM studies, thus, becomes more rational. The 3-D structure of the lead compound can be determined by X-ray crystallography or NMR analysis. X-ray crystallography can

determine the precise 3-D structure of a compound in the solid state, but it requires preparation of a high-quality crystal. If a crystal structure is determined for one member of a class of compounds, there is no need to determine others since the MM system is able to give reasonable 3-D structures based on the data from the initial compound. NMR can also supply 3-D information about the lead compound. Two-dimensional NMR techniques have become highly advanced and can determine the 3-D structure of a molecule in solution using NOE and coupling constant analysis. This is advantageous because the structure of a molecule changes in response to its environment; i. e. solvation interactions may make the minimum energy conformation in solution different from that in the crystal. The application of MM techniques without any initial structural data is very difficult, requiring *ab initio* methods and quantum mechanical calculations. This is normally unrealistic because the computer time required is so extensive even for moderate sized molecules. However, if 3-D data is already known for a compound with similar structure, the MM system can use it as a starting point in determination of the structure of the unknown molecule and thus reduce the computer time required.

Many commercial MM programs are available. Each offers specific advantages, but most include a basic set of capabilities: manipulation and visualization of the 3-D structure of a molecule; structure building, rotating bonds, molecular mechanics and dynamics, conformational analysis, molecular surface displays, electronic properties, docking algorithms and calculation of various physical properties of the molecule. The two major MM packages available are SYBYL® and Discover®. The Discover® program was used in this research and its capabilities are described below.

The Discover® Program[72]

The Discover® program enables the user to perform molecular simulations such as molecular mechanics, dynamics, energy minimizations and template forcing (forcing the conformation of one molecule to be similar to that of a template structure), calculation of interaction energies and vibrational frequencies. Using Discover®, one can also evaluate docking interactions, such as enzyme-substrate, receptor-ligand, or polymer-polymer. Discover® can also evaluate the multitude of conformations available to a drug, catalyst, or polymer and energy refine a model-built structure.

Minimization

Discover® uses different algorithms for the energy minimization process. However, the final structure reached represents one of the low energy conformations. In order to find other low energy conformations, molecular dynamics can be used to search the conformational space and hence find other minima.

Minimization with solvent attempts to take into account the interactions of solvent molecules with the substrate. This is done by placing either a layer or sphere of solvent around the substrate. The whole system is then minimized. This will tend to alter the minima acquired versus that found with minimization in the gas phase. This new minima may provide insight into how the substrate conformation changes with a solvent environment and hence what the true conformation is in biological systems.

Docking

The Docking Module is used to evaluate the non-bond energy between two molecules. This energy is frequently used as a guide to the preferred orientation of one molecule relative to another. As in the minimization process

described above, the parameters used in this calculation are stored in a force field file which calculates values for the van der Waals non-bond potential. The van der Waals interaction energy is calculated by summing the energy contributions between all atoms of the two molecules. Hydrogen bonding is also used as an indicator of a positive interaction. This is especially important in the interaction between a ligand and its receptor. (i. e. it is favorable to form more hydrogen bonds which will aid in the binding process). The primary objective of a docking calculation is to evaluate the interaction energies of many orientations of one molecule relative to another, while searching for the orientations that result in low interaction energies. The lowest energy value obtainable is used to describe a possible binding conformation of the substrate with respect to the receptor.

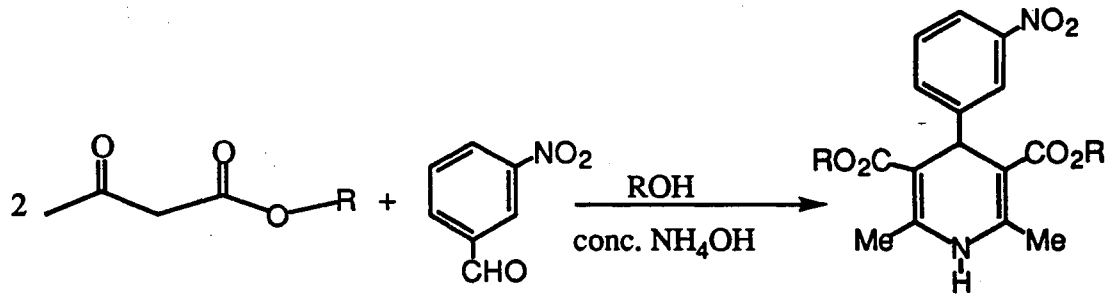
CHAPTER IV

EXPERIMENTAL

Materials. All chemicals were reagent grade materials and were used without further purification.

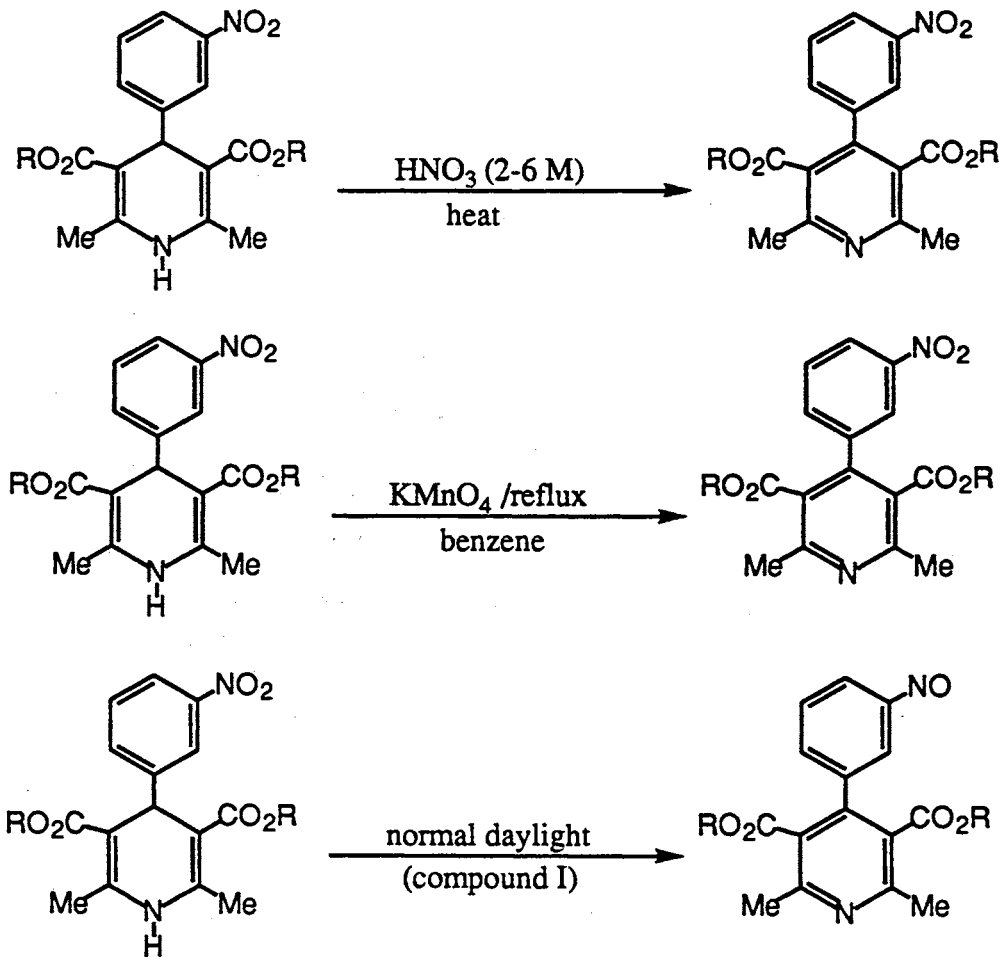
1,4-Dihydropyridine Synthesis

The synthetic procedure used to prepare the compounds of this study is known as the Hantzsch dihydropyridine synthesis[73], a " one pot" synthesis in which all the reactants are mixed in an alcohol solvent (CH_3OH, CH_3CH_2OH) and refluxed for 4-6 hours (scheme A). The product usually crystallizes out of the mother liquor, otherwise, evaporation of the alcohol solvent and replacement with another solvent usually CH_3CN, enhanced precipitation.



Scheme A: General Hantzsch Synthesis of Dialkyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-Dihydropyridines.

Decomposition was carried out by oxidation with nitric acid (HNO_3), potassium permanganate ($KMnO_4$) (Scheme B), or (compound I), by placing the sample dissolved in an alcohol solvent in normal daylight.



Scheme B: Decomposition of 1,4-Dihydropyridines

Dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)-pyridine-3,5-dicarboxylate (I)

Nifedipine (50 mg, 0.1445 mmol) (2,6-dimethyl-3,5-dicarbomethoxy-4-(2-nitrophenyl)-1,4-dihydropyridine in an ethanol solution was exposed to normal sunlight. After approximately two days, light green crystals formed. A crystal with appropriate dimensions (< 0.5 x 0.5 x 0.5 mm) was mounted on a glass fiber for use in X-ray diffraction studies. (mp=93-95 °C)[64].

Bis(2,6-dimethyl-3,5-dicarbomethoxy-4-(2-nitrophenyl)pyridine)dichloro-copper(II) (II)

A mixture of 20 mg (0.0578 mmol) of nifedipine and 9.8 mg (0.07334 mmol) copper(II) chloride in 10 mL of ethanol was allowed to sit in an open container on the bench top. Dark purple crystals were produced after several weeks.

2,6-Dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine • NO_3 • H_2O (III)

Di-*tert*-butyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-di-carboxylate-(2 g ,4.65 mmol) was mixed with 30 ml of 2 N HNO_3. The resulting solution was extracted with $CHCl_3$. The organic layer was washed twice with water and once with 5% $NaHCO_3$. The aqueous layer yielded transparent, colorless crystals.

Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (IV)

A mixture of 6 g of 2,6-dimethyl-3,5-dicarbomethoxy-4-(3-nitrophenyl)-1,4 dihydropyridine was warmed with 5 M (110 ml) nitric acid to approximately 80°C.

The reaction mixture was stirred for 30 minutes and then extracted with methylene chloride(CH_2Cl_2). The extract was washed with water, 5% aqueous. $NaHCO_3$, again with water, and then dried over Na_2SO_4. Large crystals precipitated out of the organic layer (mp =121-124 °C).

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (V)

A solution of 5g (0.0331 mole) of 3-nitrobenzaldehyde, 8.61 g (0.06618 mole) ethyl acetoacetate, and 4.56 g (0.065moles) ammonium hydroxide was refluxed for approximately 4 hours. The product precipitated out of the reaction mixture, was filtered, and recrystallized from a methanol/water mixture (mp=205-207 °C).

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (VI)

A mixture of 4g of 2,6-dimethyl-3,5-dicarboethoxy-4-(3-nitrophenyl)-1,4 dihydropyridine was warmed with 5 M nitric acid (100 ml) to approximately 80°C. The mixture was stirred at this temperature for approximately 30 minutes and extracted with $CHCl_3$. The organic layer was washed with water twice. The organic layer yielded clear crystals of diethyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate.

Dipropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VII)

A solution of propyl acetoacetate (14.417 g, 0.1 mole), 3-nitro-benzaldehyde (7.556 g, 0.05 mole), and concentrated ammonium hydroxide (0.1

mole) was refluxed for 5-6 hours in 30 ml of ethanol. Yellow plate-like crystals precipitated out of the mother liquor upon cooling (mp =144-147 °C).

Di-isopropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(VIII)

A solution of isopropyl acetoacetate (14.417 g, 0.1 mole), 3-nitrobenzaldehyde (7.556 g, 0.05 mole), and concentrated ammonium hydroxide (0.1 mole) was refluxed for 5-6 hours in 30 ml of ethanol. Yellow plate-like crystals precipitated out of the mother liquor upon cooling (mp =107-113 °C).

Dibutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (IX)

A solution of n-butyl acetoacetate(15.82 g, 0.1 mole), 3-nitrobenzaldehyde (7.556 g, 0.05 mole), and concentrated ammonium hydroxide(3.85 g, 0.1 mole) was refluxed in ethanol for approximately 4 hours. The ethanol was removed and the resulting oil dissolved in acetonitrile. Large yellow crystals formed upon slow evaporation of the acetonitrile solution (mp = 89-94 °C).

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (X)

A solution of 7.556 g (0.05 mole) of 3-nitrobenzaldehyde, 17.402 g (0.11 mole) isobutyl acetoacetate, and 3.85 g (0.11 mole) concentrated ammonium hydroxide was refluxed in ethanol for 7 hours. The product precipitated out of the reaction mixture, was filtered, and recrystallized from ethanol (mp=139-143 °C).

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XI)

A mixture of 4 g of di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (compound X) was warmed with 5N nitric acid (100ml) to approximately 80°C. The mixture was stirred for approximately 30 minutes and extracted with $CHCl_3$. The organic layer was washed twice with water. The organic layer yielded clear crystals of di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XI).

di-*tert*-Butyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(XII)

A solution of 3-nitrobenzaldehyde (7.556 g, 0.05 mole), *tert*-butyl acetoacetate (17.402 g, 0.11 mole), and ammonium hydroxide (3.85 g, 0.11 mole) was refluxed in methanol for 7 hours. The methanol was removed under reduced pressure and the solid dissolved in acetonitrile (CH_3CN). Bright yellow crystals were formed on slow evaporation of the CH_3CN solution (mp=175-178 °C).

Dipentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIII)

A solution of n-pentyl acetoacetate (17.20 g, 0.1 mole), 3-nitro-benzaldehyde (7.556 g, 0.05 mole), and concentrated ammonium hydroxide (3.85 g, 0.1 mole) were refluxed in ethanol for approximately 4 hours. Large yellow crystals formed upon slow evaporation of the ethanol solution.

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIV)

A solution of di-isopentyl acetoacetate(17.20 g, 0.1 mole), 3-nitrobenzaldehyde (7.556 g, 0.05 mole), and concentrated ammonium hydroxide (3.85 g, 0.1 mole) were refluxed in ethanol for approximately 4 hours. Large yellow crystals formed upon slow evaporation of the ethanol solution (mp = 115-117 °C).

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XV)

A solution of di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4.59g, 0.01 mole), potassium permanganate (1.58g, 0.01 mole), and montmorillonite KSF (3.42g) was refluxed in 60 ml benzene for 24 hours. The reaction mixture was filtered and subsequently solidified. The solid was recrystallized from methanol.

Di-neopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XVI)

A mixture of 4 g of di-neopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4 dihydropyridine 3,5-dicarboxylate was warmed with 5M nitric acid (100 ml) to approximately 80°C. The mixture was stirred for approximately 30 minutes and extracted with $CHCl_3$. The organic layer was washed twice with water. The organic layer yielded clear crystals of neopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate.

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XVII)

A solution of n-hexyl acetoacetate (18.60 g, 0.1 mole), 3-nitrobenzaldehyde (7.556 g, 0.05 mole), and concentrated ammonium hydroxide (3.85 g, 0.1 mole) was refluxed in methanol for approximately 4 hours. The ethanol was removed under reduced pressure and the resulting oil dissolved in acetonitrile. Large yellow crystals formed upon slow evaporation of the acetonitrile solution (mp = 75-78 °C).

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate(XVIII)

A solution of dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (0.01 mole, 5.0 g), potassium permanganate (0.01mole, 1.58 g), montmorillonite KSF (3.42 g), and 60 ml benzene was refluxed for 24 hours. After the benzene was removed, the resulting oil was dissolved in hexane which yielded clear transparent crystals upon slow evaporation.

(Diheptyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) • CH_3CN (XIX)

A solution of n-heptyl acetoacetate (20.02 g, 0.1 mole), 3-nitrobenzaldehyde (7.556 g, 0.05 mole), and concentrated ammonium hydroxide (3.85 g, 0.1 mole) were refluxed in methanol for approximately 4 hours. Acetonitrile was added to the original mixture causing compound XIX to precipitate. Large yellow crystals formed upon slow evaporation of the acetonitrile solution.

Dioctyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XX)

A solution of n-octyl acetoacetate (21.40 g, 0.1 mole), 3-nitrobenzaldehyde (7.556 g, 0.05 mole), and concentrated ammonium hydroxide (3.85 g, 0.1 mole) was refluxed in methanol for approximately 4 hours. Acetonitrile was added to the original mixture causing compound XX to precipitate. Large yellow crystals formed upon slow evaporation of the acetonitrile solution (mp = 58-67 °C).

Di-(2-Methoxyethyl) 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboylate(XXI)

A solution of 3-nitrobenzaldehyde (4.53 g,0.03 mole), 2-methoxyethyl acetoacetate (10.4 g, 0.065 mole), and ammonium hydroxide(2.275 g, 0.065 mole) was refluxed in ethanol for seven hours. The product precipitated out of the reaction mixture, was collected by filtration, and recrystallized from ethanol (mp=125-129 °C).

(Dibenzyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) • 0.5 CH_3CN (XXII)

A solution of benzyl acetoacetate (0.1 mole), 3-nitro-benzaldehyde (0.05 mole), concentrated ammonium hydroxide (0.1 mole) was refluxed in 30 ml ethanol for approximately 5-6 hours. The product crystallized from the mother liquor as a yellow precipitate. The precipitate was dissolved in acetonitrile which yielded yellow plate-like crystals.

(2,6-Dimethyl-3-carbomethoxy-5-carboethoxy-4-(3-nitrophenyl)-pyridine) • NO_3 (XXIII):

A solution of 2 g (5.55 mmole) of 2,6-dimethyl-4-(3-nitrophenyl)-3-carbomethoxy-5-carboethoxy-1,4-dihydropyridine and 2 M HNO_3 (100 ml) was refluxed for 4 hrs. The resulting solution was extracted with methylene chloride (CH_2Cl_2). The organic layer was washed twice with water, dried with Na_2SO_4 and the CH_2Cl_2 removed under reduced pressure. The resulting oil was dissolved in ethyl acetate and upon slow evaporation, yielded clear crystals suitable for X-ray diffraction.

CRYSTALLOGRAPHY

Crystals with the appropriate dimensions (<0.2 mm in all three dimensions) of each compound were chosen for X-ray diffraction. A single crystal of good quality was mounted on a glass fiber held in a brass support. The brass pin was placed in a goniometer head and mounted on a Siemens P4 automated four-circle diffractometer equipped with a PC-486DX computer (Figure 14). The crystals were irradiated with molybdenum radiation at an average wavelength of 0.71073 Å (a weighted average of kα1 and kα2). Unit cell dimensions were determined using the centered angles from 25 - 50 independent strong reflections which were refined by least-squares methods using the automated procedure in XSCANS[74]. The intensity data were collected at room temperature using a variable scan rate, a θ-2θ scan mode and a scan range of 0.6° below $k_{\alpha 1}$ and 0.6° above $k_{\alpha 2}$ to a maximum 2θ value (normally 50.0° or the observed diffraction of the crystal). Backgrounds were measured at the ends of the scan range for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections to monitor crystal decomposition. The raw intensity data collected were corrected for Lorentz, polarization, absorption, decomposition, centering and background effects, after which redundant and space group forbidden data were removed.

Observed reflections (F>4.0 σF) were used to arrive at the non-hydrogen atom positions by direct methods[75-77]. Refinement of the scale factor, positional and anisotropic thermal parameters for all atoms was carried out using either

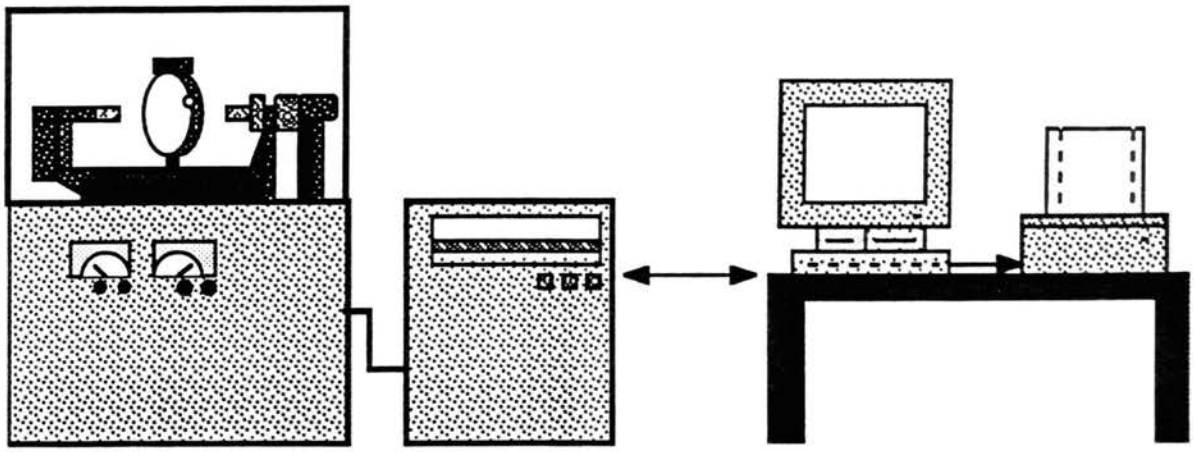


Figure 14. Siemens P4 automated 4-circle diffractometer with PC-486DX computer and printer

XLS (refinement on F) or SHELXL[78] (refinement on F^2) to convergence. Scattering factors were taken from the International Tables for Crystallography. Hydrogen atom positions were calculated using idealized geometry. The profile fitting technique for data reduction was employed. A weighting scheme $\left(w = \frac{1}{\sigma^2(F) + |g|F^2} \right)$ and extinction correction were applied at the last stages of refinement. Final refinement led to the final agreement factor, R_w.

MOLECULAR MODELING

The molecular modeling performed in this study were done on a Silicon Graphics IRIS® Workstation, which was graciously provided by the Department of Biochemistry and Molecular Biology at Oklahoma State University.. The program used for the minimization in the gas phase and in solution was Discover[72]. The coordinates of the X-ray crystal structure were introduced using FDAT file format. Minimizations were performed using these initial coordinates. The docking calculations were performed using the program Docking®[72]. The α1-subunit coordinates were obtained from Dr. David A. Langs at the Department of Molecular Biophysics, Medical Foundation of Buffalo, Inc. , Buffalo, New York. The molecules of this study as seen in their single crystal X-ray conformations were docked into the proposed receptor site and the Van der Waals interaction energy calculated.

Biological Evaluation

The biological testing procedures for the six compounds evaluated in this study were done by David J. Triggle using the method of Bolger[38] et. al. at the school of pharmacy at the University of Buffalo, State University of New York, C126 Cooke-Hochstetter Complex, Box 601200, Buffalo, NY, 14260-1200. The method used measured the displacement of 6.1×10^{-11} M [^{3}H]-(+)-PN200-110 binding in rat brain membranes. Membrane protein was incubated in Tris buffer with the labeled compound and the drug under inspection. The total assay volume was 2.5 ml in Tris buffer at a pH of 7.2 at 25°C. The tested compounds

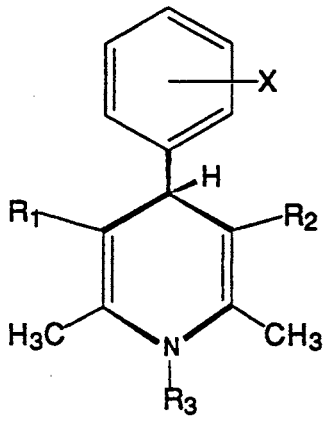
were incubated with the membrane protein and bound [^{3}H]-(+)-PN200-110 for four hours. The amount of [^{3}H]-(+)-PN200-110 that was displaced was measured using liquid scintillation counting. This gave a binding value which described the affinity of the compound being tested with respect to the labeled DHP derivative, [^{3}H]-(+)-PN200-110.

CHAPTER V

RESULTS AND DISCUSSION

Numerous structure-activity relationships (SAR's) for 1,4-dihydropyridine (DHP) derivatives are available in the literature[1]. However, the influence of the alkoxy groups at the C3 and C5 ester positions on the conformation of the rest of the molecule, and thus on the activity, is still somewhat unclear. A further understanding of 1) the effect of increasing the length and bulk of the ester alkyl groups on the overall conformation of 1,4-DHP compounds and 2) the conformational changes associated with DHP decomposition to the nitro-pyridine form and the potential effects on the calcium antagonistic activity of these changes was the focus of this study. The nine new compounds prepared, and the four prepared using literature preparations, (TABLE 4) have C3 and C5 ester alkyl groups that range from a two carbon to an eight carbon chain (compounds V, VII, VIV, XIII, XVII, XVIV, and XX). In order to observe the conformational dependence upon increased bulk of these side chains, isopropyl, isobutyl, tertiary butyl, isopentyl, and benzyl groups were also included (compounds VIII, X, XII, XIV, and XXII). The decomposition products studied were those of nifedipine (I and II), dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (IV), 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (III), diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VI), di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XI),

TABLE 4



Compound	X	R_1	R_2	Decomposition Product (R_3)
I	2-NO	CO_2CH_3	CO_2CH_3	yes
II	2-NO_2	CO_2CH_3	CO_2CH_3	yes
III	3-NO_2	CO_2H	CO_2H	yes
IV	3-NO_2	CO_2CH_3	CO_2CH_3	yes
V[26]	3-NO_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	no
VI	3-NO_2	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	yes
VII[26]	3-NO_2	$CO_2CH_2CH_2CH_3$	$CO_2CH_2CH_2CH_3$	no
VIII[26]	3-NO_2	$CO_2CH(CH_3)_2$	$CO_2CH(CH_3)_2$	no
VIV	3-NO_2	$CO_2(CH_2)_3CH_3$	$CO_2(CH_2)_3CH_3$	no
X	3-NO_2	$CO_2CH_2CH(CH_3)_2$	$CO_2CH_2CH(CH_3)_2$	no
XI	3-NO_2	$CO_2CH_2CH(CH_3)_2$	$CO_2CH_2CH(CH_3)_2$	yes
XII	3-NO_2	$CO_2C(CH_3)_3$	$CO_2C(CH_3)_3$	no
XIII	3-NO_2	$CO_2(CH_2)_4CH_3$	$CO_2(CH_2)_4CH_3$	no
XIV	3-NO_2	$CO_2(CH_2)_2CH(CH_3)_2$	$CO_2(CH_2)_2CH(CH_3)_2$	no
XV	3-NO_2	$CO_2(CH_2)_2CH(CH_3)_2$	$CO_2(CH_2)_2CH(CH_3)_2$	yes
XVI	3-NO_2	$CO_2(CH_2)C(CH_3)_3$	$CO_2(CH_2)C(CH_3)_3$	yes
XVII	3-NO_2	$CO_2(CH_2)_5CH_3$	$CO_2(CH_2)_5CH_3$	no
XVIII	3-NO_2	$CO_2(CH_2)_5CH_3$	$CO_2(CH_2)_5CH_3$	yes
XVIV	3-NO_2	$CO_2(CH_2)_6CH_3$	$CO_2(CH_2)_6CH_3$	no
XX	3-NO_2	$CO_2(CH_2)_7CH_3$	$CO_2(CH_2)_7CH_3$	no
XXI[26]	3-NO_2	$CO_2CH_2CH_2OCH_3$	$CO_2CH_2CH_2OCH_3$	no
XXII	3-NO_2	$CO_2CH_2C_6H_5$	$CO_2CH_2C_6H_5$	no
XXIII	3-NO_2	CO_2CH_3	$CO_2CH_2CH_3$	yes

di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XV), dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(XVI), dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XVIII), and nitrendipine(XXIII). To investigate the effect of inserting an oxygen in the side chain di(2-methoxyethyl) 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XXI) was synthesized. These compounds are tabulated in TABLE 4. Compounds V, VII, VIII, and XX, which had been prepared previously, but had not been examined by single crystal studies.

All of the nifedipine derivatives previously examined by single crystal X-ray diffraction[3,46] exhibit a flattened boat conformation of the 1,4-dihydropyridine ring with the nitrogen atom at the prow and the phenyl ring in pseudo-axial position at the bow. In order to quantify the effect of changes in bulk and length of the ester alkyl groups on the general conformation of the compounds in this study, specific structural parameters were defined. The parameters used were 1) the configuration of the ester carbonyl groups as sp or ap and of the phenyl substituent as *ap* or *sp*, 2) the sum of the internal torsion angles of the DHP ring to describe its planarity (SUM), 3) the deviation from orthogonality of the phenyl ring with respect to the base of the DHP boat , and 4) the cone angle of the ester groups to quantify the space occupied by the alkyl groups. The questions that I set out to answer were 1) How does the identity of the ester alkyl groups affect the deviation value of the phenyl ring, the planarity of the DHP ring, the conformation of the ester groups (ap vs sp) and that of the phenyl substituent (*ap* vs *sp*) and 2) based on these parameters, how does the identity of the ester alkyl group affect the activity? The X-ray parameters determined in this study are given in TABLE 5.

TABLE 5

Selected X-Ray Parameters for Compounds I-XXIII

Compound	Conformation of C3,C5 Esters [a]	Conformation of Phenyl Ring Substituent [b]	# Carbons in Ester Alkyl Chain	SUM (°)[c]	Deviation (°)[d]	Cone Angle(°)
(I) Dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)pyridine-3,5-dicarboxylate	-	-	1	15.134	6.265	-
(II) Dimethyl 2,6-dimethyl-4-(2-nitrophenyl)pyridine-3,5-dicarboxylate	-	-	1	11.688	5.751	-
(III) 2,6-Dimethyl-3,5-di-carboxylate-4-(3-nitrophenyl)pyridine • NO_3 • H_2O	-	-	0	6.4	32.8	-
(IV) Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate	-	-	1	12.6	33.1	-
(V) Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	ap,sp	*sp*	2	67.9	9.6	44.4
(VI) Diethyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate	-	-	2	5.19	32.95	-
(VII) Dipropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	sp,sp	*sp*	3	74.8	7.6	53.4

(VIII) Di-isopropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	ap,sp	*sp*	3	97.2	8.4	48.3
(VIV) Dibutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	ap,sp	*sp*	4	103.4	14.8	52.7
(X) Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	sp,sp	*sp*	4	100.97	8.88	56.2
(XI)DI-Isobutyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate	-	-	4	24.87	17.19	-
(XII) Di-*tert*-butyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	sp,ap	*sp*	4	73.99	33.71	48.4
(XIII) Dipentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	sp,sp	*sp*	5	90	10.1	70.3
(XIV) Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	sp,sp	*sp*	5	102.02	14.035	63.5
(XV) Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate	-	-	5	6.33	21.08	-
(XVI) Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate	-	-	5	7.3	35.2	-

(XVII) Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	sp,ap	*sp*	6	99	16.9	60.5
(XVIII) Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate	-	-	6	14.7	21.1	-
(XVIV) Diheptyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	sp,sp	*sp*	7	68.2	5.9	44.2
(XX) Dioctyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate	sp,ap	*sp*	8	103.2	21.8	64.7
(XXI) Di(2-methoxyethyl) 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate	sp,sp	*sp*	3	66.2	4.6	61.1
(XXII) (Dibenzyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydro-pyridine-3,5-dicarboxylate) • 0.5 CH_3CN	sp,sp	*sp*	7	99.6	8.0	50.0
(XXIII) Ethyl Methyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate • NO_3	-	-	1,2	6.86	39.07	-

a. The ester carbonyl groups of the decomposition products are no longer conjugated with the double bonds of the pyridine ring, therefore, they cannot be classified as sp or ap.
b. The conformation of the phenyl ring substituent is in reference to the hydrogen atom on the DHP ring. In the decomposition products, this atom is missing, therefore, this classification can not be made
c. The sum of the absolute values of the internal torsion angles of the DHP or pyridine ring.
d. The deviation from orthogonality of the phenyl ring with respect to the base of the DHP boat or pyridine ring.

The ester groups can adopt 1 of 4 different conformations, sp,sp; ap,sp; sp,ap; or ap,ap. Of the thirteen parent compounds in TABLE 4, three adopt the ap,sp conformation, 7 adopt the sp,sp conformation, and 3 adopt the sp,ap conformation. It appears that the sp,sp conformation is favored (7/13) in the solid state. However, there appears to be no correlation between the size or length of the ester groups and their conformation in the X-ray structures.

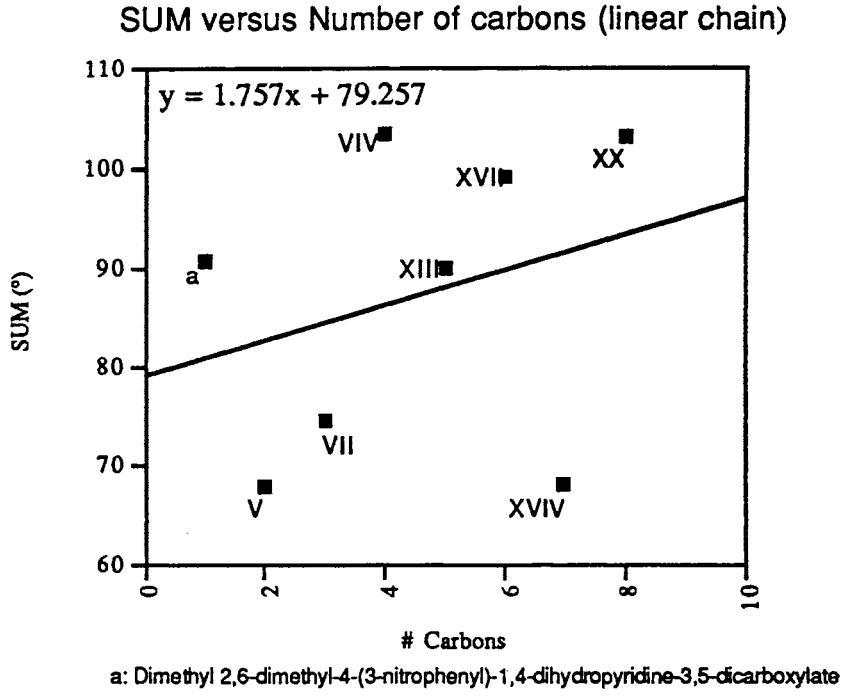
The planarity of the DHP ring is described by the sum of the absolute values of the internal torsion angles of the DHP ring (SUM). As the number of carbon atoms increases, the SUM value also increases, i.e. the DHP ring becomes less planar. This is a general trend and is not very well obeyed by compounds dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (a), VIV (n-butyl)* and XVIV (n-heptyl) (Figure 15a). A better correlation results if these compounds are not considered (Figure 15b).

The deviation of the phenyl ring from a perpendicular orientation to the base of the DHP ring is described using the C3-C4-C7-C8 torsion angle. The ideal value for this angle of the unoxidized parent compound is 60°. To arrive at the deviation value, the absolute value of the C3-C4-C7-C8 angle is subtracted from 60. The identity of the ester group appears to have an effect on this parameter. As the number of carbons in the ester alkyl chain increases, the deviation value also increases. This is represented graphically in Figure 16. This appears to be a general trend, which is not obeyed by compound XVIV, which contains a heptyl alkoxy group. This may be explained by the fact that the conformation of the ester groups are sp,sp. In the crystal lattice, the phenyl ring is flanked on both sides by heptyl chains from another molecule. Therefore, the phenyl ring would be forced to lie closer to the plane of bisection. In Figure 16a, all compounds in this study are represented. However, a better correlation exists

* The phrase in parentheses denotes the identity of the ester alkyl chain throughout text.

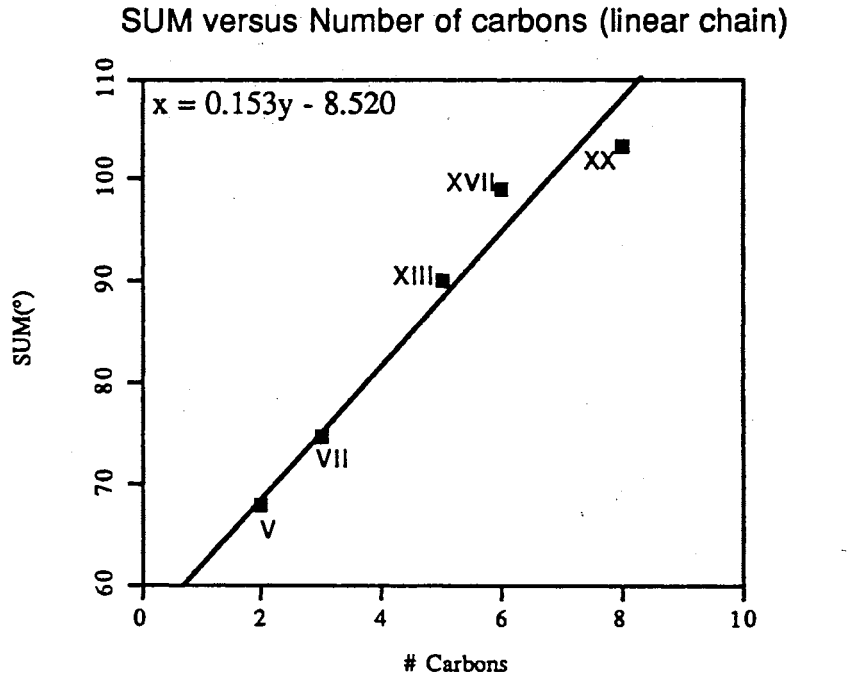
if only linear chain alkoxy groups are considered (Figure 16b). Again, this is not well obeyed by the n-heptyl compound.

The conformation of the ester groups appears to have an effect on the deviation value. In the sp conformation the alkyl esterification group is extended towards and parallel to the phenyl ring. When both ester groups are oriented sp,sp, the phenyl ring is more constricted, and therefore will have a smaller deviation value. The deviation values for compounds having the sp,sp orientation range from 4.6 to 14.035°, those with one group ap, and one group sp, range from 8.4 to 14.8. Thus, the sp,ap conformation seems to cause an increase in the deviation value.



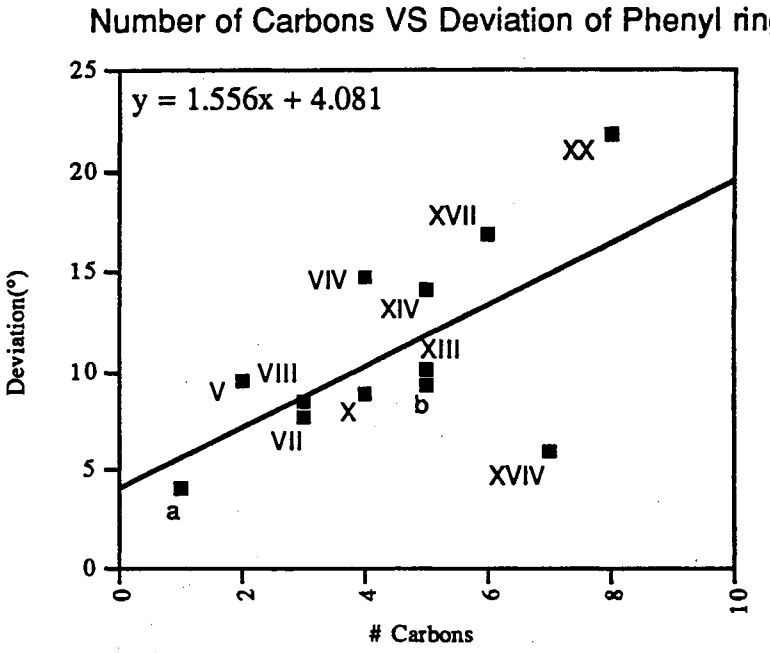
a: Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate

(a)



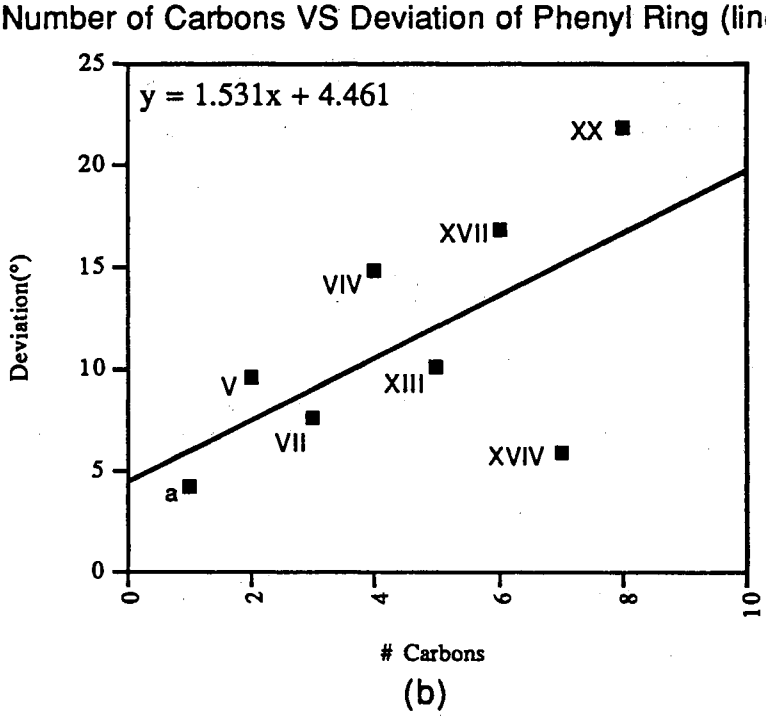
(b)

Figure 15: Plots of the SUM value versus the number of carbons in the ester groups. (a) all compounds in this study, (b) linear chain only



a: Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate
b: Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate

(a)

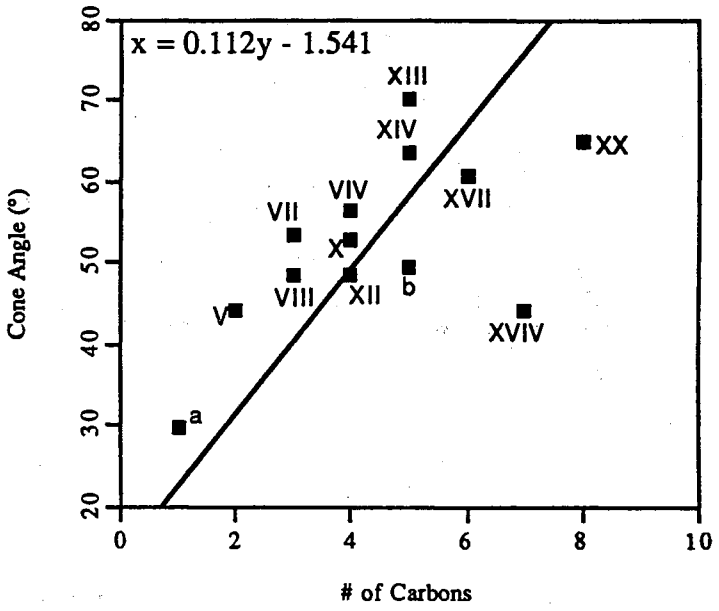


(b)

Figure 16: Plots of the deviation value versus the number of carbons in the ester alkyl group

A parameter that can be used to describe the space occupied by an ester alkyl group is the cone angle[86]. This is the angle swept out by the extent of the van der Waals radii of the group attached to the carboxy oxygen, assuming free rotation about the C3-C3' or C5-C5' bonds. These angle are given in TABLE 5. The number of carbons in the ester groups (branched and linear chain alike) appears to cause an increase in the cone angle parameter. Again, this trend is not followed as well by compound XVIV (n-heptyl). This is represented graphically in Figure 17.

Cone Angle versus the Number of Carbons in the ester alkyl chain



a: Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate
b. Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate

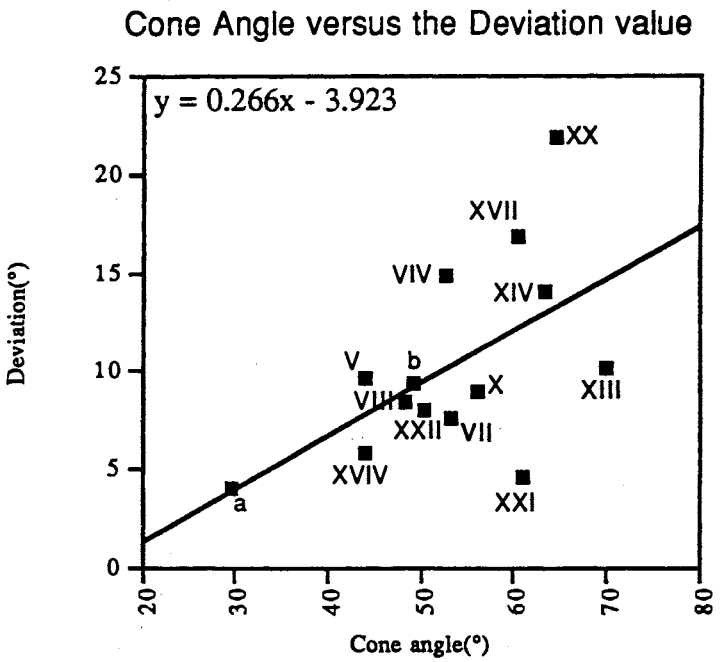
Figure 17 : Graph of the Cone Angle versus the number of carbons in the ester alkyl group

The effect of the magnitude of the cone angle on the deviation and SUM values was also investigated. The initial hypothesis was that as the cone angle increased, the deviation value would decrease. This was a logical conclusion

because the phenyl ring should be more restricted as the space occupied by the ester alkyl groups increased. This hypothesis was tested by plotting the cone angle against the deviation value (Figure 18a). The effect of the cone angle on the deviation value is exactly the opposite of that expected. As the cone angle increases, the deviation value also increases. However, three compounds do not obey this trend well, XIII (n-pentyl), XXI (2-methoxy ethyl) and XII (*t*-butyl-not shown).

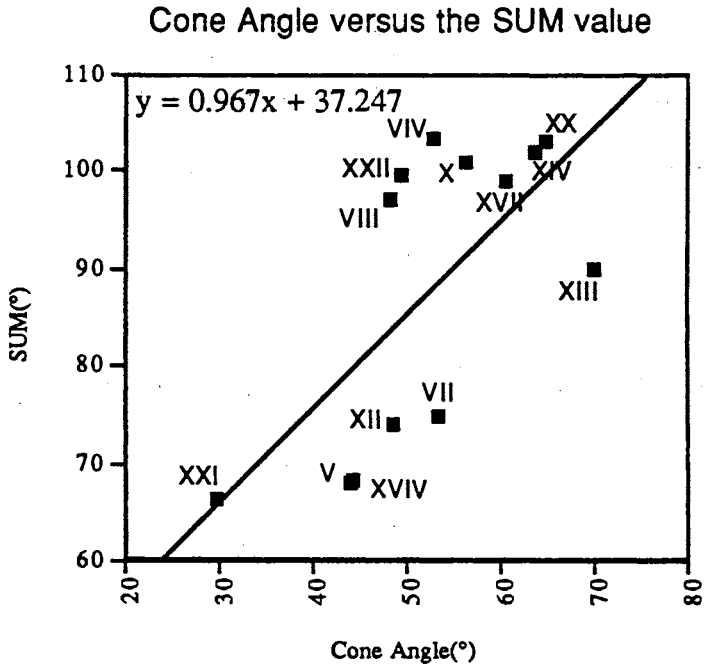
The SUM value was plotted against the cone angle (Figure 18b). There is no correlation between these two values, hence, it does not appear that the cone angle affects the SUM value in any way.

Since SAR analysis indicates that as the SUM value increases, activity decreases, it would appear that as the number of carbons increases, activity should decrease. Similarly, as the number of carbons increases, the deviation value increases, and thus activtiy should decrease. Finally, since the deviation value appears to increase with an increase in cone angle, it would be logical to assume that compounds with large cone angles would display generally lower activities.



a: Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate
b: Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate

(a)

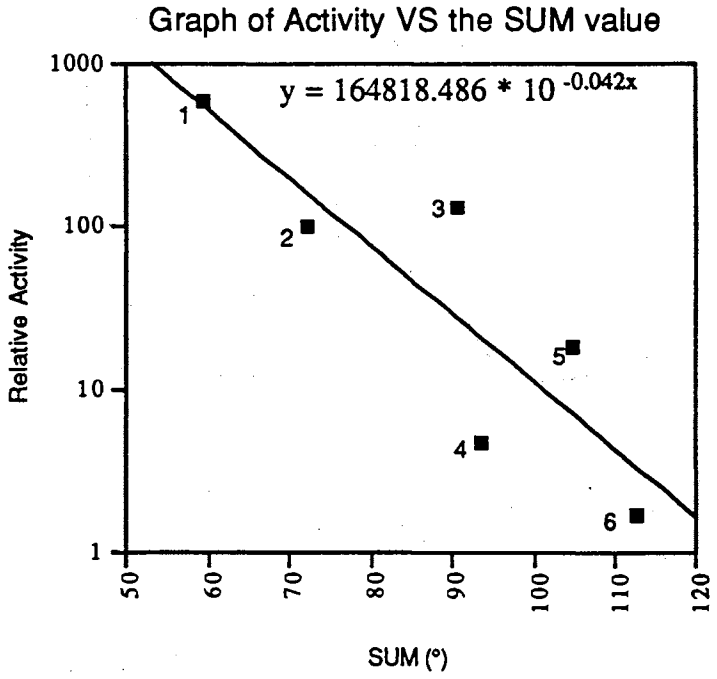


(b)

Figure 18: Cone Angle versus the a) deviation value, and b) SUM value

Activity Analysis

Structure-activity studies have demonstrated that flattening of the DHP boat conformation correlates with increased activity, presumably due to the concurrent change in position of the phenyl ring (Figure 9). As previously stated , the sum of the internal torsion angles is a measure of the planarity of the DHP ring. Published SAR's have indicated that as the SUM value decreases, calcium antagonistic activity increases. This trend is represented graphically in Figure 19[21].



1: Dimethyl 2,6-dimethyl-4-(2,3,4,5,6-pentafluorophenyl)-1,4-dihydropyridine 3,5-dicarboxylate
2: Nifedipine
3: Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine 3,5-dicarboxylate
4: Dimethyl 2,6-dimethyl-4-(3-methylphenyl)-1,4-dihydropyridine 3,5-dicarboxylate
5: Dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine 3,5-dicarboxylate
6: Dimethyl 2,6-dimethyl-4-(3-cyanophenyl)-1,4-dihydropyridine 3,5-dicarboxylate

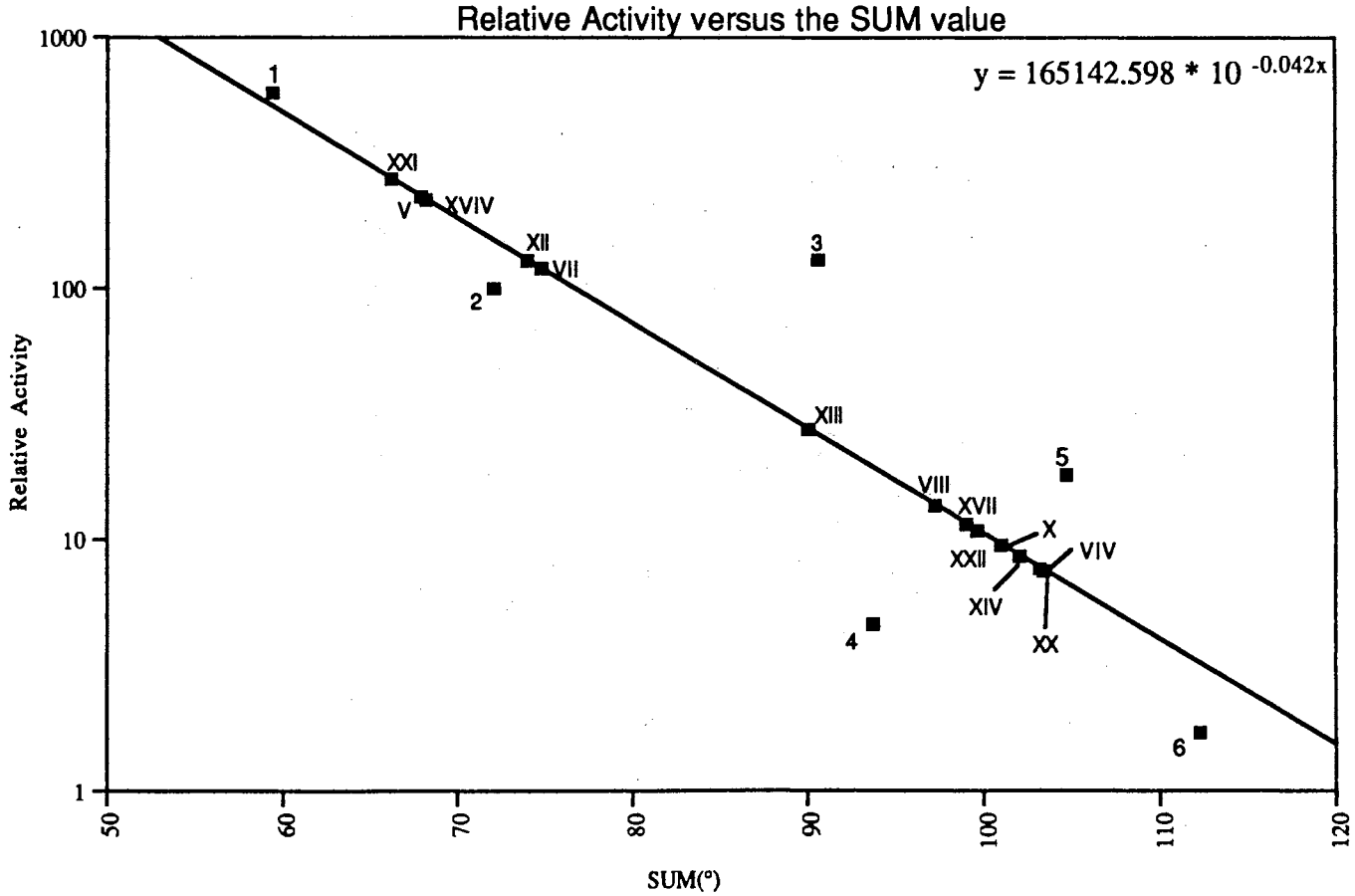
Figure 19: Graph of the Activity versus the SUM value [21]

This information may be used to predict the relative activity of compounds in which the activity has not been measured, i.e., compounds with higher SUM values should have lower activities.

The activities of the new compounds prepared in this study were estimated using this approach. Using the equation of the line (Figure 19), their activities were calculated and then plotted on the same graph (Figure 20). It was concluded that compounds V (ethyl), VII (n-propyl), XII (*t*-butyl), XVIV (n-heptyl), and XXI (2-methoxy ethyl) should be relatively active with activity values of; V (232), VII (120), XII (129), XVIV (225), and XXI (273). The SUM versus activity model predicted that compound VII (isopropyl) should have an activity value of 13.6, compound XVII (n-hexyl), 11.45, compound XII (*t*-butyl), 129, and compound XX (n-octyl), 7.6. These values are relative to the activity of nifedipine, which is assigned a value of 100. It also appears from this model that the identity of the ester group has no effect on activity.

In order to test these values, four new compounds were submitted for activity testing using the method of Bolger et al[38], actual results: VIII (isopropyl side chain; 80.6), XII (*t*-butyl; 3.7), XVII (n-hexyl; 16), and XX (n-octyl; 3.6). These values do not correspond with the values predicted from the above model.

One may also compare the order of activity of the four tested compounds. This order is VIII (isopropyl) > XVII (n-hexyl) > XII (*t*-butyl) ~ XX (n-octyl). Using the above analysis, the order calculated is XII (*t*-butyl) > VIII (isopropyl) ~ XVII (n-hexyl) > XX (n-octyl). The order is correct except for compound XII (*t*-butyl). A possible reason for this failure could be that the model was constructed using compounds having only methyl alkyl groups on the ester substituents while the substituent on the phenyl ring was varied.

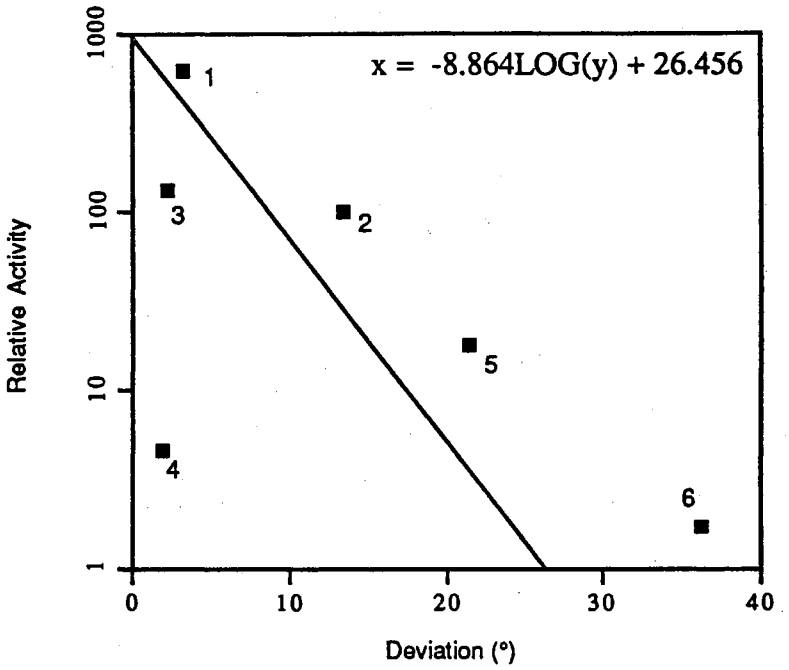


1: Dimethyl 2,6-dimethyl-4-(2,3,4,5,6-pentafluorophenyl)-1,4-dihydropyridine 3,5-dicarboxylate
2: Nifedipine
3: Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine 3,5-dicarboxylate
4: Dimethyl 2,6-dimethyl-4-(3-methylphenyl)-1,4-dihydropyridine 3,5-dicarboxylate
5: Dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine 3,5-dicarboxylate
6: Dimethyl 2,6-dimethyl-4-(3-cyanophenyl)-1,4-dihydropyridine 3,5-dicarboxylate

Figure 20: Graph of the Relative Activity versus the SUM value of six known compounds and the thirteen unoxidized parent compounds of this study

Known SAR's have indicated that as the deviation value decreases, activity increases. Therefore, a plot of relative activity versus the deviation value was prepared for the same compounds considered in Figure 17 (Figure 21).

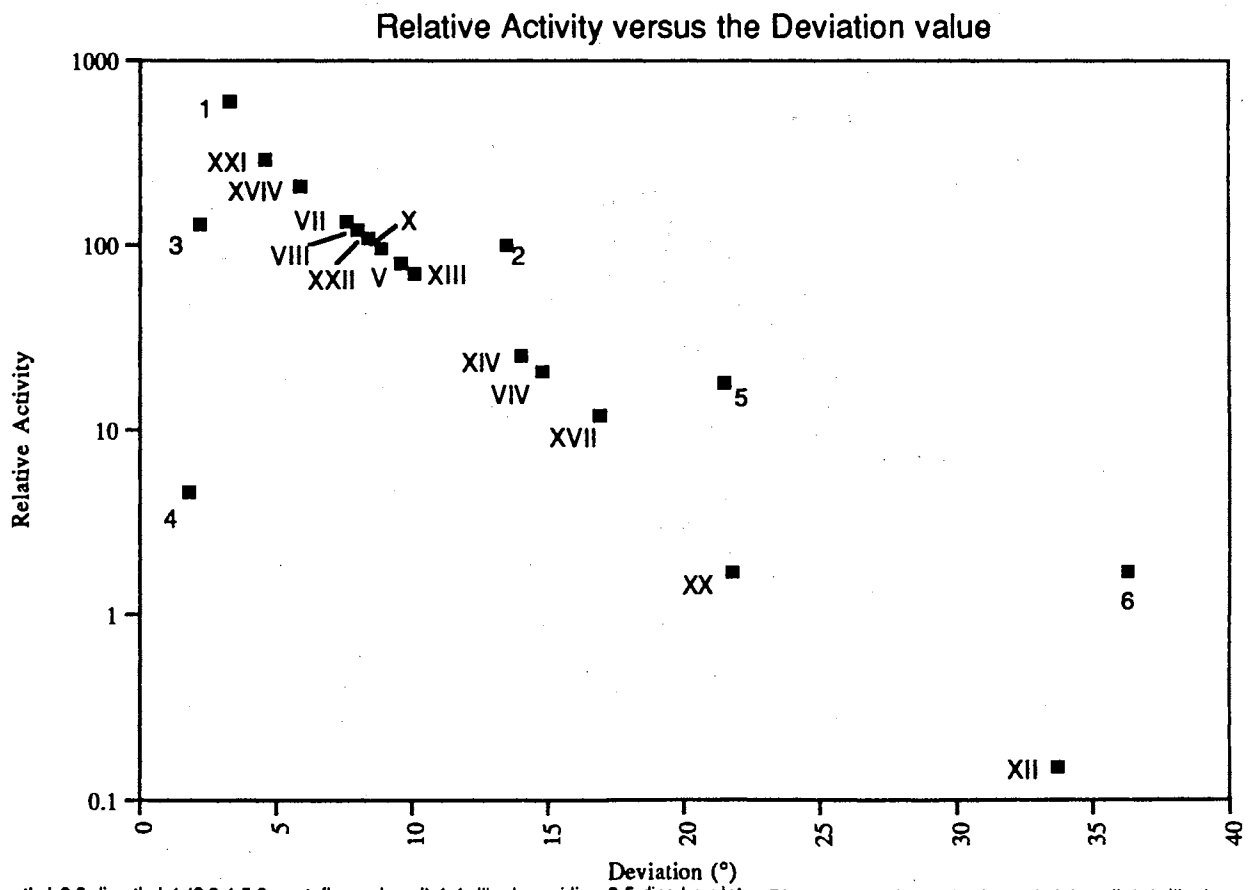
Relative Activity versus Deviation Value(Known compounds)



1: Dimethyl 2,6-dimethyl-4-(2,3,4,5,6-pentafluorophenyl)-1,4-dihydropyridine 3,5-dicarboxylate
2: Nifedipine
3: Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine 3,5-dicarboxylate
4: Dimethyl 2,6-dimethyl-4-(3-methylphenyl)-1,4-dihydropyridine 3,5-dicarboxylate
5: Dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine 3,5-dicarboxylate
6: Dimethyl 2,6-dimethyl-4-(3-cyanophenyl)-1,4-dihydropyridine 3,5-dicarboxylate

Figure 21: Graph of Deviation vs Activity of known compounds

The correlation resulting was not as good as that using SUM value versus relative activity. Nevertheless, the graph was used to predict the relative



1: Dimethyl 2,6-dimethyl-4-(2,3,4,5,6-pentafluorophenyl)-1,4-dihydropyridine 3,5-dicarboxylate
2: Nifedipine
3: Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine 3,5-dicarboxylate
4: Dimethyl 2,6-dimethyl-4-(3-methylphenyl)-1,4-dihydropyridine 3,5-dicarboxylate
5: Dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine 3,5-dicarboxylate
6: Dimethyl 2,6-dimethyl-4-(3-cyanophenyl)-1,4-dihydropyridine 3,5-dicarboxylate

Figure 22: Graph of the relative activity versus the deviation of the phenyl ring of six known compounds and thirteen unoxidized parent compounds from this study.

activities of the unoxidized compounds in this study (Figure 22). Based on this analysis, compounds V (ethyl, 80), VII (n-propyl, 134), VIII (isopropyl, 108.9), X (isobutyl, 96.13), XIII (n-pentyl, 70), XVIV (n-heptyl, 208.5), XXI (2-methoxy ethyl, 292.2), and XXII (benzyl, 121) should be active. Again, this hypothesis was tested using the compounds submitted for activity data. This model predicted that compound VIII (isopropyl) should have an activity of 109, however, the actual tests show a value of ~80. Also, it is known that compounds V (ethyl) and XXI (2-methoxy ethyl) have a relative activity of 80, but the activity versus deviation model predicts activities to be 79.73 and 292.2 respectively.

The order analysis as above, gives VIII (isopropyl) > XVII (n-hexyl) > XX (n-octyl) ~ XII (*t*-butyl), a much more consistent result. Therefore, this model may lead to a better order analysis, but not to absolute activity value predictions.

It appears that the activity is affected by the identity of the ester groups, since as the identity of the ester alkyl group increases in the number of carbon atoms in the four tested compounds, activity decreases.

It was concluded that a different combination of these two parameters would give a better model, since using each parameter by itself did not appear very satisfactory. If the SUM and deviation values are added together, the resulting sum describes both the deviation of the phenyl ring and the planarity of the DHP ring. This parameter will be termed SUM+Deviation (S+D). If one plots the S+D value of the known compounds listed below in Figure 23 against relative activity, a different correlation is obtained.

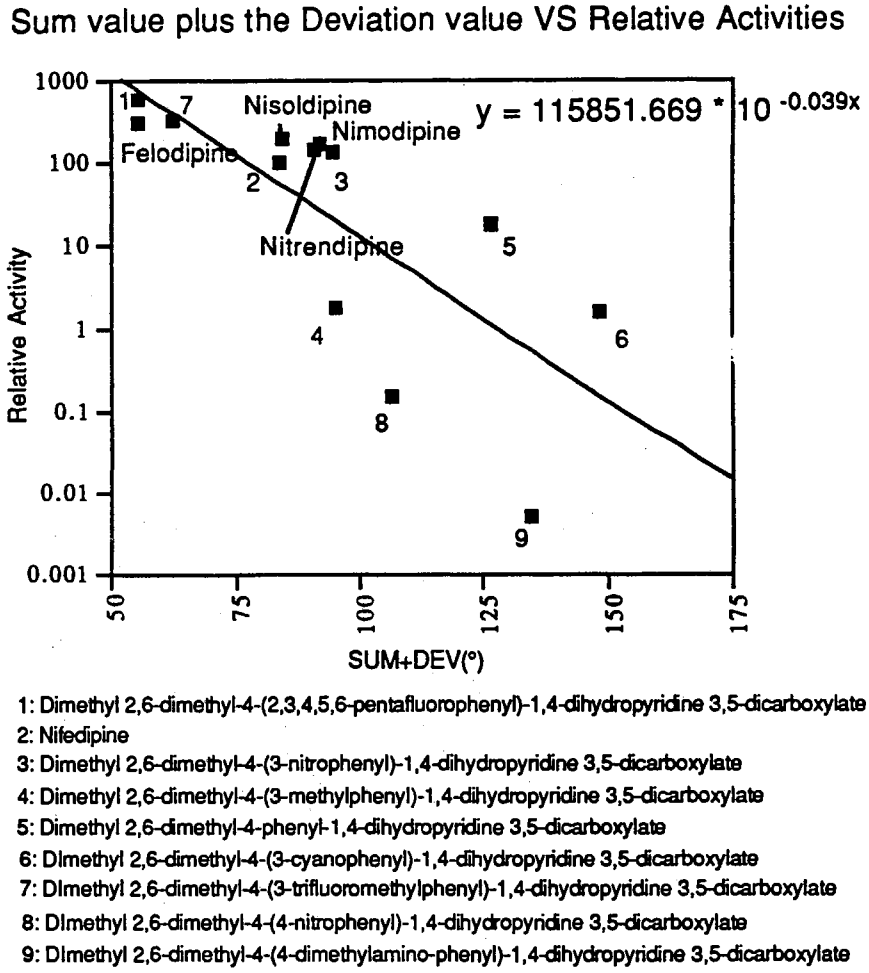
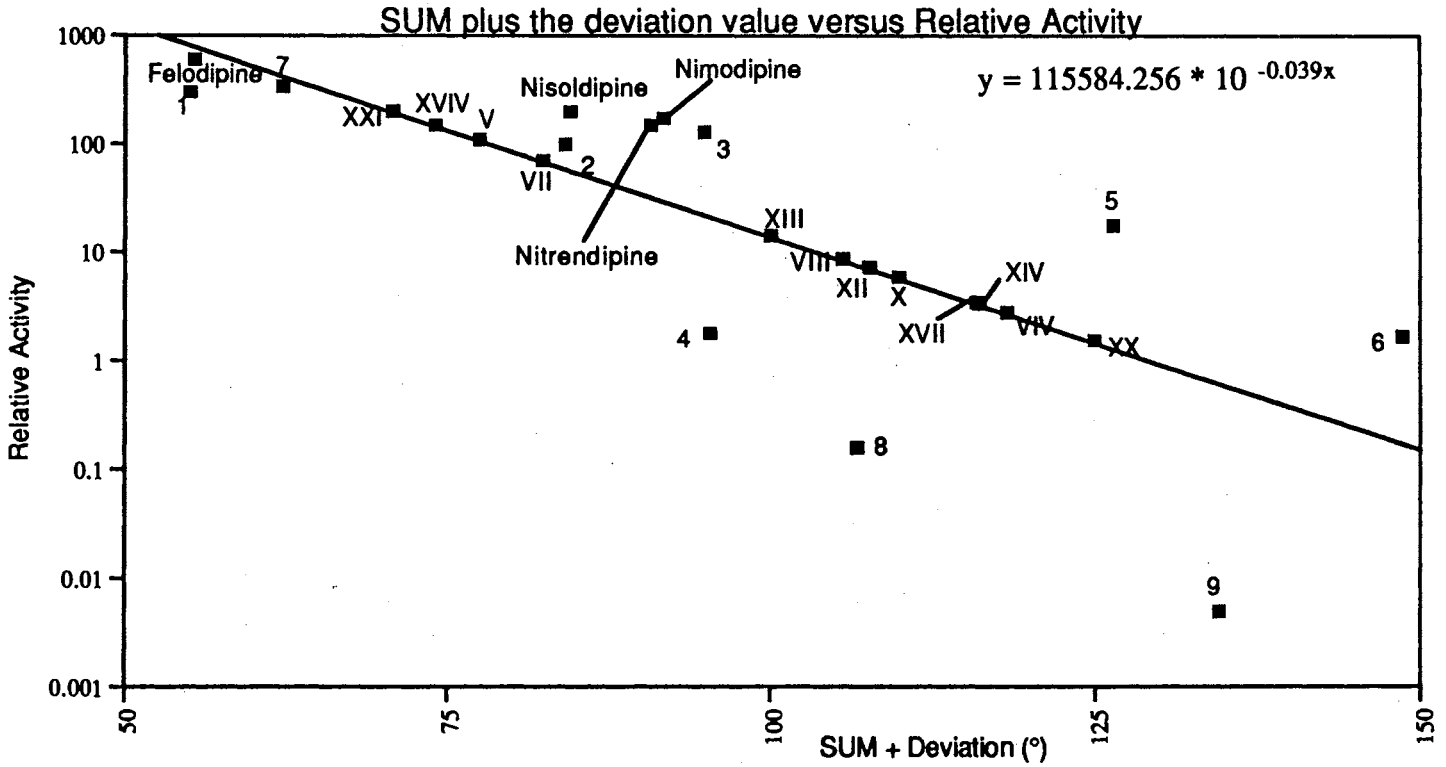


Figure 23: Graph of the SUM value + the Deviation value versus the relative activities of known compounds

Using this new parameter and compounds of known activities, the activity of the compounds in this study were calculated. This is represented graphically in Figure 24. This model predicted the most active compounds to be XXI (2-methoxy ethyl), XVIV (n-heptyl), V (ethyl), and VII (n-propyl). The order analysis gave VIII (isopropyl) > XII (t-butyl) > XVII (n-hexyl) > XX(n-octyl). This order is correct except for the position of the tertiary butyl derivative. However, testing this model with the known compound dimethyl 2,6-dimethyl-4-(2-chlorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate gave more encouraging results.



1: Dimethyl 2,6-dimethyl-4-(2,3,4,5,6-pentafluorophenyl)-1,4-dihydropyridine 3,5-dicarboxylate 2: Nifedipine

3: Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine 3,5-dicarboxylate 4: Dimethyl 2,6-dimethyl-4-(3-methylphenyl)-1,4-dihydropyridine 3,5-dicarboxylate

5: Dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine 3,5-dicarboxylate 6: Dimethyl 2,6-dimethyl-4-(3-cyanophenyl)-1,4-dihydropyridine 3,5-dicarboxylate

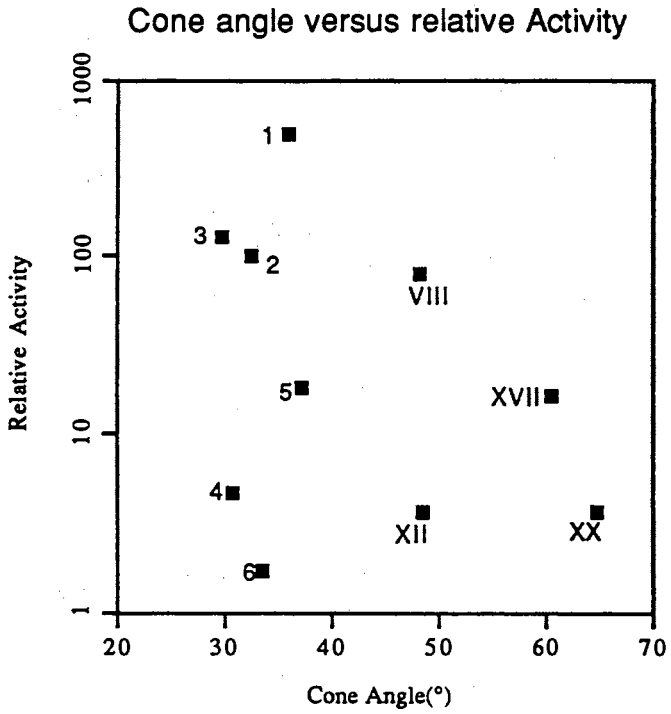
7: Dimethyl 2,6-dimethyl-4-(3-trifluoromethylphenyl)-1,4-dihydropyridine 3,5-dicarboxylate 8: Dimethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine 3,5-dicarboxylate

9: DimMethyl 2,6-dimethyl-4-(4-dimethylamino-phenyl)-1,4-dihydropyridine 3,5-dicarboxylate

Figure 24: Graph of the SUM+Deviation value versus the Relative activity of thirteen known compounds and the thirteen parent compounds of this work

This compound displays an activity of ~150, while the model calculates a theoretical activity of 145, very close to the true value.

The effect of the cone angle on activity was also investigated. A plot of the cone angle versus activity of six known compounds (including the four compounds in which activity was tested) was graphed (Figure 25). From this model it appears that the cone angle does not have a direct effect on activity, since compound XII and VII have very similar cone angles but very different activities.



1: Dimethyl 2,6-dimethyl-4-(2,3,4,5,6-pentafluorophenyl)-1,4-dihydropyridine 3,5-dicarboxylate
2: Nifedipine
3: Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine 3,5-dicarboxylate
4: Dimethyl 2,6-dimethyl-4-(3-methylphenyl)-1,4-dihydropyridine 3,5-dicarboxylate
5: Dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine 3,5-dicarboxylate
6: Dimethyl 2,6-dimethyl-4-(3-cyanophenyl)-1,4-dihydropyridine 3,5-dicarboxylate

Figure 25: Graph of the Cone Angle versus the Relative Activity of Known Compounds.

Energy Minimization

In any crystal structure, the molecule under study is affected by the packing of neighboring molecules in the crystal lattice. Therefore, it seemed logical to assume that the various parameters used in this study(the deviation value and SUM) would be affected by the packing of the molecules in the crystal lattice.

One of the continuing arguments in structural biochemistry concerns the use of X-ray structures in structure activity relationships, i. e. whether or not the X-ray structure reflects the actual conformation *in vivo*.

In order to address this issue, the molecular modeling program Discover was used to perform energy minimizations on the crystal structures of the thirteen parent compounds in the gas and aqueous phases. This program uses the expected values for bond lengths and angles to calculate a theoretical conformation of lowest energy. All thirteen parent compounds show a SUM value of approximately 50 degrees and a deviation value of approximately 60 degrees in the gas and aqueous phases. Hence, no differences were observed to correlate activity with variations in structure. Therefore, the X-ray structures were used in all subsequent analyses.

This has been approached historically by synthesizing rigid analogs which hold the structure in a predefined conformation and then examining the activity. Conformationally restrained analogs of the 1,4-DHP calcium antagonists[60] were studied in this way. Baldwin et al synthesized conformationally restricted analogs of the 1,4-DHP's where the phenyl ring was held in different positions, which then gave different deviation values[60]. Those compounds that exhibited the smallest deviation value showed the highest activtiy. Hence, Baldwin et. al. illustrated that at least one of the active conformations is that of the X-ray structure.

Decomposition Products

The decomposition products examined in this study are listed in TABLE 4. They display many differences when compared to their parent, unoxidized forms. The DHP ring has been oxidized to a pyridine ring, which has changed the overall conformation (Figure 31). Since the pyridine ring is planar, the 4-phenyl ring is not in a pseudoaxial position. The C7 and C10 carbon atoms of the phenyl ring are now coplanar with the C4 and N1 atoms of the pyridine ring and the phenyl ring is approximately perpendicular to the pyridine ring. Aromatization of the 1,4-dihydropyridine ring results in the loss of the hydrogen atom at N1, removing any possible hydrogen bonding interaction with the receptor site. However, the rotation of the 3,5 ester groups out of conjugation with the pi bonds of the ring may permit increased hydrogen bonding to these groups.

The conformation of the ester groups is changed significantly. In the majority of the more than 30 crystal structures of members of the nifedipine family, the ester groups are found to be nearly coplanar with the nearest double bond in the DHP ring, with the carbonyl group oriented either cis (sp, synperiplanar) or trans (ap, antiperiplanar) to that bond[3]. In nifedipine itself, the carbonyls of the ester groups are ap and sp and thus point in opposite directions. It is thought that only the sp conformation of the ester group permits hydrogen bonding to the carbonyl oxygen atom as an acceptor atom when the drug binds to its receptor site[25,28]. In the decomposition products, the carbonyl groups of the esters are no longer coplanar with any double bond in the pyridine ring. This could move the ester oxygens out of reach or within reach of possible H-bonding with the receptor site.

In order to observe how these conformational differences between the parent compounds and their decomposition products affected the activity, two decomposition products were submitted for activity testing. These were

compounds I and XXIII, which are decomposition products of nifedipine and nitrendipine respectively. These two compounds exhibited no activity. Therefore, it could be concluded that the conformational changes arising upon decomposition abolish the calcium antagonistic properties of the 1,4-DHP's, and that the ester position has significant interaction with the receptor site.

Receptor Docking Analysis

Since all drug molecules have specific interactions with their receptors, one of the goals of molecular modeling is to elucidate this interaction spatially using 3-dimensional models of the receptor and the ligand, and evaluating the affinity of the ligand for its receptor. This type of analysis can give insight into the different interactions occurring in the receptor-ligand model. The 3-D atomic coordinates of the receptor site proposed by Langs et al was used (Figure 12)[28]. The receptor cleft is that between the two Arginine side chains in which the phenyl ring is docked. Van der Waals interaction energy was used as a measure of the compounds affinity for the receptor site and the number of H- bonds was maximized allowing only reasonable H-Bond distances (1.9 - 2.8 Å).

Initially, compounds of known activities were docked at the receptor site to ascertain a favorable conformation. This was done using nifedipine, dimethyl 2,6-dimethyl-4-(2,3,4,5,6-pentaflourophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (5-F), nitrendipine, nisoldipine, dimethyl 2,6-dimethyl-4-(2-triflouromethylphenyl)-1,4-dihydropyridine-3,5-dicarboxylate (2-CF_3), felodipine, dimethyl 2,6-dimethyl-4-(3-cyanophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (3-CN), and dimethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (4-NO_2). Each molecule was brought slowly into contact with the receptor cavity as in Figure 12. Van der Waals interaction energy was minimized as much as possible by altering the position of the molecule. This was continued until a

minimum was found which maximized H-bonding of reasonable distances. The energy value that results can only be used as a guide to the relative activity, not as an indicator of the absolute value.

The six high activity compounds examined in the docking procedure gave interaction energy values in the range of 250 to 3000. This range was then considered as favorable. All of these compounds fit into the receptor cavity without difficulty, and with no great energy barrier (i.e. did not bump into anything before entering the receptor cavity). The number of H-bonds formed ranged from 1 to 5. The 3-CN compound, which is known to have a low activity, did not fit into the receptor without causing a very large increase in interaction energy (10^6). This was due to the large deviation value (36.28°), which caused the cyano group on the phenyl ring to bump into one of the arginine side chains protruding from the receptor cavity. The 4-NO_2 compound, also of low activity, could not fit into the receptor cavity because of negative interactions with the para-NO_2 group on the phenyl ring. The para-NO_2 group could not get past side chains extending from the receptor without a great increase in energy, therefore, the likelihood of this compound binding in the same manner as the high activity compounds above was low. This modeling provided information about the possible reasons for high or low activity.

Each of the compounds prepared in this study was modeled in the same way. These results are given in TABLE 6 below, which may be compared with modeling results of the known compounds. Conclusions were drawn about the relative binding affinities of all the compounds in this study.

The decomposition products displayed interaction energies in the range of 4.3×10^4 to 1×10^{14}. These energies were very high and therefore were not considered as indicative of a favorable interaction between the decomposition products and the receptor. The number of H-bonds varied for these compounds

(0 to 5). The decomposition product that displayed the lowest interaction energy was compound III. This compound contains carboxylic acid side chains, and hence encountered less resistance to binding than the others. All of the other decomposition products encountered much more resistance to binding. This could be explained from the fact that since the boat shaped DHP moiety is no longer present, the position of the ester side chains interfered much more. Figure 26 illustrates the binding conformation of the nitroso decomposition product of nifedipine, indicated by an arrow. When one compares this to Figure 12, it can easily be seen how structural changes on decomposition has adversely affected the binding process.

The thirteen parent compounds modeled in this way produced varying results. The main goal of this study was to elucidate the effect of the length and bulk of the ester side chains, therefore, the modeling was geared towards observing the interaction between the different ester side chains and the proposed receptor site.

Compound V, which contains ethyl alkyl groups, showed difficulty in binding because the ester group that was in the sp orientation bumped into the receptor core. This caused a great increase in interaction energy (6×10^3). Compound VII, with sp,sp propyl ester side chains, also displayed the same problem. The propyl groups tended to bump into the receptor core. This bumping interaction impedes the binding of both of these compounds. Other compounds with straight chain ester groups, compounds VIV (n-butyl), XIII (n-pentyl), XVII (n-hexyl), XVIV (n-heptyl) and XX (n-octyl) also display this problem. This adverse interaction appeared to be associated with the orientation of the ester groups. The ester orientation that seemed the most favorable for H-bonding interactions is sp, which allowed the most H-bonding to the arginine side chains from the keto oxygens. However, as the alkyl chain length increases, this

orientation becomes disadvantageous, because the ester groups hit the receptor core before binding can occur. Therefore, it would seem logical to conclude that the methyl side chains are optimum, if both esters contain the same alkyl group.

It has been reported in the literature that unsymmetrically substituted 1,4-DHP's are more active. This was observed in the modeling of the known compounds given in TABLE 6. Compounds 5-F and 2-CF3 are symmetrically substituted with methyl ester groups, only the phenyl substituents were varied. In the docking of these two compounds, there was no interference from the ester side chains. One H-bond was formed with each compound to the arginine side chain of the receptor, both times to the sp oriented ester. Nitrendipine, which contains an ethyl ester and a methyl ester, had a higher energy, but formed more H-bonds, involving both of its ester groups. Nisoldipine, which contains an isobutyl and a methyl ester, displayed one of the lowest binding energies. This was attributed to the fact that the isobutyl ester group was oriented ap, and therefore did not interfere with the binding process. The methyl ester was sp, which formed a H-bond from its keto oxygen to one of the arginine side chains.

The effect on the binding process of branching the ester alkyl groups was investigated. Compound VIII (isopropyl), had a much lower interaction energy than its straight chain counterpart. In the docking of this compound, branching in the isopropyl group did appear to be advantageous. As this compound was brought towards the receptor site, the isopropyl groups did not interfere, and once the compound was in its optimal binding position, an H-bond was formed between its sp ester and one of the arginine side chains. This favorable interaction suggests that this compound should have a relatively high activity (interaction energy : ~1500). Compound X (isobutyl) did not display such favorable interactions. Both ester groups are oriented sp, which caused the

orientation becomes disadvantageous, because the ester groups hit the receptor core before binding can occur. Therefore, it would seem logical to conclude that the methyl side chains are optimum, if both esters contain the same alkyl group.

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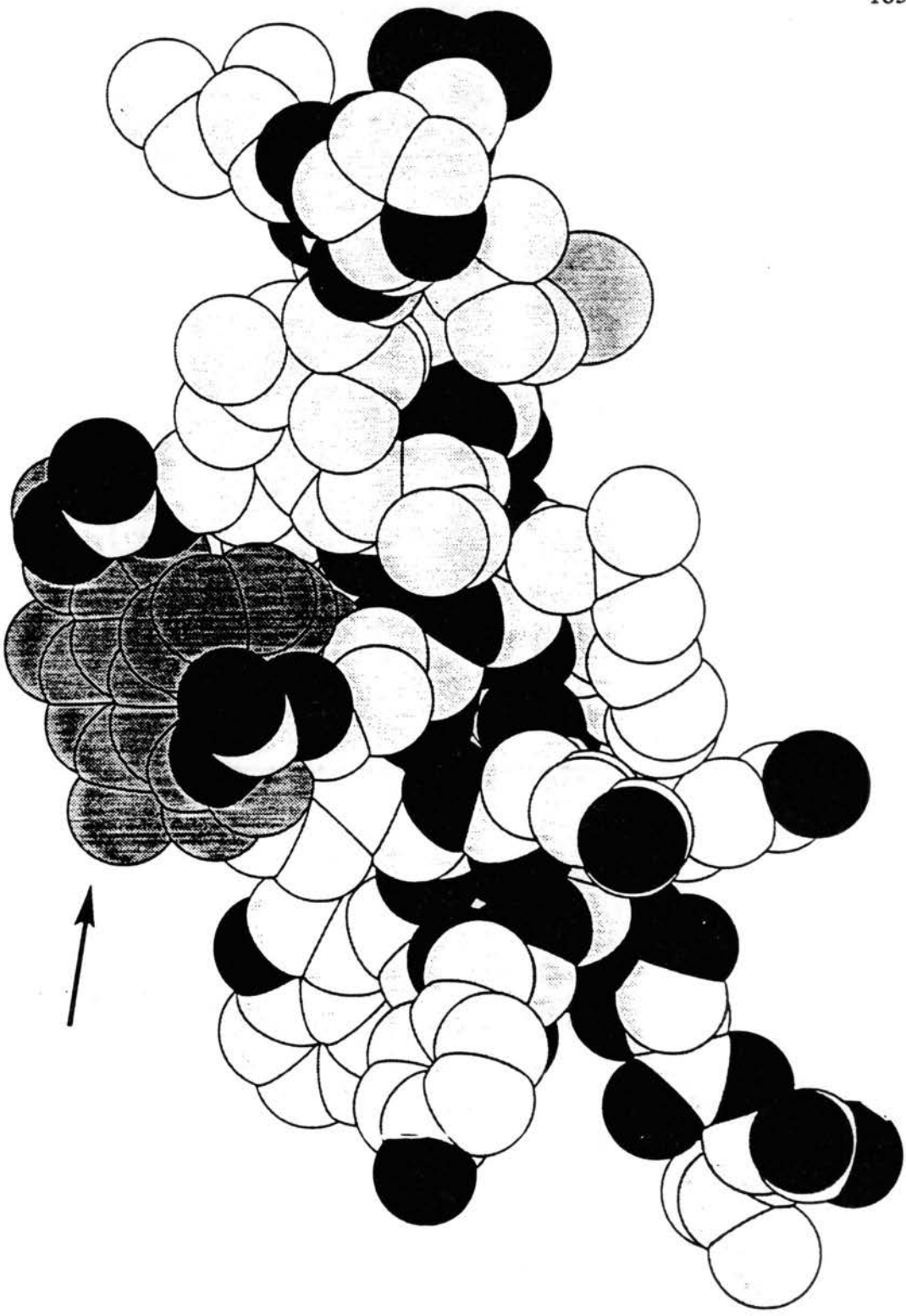

Figure 26: Nitroso Decomposition Product of Methyl 2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (Nifedipine) docked in Proposed Receptor Site

TABLE 6
Selected Docking Parameters

Compound	# H-bonds with Receptor	Relative energy of Binding
Nifedipine	2	256
Dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)-pyridine-3,5-dicarboxylate(I)	5	233402
Dimethyl 2,6-dimethyl-4-(2-nitrophenyl)-pyridine-3,5-dicarboxylate(II)	2	10^{10}
Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate	3	~7500
2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine • NO_3 • H_2O(III)	5	42607
Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate(IV)	2	653580
Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(V)	4	6000
Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate(VI)	1	10^8
Dipropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(VII)	5	79674
Di-isopropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(VIII)	3	1534
Dibutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(VIV)	5	17000
Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(X)	0	10^{10}
Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate(XI)	0	10^6
Di-*tert*-butyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(XII)	5	5.3×10^7
Dipentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(XIII)	4	10^9
Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(XIV)	0	10^{10}
Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate(XV)	0	10^{11}

Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate	5	10^{12}
Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate(XVI)	0	10^{12}
Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(XVII)	3	23256
Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate(XVIII)	0	10^{14}
Diheptyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(XVIV)	0	10^{15}
Dioctyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(XX)	0	10^{10}
Di(2-methoxy ethyl) 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(XXI)	4	10^{6}
(Dibenzyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) • 0.5 CH_3CN (XXII)	1	10^{8}
Ethyl methyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate • NO_3(XXIII)	2	71013
Nitrendipine	5	2752
5F Dimethyl 2,6-dimethyl-4-(2,3,4,5,6 pentafluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate	1	361
Nisoldipine	1	519
Felodipine	1	1500
Dimethyl 2,6-dimethyl-4-(2-trifluoromethyl-phenyl)-1,4-dihydropyridine-3,5-dicarboxylate	1	450
Dimethyl 2,6-dimethyl-4-(3-cyanophenyl)-1,4-dihydropyridine-3,5-dicarboxylate	1	10^{5}
Dimethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate	0	10^{6}

interaction energy (10^{10}) to be great. The position of both side chains impeded the approach of the molecule and hence precluded the formation of any H-bonds. Thus, compound X should not display a very high affinity for the receptor. Compound XII (*t*-butyl), encountered a different kind of problem on docking. Its

large deviation value (33.71°) impeded its approach to the receptor site and caused a high interaction energy (10^4). Therefore, this may explain why the deviation of the phenyl ring is important, i.e. lack of orthogonality interferes with the approach of the molecule to the receptor site. Compound XIV (isopentyl) encountered the same problem as the isobutyl derivative (X). Since both ester groups were oriented sp, approach to the receptor site was practically impossible without hitting the extending arginine side chains. The interaction energy was far too great to suspect any activity for this compound. Therefore, it can be concluded that branching of the side chains normally has a adverse effect on the binding process. However, this conclusion is dependent on the orientation of the ester groups. Interaction energy is less if one of the ester groups is oriented sp, and the other ap. When both esters are sp, approach to the receptor site is greatly impeded.

The ability of this model to predict relative activities was also tested using the four compounds submitted for activity analysis. The order given from the activity study was isopropyl >> n-hexyl >> t-butyl ~n-octyl. Based on the interaction energies obtained from the modeling study described above, the order is also isopropyl (1534) >> n-hexyl (23256) >> t-butyl (10^7) ~n-octyl (10^{10}) (TABLE 6). This order can be explained by the docking interactions encountered for each individual compound.

Compound VIII, which contains isopropyl ester groups is seen to slide easily underneath the two arginine side chains (Figure 27). Also, the low deviation value (nearly ideal bisection of the DHP ring) allows this compound to enter the receptor site without any great energy barrier. The interaction energy for this compound is 1534.

Compound XVII, which contains n-hexyl ester substituents has an interaction energy of 23256. This high interaction energy arises from the "

bumping" of the hexyl side chain into the receptor core. This adverse interaction occurs only for the side chain that is oriented sp (Figure 28). The ap ester group does not interfere with the binding of this molecule. The high interaction energy precludes great activity on this compounds part. Compound XX, with the octyl ester alkyl groups is known to have a lower activity than that of the n-hexyl derivative. The n-octyl derivative has two more carbon atoms in its alkyl side chain that interfere to a greater extent than that of the n-hexyl alkyl side chains (Figure 29). This is indicated by the much greater interaction energy observed for this compound (10^{10}).

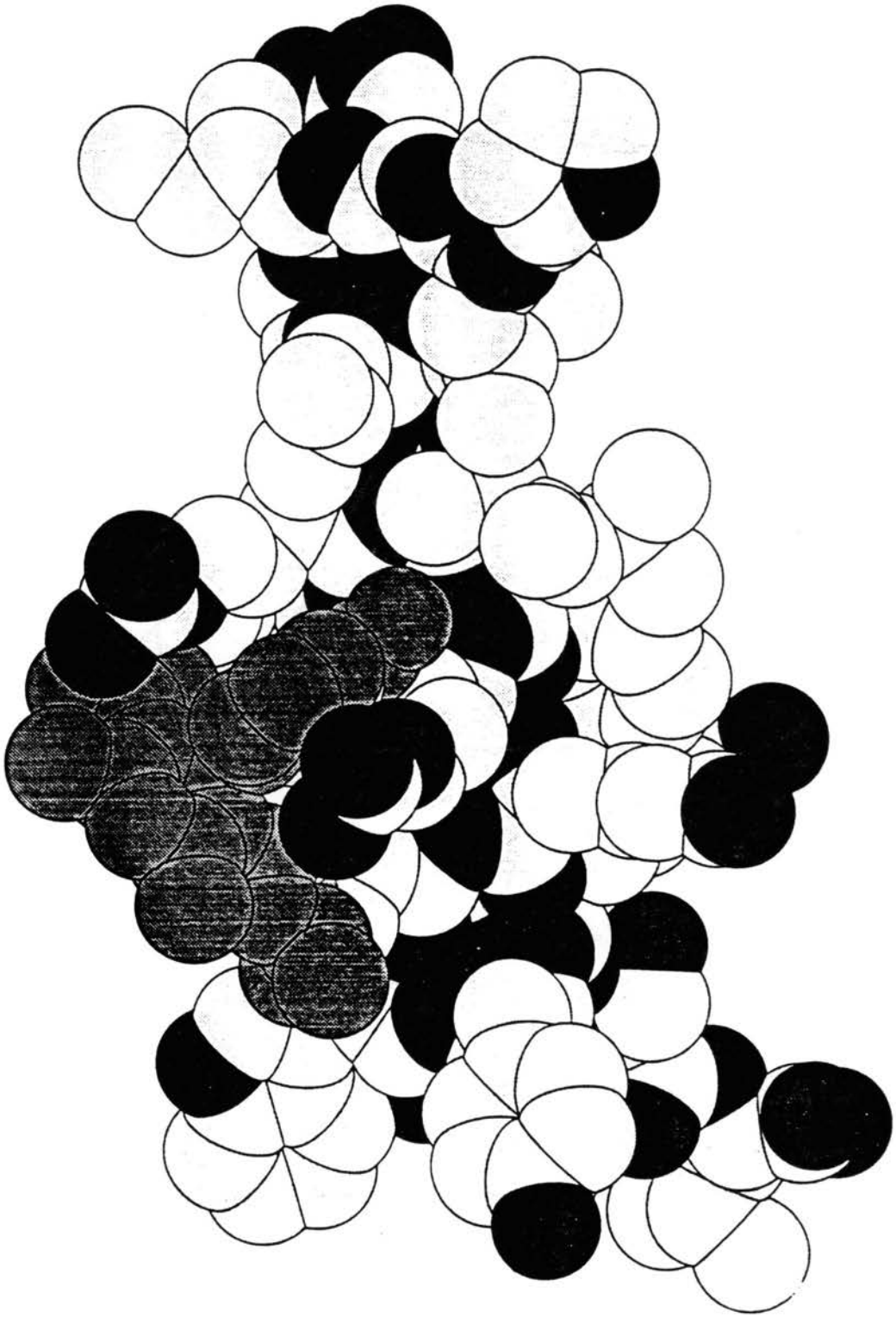

Figure 27- Di-isopropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(VIII) docked in proposed receptor site

Figure 28 - Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(VIII) docked in proposed receptor site

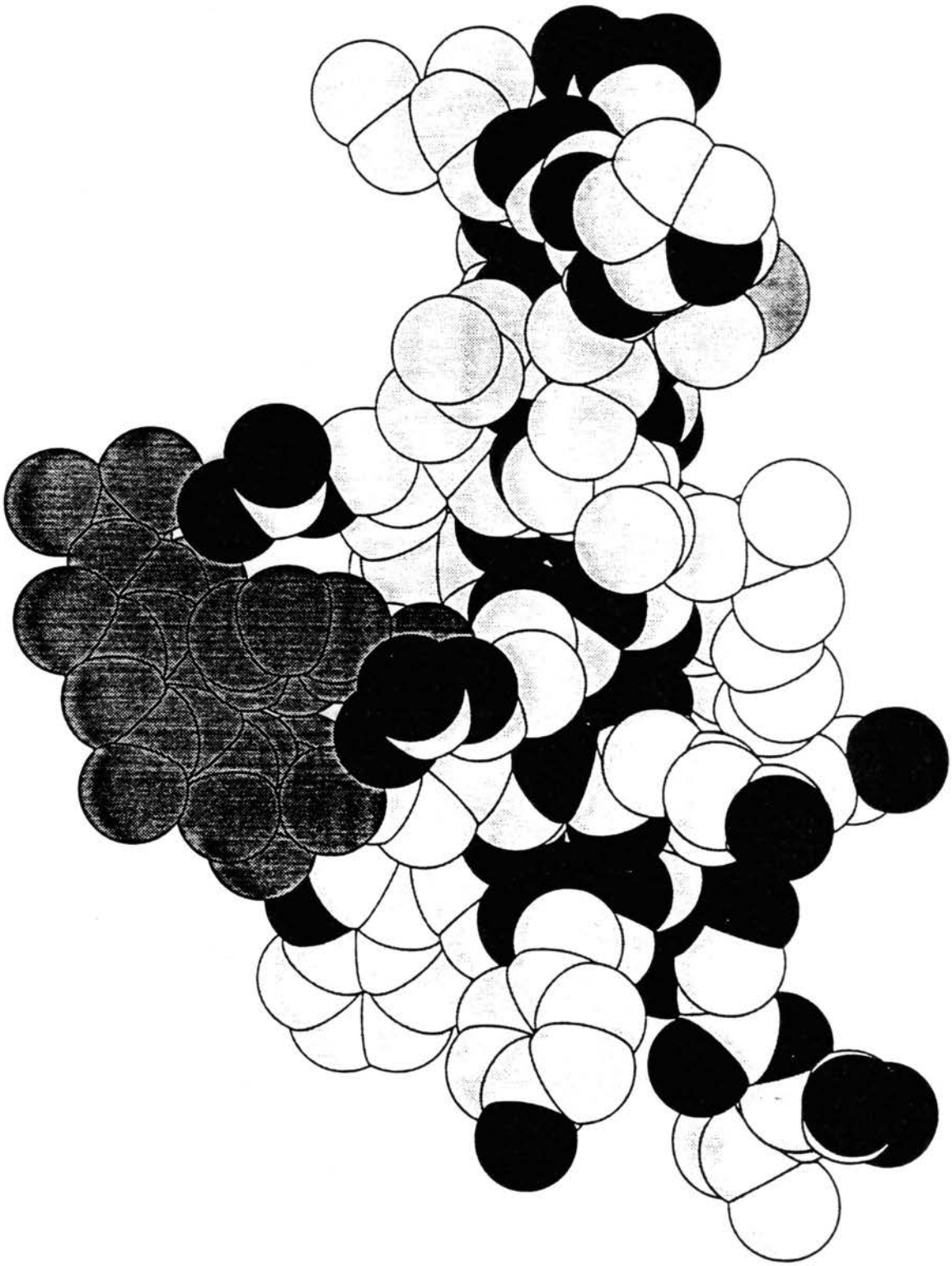

Figure 29- Dioctyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(VIII) docked in proposed receptor site

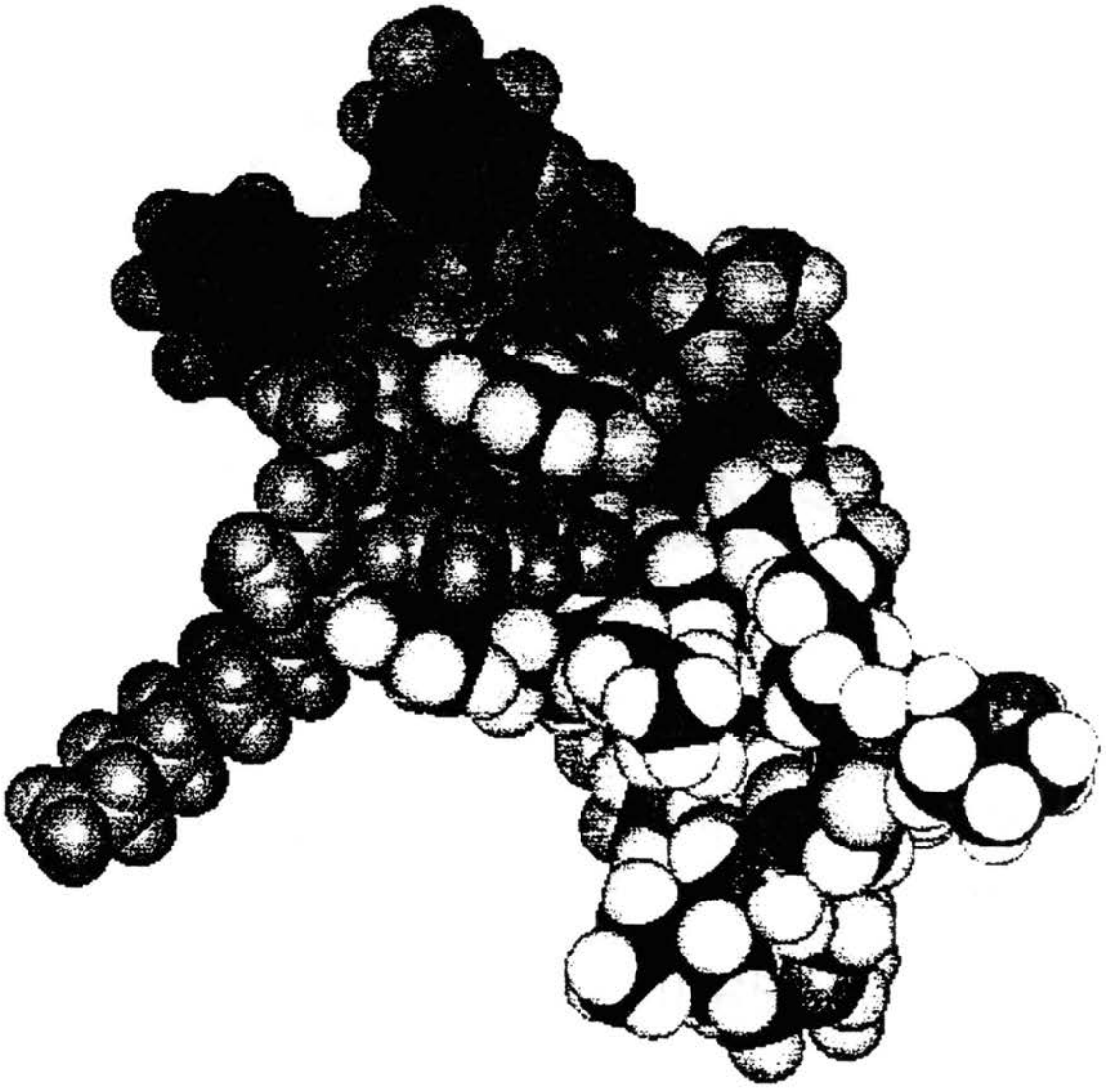

Figure 30 - Di-*tert*-butyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(VIII) docked in proposed receptor site

Conclusion

The questions to be addressed in this thesis were 1) How does the identity of the ester alkyl group affect the deviation of the phenyl ring, the planarity of the DHP ring, and the conformation of the esters (ap vs sp) and 2) based on these parameters, how does the identity of the ester alkyl group affect activity? Moreover, the conformational changes associated with decomposition to the nitro-pyridine derivatives and their potential effects on the calcium antagonistic activity of these compounds was investigated.

It appears the identity of the ester alkyl group has an effect on most of the significant parameters. The deviation value increases with the number of carbon atoms. It has been shown that as the number of carbon atoms in the chain increases, activity decreases. The SUM value is affected in the same manner by the length of the carbon chain. It has been shown that as the length of the ester group increases, the SUM increases and activity decreases. The cone angle, which is a reflection of the primary, secondary or tertiary character of the esterification group demonstrates the opposite effect of that expected. The initial hypothesis was that as the cone angle increased, the deviation value would decrease, due to increased bulk of neighboring groups. However, most bulky esterification groups exhibit ap, sp conformation of the ester groups and the phenyl ring tilts away from the bulk of the sp ester group, and thus the deviation value increases. This conclusion agrees with the fact that as the ester alkyl groups size increases, the deviation value increases and activity decreases.

Based on the molecular modeling analysis of the receptor-ligand complex, the general trend is that increasing the alkyl chain length causes a decrease in binding affinity due to increased repulsive interactions. Branching in the ester alkyl group decreases this repulsion, but only if the number of carbons is below three. One of the compounds prepared in this study, di-isopropyl 2,6-dimethyl-4-

(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VIII), exhibited an activity value comparable to the high activity compound nitrendipine .

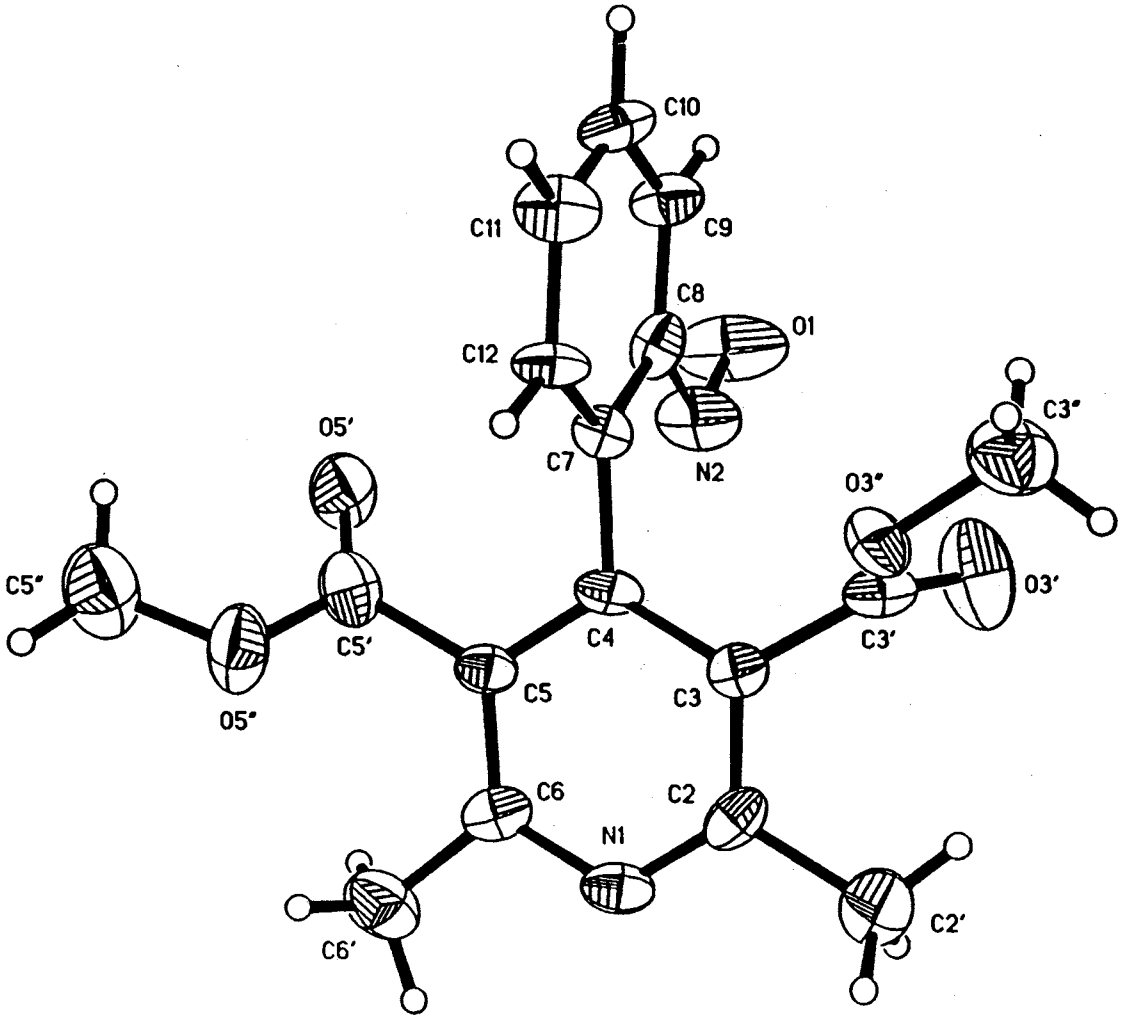

Figure 31: Projection view of Methyl 2,6-dimethyl-4-(2-nitrosophenyl)-pyridine-3,5-dicarboxylate(I)

TABLE 7

CRYSTAL DATA FOR

Dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)-pyridine-3,5-dicarboxylate (I)

Formula	$C_{17}H_{16}N_2O_5$'
M. W.	328.3 g $mole^{-1}$
a	18.171(4) Å
b	7.157(1) Å
c	26.165(5) Å
α	90.0 °
β	90.2 (1)°
γ	90.0 °
V	3402.6(13) $Å^3$
F(000)	1376
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.282 g/cm^3
Z	8
Meas refl	7522
Obs refl	1328
R	6.3%
R_w	10.0%
G. O. F.	1.136
Space Group	$P2_1/c$
Octants meas	$-1 \leq h \leq 19, -1 \leq k \leq 8, -31 \leq l \leq 31$

TABLE 8

POSITIONAL PARAMETERS FOR

Dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)-pyridine-3,5-dicarboxylate (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.2852(3)	-0.1787(8)	0.0848(2)
C2	0.3300(3)	-0.0918(10)	0.0523(2)
C2'	0.3326(3)	-0.1806(9)	0.0005(2)
C3	0.3726(3)	0.0585(10)	0.0668(2)
C3'	0.4241(4)	0.1545(10)	0.0296(3)
O3'	0.4883(2)	0.1801(8)	0.03731(15)
O3"	0.3876(2)	0.2127(8)	-0.0108(2)
C3"	0.4316(4)	0.2938(11)	-0.0510(2)
C4	0.3715(3)	0.1225(9)	0.1177(2)
C5	0.3225(3)	0.0309(9)	0.1508(2)
C5'	0.3181(3)	0.0904(11)	0.2059(3)
C5"	0.2796(3)	0.3342(9)	0.2607(2)
O5'	0.3384(3)	-0.0012(8)	0.2409(2)
O5"	0.2867(2)	0.2539(7)	0.2100(2)
C6	0.2818(3)	-0.1207(10)	0.1329(3)
C6'	0.2298(3)	-0.2199(9)	0.1683(2)
C7	0.4183(3)	0.2808(10)	0.1360(2)
C8	0.3990(3)	0.4600(10)	0.1288(2)
C9	0.4400(4)	0.6035(10)	0.1489(2)
C10	0.5028(4)	0.5665(10)	0.1773(3)
C11	0.5239(3)	0.3854(10)	0.1846(2)
C12	0.4830(3)	0.2433(10)	0.1639(2)
N2	0.5020(3)	0.0504(9)	0.1690(2)
O1A	0.5649(17)	0.0186(33)	0.1865(14)
O1B	0.5550(22)	0.0264(41)	0.1929(15)
N91	0.0632(4)	0.2394(8)	-0.0383(2)
C92	0.0034(4)	0.3288(10)	-0.0554(2)
C92'	-0.0674(3)	0.2501(9)	-0.0354(2)
C93	0.0064(3)	0.4696(10)	-0.0901(2)
C93'	-0.0625(4)	0.5461(12)	-0.1138(3)
C93"	-0.1711(14)	0.7197(44)	-0.1023(9)
C93X	-0.1492(19)	0.7960(49)	-0.1132(12)
O93'	-0.0845(2)	0.5016(7)	-0.1544(2)
O93"	-0.0903(33)	0.6592(75)	-0.0784(15)
O93X	-0.1004(29)	0.6788(61)	-0.0900(14)
C94	0.0739(4)	0.5358(10)	-0.1080(2)
C95	0.1370(4)	0.4472(10)	-0.0896(2)

TABLE 8 (Continued)

C95'	0.2129(5)	0.4977(14)	-0.1100(3)
C95"	0.2871(4)	0.7447(12)	-0.1359(2)
O95'	0.2583(3)	0.3847(10)	-0.1222(2)
O95"	0.2208(3)	0.6802(9)	-0.1111(2)
C96	0.1295(4)	0.2991(11)	-0.0556(2)
C96'	0.1932(4)	0.1850(12)	-0.0359(2)
C97	0.0749(3)	0.6917(10)	-0.1452(2)
C98	0.0605(4)	0.8694(11)	-0.1304(3)
C99	0.0592(4)	1.0135(10)	-0.1652(3)
C910	0.0735(3)	0.9826(10)	-0.2163(3)
C911	0.0855(3)	0.8038(10)	-0.2323(2)
C912	0.0881(3)	0.6577(10)	-0.1976(2)
N92	0.1012(3)	0.4688(9)	-0.2111(2)
O91	0.1145(3)	0.4430(7)	-0.2563(2)
H2'A	0.2992(3)	-0.2845(9)	-0.0009(2)
H2'B	0.3184(3)	-0.0894(9)	-0.0246(2)
H2'C	0.3816(3)	-0.2232(9)	-0.0065(2)
H3"A	0.4013(4)	0.3286(11)	-0.0796(2)
H3"B	0.4534(4)	0.4038(11)	-0.0364(2)
H3"C	0.4698(4)	0.2108(11)	-0.0623(2)
H5"A	0.2565(3)	0.4549(9)	0.2607(2)
H5"B	0.2509(3)	0.2492(9)	0.2809(2)
H5"C	0.3282(3)	0.3442(9)	0.2749(2)
H6'A	0.2309(3)	-0.1661(9)	0.2019(2)
H6'B	0.1810(3)	-0.2104(9)	0.1544(2)
H6'C	0.2439(3)	-0.3490(9)	0.1702(2)
H8A	0.3566(3)	0.4898(10)	0.1084(2)
H9A	0.4253(4)	0.7314(10)	0.1444(2)
H10A	0.5324(4)	0.6652(10)	0.1913(3)
H11A	0.5666(3)	0.3580(10)	0.2050(2)
H92'D	-0.0593(3)	0.1506(9)	-0.0114(2)
H92'E	-0.0941(3)	0.3491(9)	-0.0190(2)
H92'F	-0.0955(3)	0.2041(9)	-0.0639(2)
H93"D	-0.1942(14)	0.8002(44)	-0.0778(9)
H93"E	-0.1573(14)	0.7912(44)	-0.1318(9)
H93"F	-0.2049(14)	0.6232(44)	-0.1123(9)
H93A	-0.1680(19)	0.8804(49)	-0.0879(12)
H93B	-0.1310(19)	0.8659(49)	-0.1418(12)
H93C	-0.1879(19)	0.7142(49)	-0.1245(12)
H95"A	0.2873(4)	0.8787(12)	-0.1375(2)
H95"B	0.3288(4)	0.7027(12)	-0.1164(2)
H95"C	0.2898(4)	0.6946(12)	-0.1699(2)
H96'H	0.1732(4)	0.0877(12)	-0.0149(2)
H96'I	0.2207(4)	0.1304(12)	-0.0635(2)
H96'J	0.2252(4)	0.2626(12)	-0.0158(2)
H98J	0.0483(4)	0.8934(11)	-0.0953(3)

TABLE 8 (Continued)

H99A	0.0483(4)	1.1360(10)	-0.1523(3)
H910A	0.0756(3)	1.0859(10)	-0.2397(3)
H111G	0.0929(3)	0.7757(10)	-0.2678(2)

TABLE 9

ANISOTROPIC THERMAL PARAMETERS FOR

Methyl 2,6-dimethyl-4-(2-nitrosophenyl)-pyridine-3,5-dicarboxylate(I)

ATOM	U11	U22	U33	U23	U13	U12
N1	38(3)	68(4)	78(4)	-9(4)	-4(3)	-1(3)
C2	34(4)	53(5)	70(5)	-13(4)	-12(4)	10(4)
C2'	62(4)	111(7)	77(5)	-19(5)	-17(4)	10(5)
C3	35(4)	62(5)	63(4)	4(4)	-5(3)	6(4)
C3'	67(5)	78(6)	53(4)	-1(4)	12(4)	14(5)
O3'	50(3)	139(5)	74(3)	0(3)	5(3)	-7(4)
O3"	68(3)	147(5)	74(3)	34(4)	1(3)	8(4)
C3"	99(6)	181(10)	88(5)	17(7)	2(5)	10(7)
C4	36(4)	68(5)	62(4)	4(4)	-11(3)	9(4)
C5	40(4)	48(5)	54(4)	1(4)	-7(3)	7(4)
C5'	35(4)	64(6)	62(5)	-1(5)	0(3)	2(4)
C5"	98(6)	102(7)	86(5)	-38(5)	12(4)	-5(5)
O5'	133(4)	138(6)	74(3)	32(4)	-10(3)	58(4)
O5"	81(3)	67(4)	63(3)	-7(3)	-1(3)	10(3)
C6	41(4)	51(5)	73(5)	14(4)	7(4)	5(4)
C6'	77(5)	91(6)	106(5)	13(5)	3(4)	-18(5)
C7	33(4)	50(5)	59(4)	-2(4)	-1(3)	5(4)
C8	41(4)	50(5)	83(5)	0(4)	-12(3)	4(4)
C9	61(5)	53(5)	111(6)	-8(5)	-2(4)	9(5)
C10	55(5)	55(6)	101(5)	-14(5)	0(4)	-9(5)
C11	47(4)	55(5)	87(5)	-2(4)	-11(4)	-3(4)
C12	50(4)	43(5)	67(4)	3(4)	1(3)	3(4)
N2	65(5)	63(5)	113(5)	8(4)	-34(4)	13(4)
O1A	54(12)	46(12)	244(28)	-26(14)	-92(13)	8(9)
O1B	113(23)	146(23)	208(25)	85(18)	-81(18)	33(16)
N91	92(5)	70(5)	51(3)	16(3)	2(4)	7(4)
C92	80(5)	61(5)	40(4)	3(4)	10(4)	0(5)
C92'	92(5)	100(7)	67(4)	23(5)	2(4)	-9(5)
C93	58(4)	63(5)	34(3)	7(4)	3(3)	4(4)
C93'	60(5)	77(6)	48(5)	-3(5)	-2(4)	-14(5)
C93"	89(18)	120(25)	79(15)	-11(16)	-49(15)	59(18)
C93X	139(25)	130(31)	156(22)	43(18)	48(18)	10(20)
O93'	63(3)	140(5)	63(3)	-24(3)	-13(2)	2(3)
O93"	95(12)	186(24)	91(27)	-37(20)	-41(20)	93(13)

TABLE 9 (Continued)

O93X	139(33)	100(15)	31(7)	-28(8)	-59(11)	55(16)
C94	65(5)	59(5)	37(4)	-4(4)	2(4)	9(4)
C95	66(5)	73(6)	37(4)	9(4)	5(4)	0(5)
C95'	77(7)	94(8)	57(5)	14(6)	-15(5)	-5(7)
C95"	98(6)	221(12)	95(6)	40(7)	-4(5)	-41(8)
O95'	91(4)	171(7)	117(4)	0(4)	26(3)	48(4)
O95"	54(3)	123(5)	91(4)	7(4)	8(3)	-12(4)
C96	78(5)	77(6)	49(4)	14(4)	-9(4)	30(5)
C96'	102(6)	209(11)	88(5)	55(6)	5(5)	50(7)
C97	48(4)	50(5)	52(4)	4(4)	2(3)	1(4)
C98	101(6)	66(6)	56(4)	7(5)	0(4)	9(5)
C99	110(6)	62(6)	69(5)	-9(5)	12(5)	6(5)
C910	82(5)	54(6)	68(5)	14(4)	-2(4)	-6(5)
C911	68(5)	61(5)	53(4)	14(4)	-3(4)	-11(5)
C912	47(4)	48(5)	58(4)	-1(4)	-3(3)	4(4)
N92	86(4)	70(5)	55(3)	1(4)	8(3)	7(4)
O91	39(4)	96(4)	60(3)	-11(3)	23(3)	8(4)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE 10

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)-pyridine-3,5-dicarboxylate (I)

N1-C6	1.326(7)	C6-N1-C2	119.3(6)
N1-C2	1.332(7)	N1-C2-C3	122.2(6)
C2-C3	1.378(7)	N1-C2-C2'	113.6(6)
C2-C2'	1.500(7)	C3-C2-C2'	124.1(7)
C3-C4	1.408(7)	C2-C3-C4	120.3(6)
C3-C3'	1.518(8)	C2-C3-C3'	121.6(6)
C3'-O3'	1.197(7)	C4-C3-C3'	118.0(6)
C3'-O3"	1.315(7)	O3'-C3'-O3"	125.2(7)
O3"-C3"	1.446(6)	O3'-C3'-C3	124.3(7)
C4-C5	1.406(7)	O3"-C3'-C3	110.4(6)
C4-C7	1.495(8)	C3'-O3"-C3"	115.6(5)
C5-C6	1.394(7)	C3-C4-C5	116.2(6)
C5-C5'	1.506(7)	C3-C4-C7	122.6(6)
C5'-O5'	1.183(7)	C5-C4-C7	121.2(6)
C5'-O5"	1.307(7)	C6-C5-C4	119.5(6)
C5"-O5"	1.453(6)	C6-C5-C5'	120.8(6)
C6-C6'	1.503(7)	C4-C5-C5'	119.5(6)
C7-C8	1.343(7)	O5'-C5'-O5"	124.5(7)
C7-C12	1.407(7)	O5'-C5'-C5	124.5(7)
C8-C9	1.373(7)	O5"-C5'-C5	110.9(6)
C9-C10	1.385(7)	C5'-O5"-C5"	118.1(5)
C10-C11	1.365(8)	N1-C6-C5	122.4(6)
C11-C12	1.370(7)	N1-C6-C6'	117.9(7)
C12-N2	1.429(8)	C5-C6-C6'	119.6(6)
N2-O1B	1.16(3)	C8-C7-C12	118.2(6)
N2-O1A	1.25(3)	C8-C7-C4	122.1(6)
N91-C92	1.338(7)	C12-C7-C4	119.7(6)
N91-C96	1.358(7)	C7-C8-C9	121.3(6)
C92-C93	1.357(7)	C8-C9-C10	120.5(7)
C92-C92'	1.500(7)	C11-C10-C9 1	19.1(7)
C93-C94	1.397(7)	C10-C11-C12	119.9(6)
C93-C93'	1.501(8)	C11-C12-C7	121.0(6)
C93'-O93'	1.176(6)	C11-C12-N2	123.3(6)
C93'-O93"	1.33(5)	C7-C12-N2	115.7(6)
C93'-O93X	1.33(5)	O1A-N2-C12	115.5(12)
C93"-O93X	1.36(6)	C92-N91-C96	117.4(6)
C93"-O93"	1.65(5)	N91-C92-C93	122.9(6)
C93X-O93X	1.36(5)	N91-C92-C92'	113.7(6)
C93X-O93"	1.71(6)	C93-C92-C92'	123.3(7)
C94-C95	1.394(7)	C92-C93-C94	121.0(6)
C94-C97	1.481(8)	C92-C93-C93'	120.8(6)

TABLE 10 (Continued)

C95-C96	1.391(8)	C94-C93-C93'	118.0(6)
C95-C95'	1.525(9)	O93'-C93'-O93"	131.7(18)
C95'-O95'	1.199(8)	O93'-C93'-C93	123.7(7)
C95'-O95"	1.315(8)	O93"-C93'-C93	104.5(18)
C95"-O95"	1.445(7)	C93'-O93"-C93"	103.5(24)
C96-C96'	1.506(8)	C95-C94-C93	116.8(6)
C97-C98	1.355(8)	C95-C94-C97	123.9(6)
C97-C912	1.413(7)	C93-C94-C97	119.3(6)
C98-C99	1.376(8)	C96-C95-C94	119.1(6)
C99-C910	1.381(7)	C96-C95-C95'	119.6(7)
C910-C911	1.364(8)	C94-C95-C95'	121.0(6)
C911-C912	1.386(7)	O95'-C95'-O95"	126.1(9)
C912-N92	1.418(7)	O95'-C95'-C95	123.9(9)
N92-O91	1.221(5)	O95"-C95'-C95	110.0(8)
		C95'-O95"-C95"	114.8(7)
		N91-C96-C95	122.8(6)
		N91-C96-C96'	113.4(7)
		C95-C96-C96'	123.7(7)
		C98-C97-C912	118.2(6)
		C98-C97-C94	121.1(6)
		C912-C97-C94	120.7(6)
		C97-C98-C99	121.1(6)
		C98-C99-C910	121.2(7)
		C911-C910-C99	118.5(6)
		C910-C911-C912	120.8(6)
		C911-C912-N92	124.1(6)
		C911-C912-C97	120.0(6)
		N92-C912-C97	115.9(6)
		O91-N92-C912	114.8(6)

TABLE 11

TORSION ANGLES (°) FOR

Dimethyl 2,6-dimethyl-4-(2-nitrosophenyl)-pyridine-3,5-dicarboxylate (I)

C6-N1-C2-C3	-0.72	C6-N1-C2-C2'	175.68
N1-C2-C3-C4	1.78	C2'-C2-C3-C4	-174.23
N1-C2-C3-C3'	179.16	C2'-C2-C3-C3'	3.15
C2-C3-C3'-O3'	-126.31	C4-C3-C3'-O3'	51.13
C2-C3-C3'-O3"	56.66	C4-C3-C3'-O3"	-125.90
O3'-C3'-O3"-C3"	7.62	C3-C3'-O3"-C3"	-175.37
C2-C3-C4-C5	-3.10	C3'-C3-C4-C5	179.43
C2-C3-C4-C7	177.98	C3'-C3-C4-C7	0.51
C3-C4-C5-C6	3.48	C7-C4-C5-C6	-177.58
C3-C4-C5-C5'	179.78	C7-C4-C5-C5'	-1.29
C6-C5-C5'-O5'	65.12	C4-C5-C5'-O5'	-111.13
C6-C5-C5'-O5"	-112.74	C4-C5-C5'-O5"	71.01
O5'-C5'-O5"-C5"	3.50	C5-C5'-O5"-C5"	-178.64
C2-N1-C6-C5	1.16	C2-N1-C6-C6'	179.06
C4-C5-C6-N1	-2.64	C5'-C5'-C6'-N1	-178.89
C5'-C5-C6-C6'	3.24	C5-C4-C7-C8	-97.16
C3-C4-C7-C8	81.71	C3-C4-C7-C12	79.48
C3-C4-C7-C12	-101.66	C12-C7-C8-C9	-1.29
C4-C7-C8-C9	175.40	C7-C8-C9-C10	-0.04
C8-C9-C10-C11	0.68	C9-C10C11-C12	0.07
C10-C11-C12-C7	-1.44	C10-C11-C12-N2	178.83
C8-C7-C12-C11	2.04	C4-C7-C12-C11	-174.73
C8-C7-C12-N2	-178.21	C4-C7-C12-N2	5.02
C11-C12-N2-O1A	-11.27	C7-C12-N2-O1A	168.99
C96-N91-C92-C93	2.33	C96-N91-C92-C92'	178.36
N91-C92-C93-C94	-3.35	C92'-C92-C93-C94	-179.00
N91-C92-C93-C93'	170.84	C92'-C92-C93-C93'	-4.81
C92-C93-C93'-O93'	-98.32	C94-C93-C93'-O93'	76.05
C92-C93-C93'-O93"	78.96	C94-C93-C93'-O93"	-106.68
O93'-C93'O93"-C93"	4.07	C93-C93'-O93"-C93"	-172.89
C92-C93-C94-C95	1.62	C93'-C93'-C94-C95	-172.73
C92-C93-C94-C97	-179.00	C93'-C93-C94-C97	6.64
C93-C94-C95-C96	0.84	C97-C94-C95-C96	-178.50
C93-C94-C95-C95'	174.97	C97-C94-C95-C95'	-4.37
C96-C95-C95'-O95'	40.19	C94-C95-C95'-O95'	-133.91
C96-C95-C95'-O95"	-138.71	C94-C95-C95'-O95"	47.19
O95'-C95'-O95"-C95"	8.68	C95-C95'-O95"-C95"	-172.45
C92-N91-C96-C95	0.28	C92-N91-C96-C96'	-177.64
C94-C95-C96-N91	-1.84	C95'-C95-C96-N91	-176.05
C94-C95-C96-C96'	175.87	C95'-C95-C96-C96'	1.66
C95-C94-C97-C98	-106.40	C93-C94-C97-C98	74.28

TABLE 11 (Continued)

C95-C94-C97-C912	76.23	C93-C94-C97-C912	-103,09
C912-C97-C98-C99	-0.55	C94-C97-C98-C99	-177.98
C97-C98-C99-C910	-0.75	C98-C99-C910-C911	3.09
C99-C910-C91-C912	-4.14	C910-C911-C912-C97	2.91
C910-C911-C912-N92	-179.29	C98-C97-C912-C911	-0.50
C94-C97-C912-C911	176.94	C98-C97-C912-N92	-178.48
C94-C97-C912-N92	-1.03	C911-C912-N92-O91	4.11
C97-C912-N92-O91	-178.01		

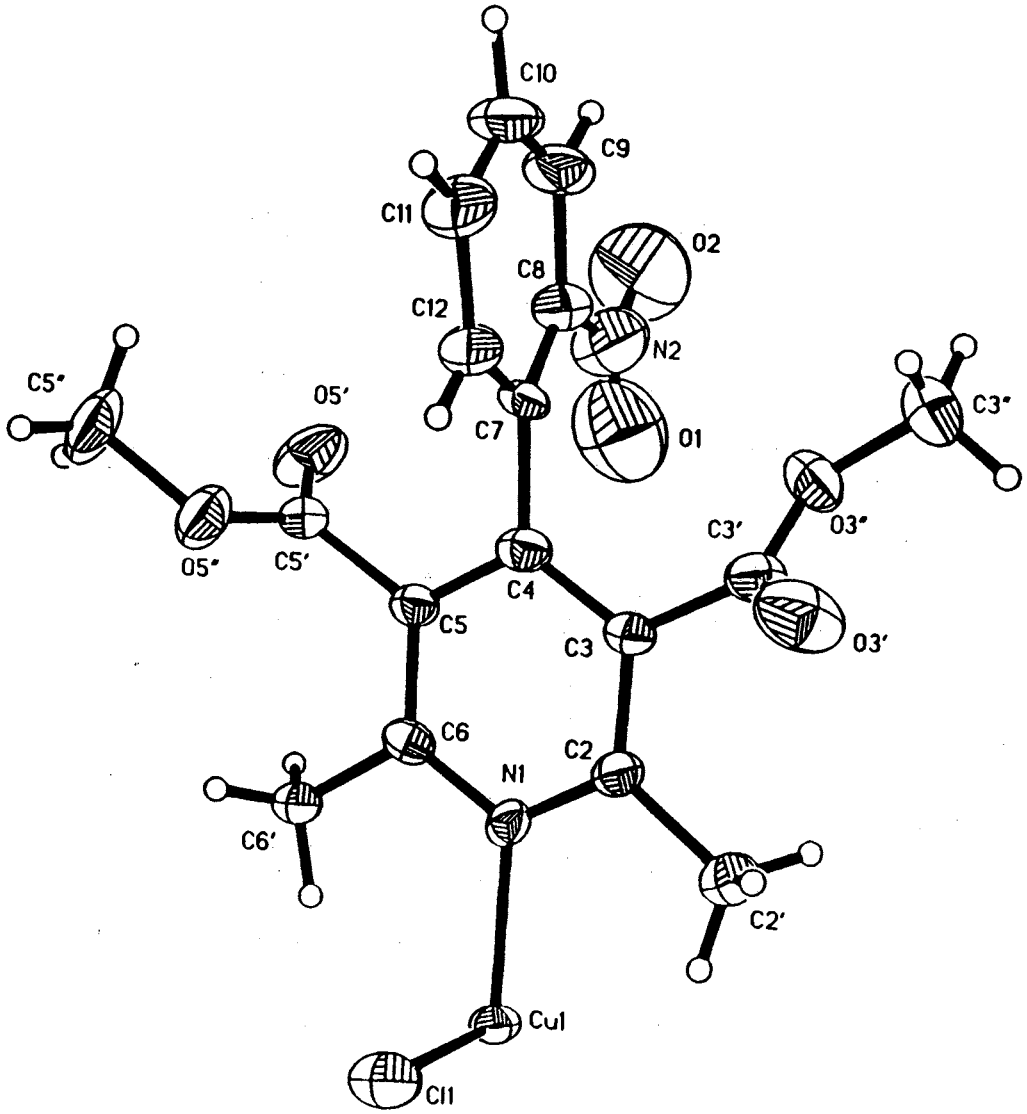

Figure 32: Projection view of Bis(2,6-dimethyl-3,5-dicarbomethoxy-4-(2-nitrophenyl)-pyridine)dichloro-copper(II)(II)

TABLE 12

CRYSTAL DATA FOR

Bis(2,6-dimethyl-3,5-dicarbomethoxy-4-(2-nitrophenyl)pyridine)$_2$dichloro-copper(II) (II)

Formula	$C_{34}\ H_{32}\ Cl_2\ Cu\ N_4\ O_{12}$
M. W.	823.1 g mole^{-1}
a	13.184(3) Å
b	7.768(2) Å
c	17.736(4) Å
α	90.0 °
β	91.5 (3)°
γ	90.0 °
V	1815.5(7) Å^3
F(000)	846
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.506 g/cm^3
Z	2
Meas refl	4231
Obs refl	1262
R	5.8%
R_w	7.1%
G. O. F.	1.70
Space Group	$P_{21/n}$
Octants meas	$-1 \le h \le 15, -1 \le k \le 9, -21 \le l \le 21$

TABLE 13

POSITIONAL PARAMETERS FOR

Bis(2,6-dimethyl-3,5-dicarbomethoxy-4-(2-nitrophenyl)pyridine)$_2$dichloro-copper(II) (II)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Cu1	0.0	0.0	0.0
Cl1	-0.1450(2)	0.1416(3)	0.0165(1)
N1	-0.0012(4)	0.069(1)	-0.1111(4)
C2	-0.0505(6)	-0.029(1)	-0.1624(5)
C2'	-0.0997(7)	-0.193(1)	-0.1338(5)
H2'A	-0.0901	-0.2002	-0.0801
H2'B	-0.1710	-0.1900	-0.1463
H2'C	-0.0693	-0.2906	-0.1572
C3	0.0540(6)	0.018(1)	-0.2384(4)
C4	-0.0068(6)	0.166(1)	-0.2615(5)
C5	0.0419(6)	0.269(1)	-0.2084(4)
C5'	0.0879(8)	0.436(1)	-0.2308(6)
C5"	0.2004(10)	0.57(1)	-0.3108(8)
H5"A	0.2489	0.5410	-0.3482
H5"B	0.1484	0.6416	-0.3332
H5"C	0.2339	0.6312	-0.2702
O5'	0.0654(7)	0.572(1)	-0.2048(5)
O5"	0.1555(5)	0.417(1)	-0.2823(4)
C6	0.0418(6)	0.219(1)	-0.1328(5)
C6'	0.0921(7)	0.326(1)	-0.0705(5)
H6'A	0.0818	0.2700	-0.0230
H6'B	0.1634	0.3329	-0.0795
H6'C	0.0640	0.4399	-0.0693
C7	-0.0173(7)	0.219(1)	-0.3432(5)
C8	-0.0988(8)	0.327(1)	-0.3643(6)
H8A	-0.1440	0.3669	-0.3264
C9	-0.1165(10)	0.371(1)	-0.4385(8)
H9A	-0.1707	0.4471	-0.4536
C10	-0.0491(13)	0.309(2)	-0.4918(7)
H10A	-0.0628	0.3365	-0.5439
C11	0.0317(11)	0.210(1)	-0.4743(6)
H11A	0.0786	0.1737	-0.5116
C12	0.0418(8)	0.167(1)	-0.3991(5)
N2	0.1249(17)	0.064(2)	-0.3867(10)
O1	0.1451(13)	0.016(2)	-0.3364(12)
O2	0.1807(10)	0.004(2)	-0.4326(9)
O3"	-0.2068(5)	-0.587(9)	-0.2975(4)

TABLE 13 (Continued)

O3'	-0.0697(6)	-0.191(1)	-0.3368(4)
C3'	-0.1103(8)	-0.094(1)	-0.2959(5)
C3"	-0.2676(8)	-0.15(1)	-0.3562(7)
H3"A	-0.3375	-0.1159	-0.3540
H3"B	-0.2429	-0.1266	-0.4056
H3"C	-0.2618	-0.2708	-0.3458

TABLE 14

ANISOTROPIC THERMAL PARAMETERS FOR

Bis(2,6-dimethyl-3,5-dicarbomethoxy-4-(2-nitrophenyl)pyridine)$_2$dichloro-copper(II) (II)

ATOM	U11	U22	U33	U23	U13	U12
N1	38(3)	68(4)	78(4)	-9(4)	-4(3)	-1(3)
Cu1	41(1)	56(1)	25(1)	1(1)	0(1)	2(1)
Cl1	55(2)	94(2)	49(1)	24(1)	2(1	4(1)
N1	26(3)	56(5)	35(4)	0(3)	-1(3)	-9(4)
C2	39(4)	42(7)	39(5)	9(4)	12(4)	-2(4)
C2'	65(6)	64(7)	32(5)	-20(5)	3(4)	0(5)
C3	43(4)	43(5)	32(4)	0(5)	6(3)	-4(5)
C4	46(5)	56(7)	33(5)	6(5)	6(4)	4(5)
C5	44(5)	36(6)	32(5)	-1(4)	2(4)	4(4)
C5'	68(7)	49(7)	39(6)	4(5)	5(5)	-3(5)
C5"	121(10)	116(11)	83(10)	-68(9)	15(8)	7(8)
O5'	42(8)	65(5)	79(6)	2(5)	31(5)	5(5)
O5"	73(5)	82(5)	63(5)	-21(4)	22(4)	3(4)
C6	36(5)	58(6)	32(5)	2(5)	0(4)	-4(5)
C6'	72(7)	63(7)	44(6)	-7(6)	-7(5)	1(5)
C7	61(6)	59(7)	25(5)	-18(5)	15(4)	-1(5)
C8	78(8)	76(8)	48(7)	-14(7)	-18(5)	23(6)
C9	87(9)	90(10)	83(10	-5(8)	-28(7)	32(8)
C10	151(13)	112(12)	33(7)	-49(11)	-1(8)	6(8)
C11	122(11)	83(9)	40(7)	-23(9)	16(6)	-14(6)
C12	66(7)	75(8)	38(6)	-3(6)	-4(5)	6(6)
N2	161(17)	133(16)	94(13)	-37(12)	-34(12)	20(11)
O1	150(12)	171(13)	215(19)	3(11)	50(14)	-9(15)
O2	142(9)	241(15)	168(13)	29(10)	63(9)	-64(11)
O3"	58(4)	98(6)	63(5)	-14(4)	-9(4)	-27(4)
O3'	95(6)	104(6)	63(5)	12(5)	-11(4)	-41(5)
C3'	52(6)	66(7)	32(6)	-13(6)	1(4)	-2(5)
C3"	70(8)	151(13)	87(9)	-27(8)	-23(6)	-48(9)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE 15

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Bis(2,6-dimethyl-3,5-dicarbomethoxy-4-(2-nitrophenyl)pyridine)$_2$dichloro-copper(II) (II)

Cu1-Cl1	2.232(2)	Cl1-Cu1-N1	90.7(2)
Cu1-N1	2.041(7)	Cl1-Cu1-Cl1	180.0(1)
Cu1-Cl1	2.232(2)	N1-Cu1-Cl1	89.3(2)
Cu1-N1	2.041(7)	Cl1-Cu1-N1	89.3(2)
N1-C2	1.34(1)	N1-Cu1-N1	180.0(1)
N1-C6	1.36(1)	Cl1-Cu1-N1	90.7(2)
C2-C2'	1.52(1)	Cu1-N1-C2	120.0(6)
C2-C3	1.40(1)	Cu1-N1-C6	120.4(5)
C3-C4	1.36(1)	C2-N1-C6	119.5(7)
C3-C3'	1.52(1)	N1-C2-C2'	116.7(7)
C4-C5	1.38(1)	N1-C2-C3	120.8(8)
C4-C7	1.51(1)	C2'-C2-C3	122.4(8)
C5-C5'	1.49(1)	C2-C3-C4	120.2(8)
C5-C6	1.40(1)	C2-C3-C3'	120.2(8)
C5'-O5'	1.20(1)	C4-C3-C3'	119.6(7)
C5'-O5"	1.30(1)	C3-C4-C5	119.0(8)
C5"-O5"	1.43(1)	C3-C4-C7	118.8(8)
C6-C6'	1.52(1)	C5-C4-C7	122.0(8)
C7-C8	1.41(1)	C4-C5-C5'	120.3(8)
C7-C12	1.34(1)	C4-C5-C6	118.9(8)
C8-C9	1.37(1)	C5'-C5-C6	120.7(8)
C9-C10	1.40(2)	C5-C5'-O5'	124.2(10)
C10-C11	1.34(2)	C5-C5'-O5"	112.4(9)
C11-C12	1.38(1)	O5'-C5'-O5"	123.5(11)
C12-N2	1.37(2)	C5'-O5-C5"	116.9(9)
N2-O1	0.99(2)	N1-C6-C5	121.5(8)
N2-O2	1.20(2)	N1-C6-C6'	116.3(7)
O3"-C3'	1.30(1)	C5-C6-C6'	122.2(8)
O3"-C3"	1.48(1)	C4-C7-C8	117.8(8)
O3'-C3'	1.19(1)	C4-C7-C12	126.2(9)
		C8-C7-C12	116.0(9)
		C7-C8-C9	120.8(10)
		C8-C9-C10	117.9(12)
		C9-C10-C11	123.6(12)
		C10-C11-C12	114.8(12)
		C7-C12-C11	126.8(11)
		C7-C12-N2	122.3(11)
		C11-C12-N2	110.9(12)
		C12-N2-O1	123.7(21)
		C12-N2-O2	128.0(17)
		O1-N2-O2	108.1(22)

TABLE 15 (Continued)

	N2-O1-O2	39.9(15)
	N2-O2-O1	32.0(12)
	C3'-O3"-C3"	115.3(8)
	C3-C3'-O3"	110.9(8)
	C3-C3'-O3'	123.8(9)
	O3"-C3'-O3'	125.2(9)

TABLE 16

TORSION ANGLES (°) FOR

Bis(2,6-dimethyl-3,5-dicarbomethoxy-4-(2-nitrophenyl)pyridine)$_2$dichloro-copper(II) (II)

CL1-CU1-N1-C6	-87.4(0.5)	C2-C3-C3'-O3"	126.0(0.8)
CL1-CU1-N1-C2	88.3(0.5)	C2-C3-C3'-O3'	-54.4(1.3)
CL1A CU1-N1-C6	92.6(0.5)	O5"-C5'-C5-C6	82.7(1.0)
CL1A CU1-N1-C2	-91.7(0.5)	O5"-C5'-C5-C4	-96.8(0.9)
CU1-N1-C6-C5	178.9(0.5)	O5'-C5'-C5-C6	-101.5(1.1)
CU1-N1-C6-C6'	-2.4(0.9)	O5'-C5'-C5-C4	79.0(1.2)
C2-N1-C6-C5	3.2(1.1)	C7-C8-N2-O2	177.7(1.6)
C2-N1-C6-C6'	-178.1(0.7)	C7-C8-N2-O1	2.2(2.9)
CU1-N1-C2-C3	-180.0(0.6)	C9-C8-N2-O2	-4.4(2.5)
CU1-N1-C2-C2'	1.7(0.9)	C9-C8-N2-O1	-179.9(2.1)
C6-N1-C2-C3	-4.3(1.1)	C7-C8-C9-C10	-3.2(1.8)
C6-N1-C2-C2'	177.4(0.7)	N2-C8-C9-C10	179.0(1.3)
C3"-O3"-C3'-C3	176.6(0.8)	C8-N2-O2-O1	-176.2(3.4)
C3"-O3"-C3'-O3'	-3.0(1.4)	C8-N2-O1-O2	176.3(3.3)
N1-C6-C5-C4	-0.4(1.1)	C7-C12-C11-C10	-1.4(1.7)
N1-C6-C5-C5'	-179.9(0.7)	C8-C9-C10-C11	2.7(2.0)
C6'-C6-C5-C4	-179.0(0.7)	C12-C11-C10-C9	-0.5(2.1)
C6'-C6-C5-C5'	1.5(1.2)	C8-C7-C12-C11	1.0(1.5)
C3-C4-C7-C8	98.9(1.2)	C4-C3-C3'-O3"	-57.8(1.1)
C3-C4-C7-C12	-84.5(1.0)	C4-C3-C3'-O3'	121.8(1.0)
C5-C4-C7-C8	-86.3(1.1)	C4-C7-C12-C11	-175.9(1.0)
C5-C4-C7-C12	90.3(1.1)		
C7-C4-C3-C2	175.0(0.7)		
C7-C4-C3-C3'	1.3(1.2)		
C5-C4-C3-C2	0.2(1.1)		
C5-C4-C3-C3'	-176.0(0.8)		
C7-C4-C5-C6	-176.2(0.7)		
C7-C4-C5-C5'	3.3(1.1)		
C3-C4-C5-C6	-1.3(1.2)		
C3-C4-C5-C5'	178.2(0.7)		
C5"-O5"-C5'-O5'	-0.7(1.5)		
C5"-O5"-C5'-C5	175.1(0.8)		
N1-C2-C3-C4	2.6(1.1)		
N1-C2-C3-C3'	178.9(0.7)		
C2'-C2-C3-C4	-179.2(0.7)		
C2'-C2-C3-C3'	-2.9(1.2)		
C4-C7-C8-N2	-4.3(1.8)		
C4-C7-C8-C9	178.0(1.0)		
C12-C7-C8-N2	179.0(1.2)		
C12-C7-C8-C9	1.4(1.6)		

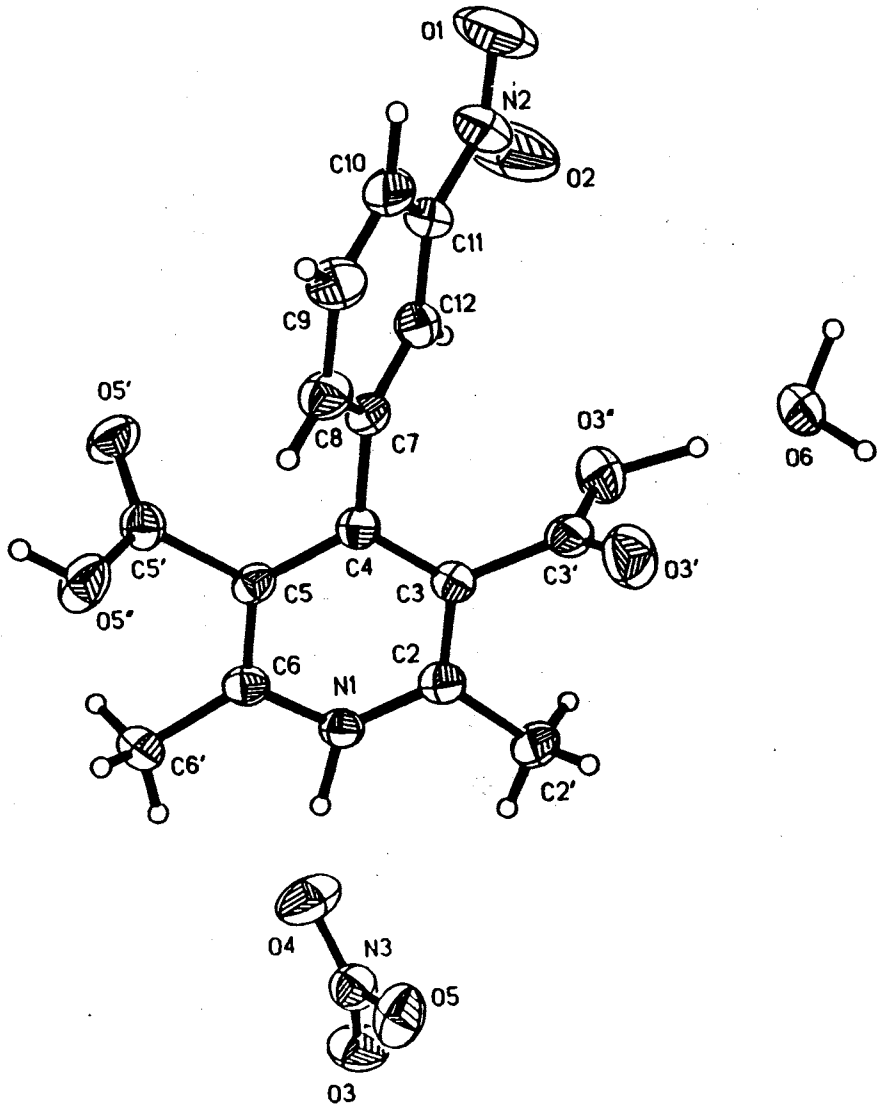

Figure 33: Projection view of 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine • NO_3 • H_2O(III)

TABLE 17

CRYSTAL DATA FOR

2,6-Dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)pyridine • NO_3 • H_2O (III)

Formula	$C_{15}H_{15}N_3O_{10}$
M. W.	397.3 g $mole^{-1}$
a	8.8130(10) Å
b	9.5970(10) Å
c	12.805(2) Å
α	70.120(0) °
β	84.450(0) °
γ	67.870(0) °
V	942.9(3) $Å^3$
F(000)	412
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.399 g/cm^3
Z	2
Meas refl	3002
Obs refl	1318
R	5.00 %
R_w	6.11 %
G. O. F.	1.29
Space Group	P-1
Octants meas	$-1 \leq h \leq 9, -9 \leq k \leq 9, -13 \leq l \leq 13$

TABLE 18

POSITIONAL PARAMETERS FOR

2,6-Dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine • NO_3 • H_2O (III)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.2679(5)	0.7168(4)	0.5523(3)
C2	0.2494(6)	0.6386(5)	0.6613(4)
C2'	0.2589(7)	0.4669(5)	0.6895(4)
C3	0.2227(6)	0.7183(5)	0.7389(4)
C3'	0.1893(9)	0.6343(6)	0.8575(5)
O3'	0.503(6)	0.6445(5)	0.8880(3)
O3"	0.3232(5)	0.5486(4)	0.9229(3)
C4	0.2149(6)	0.8788(5)	0.7039(4)
C5	0.2311(6)	0.9545(5)	0.5887(4)
C5'	0.2310(7)	1.1258(6)	0.5471(4)
O5'	0.3349(5)	1.1594(4)	0.5783(3)
O5"	0.1061(5)	0.12274(4)	0.4755(3)
C6	0.2578(6)	0.8737(6)	0.5117(4)
C6'	0.2799(7)	0.9420(6)	0.3882(4)
C7	0.1833(6)	0.9670(5)	0.7869(4)
C8	0.0483(7)	1.1132(6)	0.7700(4)
C9	0.163(8)	1.1934(6)	0.8470(5)
C10	0.1186(9)	1.1334(7)	0.9421(5)
C11	0.2512(8)	0.9899(7)	0.9579(4)
C12	0.2869(7)	0.9063(6)	0.8820(4)
N2	0.3609(9)	0.9208(8)	1.0592(4)
N3	0.2996(7)	0.4818(6)	0.3743(4)
O1	0.3282(8)	0.9913(7)	1.1268(4)
O2	0.4763(9)	0.8000(8)	1.0727(5)
O3	0.3692(6)	0.3788(5)	0.3271(3)
O4	0.3753(6)	0.5549(5)	0.3962(4)
O5	0.1510(6)	0.5088(4)	0.4032(3)
O6	0.2618(6)	0.3899(5)	1.1216(3)
H1A	0.2869	0.6719	0.4808
H2'A	0.2792	0.4385	0.6231
H2'B	0.3467	0.3964	0.7432
H2'C	0.1574	0.4584	0.7193
H2'D*	0.2242	0.4492	0.7699
H2'E*	0.3739	0.3916	0.6383
H2'F*	0.1987	0.4320	0.6352
H3"B	0.2895	0.4731	1.0162
H5"A	0.1156	1.3177	0.4511

TABLE 18 (Continued)

H6'A	0.2952	0.8636	0.3534
H6'B	0.1850	1.0346	0.3551
H6'C	0.3747	0.9710	0.3779
H6'D*	0.2065	0.9349	0.3201
H6'E*	0.2907	1.0727	0.3754
H6'F*	0.3949	0.8400	0.3366
H6A	0.2928	0.3895	1.2009
H6B	0.1592	0.3551	1.1392
H8A	-0.0221	1.1567	0.7049
H12A	0.3809	0.8093	0.8947
H9A	-0.0763	1.2915	0.8349
H10A	0.0974	1.1889	0.9949

*Disorder of methyl hydrogens on C2' and C6'

TABLE 19

ANISOTROPIC THERMAL PARAMETERS FOR

2,6-Dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine • NO_3 • H_2O (III)

ATOM	U11	U22	U33	U23	U13	U12
N1	54(3)	46(3)	47(3)	-16(2)	-4(2)	-18(2)
C2	48(4)	47(3)	53(4)	-13(3)	-4(3)	-18(3)
C2'	94(5)	49(3)	68(4)	-33(3)	9(3)	-29(3)
C3	44(3)	41(3)	44(3)	-10(3)	0(3)	-16(3)
C3'	77(5)	41(3)	54(4)	-20(3)	-5(4)	-18(3)
O3'	84(4)	109(4)	73(3)	-44(3)	20(3)	-24(2)
O3"	93(3)	69(3)	61(3)	-28(2)	-11(2)	0(2)
C4	45(3)	39(3)	46(3)	-11(3)	-3(3)	-14(3)
C5	41(3)	37(3)	52(3)	-13(2)	-4(3)	-14(3)
C5'	50(4)	47(3)	51(3)	-14(3)	-2(3)	-11(3)
O5'	80(3)	60(2)	88(3)	-36(2)	-31(2)	-10(2)
O5"	68(3)	43(2)	101(3)	-18(2)	-29(2)	-1(2)
C6	43(4)	50(3)	50(3)	-15(3)	-5(3)	-18(3)
C6'	68(4)	67(4)	43(3)	-26(3)	0(3)	-18(3)
C7	58(4)	40(3)	51(3)	-18(3)	3(3)	-18(3)
C8	69(4)	45(3)	68(4)	-14(3)	0(3)	-26(3)
C9	85(5)	58(4)	75(4)	-21(3)	10(4)	-37(3)
C10	105(5)	64(4)	64(4)	-44(4)	22(4)	-37(3)
C11	89(5)	65(4)	45(3)	-38(4)	-1(3)	-22(3)
C12	66(4)	50(3)	51(3)	-20(3)	-7(3)	-11(3)
N2	133(6)	103(5)	50(4)	-54(4)	-12(4)	-23(4)
N3	68(4)	56(3)	63(3)	-21(3)	-1(3)	-22(3)
O1	203(7)	173(5)	72(3)	-65(5)	-18(4)	-65(4)
O2	213(7)	130(5)	109(4)	17(5)	-97(5)	-40(4)
O3	110(4)	90(3)	86(3)	-32(3)	4(3)	-56(3)
O4	108(4)	110(4)	125(4)	-62(3)	25(3)	-76(3)
O5	67(3)	53(2)	104(3)	-15(2)	-3(3)	-11(2)
O6	149(4)	134(4)	48(2)	-95(4)	-7(2)	-7(2)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$$

TABLE 20

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

2,6-Dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine • NO_3 • H_2O (III)

N1-C2	1.368 (6)	C2-N1-C6	124.2(5)
N1-C6	1.386 (7)	N1-C2-C2'	116.5(5)
C2-C2'	1.532 (8)	N1-C2-C3	119.1(5)
C2-C3	1.402 (8)	C2'-C2-C3	124.4(4)
C3-C3'	1.517 (7)	C2-C3-C3'	118.3(5)
C3-C4	1.426 (7)	C2-C3-C4	120.0(4)
C3'-O3'	1.228 (9)	C3'-C3-C4	121.5(5)
C3'-O3"	1.327 (8)	C3-C3'-O3'	122.0(5)
C4-C5	1.426 (6)	C3-C3'-O3"	113.9(6)
C4-C7	1.517 (8)	O3'-C3'-O3"	124.0(5)
C5-C5'	1.545 (8)	C3-C4-C5	118.0(5)
C5-C6	1.402 (8)	C3-C4-C7	120.4(4)
C5'-O5'	1.219 (9)	C5-C4-C7	121.5(4)
C5'-O5"	1.335 (6)	C4-C5-C5'	120.1(5)
C6-C6'	1.517 (6)	C4-C5-C6	121.5(5)
C7-C12	1.410 (7)	C5'-C5-C6	118.3(4)
C7-C8	1.420 (6)	C5-C5'-O5'	122.1(4)
C12-C11	1.403 (9)	C5-C5'-O5"	112.2(5)
C11-C10	1.395 (8)	O5'-C5'-O5"	125.7(5)
C11-N2	1.493 (9)	N1-C6-C5	117.2(4)
C10-C9	1.404 (9)	N1-C6-C6'	117.1(5)
C9-C8	1.394 (9)	C5-C6-C6'	125.7(5)
N2-O1	1.223 (10)	C4-C7-C12	121.0(4)
N2-O2	1.191 (9)	C4-C7-C8	120.4(5)
N3-O3	1.264 (7)	C12-C7-C8	118.6(5)
N3-O4	1.241 (10)	C7-C12-C11	119.1(4)
N3-O5	1.279 (8)	C12-C11-C10	122.6(5)
		C12-C11-N2	117.9(5)
		C10-C11-N2	119.5(6)
		C11-C10-C9	118.0(6)
		C10-C9-C8	120.8(5)
		C7-C8-C9	120.8(5)
		C11-N2-O1	118.2(6)
		C11-N2-O2	120.2(7)
		O1-N2-O2	121.7(7)
		O3-N3-O4	120.7(6)
		O3-N3-O5	120.3(7)
		O4-N3-O5	118.9(5)

TABLE 21

TORSION ANGLES (°) FOR

2,6-Dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine • NO_3 • H_2O (III)

C6-N1-C2-C2'	178.0(0.5)	C12-C11-N2-O2	1.4(1.2)
C6-N1-C2-C3	-1.7(0.7)	C10-C11-N2-O1	1.6(1.1)
C2-N1-C6-C5	1.7(0.7)	C10-C11-N2-O2	-178.5(0.8)
C2-N1-C6-C6'	-179.5(0.5)	C11-C10-C9-C8	-1.2(1.0)
N1-C2-C3-C3'	175.3(0.5)	C10-C9-C8-C7	1.3(1.0)
N1-C2-C3-C4	0.0(0.7)		
C2'-C2-C3-C3'	-4.4(0.8)		
C2'-C2-C3-C4	-179.6(0.5)		
C2-C3-C3'-O3'	88.5(0.7)		
C2-C3-C3'-O3"	90.6(0.7)		
C4-C3-C3'-O3'	86.7(0.8)		
C4-C3-C3'-O3"	-94.2(0.6)		
C2-C3-C4-C5	1.5(0.7)		
C2-C3-C4-C7	179.0(0.5)		
C3'-C3-C4-C5	-173.6(0.5)		
C3'-C3-C4-C7	3.9(0.8)		
C3-C4-C5-C5'	-177.4(0.4)		
C3-C4-C5-C6	-1.5(0.7)		
C7-C4-C5-C5'	5.1(0.7)		
C7-C4-C5-C6	-179.0(0.5)		
C3-C4-C7-C12	57.2(0.7)		
C3-C4-C7-C8	-122.9(0.5)		
C5-C4-C7-C12	-125.4(0.5)		
C5-C4-C7-C8	54.5(0.8)		
C4-C5-C5'-O5'	61.4(0.7)		
C4-C5-C5'-O5"	-118.3(0.5)		
C6-C5-C5'-O5'	-114.6(0.6)		
C6-C5-C5'-O5"	65.7(0.6)		
C4-C5-C6-N1	0.0(0.7)		
C4-C5-C6-C6'	-178.7(0.5)		
C5'-C5-C6-N1	175.9(0.4)		
C5'-C5-C6-C6'	-2.8(0.7)		
C4-C7-C12-C11	-178.6(0.5)		
C8-C7-C12-C11	1.5(0.9)		
C4-C7-C8-C9	-178.6(0.6)		
C12-C7-C8-C9	-1.5(0.9)		
C7-C12-C11-C10	-1.4(1.0)		
C7-C12-C11-N2	178.6(0.6)		
C12-C11-C10-C9	1.2(1.1)		
N2-C11-C10-C9	-178.8(0.7)		
C12-C11-N2-O1	-178.4(0.7)		

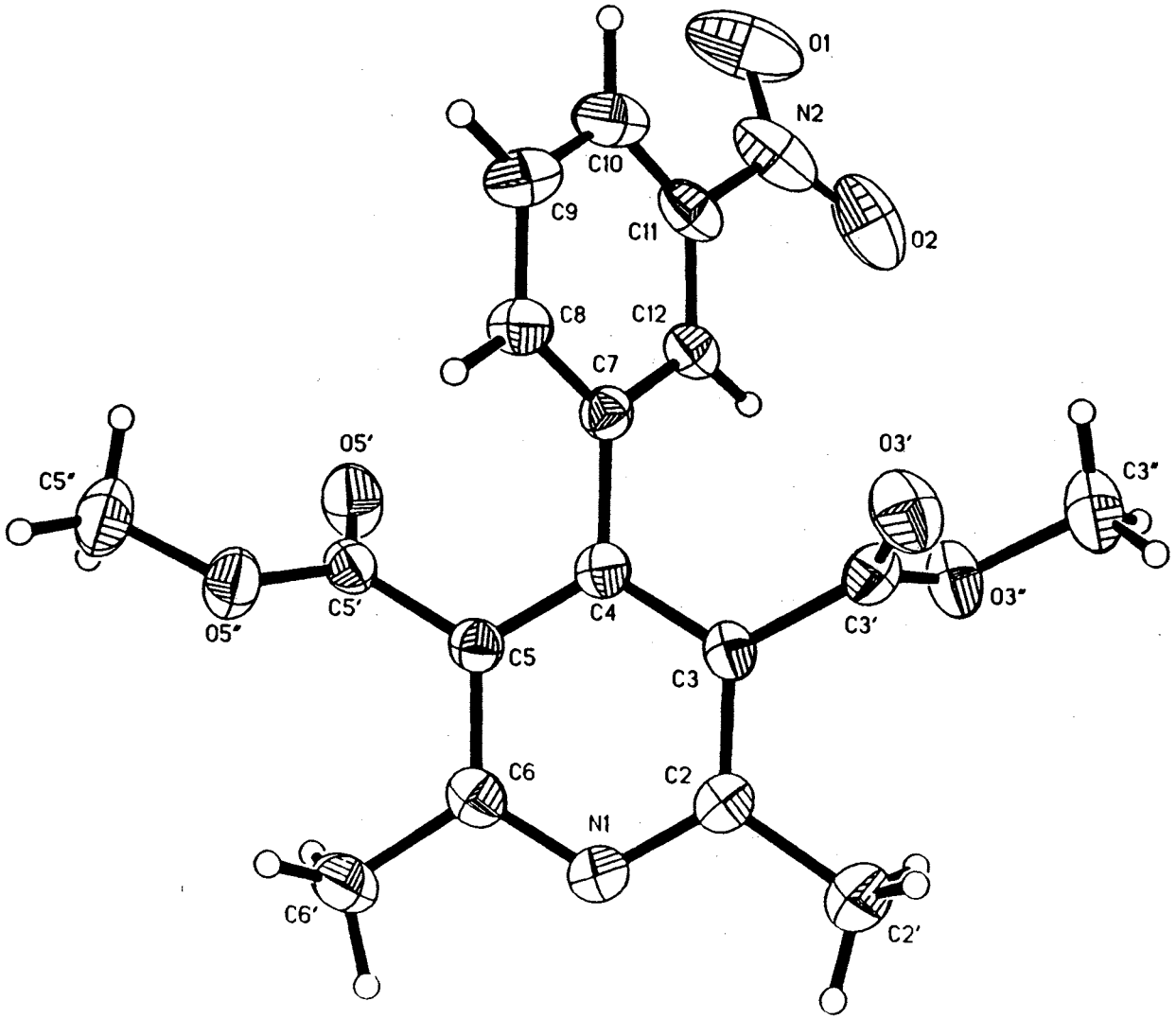

Figure 34: Projection view of Methyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine(IV)

TABLE 22

CRYSTAL DATA FOR

Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (IV)

Formula	$C_{17}H_{16}N_2O_6$
M. W.	344.3 g $mole^{-1}$
a	11.598(1) Å
b	14.526(1) Å
c	10.612(1) Å
α	90.0 °
β	111.500(10) °
γ	90.0 °
V	1663.4(2) $Å^3$
F(000)	720
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.375 g/cm^3
Z	4
Meas refl	2068
Obs refl	1173
R	4.71 %
R_w	6.48 %
G. O. F.	1.53
Space Group	$P2_1/c$
Octants meas	$-11 \leq h \leq 10, -13 \leq k \leq 1, -1 \leq l \leq 10$

TABLE 23

POSITIONAL PARAMETERS FOR

Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (IV)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.0313(3)	0.3562(3)	-0.1119(4)
C2	0.0916(4)	0.3135(3)	0.0056(5)
C2'	0.0462(4)	0.2193(3)	0.0210(5)
C3	0.1916(4)	0.3545(3)	0.1072(4)
C3'	0.2482(4)	0.3098(3)	0.2434(5)
C3"	0.3750(5)	0.1882(4)	0.3673(5)
O3'	0.2351(3)	0.3364(3)	0.3431(4)
O3"	0.3165(3)	0.2368(2)	0.2403(3)
C4	0.2343(4)	0.4406(3)	0.0850(5)
C5	0.1737(4)	0.4823(3)	-0.0402(5)
C5'	0.2280(5)	0.5664(3)	-0.0759(4)
C5"	0.1944(5)	0.7212(3)	-0.1478(5)
O5'	0.3291(3)	0.5691(2)	-0.0811(3)
O5"	0.1515(3)	0.6378(2)	-0.1037(3)
C6	0.0697(4)	0.4390(3)	-0.1358(4)
C6'	-0.0011(4)	0.4811(3)	-0.2698(5)
C7	0.3431(4)	0.4843(3)	0.1893(4)
C8	0.3354(4)	0.5711(3)	0.2391(5)
C9	0.4366(5)	0.6113(4)	0.3342(5)
C10	0.5496(5)	0.5670(4)	0.3815(5)
C11	0.5555(4)	0.4811(4)	0.3320(5)
C12	0.4559(4)	0.4384(3)	0.2378(5)
N2	0.6741(5)	0.4315(5)	0.3812(5)
O1	0.7693(4)	0.4763(4)	0.4279(5)
O2	0.6703(4)	0.3476(4)	0.3695(5)
H2'A	-0.0233	0.2030	-0.0587
H2'B	0.1123	0.1761	0.0339
H2'C	0.0220	0.2179	0.0983
H3"A	0.4222	0.1374	0.3539
H3"B	0.4290	0.2292	0.4339
H3"C	0.3122	0.1655	0.3982
H5"A	0.1341	0.7695	-0.1643
H5"B	0.2707	0.7404	-0.0789
H5"C	0.2083	0.7081	-0.2298
H6'A	-0.0676	0.4410	-0.3208
H6'B	-0.0344	0.5393	-0.2568

TABLE 23 (Continued)

H6'C	0.0534	0.4903	-0.3184
H8A	0.2574	0.6029	0.2056
H9A	0.4279	0.6711	0.3682
H10A	0.6214	0.5961	0.4459
H12A	0.4645	0.3776	0.2068

TABLE 24

ANISOTROPIC THERMAL PARAMETERS FOR

Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (IV)

ATOM	U11	U22	U33	U12	U13	U23
N1	53(2)	52(3)	55(3)	-7(2)	16(2)	-3(2)
C2	52(3)	49(3)	55(3)	-4(3)	21(3)	-2(3)
C2'	76(3)	71(4)	77(4)	-16(3)	26(3)	5(3)
C3	52(3)	47(3)	43(3)	4(3)	16(3)	6(3)
C3'	57(3)	43(3)	56(4)	-3(3)	27(3)	-3(3)
C3"	117(4)	70(4)	68(4)	20(3)	40(3)	19(3)
O3'	100(3)	85(3)	53(2)	19(2)	37(2)	1(2)
O3"	93(2)	62(2)	54(2)	20(2)	32(2)	12(2)
C4	42(3)	42(3)	50(3)	5(2)	18(3)	-3(3)
C5	42(3)	44(3)	46(3)	4(2)	15(3)	-2(3)
C5'	47(3)	46(3)	43(3)	6(3)	12(2)	1(2)
C5"	113(4)	51(3)	81(4)	2(3)	40(4)	9(3)
O5'	58(2)	80(3)	94(3)	9(2)	33(2)	27(2)
O5"	66(2)	49(2)	83(3)	5(2)	29(2)	9(2)
C6	48(3)	55(3)	48(3)	6(3)	17(3)	-2(3)
C6'	58(3)	71(4)	53(3)	1(3)	5(3)	-2(3)
C7	48(3)	44(3)	43(3)	-2(3)	19(3)	1(2)
C8	49(3)	57(3)	55(3)	-2(3)	15(3)	-7(3)
C9	70(4)	72(4)	67(4)	-16(3)	24(3)	-20(3)
C10	62(4)	96(5)	50(3)	-23(4)	17(3)	-12(3)
C11	46(4)	91(4)	40(3)	4(3)	15(3)	10(3)
C12	51(3)	60(3)	42(3)	3(3)	14(3)	6(3)
N2	64(4)	161(6)	52(3)	21(5)	14(3)	10(4)
O1	53(3)	241(6)	111(4)	2(3)	-2(3)	-38(4)
O2	101(3)	149(4)	97(4)	59(4)	33(3)	45(4)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE 25

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (IV)

N1-C2	1.337 (6)	C2-N1-C6	119.8(4)
C5'-O5"	1.327 (6)	N1-C2-C2'	116.2(4)
C5"-O5"	1.450 (6)	N1-C2-C3	121.7(4)
C6-C6'	1.489 (6)	C2'-C2-C3	122.1(4)
C7-C8	1.382 (7)	C2-C3-C3'	120.5(4)
C7-C12	1.388 (6)	C2-C3-C4	119.9(4)
C8-C9	1.368 (6)	C3'-C3-C4	119.6(4)
C9-C10	1.379 (8)	C3-C3'-O3'	124.4(4)
C10-C11	1.365 (9)	C3-C3'-O3"	112.0(5)
C11-C12	1.369 (6)	O3'-C3'-O3"	123.5(4)
C11-N2	1.469 (8)	C3'-O3"-C3"	116.4(4)
N2-O1	1.220 (8)	C3-C4-C5	117.6(3)
N2-O2	1.225 (10)	C3-C4-C7	121.0(4)
C5'-O5'	1.194 (7)	C5-C4-C7	121.3(4)
N1-C6	1.338 (7)	C4-C5-C5'	119.2(3)
C2-C2'	1.497 (7)	C4-C5-C6	119.5(4)
C2-C3	1.395 (6)	C5'-C5-C6	121.0(4)
C3-C3'	1.498 (6)	C5-C5'-O5'	123.7(4)
C3-C4	1.397 (6)	C5-C5'-O5"	112.9(5)
C3'-O3'	1.187 (7)	O5'-C5'-O5"	123.5(5)
C3'-O3"	1.331 (6)	C5'-O5"-C5"	116.4(4)
C3"-O3"	1.452 (6)	N1-C6-C5	121.4(4)
C4-C5	1.394 (6)	N1-C6-C6'	116.4(4)
C4-C7	1.482 (5)	C5-C6-C6'	122.1(4)
C5-C5'	1.485 (7)	C4-C7-C8	121.3(4)
C5-C6	1.408 (5)	C4-C7-C12	119.9(4)
		C8-C7-C12	118.8(4)
		C7-C8-C9	120.9(4)
		C8-C9-C10	120.8(5)
		C9-C10-C11	117.5(4)
		C10-C11-C12	123.2(5)
		C10-C11-N2	119.0(5)
		C12-C11-N2	117.8(5)
		C7-C12-C11	118.8(5)
		C11-N2-O1	118.3(7)
		C11-N2-O2	117.3(5)
		O1-N2-O2	124.4(6)

TABLE 26

TORSION ANGLES (°) FOR

Dimethyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (IV)

C6-N1-C2-C2'	-177.1(0.5)	C10-C11-C12-C7	0.3(0.9)
C6-N1-C2-C3	2.5(0.8)	N2-C11-C12-C7	-179.6(0.5)
C2-N1-C6-C5	0.7(0.8)	C10-C11-N2-O1	-23.5(0.9)
C2-N1-C6-C6'	178.9(0.5)	C10-C11-N2-O2	158.2(0.6)
N1-C2-C3-C3'	173.0(0.5)	C12-C11-N2-O1	156.5(0.6)
N1-C2-C3-C4	-2.9(0.8)	C12-C11-N2-O2	-21.9(0.8)
C2'-C2-C3-C3'	-7.4(0.8)	C7-C8-C9-C10	0.9(0.9)
C2'-C2-C3-C4	176.7(0.5)	C8-C9-C10-C11	-1.3(0.9)
C2-C3-C3'-O3'	-106.3(0.6)	C9-C10-C11-C12	0.6(0.9)
C2-C3-C3'-O3"	74.3(0.6)	C9-C10-C11-N2	-179.4(0.6)
C4-C3-C3'-O3'	69.5(0.7)		
C4-C3-C3'-O3"	-109.8(0.5)		
C2-C3-C4-C5	0.0(0.7)		
C2-C3-C4-C7	-177.8(0.5)		
C3'-C3-C4-C5	-175.9(0.5)		
C3'-C3-C4-C7	6.3(0.7)		
C3-C3'-O3"-C3"	-179.7(0.4)		
O3'-C3'-O3"-C3"	1.0(0.7)		
C3-C4-C5-C5'	-170.5(0.5)		
C3-C4-C5-C6	3.0(0.7)		
C7-C4-C5-C5'	7.3(0.7)		
C7-C4-C5-C6	-179.1(0.5)		
C3-C4-C7-C8	-123.8(0.5)		
C3-C4-C7-C12	56.9(0.7)		
C5-C4-C7-C8	58.4(0.7)		
C5-C4-C7-C12	-120.9(0.5)		
C4-C5-C5'-O5'	59.2(0.7)		
C4-C5-C5'-O5"	-121.9(0.5)		
C6-C5-C5'-O5'	-114.2(0.5)		
C6-C5-C5'-O5"	64.7(0.6)		
C4-C5-C6-N1	-3.5(0.8)		
C4-C5-C6-C6'	178.4(0.5)		
C5'-C5-C6-N1	169.9(0.5)		
C5'-C5-C6-C6'	-8.2(0.8)		
C5-C5'-O5"-C5"	-176.2(0.4)		
O5'-C5'-O5"-C5"	2.7(0.6)		
C4-C7-C8-C9	-179.2(0.5)		
C12-C7-C8-C9	0.1(0.8)		
C4-C7-C12-C11	178.6(0.5)		
C8-C7-C12-C11	-0.7(0.8)		

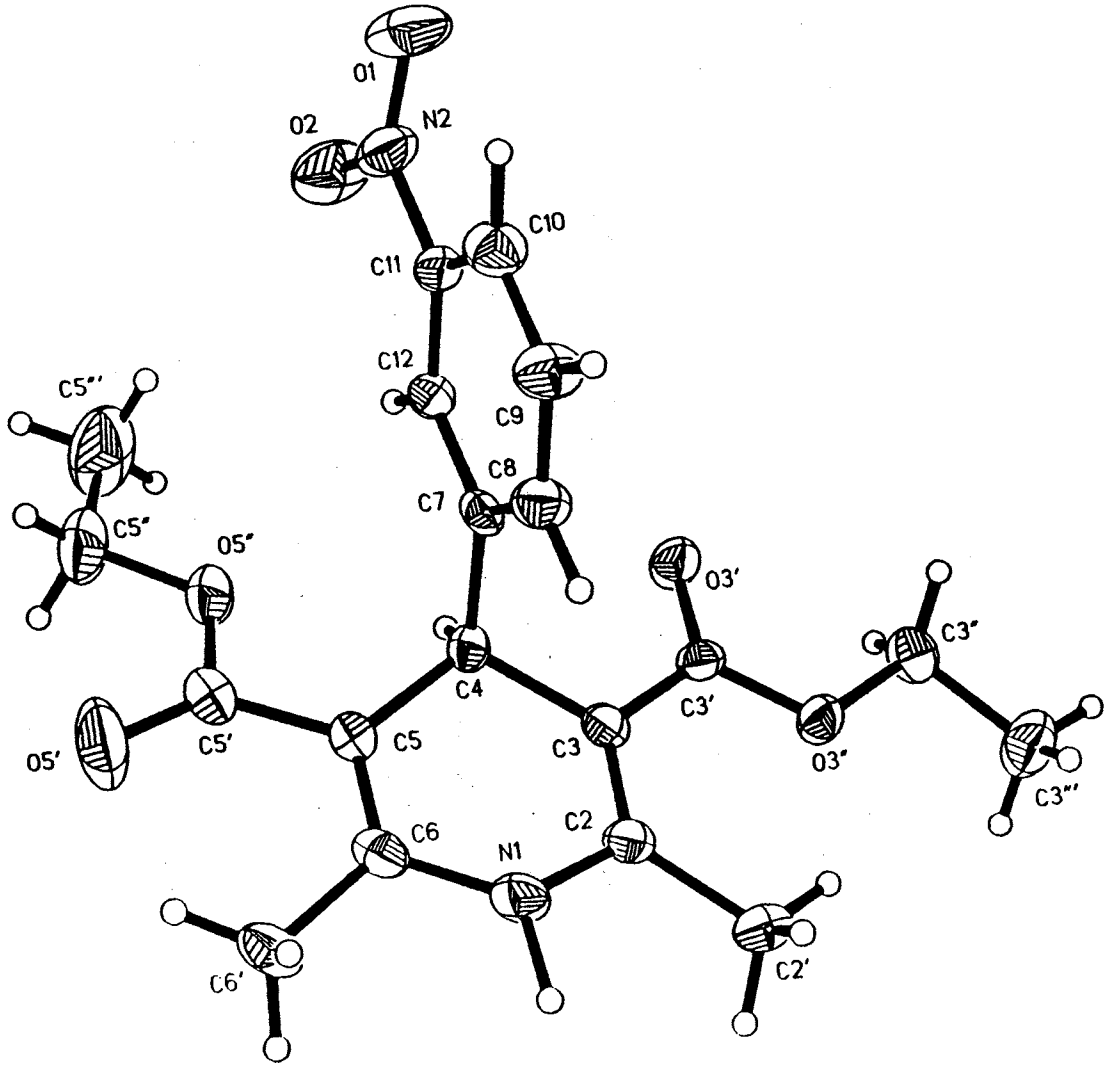

Figure 35: Projection view of Ethyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine(V)

TABLE 27

CRYSTAL DATA FOR

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine3,5-dicarboxylate (V)

Formula	$C_{19}H_{22}N_2O_6$
M. W.	374.4 g $mole^{-1}$
a	14.328(4) Å
b	15.292(3) Å
c	8.673(2) Å
α	90.0 °
β	90.0 °
γ	90.0 °
V	1900.5(8) $Å^3$
F(000)	792
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.308 Mg/m^3
Z	4
Meas refl	3024
Obs refl	1238
R	4.82 %
R_w	5.37 %
G. O. F.	1.16
Space Group	$Pna2_1$
Octants meas	$-1 \leq h \leq 18, -1 \leq k \leq 19, -1 \leq l \leq 11$

TABLE 28

POSITIONAL PARAMETERS FOR

Ethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine3,5-dicarboxylate (V)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.2054(3)	0.2890(3)	0.6351(10)
C2	0.1452(4)	0.2315(3)	0.7052(10)
C2'	0.1939(4)	0.1541(4)	0.7764(11)
C3	0.0533(4)	0.2483(4)	0.7042(10)
C3'	-0.0203(4)	0.1948(3)	0.7732(10)
C3"	-0.0609(4)	0.0644(4)	0.9072(10)
C3"'	-0.0092(5)	-0.0056(5)	0.9918(13)
O3'	-0.1022(3)	0.2123(3)	0.7656(9)
O3"	0.0094(3)	0.1224(2)	0.8472(9)
C4	0.0131(3)	0.3279(3)	0.6182(?)
C5	0.0899(4)	0.3945(3)	0.5828(10)
C5'	0.0615(4)	0.4840(4)	0.5437(12)
C5"	-0.0678(6)	0.5800(4)	0.5274(15)
C5"'	-0.1642(6)	0.5832(5)	0.5566(17)
O5'	0.1102(3)	0.5418(3)	0.4970(12)
O5"	-0.0301(3)	0.4963(2)	0.5635(9)
C6	0.1802(4)	0.3717(4)	0.5864(10)
C6'	0.2612(4)	0.4276(4)	0.5359(11)
C7	-0.0344(3)	0.3006(3)	0.4685(10)
C8	0.0098(4)	0.2474(4)	0.3629(10)
C9	-0.0327(4)	0.2266(4)	0.2253(11)
C10	-0.1207(4)	0.2572(4)	0.1882(10)
C11	-0.1637(4)	0.3099(4)	0.2939(10)
C12	-0.1224(4)	0.3324(3)	0.4332(10)
N2	-0.2567(4)	0.3435(4)	0.2612(11)
O1	-0.2986(3)	0.3143(4)	0.1489(10)
O2	-0.2914(4)	0.3974(3)	0.3482(11)
H1A	0.2707	0.2721	0.6635
H2'A	0.1483	0.1169	0.8243
H2'B	0.2259	0.1222	0.6971
H2'C	0.2380	0.1734	0.8524
H3"A	-0.0969	0.0397	0.8246
H3"B	-0.1020	0.0952	0.9757
H3"C	-0.0523	-0.0470	0.10349
H3"D	0.0319	-0.0351	0.9214
H3"E	0.0267	0.0205	0.10730
H4A	-0.0327	0.3548	0.6836
H5"A	-0.0531	0.5970	0.4237

TABLE 28 (Continued)

H5"B	-0.0402	0.6216	0.5966
H5"C	-0.1892	0.6403	0.5365
H5"D	-0.1914	0.5418	0.4866
H5"E	-0.1784	0.5665	0.6607
H6'A	0.2391	0.4839	0.5035
H6'B	0.3034	0.4346	0.6209
H6'C	0.2930	0.3997	0.4518
H8A	0.0707	0.2253	0.3871
H9A	0.0002	0.1901	0.1534
H10A	-0.1506	0.2432	0.0923
H12A	-0.1546	0.3702	0.5039

TABLE 29

ANISOTROPIC THERMAL PARAMETERS FOR

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine3,5-dicarboxylate (V)

ATOM	U11	U22	U33	U12	U13	U23
N1	27(2)	54(3)	64(4)	-2(2)	2(3)	-1(3)
C2	34(3)	44(3)	42(4)	-5(3)	-5(3)	3(3)
C2'	39(3)	59(4)	60(4)	5(3)	-10(3)	4(4)
C3	36(3)	37(3)	40(3)	-7(3)	-3(3)	-1(3)
C3'	37(3)	39(3)	38(4)	5(3)	-10(3)	-5(3)
C3"	50(4)	50(4)	51(4)	-8(3)	10(3)	5(4)
C3"'	80(5)	64(4)	101(7)	6(4)	-6(5)	30(5)
O3'	35(2)	51(2)	75(3)	2(2)	1(2)	17(3)
O3"	35(2)	43(2)	63(3)	2(2)	0(2)	13(2)
C4	39(3)	28(3)	41(4)	3(3)	0(3)	-1(3)
C5	44(3)	36(3)	49(4)	-6(3)	-5(3)	1(4)
C5'	56(4)	48(4)	75(5)	-14(4)	-6(4)	6(4)
C5"	99(6)	44(4)	137(9)	5(4)	-10(7)	22(5)
C5"'	114(7)	73(5)	177(12)	37(5)	16(8)	17(7)
O5'	82(3)	55(3)	213(8)	-11(3)	24(5)	41(5)
O5"	65(3)	34(2)	89(4)	3(2)	-9(3)	3(3)
C6	42(3)	51(4)	41(4)	-14(3)	-4(3)	-3(4)
C6'	43(3)	78(4)	83(6)	-29(3)	-9(4)	17(5)
C7	41(3)	34(3)	34(3)	-16(3)	-2(3)	4(3)
C8	42(3)	51(3)	55(4)	1(3)	-5(4)	-7(4)
C9	52(4)	64(4)	48(4)	9(3)	-4(4)	-15(4)
C10	58(4)	59(4)	42(4)	-5(4)	-4(4)	-4(4)
C11	33(3)	40(3)	52(4)	-3(3)	-7(3)	9(3)
C12	32(3)	40(3)	44(4)	-5(3)	-1(3)	3(3)
N2	44(3)	75(4)	68(4)	-1(3)	-16(4)	22(4)
O1	55(3)	128(5)	82(4)	2(3)	-29(3)	13(4)
O2	72(3)	95(4)	102(5)	40(3)	-17(4)	-20(4)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$$

TABLE 30

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine3,5-dicarboxylate (V)

N1-C2	1.374 (8)	C2-N1-C6	123.8(5)
N1-C6	1.382 (8)	N1-C2-C2'	113.1(5)
C2-C2'	1.507 (9)	N1-C2-C3	119.4(6)
C(2)-C3	1.341 (7)	C2'-C2-C3	127.4(6)
C3-C3'	1.463 (9)	C2-C3-C3'	126.7(6)
C3-C4	1.539 (8)	C2-C3-C4	121.5(6)
C3'-O3'	1.205 (7)	C3'-C3-C4	111.7(4)
C3'-O3"	1.349 (8)	C3-C3'-O3'	123.8(6)
C3"-C3"'	1.494 (11)	C3-C3'-O3"	115.2(5)
C3"-O3"	1.439 (8)	O3'-C3'-O3"	121.0(6)
C4-C5	1.531 (7)	C3"'-C3"-O3"	105.8(5)
C4-C7	1.524 (8)	C3'-O3"-C3"	117.2(4)
C5-C5'	1.468 (8)	C3-C4-C5	110.7(4)
C5-C6	1.340 (8)	C3-C4-C7	111.3(4)
C5'-O5'	1.196 (9)	C5-C4-C7	109.4(4)
C5'-O5"	1.337 (7)	C4-C5-C5'	117.9(5)
C5"-C5"'	1.405 (12)	C4-C5-C6	121.1(5)
C5"-O5"	1.424 (8)	C5'-C5-C6	121.0(5)
C6-C6'	1.506 (9)	C5-C5'-O5'	127.3(6)
C7-C12	1.386 (8)	C5-C5'-O5"	111.9(5)
C7-C8	1.378 (10)	O5'-C 5'-O5"	120.8(6)
C11-C12	1.389 (11)	C5"'-C5"-O5"	111.4(7)
C11-C10	1.367 (10)	C5'-O5"-C5"	118.1(5)
C11-N2	1.456 (8)	N1-C6-C5	119.8(5)
C10-C9	1.382 (9)	N1-C6-C6'	114.0(5)
C9-C8	1.377 (12)	C5-C6-C6'	126.1(6)
N2-O1	1.228 (11)	C4-C7-C12	119.9(6)
N2-O2	1.223 (10)	C4-C7-C8	121.5(5)
		C12-C7-C8	118.5(7)
		C7-C12-C11	119.5(6)
		C12-C11-C10	122.5(6)
		C12-C11-N2	118.2(6)
		C10-C11-N2	119.3(7)
		C11-C10-C9	117.0(7)
		C10-C9-C8	121.7(7)
		C7-C8-C9	120.6(6)
		C9-N2-O1	118.2(7)
		C9-N2-O2	119.3(7)
		O1-N2-O2	122.4(6)

TABLE 31

TORSION ANGLES (°) FOR

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine3,5-dicarboxylate (V)

C6-N1-C2-C2'	-167.9(0.8)	C12-C11-C10-C9	-0.2(1.0)
C6-N1-C2-C3	12.1(1.3)	N2-C11-C10-C9	-179.7(0.6)
C2-N1-C6-C5	-11.2(1.3)	C12-C11-N2-O1	-170.1(0.7)
C2-N1-C6-C6'	170.9(0.8)	C12-C11-N2-O2	7.7(1.0)
N1-C2-C3-C3'	-179.8(0.8)	C10-C11-N2-O1	9.4(1.0)
N1-C2-C3-C4	3.6(1.2)	C10-C11-N2-O2	-172.8(0.7)
C2'-C2-C3-C3'	0.2(1.4)	C11-C10-C9-C8	0.6(1.0)
C2'-C2-C3-C4	-176.4(0.7)	C10-C9-C8-C7	0.6(1.0)
C2-C3-C3'-O3'	-178.3(0.8)	C4-C7-C8-C9	-177.1(0.6)
C2-C3-C3'-O3"	1.4(1.2)	C12-C7-C8-C9	0.2(1.0)
C4-C3-C3'-O3'	-1.4(1.1)	C7-C12-C11-C10	-0.2(1.0)
C4-C3-C3'-O3"	178.3(0.6)	C7-C12-C11-N2	179.3(0.6)
C2-C3-C4-C5	-17.3(0.9)	C5"'-C5"-O5"-C5'	-179.0(1.0)
C2-C3-C4-C7	104.7(0.8)	C4-C7-C12-C11	177.6(0.5)
C3'-C3-C4-C5	165.6(0.6)	C8-C7-C12-C11	0.2(0.9)
C3'-C3-C4-C7	-72.4(0.7)	O5'-C5'-O5"-C5"	0.1(1.5)
C3-C3'-O3"-C3"	-175.6(0.7)		
O3'-C3'-O3"-C3"	4.1(1.1)		
C3"'-C3"-O3"-C3'	-176.1(0.7)		
C3-C4-C5-C5'	-162.3(0.7)		
C3-C4-C5-C6	18.2(0.9)		
C7-C4-C5-C5'	74.6(0.8)		
C7-C4-C5-C6	-104.9(0.8)		
C3-C4-C7-C12	132.3(0.6)		
C3-C4-C7-C8	-50.4(0.7)		
C5-C4-C7-C12	-105.0(0.6)		
C5-C4-C7-C8	72.3(0.7)		
C4-C5-C5'-O5'	-171.3(0.9)		
C4-C5-C5'-O5"	7.7(1.1)		
C6-C5-C5'-O5'	8.2(1.6)		
C6-C5-C5'-O5"	-172.8(0.8)		
C4-C5-C6-N1	-5.5(1.2)		
C4-C5-C6-C6'	172.2(0.7)		
C5'-C5-C6-N1	175.0(0.8)		
C5'-C5-C6-C6'	-7.3(1.4)		
C5-C5'-O5"-C5"	-179.0(0.9)		

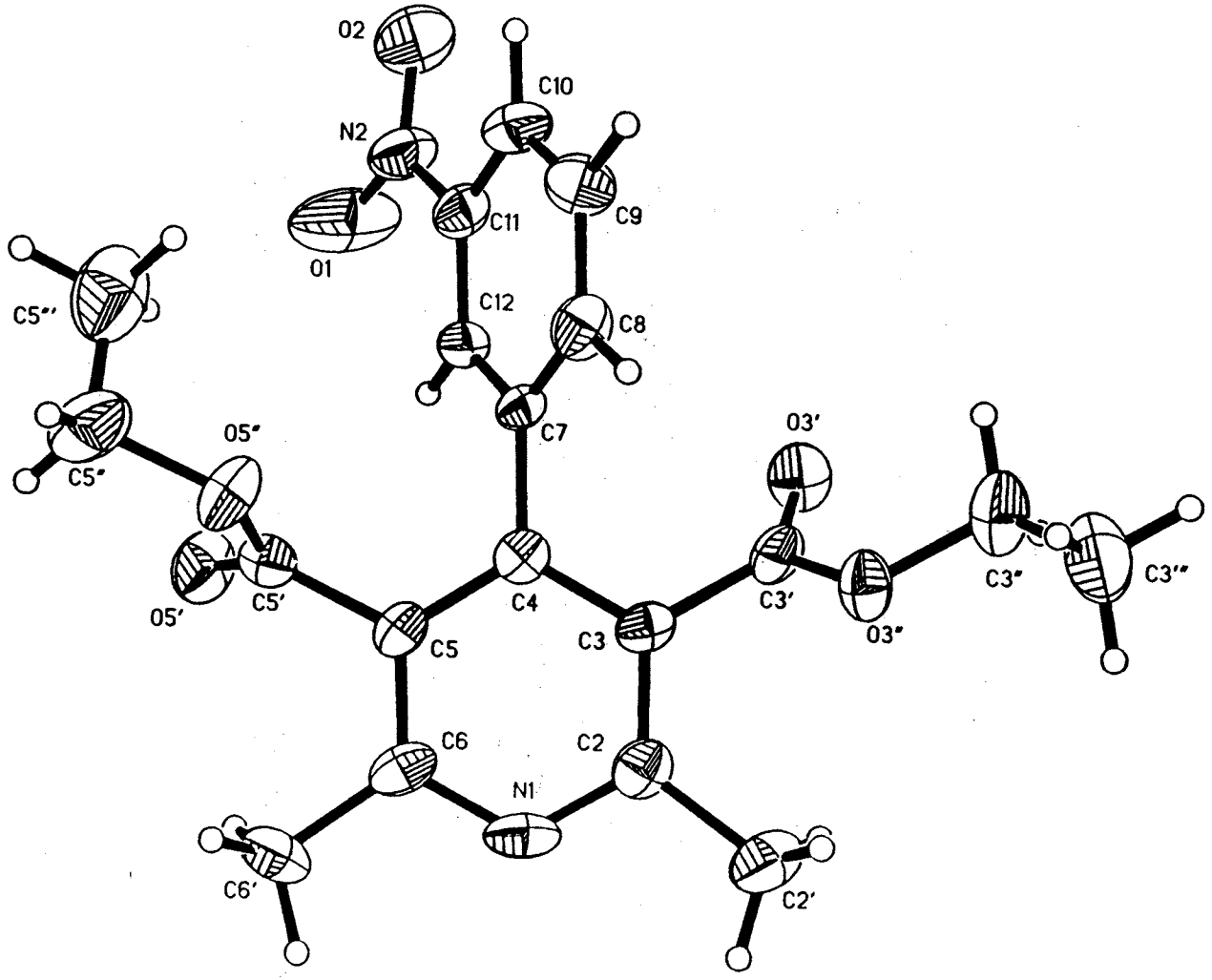

Figure 36: Projection view of Ethyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine(VI)

TABLE 32

CRYSTAL DATA FOR

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (VI)

Formula	$C_{19}\ H_{20}\ N_2\ O_6$
M. W.	372.37 g $mole^{-1}$
a	12.0180(10)Å
b	19.517(2) Å
c	8.6060(10) Å
α	90.00 °
β	109.920(10) °
γ	90.00 °
V	1897.8(3)$Å^3$
F(000)	784
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.303 g/cm^3
Z	4
Meas refl	2402
Obs refl	890
R	5.8%
R_w	14.52%
G. O. F.	0.970
Space Group	$P2_1/c$
Octants meas	$-11 \leq h \leq 11, -18 \leq k \leq 1, -1 \leq l \leq 8$

TABLE 33

POSITIONAL PARAMETERS FOR

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (VI)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.8611(6)	0.4858(3)	0.1636(8)
H1A	0.8039(6)	0.5156(3)	0.1631(8)
C2	0.8301(6)	0.4265(5)	0.0794(9)
C2'	0.6999(5)	0.4178(4)	-0.0093(8)
H2'A	0.6577(5)	0.4567(4)	0.0104(8)
H2'B	0.6855(5)	0.4136(4)	-0.1257(8)
H2'C	0.6734(5)	0.3771(4)	0.0300(8)
C3	0.9168(6)	0.3799(4)	0.0775(8)
C3'	0.8852(6)	0.3182(4)	-0.0293(9)
C3"	0.7720(6)	0.2170(4)	-0.0896(10)
H3"A	0.7411(6)	0.2281(4)	-0.2051(10)
H3"B	0.8403(6)	0.1884(4)	-0.0711(10)
C3"'	0.6838(7)	0.1807(4)	-0.0432(10)
H3'A	0.6624(7)	0.1397(4)	-0.1079(10)
H3'B	0.7150(7)	0.1690(4)	0.0720(10)
H3'C	0.6150(7)	0.2091(4)	-0.0632(10)
O3'	0.9289(4)	0.3041(2)	-0.1301(6)
O3"	0.8055(4)	0.2795(2)	0.0063(5)
C4	1.0358(6)	0.3953(4)	0.1657(8)
C5	1.0624(6)	0.4570(4)	0.2519(8)
C5'	1.1870(6)	0.4758(4)	0.3504(9)
C5"	1.3485(6)	0.4491(4)	0.5981(10)
H5"A	1.3624(6)	0.4976(4)	0.6078(10)
H5"B	1.3557(6)	0.4314(4)	0.7051(10)
C5"'	1.4337(7)	0.4160(4)	0.5364(11)
H5"C	1.5123(7)	0.4246(4)	0.6116(11)
H5"D	1.4193(7)	0.3676(4)	0.5275(11)
H5"E	1.4260(7)	0.4343(4)	0.4296(11)
O5"	1.2294(4)	0.4347(3)	0.4785(6)
O5'	1.2399(4)	0.5232(2)	0.3211(6)
C6	0.9733(7)	0.5018(4)	0.2481(9)
C6'	0.9968(6)	0.5685(3)	0.3428(9)
H6'A	0.9241(6)	0.5930(3)	0.3249(9)
H6'B	1.0334(6)	0.5590(3)	0.4585(9)
H6'C	1.0492(6)	0.5959(3)	0.3056(9)
C7	1.1307(5)	0.3458(4)	0.1698(8)
C8	1.1272(6)	0.2780(4)	0.2207(8)

TABLE 33 (Continued)

H8A	1.0624(6)	0.2632(4)	0.2537(8)
C9	1.2155(8)	0.2323(4)	0.2240(10)
H9A	1.2109(8)	0.1858(4)	0.2577(10)
C10	1.3093(7)	0.2527(5)	0.1802(10)
H10A	1.3714(7)	0.2212(5)	0.1834(10)
C11	1.3113(6)	0.3186(5)	0.1319(9)
C12	1.2243(6)	0.3654(3)	0.1221(7)
H12A	1.2281(6)	0.4109(3)	0.0821(7)
N2	1.4115(6)	0.3410(4)	0.0798(9)
O1	1.4221(6)	0.4009(4)	0.0577(11)
O2	1.4805(5)	0.2976(3)	0.0704(8)
H6'D*	0.9364	0.5811	0.4164
H6'E*	0.9680	0.6013	0.2058
H6'F*	1.1137	0.5811	0.4209

*Disorder of methyl hydrogens on C6'

TABLE 34

ANISOTROPIC THERMAL PARAMETERS FOR

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (VI)

ATOM	U11	U22	U33	U23	U13	U12
N1	38(3)	68(4)	78(4)	-9(4)	-4(3)	-1(3)
N1	60(5)	62(5)	86(5)	14(4)	48(4)	22(4)
C2	51(5)	65(6)	60(5)	4(5)	29(4)	-7(5)
C2'	52(5)	82(6)	92(6)	18(5)	22(5)	10(4)
C3	39(5)	49(5)	58(5)	12(4)	29(4)	-1(4)
C3'	35(4)	69(6)	56(6)	1(5)	20(4)	-12(4)
C3"	79(6)	92(7)	80(6)	-14(6)	26(5)	-34(5)
C3"'	110(7)	86(7)	106(7)	-22(6)	24(6)	-24(6)
O3'	73(4)	83(4)	64(4)	-5(3)	40(3)	-15(3)
O3"	63(3)	63(3)	58(3)	-8(3)	23(3)	-22(3)
C4	45(5)	51(5)	40(4)	8(4)	26(4)	-5(4)
C5	38(5)	57(5)	49(5)	5(5)	13(4)	-4(4)
C5'	60(6)	50(5)	41(5)	5(5)	22(5)	6(5)
C5"	63(6)	131(8)	102(7)	6(6)	31(6)	9(6)
C5"'	111(7)	102(7)	129(8)	23(7)	13(7)	-38(6)
O5"	45(3)	93(4)	69(4)	15(4)	6(3)	-13(3)
O5'	69(3)	63(4)	100(5)	13(3)	22(3)	-22(3)
C6	41(5)	72(6)	59(5)	18(5)	23(5)	9(5)
C6'	85(5)	51(5)	90(6)	-10(5)	53(5)	4(4)
C7	30(4)	53(5)	52(5)	-6(4)	15(4)	1(4)
C8	55(5)	67(6)	63(6)	8(5)	20(4)	-9(5)
C9	85(6)	48(5)	98(7)	11(5)	15(6)	10(6)
C10	52(6)	77(8)	88(7)	1(5)	26(5)	18(5)
C11	37(5)	71(6)	71(6)	-6(5)	23(4)	-4(5)
C12	46(4)	45(5)	50(5)	0(4)	13(4)	7(4)
N2	54(5)	98(6)	95(6)	-6(5)	24(4)	21(5)
O1	99(5)	126(6)	276(10)	63(7)	127(6)	25(5)
O2	65(4)	146(6)	159(6)	-27(5)	58(4)	8(4)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$$

TABLE 35

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (VI)

N1-C6	1.333(7)	C6-N1-C2	122.5(6)
N1-C2	1.348(8)	N1-C2-C3	119.9(6)
C2-C3	1.388(8)	N1-C2-C2'	114.9(7)
C2-C2'	1.498(8)	C3-C2-C2'	125.3(8)
C3-C4	1.405(8)	C2-C3-C4	118.9(7)
C3-C3'	1.484(9)	C2-C3-C3'	120.3(7)
C3'-O3'	1.190(7)	C4-C3-C3'	120.5(6)
C3'-O3"	1.335(7)	O3'-C3'-O3"	124.6(8)
C3"-C3"'	1.441(8)	O3'-C3'-C3	123.8(7)
C3"-O3"	1.451(7)	O3"-C3'-C3	111.6(6)
C4-C5	1.393(8)	C3"'-C3"-O3"	110.1(6)
C4-C7	1.486(8)	C3'-O3"-C3"	115.2(6)
C5-C6	1.375(8)	C5-C4-C3	118.7(6)
C5-C5'	1.493(8)	C5-C4-C7	121.0(6)
C5'-O5'	1.197(7)	C3-C4-C7	120.3(6)
C5'-O5"	1.318(7)	C6-C5-C4	120.1(6)
C5"-C5"	1.456(9)	C6-C5-C5'	118.7(7)
C5"-O5"	1.478(8)	C4-C5-C5'	121.2(6)
C6-C6'	1.510(8)	O5'-C5'-O5"	124.4(7)
C7-C12	1.376(7)	O5'-C5'-C5	124.9(7)
C7-C8	1.400(8)	O5"-C5'-C5	110.6(6)
C8-C9	1.378(9)	C5"'-C5"-O5"	107.2(7)
C9-C10	1.364(9)	C5'-O5"-C5"	118.2(6)
C10-C11	1.355(8)	N1-C6-C5	119.9(7)
C11-C12	1.369(8)	N1-C6-C6'	117.7(7)
C11-N2	1.486(9)	C5-C6-C6'	122.3(7)
N2-O1	1.197(7)	C12-C7-C8	118.1(6)
N2-O2	1.208(7)	C12-C7-C4	120.7(6)
		C8-C7-C4	121.2(6)
		C9-C8-C7	120.8(7)
		C10-C9-C8	120.6(7)
		C11-C10-C9	117.6(7)
		C10-C11-C12	124.0(7)
		C10-C11-N2	118.2(8)
		C12-C11-N2	117.8(8)
		C11-C12-C7	118.8(6)
		O1-N2-O2	124.1(9)
		O1-N2-C11	118.4(8)
		O2-N2-C11	117.4(8)

TABLE-36

TORSION-ANGLES-(°)-FOR

Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (VI)

C6-N1-C2-C3	-0.6(10)	C7-C8-C9-C10	1.0(12)
C6-N1-C2-C2'	-179.5(6)	C8-C9-C10-C11	-0.8(12)
N1-C2-C3-C4	0.7(9)	C9-C10-C11-C12	-1.1(12)
C2'-C2-C3-C4	179.4(6)	C9-C10-C11-N2	-178.5(6)
N1-C2-C3-C3'	-173.2(6)	C10-C11-C12-C7	2.6(11)
C2'-C2-C3-C3'	5.5(10)	N2-C11-C12-C7	-180.0(6)
C2-C3-C3'-O3'	123.8(8)	C8-C7-C12-C11	-2.2(9)
C4-C3-C3'-O3'	-50.0(10)	C4-C7-C12-C11	178.3(6)
C2-C3-C3'-O3"	-58.6(8)	C10-C11-N2-O1	-170.5(9)
C4-C3-C3'-O3"	127.6(6)	C12-C11-N2-O1	12.0(11)
O3'-C3'-O3"-C3"	-0.8(10)	C10-C11-N2-O2	6.0(11)
C3-C3'-O3"-C3"	-178.4(5)	C12-C11-N2-O2	-171.6(7)
C3'"-C3"-O3"-C3'	-178.6(6)		
C2-C3-C4-C5	0.0(9)		
C3'-C3-C4-C5	173.9(6)		
C2-C3-C4-C7	178.5(6)		
C3'-C3-C4-C7	-7.6(9)		
C3-C4-C5-C6	-0.8(9)		
C7-C4-C5-C6	-179.3(6)		
C3-C4-C5-C5'	178.9(6)		
C7-C4-C5-C5'	0.5(9)		
C6-C5-C5'-O5'	-64.8(9)		
C4-C5-C5'-O5'	115.5(8)		
C6-C5-C5'-O5"	112.5(7)		
C4-C5-C5'-O5"	-67.2(8)		
O5'-C5'-O5"-C5"	2.3(10)		
C5-C5'-O5"-C5"	-175.0(6)		
C5"'-C5"-O5"-C5'	-86.2(8)		
C2-N1-C6-C5	-0.2(10)		
C2-N1-C6-C6'	-177.7(6)		
C4-C5-C6-N1	0.9(10)		
C5'-C5-C6-N1	-178.8(6)		
C4-C5-C6-C6'	178.4(6)		
C5'-C5-C6-C6'	-1.4(10)		
C5-C4-C7-C12	-56.6(8)		
C3-C4-C7-C12	125.0(6)		
C5-C4-C7-C8	124.0(7)		
C3-C4-C7-C8	-54.4(8)		
C12-C7-C8-C9	0.5(10)		
C4-C7-C8-C9	179.9(7)		

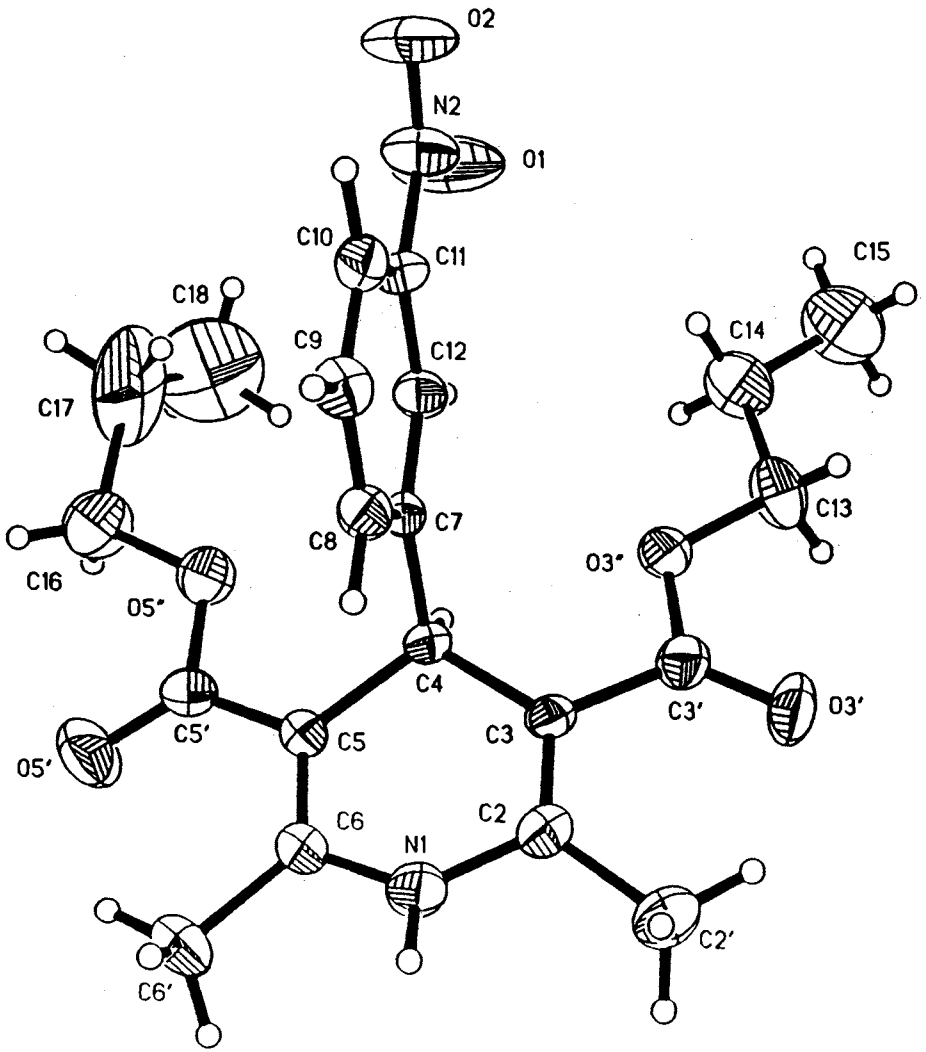
O2
N2
O1
C10
C11
C18
C15
C9
C12
C14
C17
C13
C8
C7
C16
O5'
O3'
C4
C5'
C3'
O3'
O5'
C5
C3
C6
C2
N1
C2'
C6'

TABLE 37

CRYSTAL DATA FOR

Dipropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(VII)

Formula	$C_{21}H_{26}N_2O_6$
M. W.	402.4 g $mole^{-1}$
a	9.452(1) Å
b	10.718(1) Å
c	12.081(2) Å
α	103.36(1) °
β	96.10(1) °
γ	104.53(1) °
V	1054.6(2) $Å^3$
F(000)	428
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
Dcalc	1.267 g/cm^3
Z	2
Meas refl	4398
Obs refl	1390
R	6.05 %
R_w	7.36 %
G. O. F.	1.50
Space Group	P-1
Octants meas	$-1 \leq h \leq 11, -12 \leq k \leq 11, -14 \leq l \leq 14$

TABLE 38

POSITIONAL PARAMETERS FOR

Dipropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.3377(6)	-0.3553(5)	0.2676(5)
C2	0.3041(7)	-0.2822(6)	0.1978(5)
C2'	0.1508(7)	-0.3739(6)	0.1061(5)
C3	0.4029(6)	-0.1429(5)	0.2183(4)
C3'	0.3615(8)	-0.0593(6)	0.1494(5)
O3'	0.2415(6)	-0.1015(5)	0.0773(4)
O3"	0.4790(4)	0.0744(4)	0.1781(3)
C4	0.5582(6)	-0.0663(5)	0.3077(4)
C5	0.5567(6)	-0.1490(6)	0.3968(4)
C5'	0.6791(7)	-0.0758(6)	0.5056(5)
O5'	0.6900(6)	-0.1210(5)	0.5872(4)
O5"	0.7866(5)	0.0531(4)	0.5065(3)
C6	0.4499(7)	-0.2875(6)	0.3711(5)
C6'	0.4425(8)	-0.3855(7)	0.4435(6)
C7	0.6989(6)	-0.0452(5)	0.2496(4)
C8	0.7232(7)	-0.1605(6)	0.1918(4)
C9	0.8483(7)	-0.1431(6)	0.1384(4)
C10	0.9556(7)	-0.0068(6)	0.1413(5)
C11	0.9326(6)	0.1069(6)	0.1972(5)
C12	0.8072(6)	0.0905(5)	0.2523(4)
C13	0.4554(9)	0.1703(7)	0.1200(6)
C14	0.5932(9)	0.3120(7)	0.1649(7)
C15	0.5777(11)	0.4210(8)	0.1147(8)
C16	0.9218(9)	0.1284(8)	0.6043(6)
N2	0.10433(7)	0.2523(6)	0.2017(5)
O2	0.11482(6)	0.2684(5)	0.1497(5)
O1	0.10258(7)	0.3535(5)	0.2546(5)
C17	0.10452(14)	0.2556(11)	0.5725(10)
C18	0.10125(15)	0.3521(10)	0.5723(11)
H1A	0.2838	-0.4521	0.2437
H2'A	0.1324	-0.3171	0.0608
H2'B	0.1597	-0.4527	0.0559
H2'C	0.0631	-0.4106	0.1425
H4A	0.5710	0.0270	0.3492
H6'A	0.5238	-0.3321	0.5145
H6'B	0.3394	-0.4212	0.4618
H6'C	0.4581	-0.4649	0.4017

TABLE 38 (Continued)

H8A	0.6483	-0.2557	0.1888
H9A	0.8596	-0.2259	0.0986
H10A	1.0452	0.0085	0.1059
H12A	0.7951	0.1731	0.2912
H13A	0.3609	0.1787	0.1332
H13B	0.4435	0.1330	0.0375
H14A	0.6864	0.3029	0.1489
H14B	0.6075	0.3456	0.2481
H15A	0.6703	0.5129	0.1463
H15B	0.5644	0.3873	0.0316
H15C	0.4849	0.4304	0.1315
H16A	0.9620	0.0650	0.6224
H16B	0.8918	0.1697	0.6715
H17A	1.0512	0.2178	0.4939
H17B	1.1490	0.2964	0.6232
H18A	1.0839	0.4306	0.5490
H18B	0.9082	0.3085	0.5217
H18C	1.0063	0.3873	0.6514

TABLE 39

ANISOTROPIC THERMAL PARAMETERS FOR

Dipropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VII)

ATOM	U11	U22	U33	U12	U13	U23
N1	54(3)	43(3)	97(4)	3(3)	-4(3)	31(3)
C2	42(4)	58(4)	70(4)	13(3)	2(3)	25(3)
C2'	60(4)	57(4)	85(4)	-1(3)	-11(4)	17(3)
C3	32(3)	45(3)	60(4)	17(3)	13(3)	24(3)
C3'	48(4)	56(4)	69(4)	27(3)	13(3)	24(3)
O3'	63(3)	90(3)	100(3)	32(2)	-16(3)	42(3)
O3"	52(3)	61(3)	97(3)	23(2)	12(2)	49(2)
C4	32(3)	39(3)	51(3)	10(2)	7(3)	18(3)
C5	43(3)	54(4)	48(3)	15(3)	7(3)	26(3)
C5'	47(4)	75(4)	63(4)	26(3)	23(3)	35(4)
O5'	108(4)	106(4)	71(3)	28(3)	5(3)	52(3)
O5"	62(3)	73(3)	52(2)	10(2)	-5(2)	16(2)
C6	50(4)	62(4)	78(5)	16(3)	8(4)	43(3)
C6'	84(5)	92(5)	123(6)	15(4)	1(5)	78(5)
C7	34(3)	37(3)	39(3)	13(3)	2(2)	15(2)
C8	50(4)	43(3)	56(4)	21(3)	10(3)	18(3)
C9	61(4)	56(4)	51(4)	30(3)	15(3)	15(3)
C10	49(4)	72(4)	57(4)	33(4)	15(3)	29(3)
C11	32(3)	43(3)	56(4)	7(3)	11(3)	17(3)
C12	46(4)	38(3)	55(4)	11(3)	8(3)	17(3)
C13	103(6)	97(6)	132(6)	62(5)	21(5)	79(5)
C14	102(6)	73(5)	167(8)	25(5)	13(6)	81(5)
C15	145(8)	85(5)	181(8)	46(6)	31(7)	68(6)
C16	80(6)	89(5)	81(5)	-1(5)	-21(5)	16(4)
N2	68(4)	61(4)	98(5)	12(3)	36(3)	33(4)
O2	79(3)	85(3)	156(5)	23(3)	74(4)	55(3)
O1	121(5)	40(3)	202(6)	8(3)	89(4)	27(3)
C17A	185(12)	98(8)	159(10)	30(9)	-115(9)	-24(8)
C18A	215(15)	98(9)	203(13)	21(9)	-7(11)	-12(9)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$$

TABLE 40

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Dipropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VII)

N1-C2	1.371 (10)	C2-N1-C6	122.9(5)
N1-C6	1.370 (7)	N1-C2-C2'	113.1(5)
C2-C2'	1.505 (7)	N1-C2-C3	119.3(5)
C2-C3	1.337 (7)	C2'-C2-C3	127.6(6)
C3-C3'	1.488 (10)	C2-C3-C3'	119.9(5)
C3-C4	1.499 (6)	C2-C3-C4	122.3(6)
C3'-O3'	1.196 (8)	C3'-C3-C4	117.9(4)
C3'-O3"	1.333 (6)	C3-C3'-O3'	126.9(5)
O3"-C13	1.445 (10)	C3-C3'-O3"	110.6(5)
C4-C5	1.541 (9)	O3'-C3'-O3"	122.5(7)
C4-C7	1.528 (8)	C3'-O3"-C13	117.3(5)
C5-C5'	1.460 (7)	C3-C4-C5	110.5(4)
C5-C6	1.340 (7)	C3-C4-C7	111.0(4)
C5'-O5'	1.207 (9)	C5-C4-C7	110.8(5)
C5'-O5"	1.329 (7)	C4-C5-C5'	118.6(4)
O5"-C16	1.436 (7)	C4-C5-C6	120.1(5)
C6-C6'	1.499 (11)	C5'-C5-C6	121.1(6)
C7-C8	1.393 (9)	C5-C5'-O5'	127.3(5)
C7-C12	1.378 (7)	C5-C5'-O5"	111.6(6)
C8-C9	1.373 (9)	O5'-C5'-O5"	121.1(5)
C9-C10	1.379 (8)	C5'-O5"-C16	116.2(5)
C10-C11	1.364 (9)	N1-C6-C5	120.4(6)
C11-C12	1.389 (8)	N1-C6-C6'	113.1(5)
C11-N2	1.456 (8)	C5-C6-C6'	126.4(5)
C13-C14	1.457 (8)	C4-C7-C8	122.0(4)
C14-C15	1.485 (14)	C4-C7-C12	120.7(5)
C16-C17A	1.544 (13)	C8-C7-C12	117.3(5)
N2-O2	1.203 (9)	C7-C8-C9	122.6(5)
N2-O1)	1.210 (9)	C8-C9-C10	119.6(6)
C17A)-C18A	1.196 (20)	C9-C10-C11	118.4(6)
		C10-C11-C12	122.5(5)
		C10-C11-N2	119.8(6)
		C12-C11-N2	117.7(6)
		C7-C12-C11	119.7(5)
		O3"-C13-C14	109.5(6)
		C13-C14-C15	113.8(7)
		O5"-C16-C17A	106.5(7)
		C11-N2-O2	118.8(6)
		C11-N2-O1	119.7(6)
		O2-N2-O1	121.4(6)
		C16-C17A-C18A	115.8(12)

TABLE 41

TORSION ANGLES (°) FOR

Dipropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VII)

C6-N1-C2-C2'	-165.3(0.6)	C9-C10-C11-C12	0.9(0.9)
C6-N1-C2-C3	13.1(1.0)	C9-C10-C11-N2	-179.8(0.6)
C2-N1-C6-C5	-14.8(1.1)	C10-C11-C12-C7	-1.1(0.9)
C2-N1-C6-C6'	168.2(0.6)	N2-C11-C12-C7	179.5(0.5)
N1-C2-C3-C3'	-175.2(0.6)	C10-C11-N2-O2	4.3(0.9)
N1-C2-C3-C4	6.1(0.9)	C8-C9-C10-C11	-0.3(0.9)
C2'-C2-C3-C3'	2.9(1.0)	C7-C8-C9-C10	0.1(0.9)
C2'-C2-C3-C4	-175.8(0.6)	C10-C11-N2- O1	-177.6(0.6)
C2-C3-C3'-O3'	3.5(1.1)	C12-C11-N2-O2	-176.3(0.6)
C2-C3-C3'-O3"	-176.4(0.6)	C12-C11-N2-O1	1.7(0.9)
C4-C3-C3'-O3'	-177.8(0.7)	O3"-C13-C14-C15	-177.3(0.7)
C4-C3-C3'-O3"	2.4(0.8)	O5"-C16-C17A-C18A	71.9(1.1)
C2-C3-C4-C5	-20.2(0.8)	C8-C7-C12-C11	0.8(0.8)
C2-C3-C4-C7	103.2(0.7)		
C3'-C3-C4-C5	161.0(0.5)		
C3'-C3-C4-C7	-75.6(0.7)		
C3-C3'-O3"-C13	-178.8(0.6)		
O3'-C3'-O3"-C13	1.3(1.0)		
C3'-O3"-C13-C14	178.3(0.7)		
C3-C4-C5-C5'	-165.3(0.6)		
C3-C4-C5-C6	18.2(0.8)		
C7-C4-C5-C5'	71.2(0.6)		
C7-C4-C5-C6	-105.3(0.6)		
C3-C4-C7-C8	-67.6(0.7)		
C3-C4-C7-C12	112.2(0.5)		
C5-C4-C7-C8	55.7(0.6)		
C5-C4-C7-C12	-124.6(0.5)		
C4-C5-C5'-O5'	175.3(0.7)		
C4-C5-C5'-O5"	-5.8(0.9)		
C6-C5-C5'-O5'	-8.3(1.2)		
C6-C5-C5'-O5"	170.7(0.7)		
C4-C5-C6-N1	-2.4(1.0)		
C4-C5-C6-C6'	174.2(0.7)		
C5'-C5-C6-N1	-178.8(0.6)		
C5'-C5-C6-C6'	-2.1(1.2)		
C5-C5'-O5"-C16	-173.7(0.6)		
O5'-C5'-O5"-C16	5.3(1.0)		
C5'-O5"-C16-C17A	167.4(0.8)		
C4-C7-C8-C9	179.4(0.5)		
C12-C7-C8-C9	-0.3(0.8)		
C4-C7-C12-C11	-178.9(0.5)		

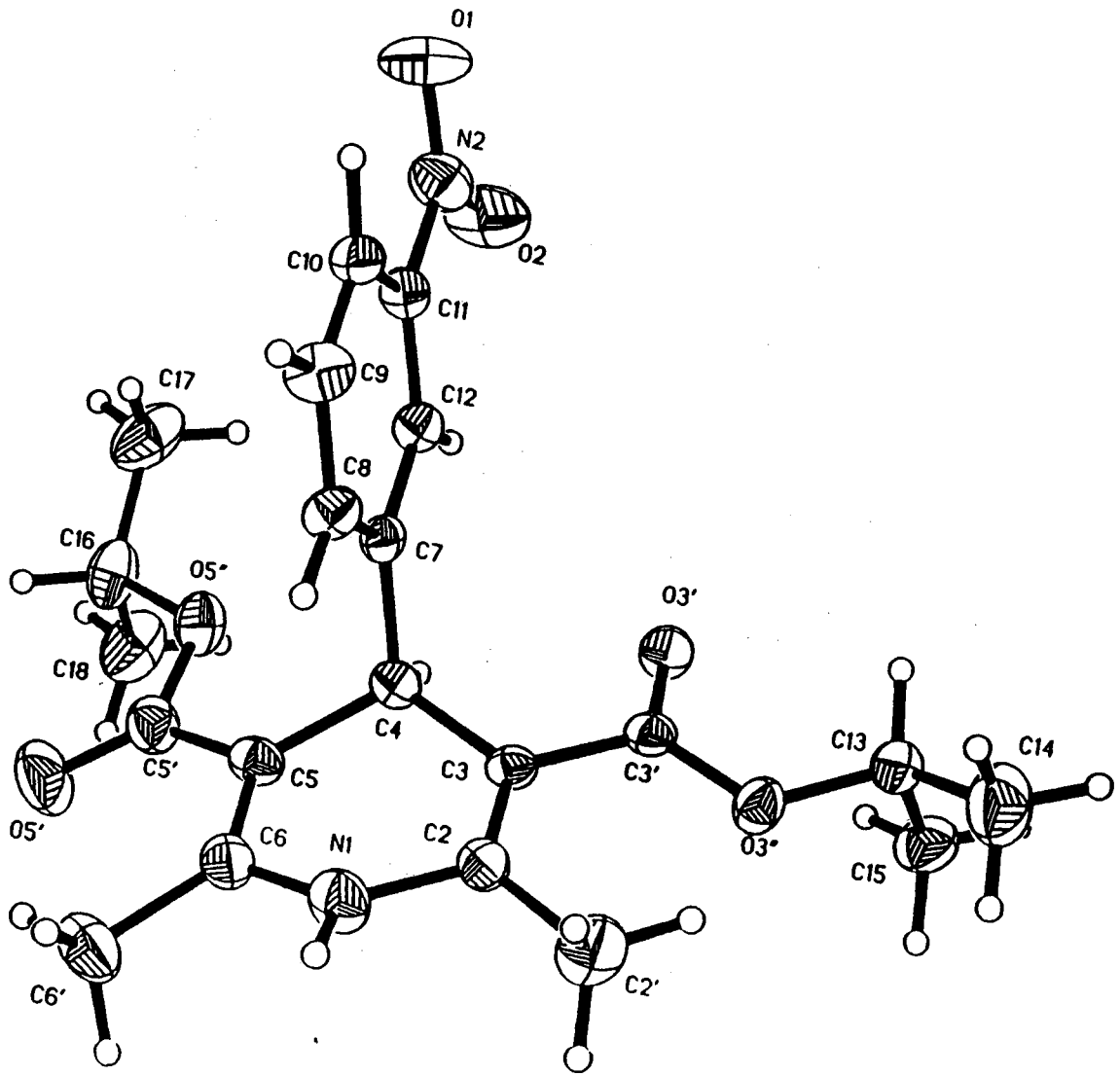

Figure 37: Projection view of Propyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine(VII)

TABLE 42

CRYSTAL DATA FOR

Di-isopropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VIII)

Formula	$C_{21}H_{26}N_2O_6$
M. W.	402.4 g $mole^{-1}$
a	7.612(2) Å
b	11.441(2) Å
c	12.938(2) Å
α	75.83(1) °
β	89.61(1) °
γ	73.18(2) °
V	1043.3(4) $Å^3$
F(000)	428
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.281 g/cm^3
Z	2
Meas refl	4521
Obs refl	1380
R	4.94 %
R_w	5.43 %
G. O. F.	1.06
Space Group	P-1
Octants meas	$-1 \leq h \leq 8, -12 \leq k \leq 13, -15 \leq l \leq 15$

TABLE 43

POSITIONAL PARAMETERS FOR

Di-isopropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VIII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.5182(6)	1.0668(4)	0.3075(3)
C2	0.4243(7)	0.9790(5)	0.3322(3)
C2'	0.5495(7)	0.8480(5)	0.3832(4)
C3	0.2405(7)	1.0170(4)	0.3092(3)
C3'	0.1198(8)	0.9375(5)	0.3407(4)
O3'	-0.0454(5)	0.9753(3)	0.3172(3)
O3"	0.2043(4)	0.8202(3)	0.3992(3)
C4	0.1463(6)	1.1482(4)	0.2403(3)
C5	0.2505(7)	1.2392(5)	0.2502(4)
C5'	0.1516(9)	1.3760(5)	0.2222(4)
O5'	0.2126(6)	1.4589(4)	0.2295(3)
O5"	-0.213(5)	1.3950(3)	0.1857(3)
C6	0.4310(8)	1.1974(5)	0.2798(4)
C6'	0.5594(8)	1.2728(5)	0.2873(4)
C7	0.1229(7)	1.1461(4)	0.1237(3)
C8	0.2714(7)	1.1208(4)	0.0621(4)
C9	0.2513(7)	1.1177(5)	-0.0425(4)
C10	0.0791(8)	1.1423(4)	-0.0895(4)
C11	-0.0684(7)	1.1688(4)	-0.0300(4)
C12	-0.0512(7)	1.1706(4)	0.0764(4)
C13	0.0997(7)	0.7312(5)	0.4238(4)
C14	0.2387(9)	0.6036(5)	0.4342(5)
C15	0.0071(7)	0.7414(5)	0.5249(4)
C16	-0.1352(8)	1.5256(5)	0.1469(5)
C17	-0.2642(9)	1.5239(5)	0.0609(5)
C18	-0.2344(9)	1.5701(5)	0.2373(4)
N2	-0.2540(7)	1.1962(4)	-0.0791(4)
O1	-0.2720(6)	1.2001(4)	-0.1726(3)
O2	-0.3810(6)	1.2094(4)	-0.0216(3)
H1A	0.6418	1.0389	0.3092
H2'A	0.4773	0.7903	0.3990
H2'B	0.6406	0.8219	0.3352
H2'C	0.6092	0.8486	0.4481
H4A	0.0264	1.1775	0.2652
H6'A	0.4920	1.3609	0.2675
H6'B	0.6121	1.2502	0.3593

TABLE 43 (Continued)

H6'C	0.6557	1.2562	0.2398
H8A	0.3921	1.1044	0.0945
H9A	0.3578	1.1006	-0.0829
H10A	0.0623	1.1394	-0.1622
H12A	-0.1579	1.1878	0.1167
H13A	0.0098	0.7480	0.3662
H14A	0.2938	0.6005	0.3676
H14B	0.3321	0.5908	0.4888
H14C	0.1794	0.5386	0.4536
H15A	-0.0807	0.8235	0.5139
H15B	-0.0547	0.6779	0.5454
H15C	0.0980	0.7302	0.5805
H16A	-0.0605	1.5785	0.1169
H17A	-0.1946	1.4970	0.0043
H17B	-0.3307	1.4653	0.0907
H17C	-0.3493	1.6063	0.0331
H18A	-0.1448	1.5711	0.2886
H18B	-0.3190	1.6533	0.2124
H18C	-0.3004	1.5123	0.2700
H2'D*	0.5024	0.8432	0.4589
H2'E*	0.6774	0.8555	0.3787
H2'F*	0.5027	0.7868	0.3334
H6'D*	0.5291	1.3528	0.2017
H6'E*	0.5139	1.3451	0.3668
H6'F*	0.7305	1.1994	0.3161

*Disorder of methyl hydrogens on C2' and C6'

TABLE 44

ANISOTROPIC THERMAL PARAMETERS FOR

Di-isopropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VIII)

ATOM	U11	U22	U33	U23	U13	U12
N1	38(3)	63(3)	64(3)	-19(3)	7(2)	-15(3)
C2	42(4)	45(4)	37(3)	-17(3)	6(3)	-12(3)
C2'	38(4)	68(4)	84(4)	-7(3)	-6(3)	0(3)
C3	29(3)	41(3)	35(3)	-8(3)	-1(2)	-8(2)
C3'	44(4)	42(3)	31(3)	-13(3)	1(3)	-13(2)
O3'	32(2)	49(2)	59(2)	-10(2)	-4(2)	-4(2)
O3"	41(2)	43(2)	53(2)	-10(2)	-2(2)	1(2)
C4	27(3)	40(3)	42(3)	-7(3)	4(2)	-14(2)
C5	35(3)	54(4)	41(3)	-16(3)	5(3)	-17(3)
C5'	64(4)	49(4)	54(4)	-22(4)	8(3)	-18(3)
O5'	101(4)	54(3)	111(4)	-37(3)	0(3)	-30(2)
O5"	55(3)	33(2)	71(3)	-5(2)	8(2)	-11(2)
C6	66(4)	55(4)	37(3)	-30(3)	10(3)	-18(3)
C6'	62(4)	82(5)	80(4)	-40(4)	8(3)	-28(3)
C7	40(3)	26(3)	36(3)	-6(2)	1(3)	-7(2)
C8	35(3)	48(3)	42(3)	-7(3)	2(3)	-6(3)
C9	37(4)	61(4)	48(4)	-3(3)	9(3)	-18(3)
C10	63(4)	44(3)	37(3)	-18(3)	-1(3)	-10(3)
C11	32(3)	37(3)	46(3)	-8(2)	0(3)	-8(3)
C12	36(3)	40(3)	42(3)	-9(3)	3(3)	-8(2)
C13	56(4)	54(4)	46(3)	-25(3)	0(3)	-5(3)
C14	111(6)	55(4)	94(5)	-22(4)	11(4)	-19(3)
C15	65(4)	82(5)	48(4)	-31(4)	4(3)	-4(3)
C16	68(5)	32(4)	77(4)	-5(3)	17(4)	-7(3)
C17	110(6)	54(4)	71(4)	10(4)	-5(4)	2(3)
C18	105(5)	46(4)	84(4)	3(4)	16(4)	-16(3)
N2	50(4)	66(3)	70(4)	-17(3)	-3(3)	-22(3)
O1	83(3)	125(4)	58(3)	-14(3)	-24(2)	-33(3)
O2	39(3)	141(4)	86(3)	-24(3)	-7(3)	-33(3)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$$

TABLE 45

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Di-isopropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VIII)

N1-C2	1.370 (8)	C2-N1-C6	123.2(4)
N1-C6	1.404 (7)	N1-C2-C2'	112.3(4)
C2-C2'	1.512 (6)	N1-C2-C3	118.7(4)
C2-C3	1.352 (7)	C2'-C2-C3	128.9(5)
C3-C3'	1.461 (8)	C2-C3-C3'	124.9(4)
C3-C4	1.514 (6)	C2-C3-C4	120.2(5)
C3'-O3'	1.219 (6)	C3'-C3-C4	114.8(4)
C3'-O3"	1.340 (5)	C3-C3'-O3'	122.8(4)
O3"-C13	1.442 (7)	C3-C3'-O3"	114.8(4)
C4-C5	1.507 (8)	O3'-C3'-O3"	122.5(5)
C4-C7	1.526 (7)	C3'-O3"-C13	118.4(4)
C5-C5'	1.481 (7)	C3-C4-C5	111.1(4)
C5-C6	1.342 (8)	C3-C4-C7	110.9(4)
C5'-O5'	1.194 (9)	C5-C4-C7	110.7(4)
C5'-O5"	1.340 (8)	C4-C5-C5'	118.7(5)
O5"-C16	1.458 (5)	C4-C5-C6	120.7(5)
C6-C6'	1.496 (10)	C5'-C5-C6	120.6(6)
C7-C8	1.382 (7)	C5-C5'-O5'	126.7(6)
C7-C12	1.386 (7)	C5-C5'-O5"	109.6(6)
C8-C9	1.373 (7)	O5'-C5'-O5"	123.7(5)
C9-C10	1.371 (8)	C5'-O5"-C16	117.0(5)
C10-C11	1.360 (8)	N1-C6-C5	118.6(6)
C11-C12	1.389 (7)	N1-C6-C6'	112.9(5)
C11-N2	1.469 (8)	C5-C6-C6'	128.5(5)
C13-C14	1.510 (7)	C4-C7-C8	121.9(4)
C13-C15	1.495 (7)	C4-C7-C12	120.2(4)
C16-C17	1.496 (9)	C8-C7-C12	117.9(4)
C16-C18	1.501 (9)	C7-C8-C9	122.2(5)
N2-O1	1.207 (7)	C8-C9-C10	119.9(5)
N2-O2	1.213 (7)	C9-C10-C11	118.4(5)
		C10-C11-C12	122.7(5)
		C10-C11-N2	119.2(5)
		C12-C11-N2	118.1(5)
		C7-C12-C11	118.9(4)
		O3"-C13-C14	105.1(5)
		O3"-C13-C15	109.3(5)
		C14-C13-C15	112.4(4)
		O5"-C16-C17	105.1(5)
		O5"-C16-C18	109.6(4)

TABLE 45 (Continued)

	C17-C16-C18	112.4(5)
	C11-N2-O1	119.0(5)
	C11-N2-O2	117.5(5)
	O1-N2-O2	123.5(5)

TABLE 46

TORSION ANGLES (°) FOR

Di-isopropyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (VIII)

C6-N1-C2-C2'	-166.8(0.5)	C8-C7-C12-C11	-0.1(0.7)
C6-N1-C2-C3	13.4(0.7)	C7-C8-C9-C10	1.1(0.8)
C2-N1-C6-C5	-17.0(0.7)	C8-C9-C10-C11	-0.3(0.8)
C2-N1-C6-C6'	163.3(0.5)	C9-C10-C11-C12	-0.6(0.8)
N1-C2-C3-C3'	-173.2(0.5)	C9-C10-C11-N2	179.6(0.5)
N1-C2-C3-C4	10.7(0.7)	C10-C11-C12-C7	0.9(0.7)
C2'-C2-C3-C3'	7.0(0.9)	N2-C11-C12-C7	-179.4(0.4)
C2'-C2-C3-C4	-169.1(0.5)	C10-C11-N2-O1	-3.2(0.7)
C2-C3-C3'-O3'	-179.2(0.5)	C10-C11-N2-O2	174.2(0.5)
C2-C3-C3'-O3"	1.9(0.7)	C12-C11-N2-O1	177.1(0.5)
C4-C3-C3'-O3'	-2.9(0.7)	C12-C11-N2-O2	-5.5(0.7)
C4-C3-C3'-O3"	178.2(0.4)	C12-C7-C8-C9	-0.9(0.7)
C2-C3-C4-C5	-28.0(0.6)	C4-C7-C12-C11	179.6(0.4)
C2-C3-C4-C7	95.6(0.6)	C4-C7-C8-C9	179.4(0.4)
C3'-C3-C4-C5	155.6(0.4)		
C3'-C3-C4-C7	-80.9(0.5)		
C3-C3'-O3"-C13	-173.3(0.4)		
O3'-C3'-O3"-C13	7.8(0.7)		
C3'-O3"-C13-C14	150.7(0.4)		
C3'-O3"-C13-C15	-88.4(0.5)		
C3-C4-C5-C5'	-158.3(0.4)		
C3-C4-C5-C6	24.3(0.6)		
C7-C4-C5-C5'	78.1(0.5)		
C7-C4-C5-C6	-99.4(0.5)		
C3-C4-C7-C8	-68.4(0.6)		
C3-C4-C7-C12	111.9(0.5)		
C5-C4-C7-C8	55.4(0.5)		
C5-C4-C7-C12	-124.3(0.5)		
C4-C5-C5'-O5'	177.1(0.5)		
C4-C5-C5'-O5"	-3.3(0.6)		
C6-C5-C5'-O5'	-5.5(0.8)		
C6-C5-C5'-O5"	174.1(0.5)		
C4-C5-C6-N1	-3.8(0.7)		
C4-C5-C6-C6'	175.7(0.5)		
C5'-C5-C6-N1	178.8(0.4)		
C5'-C5-C6-C6'	-1.6(0.8)		
C5-C5'-O5"-C16	-175.6(0.4)		
O5'-C5'-O5"-C16	3.9(0.8)		
C5'-O5"-C16-C17	149.0(0.5)		
C5'-O5"-C16-C18	-90.0(0.6)		

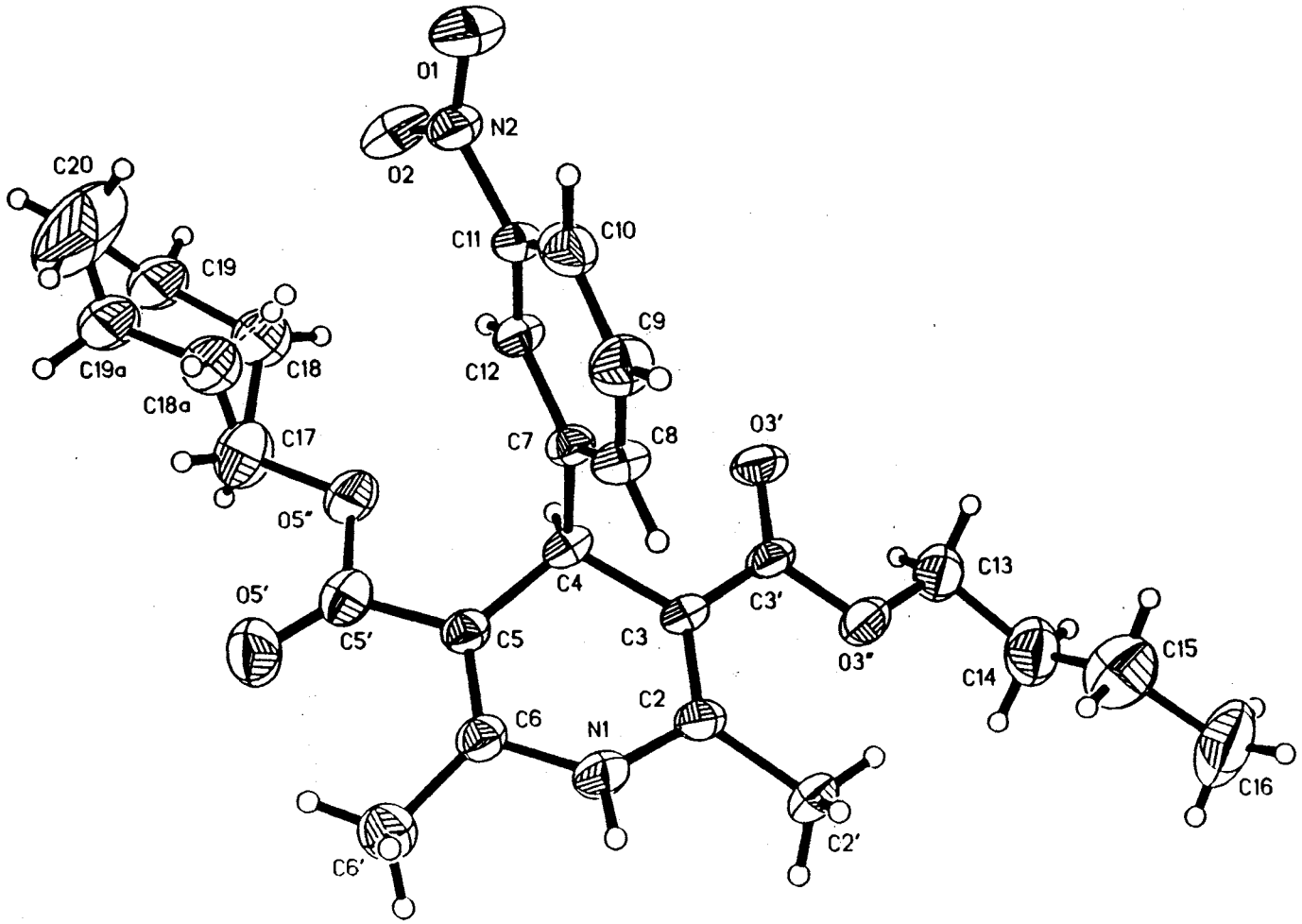

Figure 39: Projection view of Butyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine(VIV)

TABLE 47

CRYSTAL DATA FOR

Dibutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-Dihydropyridine-3,5-dicarboxylate (VIV)

Formula	$C_{23}H_{30}N_2O_6$
M. W.	430.5 g $mole^{-1}$
a	11.358(4) Å
b	16.352(6) Å
c	12.999(5) Å
α	90.0 °
β	101.56(1) °
γ	90.0 °
V	2364.9(15) $Å^3$
F(000)	920
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.209 g/cm^3
Z	4
Meas refl	5197
Obs refl	1458
R	5.6 %
R_w	6.12 %
G. O. F.	1.13
Space Group	$P2_1/c$
Octants meas	$-1 \leq h \leq 13, -1 \leq k \leq 19, -15 \leq l \leq 15$

TABLE 48

POSITIONAL PARAMETERS FOR

Dibutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-Dihydropyridine-3,5-dicarboxylate (IX)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.8738(4)	0.1670(3)	0.3466(3)
N2	1.0175(5)	0.0910(4)	-0.1728(4)
O1	0.9788(4)	0.0460(3)	-0.2493(4)
O2	1.1108(5)	0.1320(3)	-0.1632(3)
C2	0.8040(4)	0.2257(4)	0.2851(4)
C2'	0.6925(4)	0.2491(3)	0.3277(4)
C3	0.8420(4)	0.2573(3)	0.2001(4)
C3'	0.7863(4)	0.3253(3)	0.1353(4)
O3'	0.8149(3)	0.3487(2)	0.0536(3)
O3"	0.6984(3)	0.3675(2)	0.1724(3)
C4	0.9526(4)	0.2196(3)	0.1650(4)
C5	1.0376(4)	0.1813(3)	0.2584(4)
C5'	1.1678(6)	0.1713(4)	0.2552(5)
O5'	1.2451(4)	0.1392(3)	0.3204(4)
O5"	1.1933(3)	0.2067(3)	0.1678(3)
C6	0.9943(5)	0.1510(3)	0.3422(4)
C6'	1.0610(5)	0.1039(4)	0.4347(4)
C7	0.9177(4)	0.1577(3)	0.0747(3)
C8	0.9775(4)	0.1547(3)	-0.0105(4)
C9	0.9469(5)	0.0949(4)	-0.0870(4)
C10	0.8570(5)	0.0368(4)	-0.0860(4)
C11	0.7992(5)	0.0403(4)	-0.008(5)
C12	0.8293(5)	0.0991(4)	0.0781(4)
C13	0.6497(5)	0.4405(4)	0.1144(5)
C14	0.5579(6)	0.4803(5)	0.1673(6)
C15	0.4467(7)	0.4379(5)	0.1638(7)
C16	0.3473(7)	0.4826(5)	0.2065(8)
C17	1.3171(5)	0.2006(5)	0.1532(6)
C18	1.3232(9)	0.2269(11)	0.0427(9)
C18A	1.3411(28)	0.1750(36)	0.0783(28)
C19	1.4455(10)	0.2184(10)	0.0134(11)
C19A	1.4621(27)	0.1693(28)	0.0615(25)
C20	1.4820(9)	0.1439(8)	-0.0166(10)
H1A	0.8389	0.1370	0.3903
H2'A	0.6486	0.2905	0.2836
H2'B	0.6430	0.2014	0.3267
H2'C	0.7149	0.2693	0.3982

TABLE 48 (Continued)

H2'D*	0.7005	0.3069	0.3822
H2'E*	0.6921	0.2059	0.4221
H2'F*	0.6277	0.2434	0.2880
H4A	0.9958	0.2632	0.1397
H6'A	1.1425	0.0954	0.4273
H6'B	1.0602	0.1338	0. 4981
H6'C	1.0224	0.0520	0.4377
H6'D*	1.0904	0.0427	0.4381
H6'E*	1.1398	0.1391	0.4969
H6'F*	1.0146	0.0861	0. 5138
H8A	1.0390	0.1939	-0.0154
H10A	0.8364	-0.0022	-0.1420
H11A	0.7387	0.0003	0.0040
H12A	0.7884	0.0994	0.1359
H13A	0.6104	0.4253	0.0446
H13B	0.7133	0.4781	0.1097
H14A	0.5384	0.5343	0.1399
H14B	0.5941	0.4854	0.2403
H15A	0.4637	0.3867	0.2000
H15B	0.4155	0.4266	0.0910
H16A	0.2749	0.4511	0.1995
H16B	0.3786	0.4933	0.2795
H16C	0.3302	0.5335	0.1697
H17A	1.3460	0.1461	0.1706
H17B	1.3667	0.2383	0.1992
H18A	1.2930	0.2813	0.0275
H18B	1.2697	0.1900	-0.0014
H18C	1.2898	0.1973	0.0169
H18D	1.3184	0.1187	0.0825
H19A	1.5055	0.2294	0.0752
H19B	1.4520	0.2601	-0.0372
H19C	1.4902	0.2248	0.0665
H19D	1.5123	0.1391	0.1168
H20A	1.5611	0.1450	-0.0323
H20B	1.4781	0.1018	0.0341
H20C	1.4240	0.1329	-0.0796

*Disorder of methyl hydrogens on C2' and C6'

TABLE 49

ANISOTROPIC THERMAL PARAMETERS FOR

Dibutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-Dihydropyridine-3,5-dicarboxylate (IX)

ATOM	U11	U22	U33	U23	U13	U12
N1	61(3)	67(3)	55(3)	-7(3)	27(2)	4(3)
N2	91(4)	79(4)	50(3)	31(4)	22(3)	-3(3)
O1	133(4)	129(4)	64(3)	23(3)	26(3)	-27(3)
O2	108(3)	100(4)	82(3)	5(3)	58(3)	-12(3)
C2	56(3)	59(4)	40(3)	-2(3)	16(3)	-3(3)
C2'	53(3)	91(5)	62(3)	2(3)	30(3)	-1(3)
C3	51(3)	50(4)	41(3)	1(3)	20(2)	-6(3)
C3'	56(3)	61(4)	43(3)	1(3)	22(3)	-13(3)
O3'	89(3)	87(3)	48(2)	19(2)	32(2)	11(2)
O3"	68(2)	76(3)	67(2)	13(2)	32(2)	6(2)
C4	55(3)	53(4)	48(3)	0(3)	25(3)	-9(3)
C5	52(3)	52(4)	47(3)	-2(3)	14(3)	-9(3)
C5'	59(4)	61(4)	80(4)	-3(4)	21(4)	-6(4)
O5'	64(3)	140(5)	106(4)	16(3)	19(3)	28(3)
O5"	52(2)	121(4)	78(3)	-3(2)	29(2)	1(3)
C6	54(4)	58(4)	51(3)	-1(3)	15(3)	-9(3)
C6'	84(4)	70(4)	68(4)	11(4)	18(4)	6(4)
C7	59(3)	43(4)	42(3)	6(3)	17(3)	-2(3)
C8	60(3)	64(4)	45(3)	6(3)	22(3)	-2(3)
C9	67(4)	72(4)	36(3)	20(4)	14(3)	-3(4)
C10	75(4)	64(5)	57(4)	6(4)	3(3)	-10(4)
C11	73(4)	81(5)	79(4)	-7(4)	26(4)	8(4)
C12	68(4)	67(4)	47(3)	-2(4)	22(3)	-7(4)
C13	70(4)	91(5)	85(4)	15(4)	23(4)	14(4)
C14	80(5)	107(6)	120(6)	23(5)	19(4)	1(5)
C15	128(7)	117(7)	143(7)	-1(6)	50(6)	2(6)
C16	101(6)	182(9)	208(10)	55(6)	74(7)	45(8)
C17	57(4)	163(8)	119(6)	-6(5)	34(4)	8(6)
C18	62(5)	145(13)	86(8)	-9(8)	31(5)	19(9)
C18A	62(5)	145(13)	86(8)	-9(8)	31(5)	19(9)
C19	79(6)	157(14)	80(9)	5(8)	40(7)	9(8)
C19A	79(6)	157(14)	80(9)	5(8)	40(7)	9(8)
C20	125(8)	344(20)	282(16)	-33(11)	134(10)	-76(14)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$$

TABLE 50

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Dibutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-Dihydropyridine-3,5-dicarboxylate (IX)

N1-C2	1.391 (7)	C2-N1-C6	123.5(5)
N1-C6	1.406 (7)	O1-N2-O2	123.9(6)
N2-O1	1.244 (7)	O1-N2-C9	117.7(6)
N2-O2	1.238 (8)	O2-N2-C9	118.4(5)
N2-C9	1.499 (8)	N1-C2-C2'	112.5(4)
C2-C2'	1.528 (8)	N1-C2-C3	119.3(5)
C2-C3	1.366 (7)	C2'-C2-C3	128.1(5)
C3-C3'	1.461 (7)	C2-C3-C3'	125.7(5)
C3-C4	1.548 (7)	C2-C3-C4	119.6(4)
C3'-O3'	1.232 (7)	C3'-C3-C4	114.6(4)
C3'-O3"	1.378 (7)	C3-C3'-O3'	125.1(5)
O3"-C13	1.460 (7)	C3-C3'-O3"	116.1(5)
C4-C5	1.526 (6)	O3'-C3'-O3"	118.8(5)
C4-C7	1.540 (7)	C3'-O3"-C13	117.0(4)
C5-C5'	1.496 (8)	C3-C4-C5	110.5(4)
C5-C6	1.375 (8)	C3-C4-C7	112.7(4)
C5'-O5'	1.211 (8)	C5-C4-C7	111.2(4)
C5'-O5"	1.357 (8)	C4-C5-C5'	119.6(5)
O5"-C17	1.459 (7)	C4-C5-C6	120.5(5)
C6-C6'	1.499 (7)	C5'-C5-C6	119.7(5)
C7-C12	1.395 (8)	C5-C5'-O5'	127.6(6)
C7-C8	1.411 (7)	C5-C5'-O5"	110.8(5)
C12-C11	1.396 (8)	O5'-C5'-O5"	121.6(6)
C11-C10	1.398 (9)	C5'-O5"-C17	116.9(5)
C10-C9	1.397 (9)	N1-C6-C5	118.1(4)
C9-C8	1.388 (8)	N1-C6-C6'	113.8(5)
C13-C14	1.506 (10)	C5-C6-C6'	128.1(5)
C14-C15	1.434 (11)	C4-C7-C12	120.3(5)
C15-C16	1.539 (13)	C4-C7-C8	122.0(4)
C17-C18	1.514 (15)	C12-C7-C8	117.6(5)
C17-C18A	1.142 (43)	C7-C12-C11	121.5(5)
C18-C19	1.519 (17)	C12-C11-C10	121.7(6)
C19-C20	1.369 (20)	C11-C10-C9	116.1(5)
C20-C19A	1.160 (38)	N2-C9-C10	118.6(5)
C18A-C19A	1.438 (47)	N2-C9-C8	117.9(5)
		C10-C9-C8	123.4(5)
		C7-C8-C9	119.7(5)
		O3"-C13-C14	110.1(5)
		C13-C14-C15	117.5(7)
		C14-C15-C16	117.6(7)

TABLE 50 (Continued)

	O5"-C17-C18	109.4(6)
	O5"-C17-C18A	122.4(17)
	C17-C18-C19	115.5(9)
	C18-C19-C20	119.8(13)
	C17-C18A-C19A	123.5(31)
	C20-C19A-C18A	121.0(28)

TABLE 51

TORSION ANGLES (°) FOR

Dibutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-Dihydropyridine-3,5-dicarboxylate (IX)

C6-N1-C2-C2'	-162.3(0.5)	C8-C7-C12-C11	-1.1(0.8)
C6-N1-C2-C3	15.2(0.7)	C4-C7-C8-C9	176.6(0.5)
C2-N1-C6-C5	-14.7(0.7)	C12-C7-C8-C9	0.2(0.7)
C2-N1-C6-C6'	163.4(0.5)	C7-C12-C11-C10	0.8(0.9)
O1-N2-C9-C10	12.9(0.8)	C12-C11-C10-C9	0.4(0.8)
O1-N2-C9-C8	-169.4(0.5)	C11-C10-C9-N2	176.2(0.5)
O2-N2-C9-C10	-166.6(0.5)	C11-C10-C9-C8	-1.4(0.8)
O2-N2-C9-C8	11.1(0.8)	N2-C9-C8-C7	-176.5(0.5)
N1-C2-C3-C3'	-172.7(0.5)	C10-C9-C8-C7	1.1(0.8)
N1-C2-C3-C4	8.0(0.7)	O3"-C13-C14-C15	-69.0(0.7)
C2'-C2-C3-C3'	4.4(0.8)	C13-C14-C15-C16	-173.2(0.7)
C2'-C2-C3-C4	-174.9(0.5)	O5"-C17-C18-C19	-176.1(1.1)
C2-C3-C3'-O3'	-173.4(0.5)	O5"-C17-C18A-C19A	179.2(3.4)
C2-C3-C3'-O3"	9.3(0.7)	C17-C18-C19-C20	81.0(1.6)
C4-C3-C3'-O3'	5.9(0.7)	O5'-C5'-O5"-C17	3.0(0.9)
C4-C3-C3'-O3"	-171.4(0.4)	C5'-O5"-C17-C18	168.1(0.9)
C2-C3-C4-C5	-27.9(0.6)	C5'-O5"-C17-C18A	126.0(3.3)
C2-C3-C4-C7	97.3(0.5)	C4-C7-C12-C11	-177.5(0.5)
C3'-C3-C4-C5	152.8(0.4)		
C3'-C3-C4-C7	-82.0(0.5)		
C3-C3'-O3"-C13	174.2(0.4)		
O3'-C3'-O3"-C13	-3.3(0.7)		
C3'-O3"-C13-C14	-178.3(0.4)		
C3-C4-C5-C5'	-155.8(0.5)		
C3-C4-C5-C6	28.5(0.6)		
C7-C4-C5-C5'	78.2(0.6)		
C7-C4-C5-C6	-97.6(0.6)		
C3-C4-C7-C12	-45.2(0.6)		
C3-C4-C7-C8	138.6(0.5)		
C5-C4-C7-C12	79.6(0.6)		
C5-C4-C7-C8	-96.6(0.6)		
C4-C5-C5'-O5'	-176.6(0.6)		
C4-C5-C5'-O5"	5.6(0.7)		
C6-C5-C5'-O5'	-0.8(0.9)		
C6-C5-C5'-O5"	-178.6(0.5)		
C4-C5-C6-N1	-9.1(0.7)		
C4-C5-C6-C6'	173.0(0.5)		
C5'-C5-C6-N1	175.2(0.5)		
C5'-C5-C6-C6'	-2.7(0.8)		
C5-C5'-O5"-C17	-179.0(0.5)		

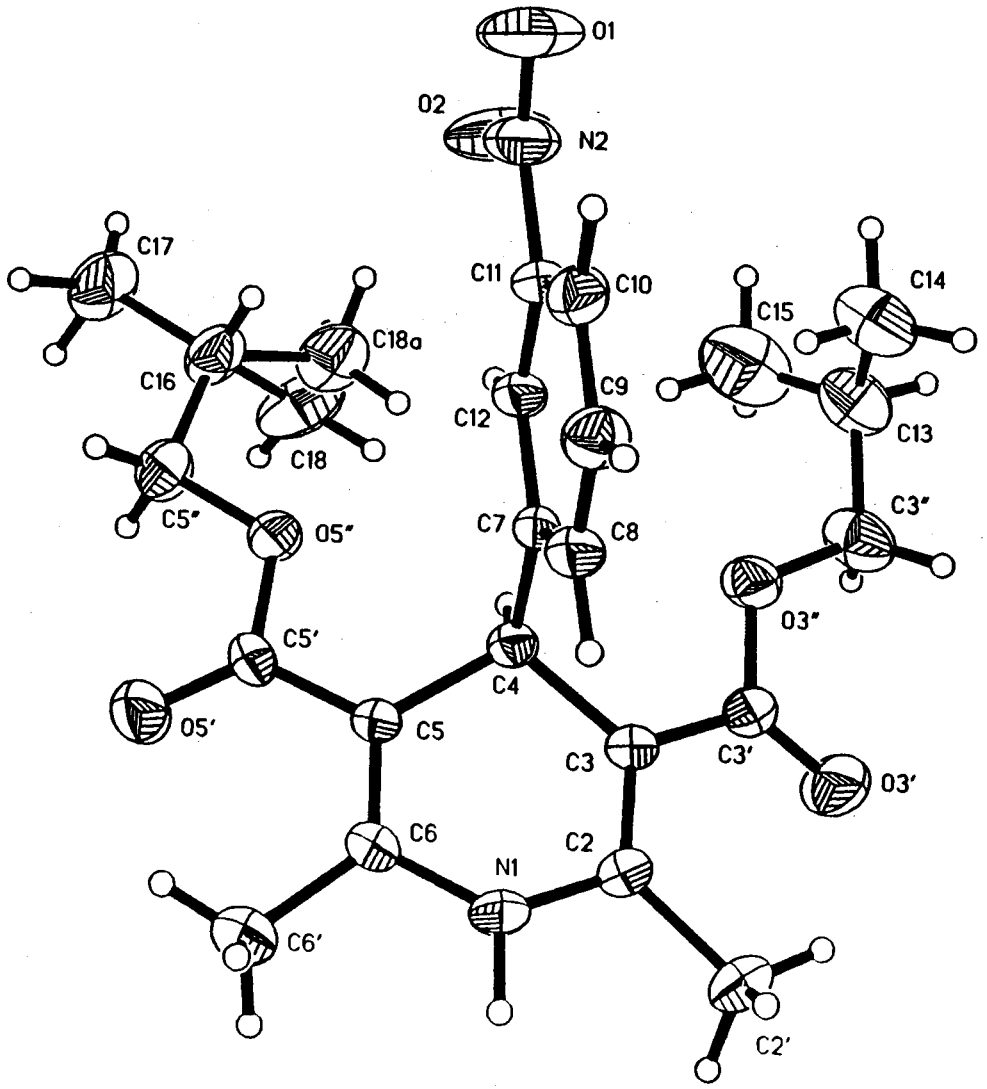

Figure 40: Projection view of Isobutyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine(X)

TABLE 52

CRYSTAL DATA FOR

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate(X)

Formula	$C_{23}H_{30}N_2O_6$
M. W.	430.49 g $mole^{-1}$
a	9.7150(10) Å
b	10.9320(10) Å
c	12.5010(10) Å
α	99.290(10) °
β	97.270(10) °
γ	116.350(10) °
V	1144.2(2) $Å^3$
F(000)	460
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.249 g/cm^3
Z	2
Meas refl	2623
Obs refl	1557
R	5.7%
R_w	15.95%
G. O. F.	1.13
Space Group	P-1
Octants meas	$-1 \leq h \leq 9, -10 \leq k \leq 9, -12 \leq l \leq 12$

TABLE 53

POSITIONAL PARAMETERS FOR

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (X)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.1571(4)	1.3679(3)	0.7555(3)
C2	0.0591(4)	1.3042(4)	0.6512(3)
C2'	0.0753(5)	1.4042(4)	0.5777(4)
C3	-0.0388(4)	1.1638(4)	0.6240(3)
C3'	-0.1340(5)	1.0906(5)	0.5124(4)
C3"	-0.3525(6)	0.8808(5)	0.4012(4)
O3'	-0.1169(4)	1.1333(4)	0.4300(3)
O3"	-0.2489(3)	0.9624(3)	0.5082(2)
C4	-0.0529(4)	1.0797(4)	0.7123(3)
C5	0.0995(4)	1.1536(4)	0.8032(3)
C5'	0.1406(5)	1.0687(4)	0.8656(3)
C5"	0.0532(5)	0.8416(4)	0.9004(4)
O5'	0.2639(4)	1.1076(3)	0.9309(3)
O5"	0.0256(3)	0.9368(3)	0.8438(2)
C6	0.1930(4)	1.2933(4)	0.8231(3)
C6'	0.3382(5)	1.3819(4)	0.9120(4)
C7	-0.1957(4)	1.0546(4)	0.7612(3)
C8	-0.2262(5)	1.1634(4)	0.8022(3)
C9	-0.3535(5)	1.1411(4)	0.8491(3)
C10	-0.4573(5)	1.0072(5)	0.8554(3)
C11	-0.4266(4)	0.9001(4)	0.8146(3)
C12	-0.2981(4)	0.9218(4)	0.7678(3)
C13	-0.4830(6)	0.7517(5)	0.4119(4)
C14	-0.5874(6)	0.7760(6)	0.4794(5)
C15	-0.4303(9)	0.6617(8)	0.4486(7)
C16	-0.0779(6)	0.6970(4)	0.8513(4)
C17	-0.0544(7)	0.5961(5)	0.9142(4) 0
C18	-0.0631(29)	0.6610(36)	0.7342(35)
C18A	-0.1395(29)	0.6372(34)	0.7297(32)
O1	-0.6409(5)	0.7386(4)	0.8662(4)
O2	-0.5118(5)	0.6613(4)	0.7774(4)
N2	-0.5339(5)	0.7577(5)	0.8197(4)
H1A	0.2307(4)	1.4611(3)	0.7608(3)
H2'A	0.0048(5)	1.3544(4)	0.5062(4)
H2'B	0.0507(5)	1.4746(4)	0.6125(4)
H2'C	0.1819(5)	1.4484(4)	0.5687(4)

TABLE 53 Continued

H2'D*	0.1146	1.3748	0.5039.
H2'E*	-0.0311	1.3951	0.5468
H2'F*	0.1323	1.4942	0.6276
H3"A	-0.2939(6)	0.8570(5)	0.3531(4)
H3"B	-0.3927(6)	0.9357(5)	0.3690(4)
H4A	-0.0656(4)	0.9895(4)	0.6768(3)
H5"A	0.0596(5)	0.8691(4)	0.9785(4)
H5"B	0.1505(5)	0.8437(4)	0.8903(4)
H6'A	0.3558(5)	1.3237(4)	0.9560(4)
H6'B	0.4268(5)	1.4253(4)	0.8794(4)
H6'C	0.3256(5)	1.4535(4)	0.9585(4)
H8A	-0.1558(5)	1.2564(4)	0.7969(3)
H9A	-0.3688(5)	1.2199(4)	0.8781(3)
H10A	-0.5470(5)	0.9898(5)	0.8875(3)
H12A	-0.2802(4)	0.8440(4)	0.7408(3)
H13A	-0.5468(6)	0.7037(5)	0.3381(4)
H14A	-0.6697(6)	0.6879(6)	0.4847(5)
H14B	-0.5259(6)	0.8315(6)	0.5526(5)
H14C	-0.6331(6)	0.8259(6)	0.4450(5)
H15A	-0.5190(9)	0.5790(8)	0.4556(7)
H15B	-0.3784(9)	0.6351(8)	0.3960(7)
H15C	-0.3578(9)	0.7094(8)	0.5196(7)
H16A	-0.1730(6)	0.6980(4)	0.8636(4)
H17A	-0.0203(7)	0.6477(5)	1.0042(4)
H17B	-0.1197(7)	0.5209(5)	0.9002(4)
H17C	0.0626(7)	0.6111(5)	0.9137(4)
H18A	-0.0773(29)	0.7220(36)	0.6918(35)
H18B	0.0336(29)	0.6595(36)	0.7276(35)
H18C	-0.1497(29)	0.5675(36)	0.7064(35)
H18D	-0.1500(29)	0.7088(34)	0.6996(32)
H18E	-0.0608(29)	0.6195(34)	0.7017(32)
H18F	-0.2386(29)	0.5523(34)	0.7082(32)

*Disorder of methyl hydrogens on C2'

TABLE 54

ANISOTROPIC THERMAL PARAMETERS FOR

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (X)

ATOM	U11	U22	U33	U23	U13	U12
N1	53(2)	30(2)	66(2)	17(2)	6(2)	5(2)
C2	47(2)	44(3)	54(3)	22(2)	14(2)	17(2)
C2'	77(3)	54(3)	81(3)	36(2)	15(3)	23(2)
C3	39(2)	39(2)	49(3)	15(2)	10(2)	13(2)
C3'	49(3)	63(3)	51(3)	24(2)	14(2)	20(3)
C3"	68(3)	83(3)	58(3)	-8(3)	7(3)	13(3)
O3'	97(3)	98(2)	55(2)	33(2)	9(2)	10(2)
O3"	57(2)	54(2)	47(2)	55(13)	38(14)	7(2)
C4	39(2)	35(2)	51(2)	15(2)	9(2)	15(2)
C5	34(2)	39(2)	49(2)	15(2)	6(2)	11(2)
C5'	36(3)	55(3)	57(3)	17(2)	0(2)	18(2)
C5"	76(3)	59(3)	90(3)	35(3)	6(3)	35(3)
O5'	66(2)	71(2)	112(3)	39(2)	-12(2)	21(2)
O5"	51(2)	42(2)	78(2)	288(14)	39(14)	18(2)
C6	38(2)	43(3)	53(2)	12(2)	2(2)	8(2)
C6'	63(3)	55(3)	80(3)	16(2)	-6(3)	6(2)
C7	34(2)	32(2)	40(2)	11(2)	3(2)	11(2)
C8	44(3)	42(2)	61(3)	17(2)	9(2)	14(2)
C9	61(3)	53(3)	69(3)	17(2)	17(2)	29(2)
C10	55(3)	73(3)	63(3)	31(2)	21(2)	34(3)
C11	39(3)	43(3)	59(3)	25(2)	11(2)	7(2)
C12	40(2)	35(2)	56(2)	15(2)	9(2)	11(2)
C13	75(4)	62(3)	85(4)	-14(3)	1(3)	19(3)
C14	69(4)	112(4)	116(5)	11(4)	19(3)	28(3)
C16	93(4)	051(3)	71(3)	27(2)	14(3)	31(3)
C17	124(5)	54(3)	110(4)	38(3)	14(4)	39(3)
C18	159(27)	66(15)	104(17)	35(12)	66(24)	52(21)
C18A	119(19)	49(10)	85(12)	10(8)	16(15)	33(13)
N2	52(3)	68(3)	114(3)	45(3)	31(2)	17(2)
O1	81(3)	98(3)	201(4)	81(3)	83(3)	32(2)
O2	117(3)	47(2)	174(4)	36(2)	81(3)	14(2)
C15	109(5)	119(5)	177(7)	13(5)	22(5)	43(5)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$$

TABLE 55

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (X)

N1-C2	1.376(5)	C2-N1-C6	122.5(3)
N1-C6	1.379(5)	C3-C2-N1	119.5(3)
C2-C3	1.353(5)	C3-C2-C2'	126.6(4)
C2-C2'	1.507(5)	N1-C2-C2'	113.9(3)
C3-C3'	1.448(5)	C2-C3-C3'	121.3(3)
C3-C4	1.529(5)	C2-C3-C4	120.0(3)
C3'-O3'	1.199(5)	C3'-C3-C4	118.7(3)
C3'-O3"	1.336(5)	O3'-C3'-O3"	121.0(4)
C3"-O3"	1.440(5)	O3'-C3'-C3	126.9(4)
C3"-C13	1.460(6)	O3"-C3'-C3	112.2(3)
C4-C7	1.519(5)	O3"-C3"-C13	110.6(4)
C4-C5	1.534(5)	C3'-O3"-C3"	116.9(3)
C5-C6	1.344(5)	C7-C4-C3	112.2(3)
C5-C5'	1.453(5)	C7-C4-C5	111.4(3)
C5'-O5'	1.213(4)	C3-C4-C5	110.0(3)
C5'-O5"	1.330(5)	C6-C5-C5'	121.3(3)
C5"-O5"	1.446(5)	C6-C5-C4	120.4(3)
C5"-C16	1.483(6)	C5'-C5-C4	118.4(3)
C6-C6'	1.485(6)	O5'-C5'-O5"	121.0(4)
C7-C12	1.372(5)	O5'-C5'-C5	126.5(4)
C7-C8	1.385(5)	O5"-C5'-C5	112.5(3)
C12-C11	1.387(5)	O5"-C5"-C16	108.5(3)
C11-C10	1.370(6)	C5'-O5"-C5"	117.7(3)
C11-N2	1.457(5)	C5-C6-N1	119.3(3)
C10-C9	1.383(5)	C5-C6-C6'	127.2(4)
C9-C8	1.376(6)	N1-C6-C6'	113.5(3)
C13-C15	1.405(8)	C12-C7-C8	117.7(3)
C13-C14	1.481(7)	C12-C7-C4	120.3(3)
C16-C18A	1.48(4)	C8-C7-C4	121.9(3)
C16-C18	1.50(4)	C7-C12-C11	120.0(3)
C16-C17	1.531(6)	C10-C11-C12	122.6(3)
N2-O2	1.220(5)	C10-C11-N2	118.7(4)
N2-O1	1.209(5)	C12-C11-N2	118.7(4)
		C11-C10-C9	117.2(4)
		C10-C9-C8	120.6(4)
		C9-C8-C7	121.9(3)
		C15-C13-C3"	111.7(5)
		C15-C13-C14	112.0(6)
		C3"-C13-C14	113.9(4)
		C5"-C16-C18A	122.9(13)

TABLE 55 (Continued)

	C5"-C16-C18	105.1(12)
	C5"-C16-C17	109.1(4)
	C18A-C16-C17	114.0(15)
	C18-C16-C17	109.3(16)
	O1-N2-O2	122.0(4)
	O1-N2-C11	119.4(5)
	O2-N2-C11	118.6(4)

TABLE 56

TORSION ANGLES (°) FOR

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (X)

C6-N1-C2-C3	18.24(0.55)	C12-C7-C8-C9	0.55(0.55)
C6-N1-C2-C2'	-161.46(0.37)	C4-C7-C8-C9	-178.27(0.33)
N1-C2-C3-C3'	-174.70(0.35)	O3"-C3"-C13-C15	-64.70(0.62)
C2'-C2-C3-C3'	4.96(0.62)	O3"-C3"-C13-C14	63.44(0.64)
N1-C2-C3-C4	6.58(0.54)	O5"-C5"-C16-C18A	45.34(1.53)
C2'-C2-C3-C4	-173.76(0.37)	O5"-C5"-C16-C18	65.62(1.61)
C2-C3-C3'-O3'	16.18(0.68)	O5"-C5"-C16-C17	-177.29(0.39)
C4-C3-C3'-O3'	-165.08(0.44)	C10-C11-N2-O1	-4.85(0.63)
C2-C3-C3'-O3"	-164.72(0.34)	C12-C11-N2-O1	175.58(0.40)
C4-C3-C3'-O3"	14.03(0.50)	C10-C11-N2-O2	175.68(0.43)
O3'-C3'-O3"-C3"	-1.71(0.60)	C12-C11-N2-O2	-3.89(0.63)
C3-C3'-O3"-C3"	179.13(0.36)	C12-C11-C10-C9	-0.35(0.59)
C13-C3"-O3"-C3'	-172.79(0.40)	C7-C12-C11-N2	179.56(0.33)
C2-C3-C4-C7	98.10(0.39)	N2-C11-C10-C9	-179.90(0.35)
C3'-C3-C4-C7	-80.66(0.41)	C11-C10-C9-C8	0.79(0.60)
C2-C3-C4-C5	-26.44(0.47)	C10-C9-C8-C7	-0.92(0.61)
C3'-C3-C4-C5	154.80(0.33)	C7-C12-C11-C10	0.00(0.57)
C7-C4-C5-C6	-99.36(0.39)	C4-C7-C12-C11	178.75(0.31)
C3-C4-C5-C6	25.68(0.47)		
C7-C4-C5-C5'	81.52(0.39)		
C3-C4-C5-C5'	-153.44(0.33)		
C6-C5-C5'-O5'	-7.79(0.65)		
C4-C5-C5'-O5'	171.33(0.39)		
C6-C5-C5'-O5"	172.43(0.33)		
C4-C5-C5'-O5"	-8.46(0.48)		
O5'-C5'-O5"-C5"	-0.24(0.57)		
C5-C5'-O5"-C5"	179.56(0.34)		
C16-C5"-O5"-C5'	-171.23(0.36)		
C5'-C5-C6-N1	174.16(0.34)		
C4-C5-C6-N1	-4.93(0.54)		
C5'-C5-C6-C6'	-5.02(0.65)		
C4-C5-C6-C6'	175.88(0.39)		
C2-N1-C6-C5	-19.10(0.55)		
C2-N1-C6-C6'	160.19(0.38)		
C3-C4-C7-C12	130.09(0.35)		
C5-C4-C7-C12	-106.15(0.36)		
C3-C4-C7-C8	-51.12(0.44)		
C5-C4-C7-C8	72.64(0.41)		
C8-C7-C12-C11	-0.09(0.52)		

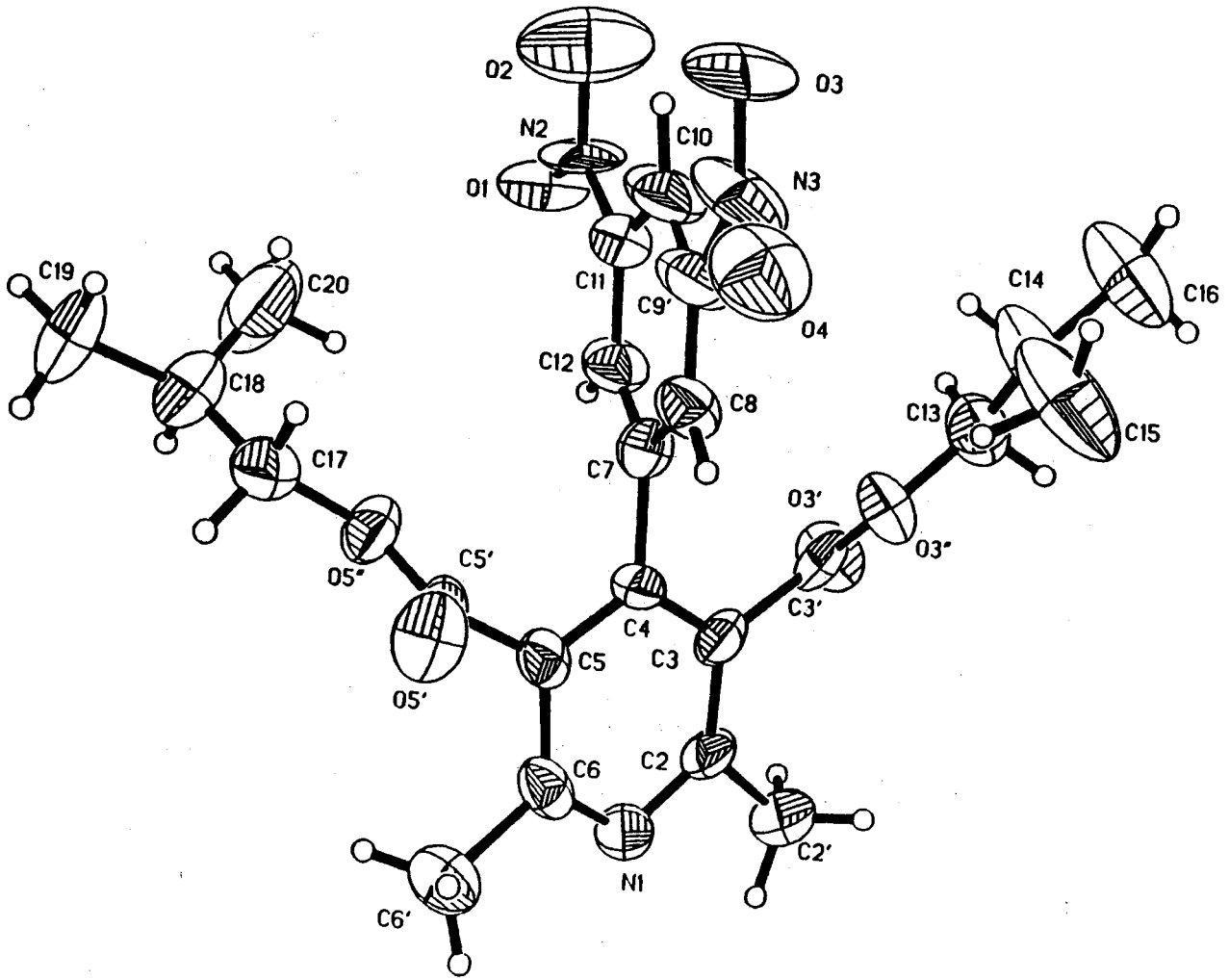

Figure 41: Projection view of Isobutyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine(XI)

TABLE 57

CRYSTAL DATA FOR

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XI)

Formula	$C_{23}H_{34}N_2O_6$
M. W.	434.52 g $mole^{-1}$
a	20.059(9) Å
b	6.340(3) Å
c	21.722(10) Å
α	90.00°
β	115.91(1)°
γ	90.00°
V	2484.8(20) $Å^3$
F(000)	936
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.162 g/cm^3
Z	4
Meas refl	5608
Obs refl	896
R	11.79%
R_w	21.54%
G. O. F.	1.009
Space Group	$P2_1/c$
Octants meas	$-1 \leq h \leq 23, -1 \leq k \leq 7, -25 \leq l \leq 23$

TABLE 58

POSITIONAL PARAMETERS FOR

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XI)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.5318(5)	0.0171(19)	0.8990(5)
C2	0.5854(7)	-0.1245(23)	0.9401(6)
C2'	0.5561(6)	-0.2643(21)	0.9789(6)
H2'A	0.5041(6)	-0.2407(21)	0.9644(6)
H2'B	0.5640(6)	-0.4082(21)	0.9701(6)
H2'C	0.5825(6)	-0.2360(21)	1.0270(6)
C3	0.6569(6)	-0.1169(21)	0.9466(5)
C3'	0.7161(9)	-0.2756(24)	0.9980(7)
O3'	0.7064(5)	-0.4570(15)	0.9979(4)
O3"	0.7747(5)	-0.1547(13)	1.0388(4)
C4	0.6745(6)	0.0168(21)	0.9058(5)
C5	0.6220(6)	0.1638(20)	0.8612(5)
C5'	0.6367(7)	0.3162(29)	0.8150(7)
O5'	0.6390(6)	0.5062(16)	0.8208(4)
O5"	0.6480(4)	0.2078(13)	0.7676(4)
C6	0.5502(7)	0.1581(21)	0.8624(6)
C6'	0.4896(6)	0.3097(17)	0.8152(5)
H6'A	0.4459(6)	0.2882(17)	0.8221(5)
H6'B	0.5064(6)	0.4525(17)	0.8268(5)
H6'C	0.4783(6)	0.2836(17)	0.7682(5)
C7	0.7529(7)	0.0229(22)	0.9091(5)
C8	0.8007(7)	0.2005(21)	0.9405(5)
H8A	0.7807(7)	0.3164(21)	0.9555(5)
C9'	0.8713(9)	0.2146(37)	0.9442(9)
C10	0.8980(8)	0.0476(40)	0.9204(9)
H10A	0.9451(8)	0.0620(40)	0.9193(9)
C11	0.8507(8)	-0.1270(34)	0.8877(7)
C12	0.7784(6)	-0.1402(23)	0.8841(6)
H12A	0.7461(6)	-0.2561(23)	0.8617(6)
C13	0.8373(8)	-0.2788(23)	1.0879(7)
H13A	0.8475(8)	-0.4000(23)	1.0670(7)
H13B	0.8274(8)	-0.3219(23)	1.1255(7)
C14	0.9019(10)	-0.1501(35)	1.1205(9)
H14A	0.9146(10)	-0.1091(35)	1.0844(9)
C15	0.8994(10)	0.0679(31)	1.1408(9)
H15A	0.8624(10)	0.1557(31)	1.0975(9)
H15B	0.8831(10)	0.0100(31)	1.1616(9)

TABLE 58 (Continued)

H15C	0.9451(10)	0.1372(31)	1.1523(9)
C16	0.9667(8)	-0.2706(27)	1.1699(8)
H16A	1.0118(8)	-0.1911(27)	1.1906(8)
H16B	0.9502(8)	-0.3057(27)	1.2040(8)
H16C	0.9752(8)	-0.3977(27)	1.1504(8)
C17	0.6638(6)	0.3300(22)	0.7195(7)
H17A	0.7091(6)	0.4070(22)	0.7431(7)
H17B	0.6243(6)	0.4278(22)	0.6954(7)
C18	0.6725(9)	0.2007(28)	0.6663(8)
H18A	0.6280(9)	0.1186(28)	0.6447(8)
C19	0.6813(8)	0.3295(23)	0.6130(6)
H19A	0.6864(8)	0.2545(23)	0.5769(6)
H19B	0.6376(8)	0.4156(23)	0.5940(6)
H19C	0.7240(8)	0.4173(23)	0.6365(6)
C20	0.7250(11)	0.0447(32)	0.6937(8)
H20A	0.7280(11)	-0.0751(32)	0.6608(8)
H20B	0.7681(11)	0.1104(32)	0.7111(8)
H20C	0.7179(11)	-0.0463(32)	0.7279(8)
N2	0.8780(18)	-0.2672(87)	0.8576(22)
N3	0.9313(18)	0.3322(96)	0.9718(20)
O1	0.8417(20)	-0.4076(63)	0.8266(15)
O2	0.9408(15)	-0.2465(33)	0.8602(13)
O3	0.9927(14)	0.3328(45)	0.9714(12)
O4	0.9086(20)	0.5026(97)	0.9895(15)

TABLE 59

ANISOTROPIC THERMAL PARAMETERS FOR

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XI)

ATOM	U11	U22	U33	U23	U13	U12
N1	60(7)	91(8)	71(6)	3(6)	31(6)	-8(7)
C2	61(8)	116(12)	66(7)	0(8)	42(7)	-13(9)
C2'	84(9)	186(15)	98(9)	7(10)	55(8)	6(10)
C3	75(9)	93(11)	54(7)	-10(8)	39(7)	-18(8)
C3'	111(12)	68(10)	66(9)	3(9)	66(9)	0(11)
O3'	98(6)	70(6)	112(7)	7(6)	33(5)	-7(7)
O3"	78(5)	71(6)	77(5)	6(5)	3(4)	3(6)
C4	40(7)	87(10)	59(7)	-5(8)	20(6)	2(7)
C5	64(8)	75(10)	50(7)	-19(8)	11(6)	3(8)
C5'	72(8)	130(15)	48(8)	15(11)	20(7)	-7(11)
O5'	143(8)	79(7)	94(6)	-15(6)	50(6)	-19(8)
O5"	99(6)	99(7)	72(5)	8(5)	50(5)	-9(5)
C6	66(9)	70(10)	58(7)	-16(8)	5(7)	12(9)
C6'	79(8)	80(10)	106(9)	11(8)	31(7)	5(8)
C7	77(9)	65(10)	58(7)	-15(7)	29(7)	-5(9)
C8	70(9)	76(10)	80(8)	2(8)	21(7)	15(8)
C9'	50(11)	154(20)	122(13)	51(13)	24(9)	14(13)
C10	45(10)	178(21)	140(14)	48(14)	28(10)	-5(14)
C11	65(10)	160(18)	85(10)	22(11)	34(9)	28(14)
C12	55(8)	102(12)	95(9)	2(9)	27(7)	-13(9)
C13	97(10)	128(14)	92(9)	15(11)	26(8)	5(12)
C14	121(15)	159(19)	127(14)	15(16)	-33(12)	0(18)
C15	132(15)	166(19)	214(20)	44(18)	-47(14)	-50(17)
C16	125(13)	243(23)	171(15)	35(16)	-30(12)	13(16)
C17	75(9)	143(14)	104(10)	33(12)	40(8)	9(9)
C18	143(15)	143(17)	111(12)	14(13)	81(11)	-6(12)
C19	216(17)	172(17)	104(10)	16(11)	110(11)	-10(14)
C20	332(28)	294(28)	203(20)	135(20)	212(21)	186(26)
N2	45(19)	162(41)	173(31)	2(28)	71(20)	-23(22)
N3	45(25)	128(44)	168(29)	16(29)	2(17)	-34(22)
O1	75(19)	142(28)	193(21)	-21(18)	74(17)	4(18)
O2	179(25)	152(21)	386(34)	-86(21)	176(22)	-28(18)
O3	51(18)	244(33)	227(28)	-1(23)	67(17)	-54(19)
O4	126(23)	147(41)	171(22)	4(23)	48(18)	-37(25)

The anisotropic displacement exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE 60

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XI)

N1-C6	1.349(13)	C6-N1-C2	118.3(10)
N1-C2	1.386(13)	N1-C2-C3	121.5(12)
C2-C3	1.378(13)	N1-C2-C2'	111.0(10)
C2-C2'	1.509(14)	C3-C2-C2'	127.3(13)
C3-C4	1.380(13)	C2-C3-C4	120.1(12)
C3-C3'	1.58(2)	C2-C3-C3'	118.4(13)
C3'-O3'	1.166(13)	C4-C3-C3'	121.3(10)
C3'-O3"	1.357(14)	O3'-C3'-O3"	130.9(14)
O3"-C13	1.471(13)	O3'-C3'-C3	123.5(15)
C4-C5	1.423(14)	O3"-C3'-C3	105.6(11)
C4-C7	1.544(14)	C3'-O3"-C13	113.1(10)
C5-C6	1.454(15)	C3-C4-C5	121.3(11)
C5-C5'	1.51(2)	C3-C4-C7	121.9(11)
C5'-O5'	1.210(15)	C5-C4-C7	116.8(12)
C5'-O5"	1.336(15)	C4-C5-C6	114.6(12)
O5"-C17	1.443(13)	C4-C5-C5'	124.7(12)
C6-C6'	1.537(13)	C6-C5-C5'	120.7(12)
C7-C12	1.366(14)	O5'-C5'-O5"	125.6(14)
C7-C8	1.443(14)	O5'-C5'-C5	125.1(15)
C8-C9'	1.39(2)	O5"-C5'-C5	109.3(14)
C9'-N3	1.32(4)	C5'-O5"-C17	116.5(11)
C9'-C10	1.38(2)	N1-C6-C5	123.7(12)
C10-C11	1.43(2)	N1-C6-C6'	117.8(12)
C11-N2	1.35(5)	C5-C6-C6'	118.3(13)
C11-C12	1.42(2)	C12-C7-C8	119.5(11)
C13-C14	1.43(2)	C12-C7-C4	120.9(12)
C14-C16	1.48(2)	C8-C7-C4	119.6(12)
C14-C15	1.46(2)	C9'-C8-C7	121.9(15)
C17-C18	1.49(2)	N3-C9'-C10	100.2(35)
C18-C20	1.38(2)	N3-C9'-C8	140.4(38)
C18-C19	1.49(2)	C10-C9'-C8	118.7(19)
O1-N2	1.16(3)	C9'-C10-C11	119.8(16)
O4-N3	1.29(3)	N2-C11-C10	115.4(27)
O2-N2	1.24(3)	N2-C11-C12	123.7(27)
O3-N3	1.23(4)	C10-C11-C12	120.9(16)
		C7-C12-C11	118.9(15)
		C14-C13-O3"	110.8(12)
		C13-C14-C16	112.4(17)
		C13-C14-C15	123.1(18)
		C16-C14-C15	113.8(16)
		O5"-C17-C18	113.8(12)

TABLE 60 (Continued)

	C20-C18-C17	112.8(15)
	C20-C18-C19	113.7(15)
	C17-C18-C19	113.3(14)
	O1-N2-O2	118.2(48)
	O1-N2-C11	120.0(26)
	O2-N2-C11	121.7(50)
	O3-N3-O4	118.7(43)
	O3-N3-C9'	135.6(63)
	O4-N3-C9'	103.8(38)

TABLE 61

TORSION ANGLES (°) FOR

Di-isobutyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XI)

C6-N1-C2-C3	3.16(1.60)	C9'-C10-C11-N2	170.95(1.80)
C6-N1-C2-C2'	178.00(0.94)	C9'-C10-C11-C12	-5.26(2.17)
N1-C2-C3-C4	-7.78(1.70)	C8-C7-C12-C11	-2.15(1.62)
C2'-C2-C3-C4	178.29(1.07)	C4-C7-C12-C11	179.49(1.03)
N1-C2-C3-C3'	176.42(0.98)	N2-C11-C12-C7	-172.16(1.80)
C2'-C2-C3-C3'	2.48(1.80)	C10-C11-C12-C7	3.72(1.84)
C2-C3-C3'-O3'	50.91(1.66)	C3'-O3"-C13-C14	169.17(1.23)
C4-C3-C3'-O3'	-124.84(1.41)	O3"-C13-C14-C16	-179.23(1.33)
C2-C3-C3'-O3"	-128.19(1.09)	O3"-C13-C14-C15	38.46(2.34)
C4-C3-C3'-O3"	56.05(1.25)	C5'-O5"-C17-C18	-177.46(1.11)
O3'-C3'-O3"-C13	3.95(1.90)	O5"-C17-C18-C20	-54.63(1.80)
C3-C3'-O3"-C13	-177.04(0.88)	O5"-C17-C18-C19	174.33(1.07)
C2-C3-C4-C5	6.24(1.63)	C10-C11-N2-O1	-175.79(2.65)
C3'-C3-C4-C5	-178.08(0.98)	C12-C11-N2-O1	0.30(4.17)
C2-C3-C4-C7	-177.10(1.12)	C10-C11-N2-O2	1.66(3.69)
C3'-C3-C4-C7	-1.42(1.64)	C8-C9'-C10-C11	5.11(2.24)
C3-C4-C5-C6	-0.45(1.46)	C12-C11-N2-O2	177.74(2.33)
C7-C4-C5-C6	-177.27(0.99)	C10-C9'-N3-O3	10.86(4.54)
C3-C4-C5-C5'	179.79(1.15)	C8-C9'-N3-O3	-179.00(2.90)
C7-C4-C5-C5'	2.97(1.61)	C10-C9'-N3-O4	174.00(2.61)
C4-C5-C5'-O5'	-113.65(1.61)	C8-C9'-N3-O4	-15.85(4.50)
C6-C5-C5'-O5'	66.60(1.81)	C7-C8-C9'-C10	-3.65(1.97)
C4-C5-C5'-O5"	65.29(1.36)	N3-C9'-C10-C11	177.96(1.76)
C6-C5-C5'-O5"	-114.45(1.17)	C7-C8-C9'-N3	-172.57(2.60)
O5'-C5'-O5"-C17	-0.41(1.89)	C4-C7-C8-C9'	-179.45(1.10)
C5-C5'-O5"-C17	-179.35(0.89)		
C2-N1-C6-C5	2.98(1.57)		
C2-N1-C6-C6'	178.09(0.88)		
C4-C5-C6-N1	-4.26(1.52)		
C5'-C5-C6-N1	175.51(1.10)		
C4-C5-C6-C6'	-179.36(0.85)		
C5'-C5-C6-C6'	0.42(1.60)		
C3-C4-C7-C12	71.17(1.37)		
C5-C4-C7-C12	-112.03(1.25)		
C3-C4-C7-C8	-107.19(1.30)		
C5-C4-C7-C8	69.61(1.22)		
C12-C7-C8-C9'	2.17(1.67)		

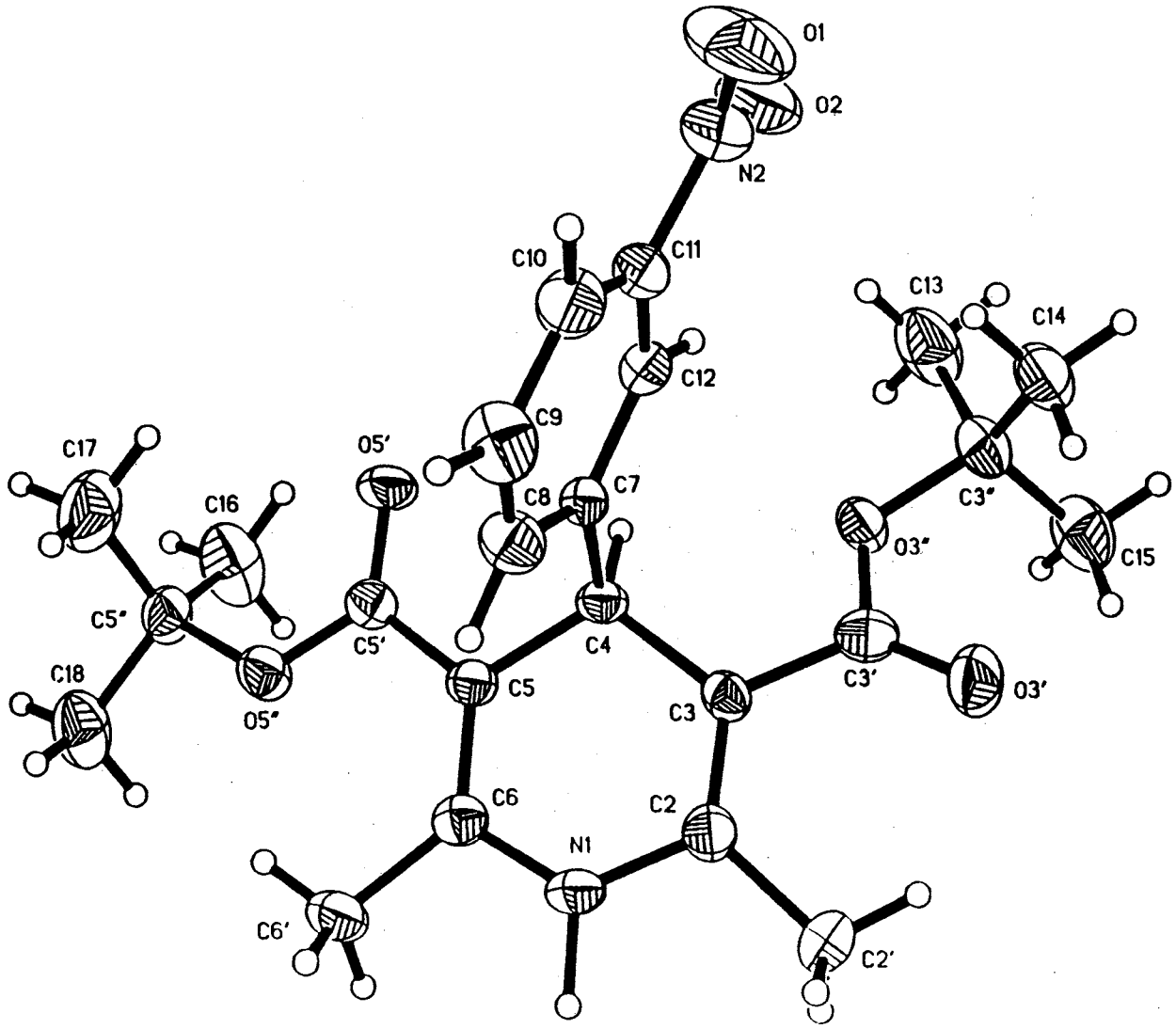

Figure 42: Projection view of *Tertiary*-butyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine(XII)

TABLE 62

CRYSTAL DATA FOR

Di-*tert*-butyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XII)

Formula	C23 H30 N2 O6
M. W.	430.49 g mole^{-1}
a	11.1420(10) Å
b	16.803(2) Å
c	13.3840(10) Å
α	90.00 °
β	109.900(10) °
γ	90.00 °
V	2356.1(4) Å^3
F(000)	920
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.214 g/cm^3
Z	4
Meas refl	2898
Obs refl	1383
R	5.42%
R_w	12.09%
G. O. F.	1.123
Space Group	$P2_1/n$
Octants meas	$-1 \leq h \leq 10$, $-1 \leq k \leq 16$, $-12 \leq l \leq 12$

TABLE 63

POSITIONAL PARAMETERS FOR

Di-*tert*-butyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.2005(3)	0.2790(2)	0.2687(3)
C2	0.1253(5)	0.3456(3)	0.2626(4)
C2'	0.1766(5)	0.4011(3)	0.3560(4)
C3	0.0222(4)	0.3576(3)	0.1770(3)
C3'	-0.0543(4)	0.4308(3)	0.1659(4)
C3"	-0.2107(5)	0.5140(3)	0.0333(4)
O3'	-0.0569(3)	0.4730(2)	0.2389(3)
O3"	-0.1237(3)	0.4454(2)	0.0645(3)
C4	-0.0235(4)	0.2945(3)	0.0902(3)
C5	0.0825(4)	0.2369(3)	0.0938(3)
C5'	0.0597(5)	0.1938(3)	-0.0061(4)
C5"	0.1547(5)	0.1038(3)	-0.1047(4)
O5'	-0.0373(3)	0.2026(2)	-0.0818(3)
O5"	0.1557(3)	0.1459(2)	-0.0080(2)
C6	0.1864(4)	0.2291(3)	0.1830(4)
C6'	0.2957(4)	0.1705(3)	0.2042(4)
C7	-0.1419(4)	0.2523(3)	0.0980(3)
C8	-0.1328(5)	0.1909(3)	0.1701(4)
C9	-0.2408(6)	0.1568(3)	0.1795(5)
C10	-0.3596(5)	0.1851(4)	0.1233(5)
C11	-0.3679(5)	0.2456(3)	0.0524(4)
C12	-0.2622(5)	0.2790(3)	0.0382(4)
C13	-0.2619(6)	0.5080(4)	-0.0860(4)
C14	-0.3173(5)	0.5039(3)	0.0776(5)
C15	-0.1387(5)	0.5911(3)	0.0685(5)
C16	0.1405(6)	0.1618(4)	-0.1936(4)
C17	0.0516(6)	0.0426(4)	-0.1351(5)
C18	0.2851(5)	0.0652(3)	-0.0693(5)
N2	-0.4927(5)	0.2780(3)	-0.0067(5)
O1	-0.5837(4)	0.2592(3)	0.0187(4)
O2	-0.5019(4)	0.3253(3)	-0.0779(4)
H1A	0.2948(3)	0.2802(2)	0.3243(3)
H2'A	0.1214(5)	0.4463(3)	0.3480(4)
H2'B	0.1823(5)	0.3730(3)	0.4199(4)
H2'C	0.2600(5)	0.4187(3)	0.3600(4)
H2'D*	0.1001	0.3956	0.4012

TABLE 63 (Continued)

H2'E*	0.2037	0.4652	0.3614
H2'F*	0.2576	0.3640	0.3986
H4A	-0.0582(4)	0.3239(3)	0.0043(3)
H6'A	0.2815(4)	0.1367(3)	0.1434(4)
H6'B	0.3738(4)	0.1996(3)	0.2172(4)
H6'C	0.3017(4)	0.1386(3)	0.2652(4)
H6'D*	0.3295	0.1842	0.1387
H6'E*	0.2444	0.1123	0.1786
H6'F*	0.3523	0.1819	0.2787
H8A	-0.0496(5)	0.1731(3)	0.2139(4)
H9A	-0.2324(6)	0.1123(3)	0.2264(5)
H10A	-0.4349(5)	0.1634(4)	0.1326(5)
H12A	-0.2726(5)	0.3211(3)	-0.0124(4)
H13A	-0.3085(6)	0.4590(4)	-0.1050(4)
H13B	-0.3172(6)	0.5519(4)	-0.1170(4)
H13C	-0.1914(6)	0.5076(4)	-0.1119(4)
H14A	-0.3612(5)	0.4550(3)	0.0512(5)
H14B	-0.2814(5)	0.5017(3)	0.1537(5)
H14C	-0.3764(5)	0.5475(3)	0.0569(5)
H15A	-0.0734(5)	0.5952(3)	0.0370(5)
H15B	-0.1950(5)	0.6360(3)	0.0477(5)
H15C	-0.1001(5)	0.5902(3)	0.1445(5)
H16A	0.0567(6)	0.1849(4)	-0.2161(4)
H16B	0.2032(6)	0.2030(4)	-0.1679(4)
H16C	0.1536(6)	0.1353(4)	-0.2526(4)
H17A	-0.0298(6)	0.0688(4)	-0.1578(5)
H17B	0.0588(6)	0.0104(4)	-0.1920(5)
H17C	0.0590(6)	0.0096(4)	-0.0748(5)
H18A	0.2917(5)	0.0277(3)	-0.0135(5)
H18B	0.2987(5)	0.0383(3)	-0.1278(5)
H18C	0.3483(5)	0.1060(3)	-0.0431(5)

*Disorder of methyl hydrogens on C2' and C6'

TABLE 64

ANISOTROPIC THERMAL PARAMETERS FOR

Di-*tert*-butyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XII)

ATOM	U11	U22	U33	U23	U13	U12
N1	42(2)	63(3)	39(3)	-3(2)	0(2)	3(2)
C2	53(3)	46(3)	46(3)	0(3)	16(3)	4(3)
C2'	67(4)	57(3)	59(3)	-18(3)	12(3)	0(3)
C3	42(3)	35(3)	43(3)	7(3)	13(3)	4(3)
C3'	49(3)	61(4)	47(4)	5(3)	14(3)	-2(3)
C3"	58(3)	50(4)	71(4)	11(3)	26(3)	11(3)
O3'	97(3)	75(3)	59(2)	-14(2)	22(2)	25(2)
O3"	51(2)	48(2)	55(2)	5(2)	17(2)	15(2)
C4	34(3)	50(3)	33(3)	-2(2)	7(2)	3(3)
C5	38(3)	42(3)	39(3)	1(2)	10(3)	0(2)
C5'	44(3)	49(3)	45(3)	2(3)	16(3)	2(3)
C5"	73(4)	55(3)	45(3)	-8(3)	19(3)	11(3)
O5'	49(2)	82(3)	43(2)	-13(2)	-5(2)	13(2)
O5"	57(2)	67(2)	44(2)	-5(2)	15(2)	18(2)
C6	45(3)	48(3)	42(3)	1(3)	12(3)	-1(3)
C6'	55(3)	78(4)	49(3)	-4(3)	0(3)	22(3)
C7	38(3)	42(3)	39(3)	-6(3)	10(3)	5(3)
C8	60(4)	58(4)	58(3)	9(3)	19(3)	4(3)
C9	77(4)	62(4)	93(4)	13(3)	45(4)	-4(4)
C10	55(4)	72(4)	93(4)	-17(4)	37(4)	-9(3)
C11	39(4)	54(4)	67(4)	-10(3)	18(3)	1(3)
C12	46(3)	45(3)	48(3)	-9(2)	14(3)	-2(3)
C13	112(5)	98(5)	79(5)	26(4)	26(4)	49(4)
C14	59(3)	62(4)	119(5)	-4(4)	27(4)	13(3)
C15	86(4)	51(4)	122(5)	20(4)	45(4)	8(4)
C16	142(6)	101(5)	69(4)	15(4)	59(4)	42(5)
C17	114(5)	87(5)	116(5)	-38(4)	53(4)	0(5)
C18	107(5)	78(4)	83(4)	-2(4)	48(4)	26(4)
N2	48(4)	84(4)	106(5)	-11(3)	19(4)	1(3)
O1	49(3)	147(5)	203(6)	33(4)	43(3)	0(3)
O2	62(3)	128(4)	102(3)	6(3)	4(3)	23(3)

The anisotropic displacement exponent takes the form:$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE 65

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Di-*tert*-butyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XII)

N1-C2	1.384(6)	C2-N1-C6	123.0(4)
N1-C6	1.385(5)	C3-C2-N1	120.0(4)
C2-C3	1.333(6)	C3-C2-C2'	126.3(5)
C2-C2'	1.508(6)	N1-C2-C2'	113.6(4)
C3-C3'	1.475(7)	C2-C3-C3'	120.8(4)
C3-C4	1.526(6)	C2-C3-C4	121.1(4)
C3'-O3'	1.216(5)	C3'-C3-C4	118.1(4)
C3'-O3"	1.336(5)	O3'-C3'-O3"	123.0(5)
C3"-O3"	1.472(5)	O3'-C3'-C3	125.2(5)
C3"-C13	1.506(7)	O3"-C3'-C3	111.7(5)
C3"-C14	1.507(7)	O3"-C3"-C13	102.9(4)
C3"-C15	1.511(7)	O3"-C3"-C14	109.3(4)
C4-C5	1.516(6)	C13-C3"-C14	110.2(5)
C4-C7	1.532(6)	O3"-C3"-C15	110.8(4)
C5-C6	1.357(6)	C13-C3"-C15	111.0(5)
C5-C5'	1.464(6)	C14-C3"-C15	112.3(4)
C5'-O5'	1.213(5)	C3'-O3"-C3"	122.0(4)
C5'-O5"	1.345(5)	C5-C4-C3	111.4(3)
C5"-O5"	1.473(5)	C5-C4-C7	112.5(4)
C5"-C17	1.491(7)	C3-C4-C7	109.9(3)
C5"-C16	1.505(7)	C6-C5-C5'	125.9(4)
C5"-C18	1.512(6)	C6-C5-C4	120.8(4)
C6-C6'	1.515(6)	C5'-C5-C4	113.3(4)
C7-C12	1.381(6)	O5'-C5'-O5"	123.0(4)
C7-C8	1.393(6)	O5'-C5'-C5	122.1(5)
C12-C11	1.375(6)	O5"-C5'-C5	114.9(4)
C11-C10	1.372(7)	O5"-C5"-C17	110.2(4)
C11-N2	1.452(7)	O5"-C5"-C16	110.5(4)
C10-C9	1.366(7)	C17-C5"-C16	111.5(5)
C9-C12	1.377(6)	O5"-C5"-C18	102.2(4)
N2-O1	1.215(6)	C17-C5"-C18	111.0(5)
N2-O2	1.218(6)	C16-C5"-C18	110.9(5)
		C5'-O5"-C5"	122.4(4)
		C5-C6-N1	119.5(4)
		C5-C6-C6'	128.1(4)
		N1-C6-C6'	112.4(4)
		C12-C7-C8	118.0(4)
		C12-C7-C4	119.9(4)
		C8-C7-C4	121.9(4)

TABLE 65 (Continued)

C11-C12-C7	119.7(5)
C10-C11-C1	122.6(5)
C10-C11-N2	118.7(5)
C12-C11-N2	118.6(5)
C9-C10-C11	117.6(5)
C10-C9-C8	121.2(5)
C9-C8-C7	120.8(5)
O1-N2-O2	122.2(6)
O1-N2-C11	119.0(6)
O2-N2-C11	118.7(6)

TABLE 66

TORSION ANGLES (°) FOR

Di-*tert*-butyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XII)

C6-N1-C2-C3	10.37(0.66)	N2-C11-C10-C9	-178.67(0.47)
C6-N1-C2-C2'	-166.31(0.40)	C11-C10-C9-C8	3.80(0.79)
N1-C2-C3-C3'	-175.94(0.40)	C10-C9-C8-C7	-3.80(0.80)
C2'-C2-C3-C3'	0.28(0.72)	C12-C7-C8-C9	1.28(0.68)
N1-C2-C3-C4	6.89(0.66)	C4-C7-C8-C9	176.50(0.44)
C2'-C2-C3-C4	-176.89(0.41)	C12-C11-C10-C9	-1.44(0.75)
C2-C3-C3'-O3'	-22.40(0.72)	C10-C11-N2-O1	10.56(0.77)
C4-C3-C3'-O3'	154.85(0.46)	C12-C11-N2-O1	-166.78(0.52)
C2-C3-C3'-O3"	158.57(0.41)	C10-C11-N2-O2	-172.00(0.51)
C4-C3-C3'-O3"	-24.18(0.54)	C12-C11-N2-O2	10.65(0.74)
O3'-C3'-O3"-C3"	-0.70(0.68)	C8-C7-C12-C11	1.04(0.62)
C3-C3'-O3"-C3"	178.35(0.36)	C4-C7-C12-C11	-174.28(0.39)
C13-C3"-O3"-C3'	177.57(0.42)	C7-C12-C11-C10	-0.97(0.69)
C14-C3"-O3"-C3'	-65.36(0.54)	C7-C12-C11-N1	176.27(0.43)
C15-C3"-O3"-C3'	58.94(0.55)	C3-C4-C7-C8	-81.41(0.51)
C2-C3-C4-C5	-20.62(0.57)	C5-C4-C7-C8	43.33(0.56)
C3'-C3-C4-C5	162.14(0.38)	C5-C4-C7-C12	-141.54(0.40)
C2-C3-C4-C7	104.75(0.48)	C3-C4-C7-C12	93.71(0.47)
C3'-C3-C4-C7	-72.49(0.49)	C2-N1-C6-C6'	168.84(0.41)
C3-C4-C5-C6	19.66(0.57)	C2-N1-C6-C5	-11.20(0.65)
C7-C4-C5-C6	-104.27(0.47)		
C3-C4-C5-C5'	-159.91(0.36)		
C7-C4-C5-C5'	76.16(0.46)		
C6-C5-C5'-O5'	178.16(0.46)		
C4-C5-C5'-O5'	-2.30(0.62)		
C6-C5-C5'-O5"	-3.62(0.65)		
C4-C5-C5'-O5"	175.92(0.36)		
O5'-C5'-O5"-C5"	4.01(0.68)		
C5-C5'-O5"-C5"	-174.19(0.39)		
C17-C5"-O5"-C5'	-66.84(0.56)		
C16-C5"-O5"-C5'	56.93(0.60)		
C18-C5"-O5"-C5'	175.04(0.40)		
C5'-C5-C6-N1	174.26(0.40)		
C4-C5-C6-N1	-5.25(0.65)		
C5'-C5-C6-C6'	-5.78(0.76)		
C4-C5-C6-C6'	174.71(0.43)		

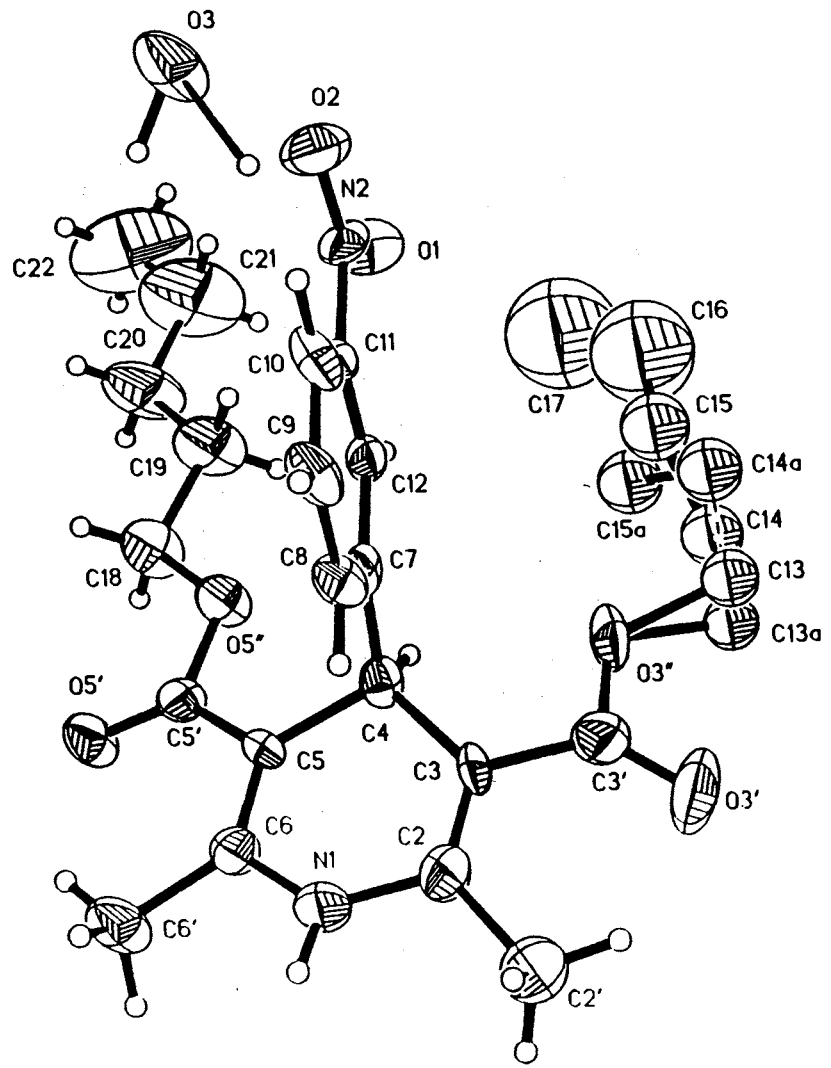

Figure 43: Projection view of Pentyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine(XIII)

TABLE 67

CRYSTAL DATA FOR

Dipentyl2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIII)

Formula	$C_{25}H_{34}N_2O_6$
M. W.	458.54 g mole^{-1}
a	12.626(2) Å
b	14.079(3) Å
c	16.098(3) Å
α	90.0°
β	110.28(0)°
γ	90.0°
V	2684.2(8) Å^3
F(000)	980
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.152 g/cm^3
Z	4
Meas refl	5878
Obs refl	1393
R	9.76 %
R_w	10.38 %
G. O. F.	1.75
Space Group	$P2_1/c$
Octants meas	$-1 \leq h \leq 15$, $-1 \leq k \leq 16$, $-19 \leq l \leq 18$

TABLE 68

POSITIONAL PARAMETERS FOR

Dipentyl2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	-0.3721(7)	0.3346(8)	0.2570(7)
C2	-0.3458(11)	0.4283(9)	0.2756(8)
C2'	-0.4483(10)	0.4912(9)	0.2628(9)
C3	-0.2393(11)	0.4550(7)	0.3000(8)
C3'	-0.2091(12)	0.5523(10)	0.3247(9)
O3'	-0.2666(9)	0.6196(6)	0.3292(8)
O3"	-0.0964(8)	0.5640(5)	0.3516(6)
C4	-0.1463(8)	0.3875(7)	0.3000(7)
C5	-0.1840(9)	0.2854(7)	0.3070(7)
C5'	-0.0982(11)	0.2113(9)	0.3381(8)
O5'	-0.1119(6)	0.1287(5)	0.3498(6)
O5"	0.0068(6)	0.2473(5)	0.3570(5)
C6	-0.2925(10)	0.2627(8)	0.2812(8)
C6'	-0.3448(9)	0.1659(8)	0.2766(8)
C7	-0.1111(10)	0.3998(6)	0.2191(8)
C8	-0.1923(10)	0.4016(7)	0.1348(8)
C9	-0.1616(10)	0.4083(7)	0.0610(8)
C10	-0.0509(12)	0.4164(8)	0.0683(9)
C11	0.0256(10)	0.4148(7)	0.1514(10)
C12	0.0016(9)	0.4089(7)	0.2290(8)
C13	-0.0461(22)	0.6640(20)	0.3672(41)
C13A	-0.0506(26)	0.6548(22)	0.4109(46)
C14	0.0681(27)	0.6441(21)	0.4470(28)
C14A	0.0730(29)	0.6578(22)	0.3807(28)
C15	0.1429(34)	0.6155(28)	0.4002(26)
C15A	0.418(28)	0.5806(23)	0.4548(21)
C16	0.2768(31)	0.6050(25)	0.4594(21)
C17	0.3130(31)	0.5378(28)	0.4608(23)
C18	0.0975(9)	0.1812(8)	0.3869(9)
C19	0.2057(10)	0.2339(10)	0.4018(10)
C20	0.3075(11)	0.1700(11)	0.4337(11)
C21	0.4138(13)	0.2154(15)	0.4501(13)
C22	0.5097(13)	0.1536(16)	0.4813(13)
N2	0.1498(10)	0.4230(7)	0.1653(8)
O1	0.2181(7)	0.4238(7)	0.2404(7)
O2	0.1744(7)	0.4231(6)	0.0991(6)
O3	0.3896(6)	0.2862(6)	0.1960(8)

TABLE 68 (Continued)

H1A	-0.4448	0.3183	0.2295
H2'A	-0.4237	0.5557	0.2763
H2'B	-0.4983	0.4872	0.2024
H2'C	-0.4873	0.4710	0.3014
H3A	0.3412	0.2437	0.2246
H3B	0.2624	0.3465	0.1839
H4A	-0.0813	0.4004	0.3515
H6'A	-0.2855	0.1195	0.2930
H6'B	-0.3862	0.1622	0.3165
H6'C	-0.3948	0.1538	0.2173
H8A	-0.2704	0.3971	0.1292
H9A	-0.2195	0.4112	0.0037
H10A	-0.0275	0.4204	0.0177
H12A	0.0593	0.4111	0.2865
H18A	0.0908	0.1343	0.3421
H18B	0.0983	0.1501	0.4402
H19A	0.2138	0.2784	0.4488
H19B	0.2016	0.2683	0.3493
H20A	0.3005	0.1265	0.3861
H20B	0.3103	0.1343	0.4852
H21A	0.4193	0.2613	0.4955
H21B	0.4141	0.2479	0.3977
H22A	0.5807	0.1858	0.4951
H22B	0.5069	0.1215	0.5331
H22C	0.5017	0.1081	0.4351

TABLE 69

ANISOTROPIC THERMAL PARAMETERS FOR

Dipentyl2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIII)

ATOM	U11	U22	U33	U12	U13	U23
N1	40(7)	67(7)	122(10)	-1(7)	31(6)	-6(7)
C2	58(10)	53(9)	101(11)	12(8)	29(8)	1(8)
C2'	62(9)	83(10)	184(16)	20(9)	40(10)	11(11)
C3	63(9)	20(6)	85(10)	-2(7)	31(7)	1(6)
C3'	59(10)	77(11)	83(10)	-10(9)	27(8)	-16(9)
O3'	125(10)	65(6)	203(12)	25(6)	56(8)	-35(7)
O3"	98(7)	38(5)	133(9)	-18(5)	41(7)	-32(5)
C4	42(7)	38(7)	51(8)	7(6)	5(6)	5(6)
C5	42(8)	39(7)	73(9)	-12(7)	29(7)	-5(7)
C5'	65(9)	45(7)	57(9)	7(8)	35(7)	19(7)
O5'	57(6)	44(5)	130(8)	8(5)	29(5)	29(6)
O5"	42(5)	56(5)	99(7)	9(4)	16(5)	24(5)
C6	44(8)	47(8)	72(9)	8(7)	22(7)	8(7)
C6'	40(8)	67(9)	148(14)	3(7)	22(8)	24(9)
C7	66(9)	22(6)	55(9)	13(6)	25(7)	14(6)
C8	63(8)	48(7)	53(9)	-2(7)	19(8)	21(7)
C9	57(9)	56(8)	57(10)	-17(7)	-3(7)	6(7)
C10	83(10)	45(8)	59(10)	-22(8)	14(9)	6(7)
C11	39(8)	24(6)	107(12)	-6(6)	41(9)	-9(8)
C12	38(8)	38(7)	81(11)	-4(6)	21(7)	-14(7)
C18	54(8)	66(9)	126(12)	22(8)	16(8)	44(9)
C19	48(9)	105(12)	161(15)	25(9)	25(10)	47(11)
C20	51(9)	153(16)	172(17)	-11(12)	24(10)	43(13)
C21	73(12)	260(28)	234(25)	31(17)	15(15)	69(20)
C22	94(15)	433(42)	199(23)	41(23)	10(15)	16(24)
N2	98(10)	49(6)	59(8)	18(7)	59(8)	15(7)
O1	75(7)	121(8)	82(7)	13(6)	32(6)	18(7)
O2	89(7)	102(7)	92(7)	10(5)	58(6)	4(6)
O3	45(5)	91(7)	279(13)	1(5)	57(7)	33(8)

The anisotropic displacement exponent takes the form:$-2\pi^2(h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12})$

TABLE 70

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Dipentyl2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIII)

N1-C2	1.367 (17)	C2-N1-C6	123.1(9)
N1-C6	1.384 (15)	N1-C2-C2'	113.6(11)
C2-C2'	1.523 (18)	N1-C2-C3	119.1(12)
C2-C3	1.319 (19)	C2'-C2-C3	127.2(11)
C3-C3'	1.440 (17)	C2-C3-C3'	119.9(12)
C3-C4	1.511 (17)	C2-C3-C4	122.1(10)
C3'-O3'	1.211 (18)	C3'-C3-C4	117.9(11)
C3'-O3"	1.346 (17)	C3-C3'-O3'	130.8(14)
O3"-C13	1.529 (29)	C3-C3'-O3"	110.8(12)
O3"-C13A	1.580 (43)	O3'-C3'-O3"	118.3(12)
C4-C5	1.530 (15)	C3'-O3"-C13	119.9(13)
C4-C7	1.526 (19)	C3'-O3"-C13A	114.7(16)
C5-C5'	1.461 (16)	C3-C4-C5	109.3(10)
C5-C6	1.326 (16)	C3-C4-C7	112.6(9)
C5'-O5'	1.200 (14)	C5-C4-C7	111.1(9)
C5'-O5"	1.352 (15)	C4-C5-C5'	118.9(10)
O5"-C18	1.423 (13)	C4-C5-C6	121.1(9)
C6-C6'	1.505 (16)	C5'-C5-C6	119.9(10)
C7-C8	1.389 (15)	C5-C5'-O5'	128.0(12)
C7-C12	1.382 (17)	C5-C5'-O5"	111.2(10)
C8-C9	1.375 (21)	O5'-C5'-O5"	120.7(11)
C9-C10	1.365 (21)	C5'-O5"-C18	116.3(9)
C10-C11	1.352 (18)	N1-C6-C5	118.9(10)
C11-C12	1.386 (23)	N1-C6-C6'	112.7(10)
C11-N2	1.510 (18)	C5-C6-C6'	128.4(10)
C18-C19	1.499 (17)	C4-C7-C8	120.1(11)
C19-C20	1.506 (18)	C4-C7-C12	120.4(10)
C20-C21	1.425 (22)	C8-C7-C12	119.6(13)
C21-C22	1.433 (25)	C7-C8-C9	120.7(12)
N2-O1	1.218 (14)	C8-C9-C10	121.2(10)
N2-O2	1.209 (18)	C9-C10-C11	116.3(14)
C13-C14	1.589 (49)	C10-C11-C12	126.0(13)
C13A-C14	1.416 (44)	C10-C11-N2	119.6(15)
C13A-C14A	1.789 (68)	C12-C11-N2	114.3(11)
C14-C15	1.455 (66)	C7-C12-C11	116.1(10)
C14A-C15A	1.624 (46)	O5"-C18-C19	108.3(9)
C15-C16	1.634 (50)	C18-C19-C20	112.5(11)
C15A-C16	1.716 (54)	C19-C20-C21	115.7(14)
C16-C17	1.048 (53)	C20-C21-C22	114.8(17)
		C11-N2-O1	119.2(13)
		C11-N2-O2	116.1(10)

TABLE 70 (Continued)

	O1-N2-O2	124.5(12)
	O3"-C13-C14	100.3(23)
	O3"-C13A-C14A	91.5(32)
	C13-C14-C15	101.6(36)
	C13A-C14A-C15A	94.6(31)
	C14-C15-C16	116.7(31)
	C14A-C15A-C16	99.7(26)
	C15-C16-C17	116.7(34)
	C15A-C16-C17	03.8(36)

TABLE 71

TORSION ANGLES (°) FOR

Dipentyl2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIII)

C6-N1-C2-C2'	-166.1(1.2)	C14A-C15A-C16-C17	-136.9(3.3)
C6-N1-C2-C3	15.3(2.0)	C14-C15-C16-C17	119.4(4.6)
C2-N1-C6-C5	-14.4(2.0)	C13A-C14A-C15A-C16	-160.7(2.5)
C2-N1-C6-C6'	163.9(1.2)	C13-C14-C15-C16	170.4(2.8)
N1-C2-C3-C3'	-176.4(1.2)	O3"-C13A-C14A-C15A	-83.8(2.7)
N1-C2-C3-C4	5.7(2.0)	O3"-C13-C14-C15	85.9(3.6)
C2'-C2-C3-C3'	5.2(2.2)	C19-C20-C21-C22	179.3(1.7)
C2'-C2-C3-C4	-172.7(1.2)	C18-C19-C20-C21	-179.5(1.6)
C2-C3-C3'-O3'	1.3(2.4)	O5"-C18-C19-C20	-180.0(1.2)
C2-C3-C3'-O3"	176.9(1.2)	C12-C11-N2-O2	176.1(0.9)
C4-C3-C3'-O3'	179.3(1.5)	C12-C11-N2-O1	0.1(1.4)
C4-C3-C3'-O3"	-5.2(1.7)	C10-C11-N2-O2	-5.7(1.4)
C2-C3-C4-C5	-23.4(1.6)	C10-C11-N2-O1	178.3(1.0)
C2-C3-C4-C7	100.6(1.4)	N2-C11-C12-C7	-179.0(0.8)
C3'-C3-C4-C5	158.7(1.1)	C10-C11-C12-C7	2.9(1.5)
C3'-C3-C4-C7	-77.3(1.3)	C9-C10-C11-N2	179.7(0.9)
C3-C3'-O3"-C13	170.4(3.0)	C9-C10-C11-C12	-2.3(1.6)
C3-C3'-O3"-C13A	-159.3(2.8)	C8-C9-C10-C11	1.8(1.6)
O3'-C3'-O3"-C13	-13.4(3.4)	C7-C8-C9-C10	-2.2(1.6)
O3'-C3'-O3"-C13A	16.9(3.1)	C8-C7-C12-C11	-2.9(1.4)
C3'-O3"-C13-C14	146.4(2.3)	C5'-O5"-C18-C19	178.4(1.1)
C3'-O3"-C13A-C14A	-156.0(1.6)	C4-C7-C8-C9	-177.0(0.9)
C3-C4-C5-C5'	-159.4(1.0)	C12-C7-C8-C9	2.7(1.5)
C3-C4-C5-C6	24.0(1.5)	C4-C7-C12-C11	176.8(0.8)
C7-C4-C5-C5'	75.8(1.2)		
C7-C4-C5-C6	-100.8(1.3)		
C3-C4-C7-C8	-49.9(1.2)		
C3-C4-C7-C12	130.4(0.9)		
C5-C4-C7-C8	73.1(1.1)		
C5-C4-C7-C12	-106.6(1.0)		
C4-C5-C5'-O5'	177.9(1.2)		
C4-C5-C5'-O5"	0.2(1.6)		
C6-C5-C5'-O5'	-5.4(2.1)		
C6-C5-C5'-O5"	176.8(1.1)		
C4-C5-C6-N1	-7.2(1.9)		
C4-C5-C6-C6'	174.8(1.2)		
C5'-C5-C6-N1	176.2(1.1)		
C5'-C5-C6-C6'	-1.8(2.1)		
C5-C5'-O5"-C18	-179.2(1.1)		
O5'-C5'-O5"-C18	2.9(1.7)		

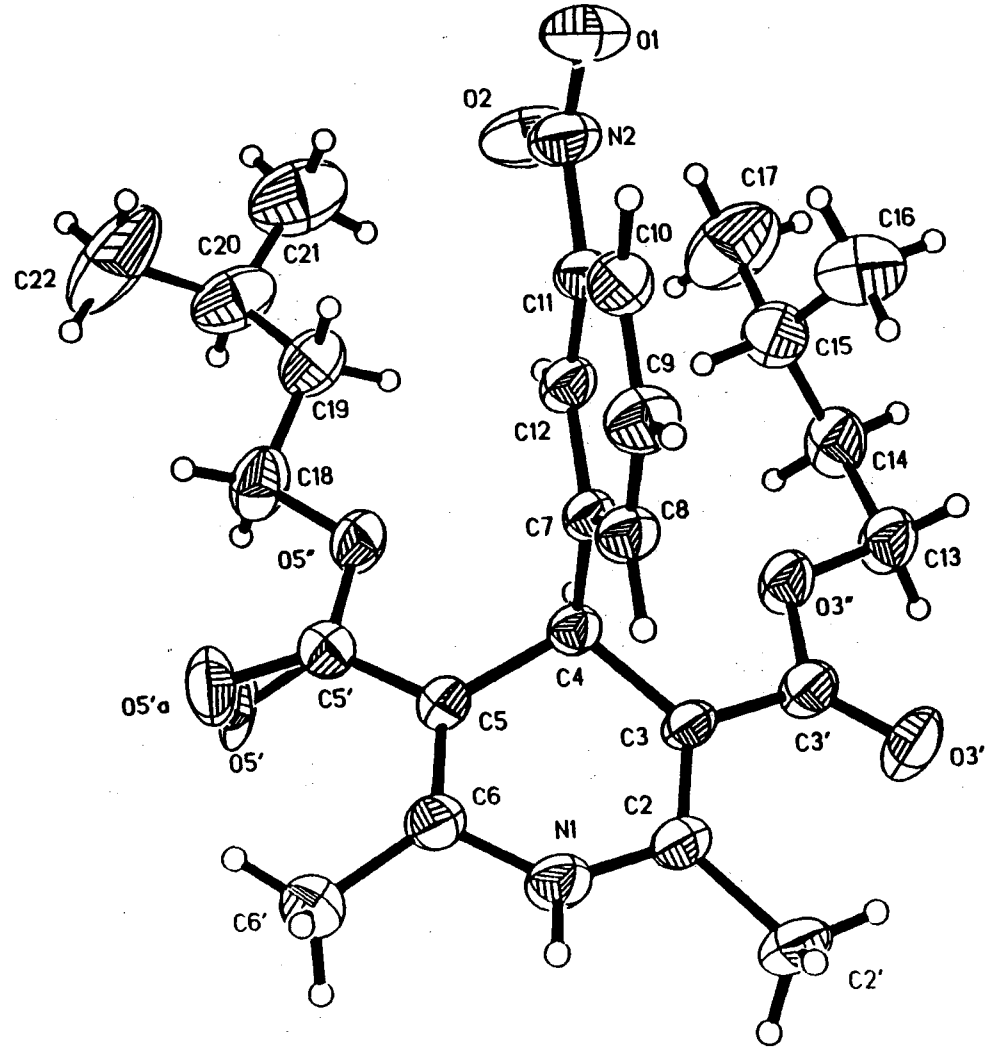

Figure 44: Projection view of Isopentyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine(XIV)

TABLE 72

CRYSTAL DATA FOR

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIV)

Formula	$C_{17}H_{17}N_2O_6$
M. W.	345.33 g $mole^{-1}$
a	10.744(1) Å
b	10.887(1) Å
c	12.223(1) Å
α	103.07(1) °
β	97.39(1) °
γ	109.51(1) °
V	1279.9(2) $Å^3$
F(000)	492
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.190 g/cm^3
Z	2
Meas refl	5249
Obs refl	N/A(refinement on F^2)
R	5.8 %
R_w	12.42 %
G. O. F.	0.796
Space Group	P-1
Octants meas	$-1 \leq h \leq 12, -12 \leq k \leq 11, -14 \leq l \leq 14$

TABLE 73

POSITIONAL PARAMETERS FOR

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIV)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.3382(4)	-0.0013(3)	0.1233(3)
H1A	0.3415(4)	-0.0774(3)	0.0781(3)
C2	0.2131(4)	0.0012(3)	0.1326(3)
C2'	0.0996(4)	-0.1378(3)	0.0914(4)
H2'A	0.0154(4)	-0.1288(3)	0.1005(4)
H2'B	0.0938(4)	-0.1786(3)	0.0117(4)
H2'C	0.1181(4)	-0.1942(3)	0.1362(4)
H2'D*	0.0365	-0.1050	0.0079
H2'E*	0.1591	-0.2055	0.0731
H2'F*	0.0808	-0.1554	0.1633
C3	0.2015(4)	0.1211(3)	0.1737(3)
C3'	0.0725(4)	0.1280(4)	0.1960(3)
O3'	-0.0363(3)	0.0371(3)	0.1731(3)
O3"	0.0892(2)	0.2574(2)	0.2489(2)
C4	0.3223(3)	0.2527(3)	0.1976(3)
H4A	0.3176(3)	0.3150(3)	0.2650(3)
C5	0.4532(4)	0.2303(3)	0.2240(3)
C5'	0.5738(5)	0.3436(4)	0.2981(4)
O5'	0.6635(69)	0.3248(64)	0.3362(52)
O5'A	0.6922(48)	0.3512(44)	0.3222(27)
O5"	0.5450(3)	0.4552(3)	0.3331(2)
C6	0.4596(4)	0.1067(4)	0.1796(3)
C6'	0.5787(4)	0.0680(4)	0.1874(4)
H6'A	0.6584(4)	0.1471(4)	0.2271(4)
H6'B	0.5668(4)	0.0018(4)	0.2293(4)
H6'C	0.5886(4)	0.0300(4)	0.1116(4)
H6'D*	0.6284	0.1042	0.2805
H6'E*	0.5125	-0.0673	0.1275
H6'F*	0.6444	0.1192	0.1440
C7	0.3197(3)	0.3164(3)	0.0998(3)
C8	0.2917(4)	0.2407(4)	-0.0145(3)
H8A	0.2754(4)	0.1456(4)	-0.0305(3)
C9	0.2885(4)	0.2993(4)	-0.1030(4)
H9A	0.2682(4)	0.2430(4)	-0.1808(4)
C10	0.3103(4)	0.4359(4)	-0.0814(4)
H10A	0.3107(4)	0.4780(4)	-0.1425(4)

TABLE 73 (Continued)

C11	0.3361(4)	0.5090(4)	0.0316(4)
C12	0.3420(4)	0.4541(3)	0.1220(3)
H12A	0.3614(4)	0.5104(3)	0.1997(3)
C13	-0.0281(4)	0.2799(4)	0.2778(4)
H13A	-0.0720(4)	0.2171(4)	0.3177(4)
H13B	-0.0908(4)	0.2674(4)	0.2090(4)
C14	0.0191(4)	0.4251(4)	0.3498(4)
H14A	0.0782(4)	0.4340(4)	0.4195(4)
H14B	-0.0564(4)	0.4459(4)	0.3701(4)
C15	0.0980(5)	0.5304(4)	0.2988(5)
H15A	0.1797(5)	0.5159(4)	0.2887(5)
C16	0.0236(6)	0.5164(5)	0.1810(5)
H16A	0.0767(6)	0.5827(5)	0.1483(5)
H16B	0.0027(6)	0.4267(5)	0.1314(5)
H16C	-0.0589(6)	0.5300(5)	0.1890(5)
C17	0.1364(6)	0.6712(5)	0.3747(5)
H17A	0.1846(6)	0.7380(5)	0.3400(5)
H17B	0.0562(6)	0.6856(5)	0.3903(5)
H17C	0.1932(6)	0.6794(5)	0.4454(5)
C18	0.6528(4)	0.5755(4)	0.4104(4)
H18A	0.7335(4)	0.5970(4)	0.3808(4)
H18B	0.6721(4)	0.5613(4)	0.4844(4)
C19	0.6014(5)	0.6887(4)	0.4201(4)
H19A	0.5167(5)	0.6609(4)	0.4433(4)
H19B	0.5850(5)	0.7022(4)	0.3454(4)
C20	0.6922(6)	0.8192(5)	0.5049(4)
H20A	0.7103(6)	0.8013(5)	0.5774(4)
C21	0.6249(7)	0.9199(5)	0.5227(5)
H21A	0.6805(7)	1.0067(5)	0.5763(5)
H21B	0.5977(7)	0.9320(5)	0.4492(5)
H21C	0.5460(7)	0.8792(5)	0.5505(5)
C22	0.8233(7)	0.8795(6)	0.4806(6)
H22A	0.8655(7)	0.8139(6)	0.4750(6)
H22B	0.8075(7)	0.8965(6)	0.4073(6)
H22C	0.8816(7)	0.9627(6)	0.5375(6)
N2	0.3571(4)	0.6553(4)	0.0594(5)
O1	0.3452(4)	0.7036(3)	-0.0192(3)
O2	0.3850(4)	0.7207(3)	0.1593(4)

*Disorder of methyl hydrogens on C2' and C6'

TABLE 74

ANISOTROPIC THERMAL PARAMETERS FOR

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIV)

ATOM	U11	U22	U33	U23	U13	U12
N1	71(2)	43(2)	86(2)	8(2)	23(2)	22(2)
C2	63(3)	43(2)	64(3)	15(2)	12(2)	14(2)
C2'	89(3)	41(2)	99(3)	14(2)	11(3)	11(2)
C3	54(2)	37(2)	60(2)	14(2)	10(2)	9(2)
C3'	60(3)	52(3)	72(3)	13(2)	18(2)	15(2)
O3'	61(2)	61(2)	134(3)	3(2)	29(2)	1(2)
O3"	51(2)	57(2)	108(2)	7(2)	27(2)	19(1)
C4	50(2)	41(2)	54(2)	9(2)	12(2)	16(2)
C5	48(2)	46(2)	56(2)	13(2)	8(2)	12(2)
C5'	60(3)	61(3)	75(3)	17(2)	13(3)	24(3)
O5'	24(15)	56(16)	109(25)	-24(16)	-2(11)	-9(14)
O5'A	43(10)	89(9)	170(10)	7(9)	0(7)	21(8)
O5"	56(2)	53(2)	97(2)	1(2)	-2(2)	8(1)
C6	60(3)	53(2)	81(3)	24(2)	26(2)	22(2)
C6'	71(3)	68(3)	111(4)	23(2)	25(3)	32(2)
C7	44(2)	38(2)	67(3)	11(2)	16(2)	14(2)
C8	65(3)	47(2)	68(3)	12(2)	14(2)	20(2)
C9	88(3)	69(3)	69(3)	20(2)	17(3)	25(3)
C10	65(3)	83(3)	88(3)	44(3)	27(3)	28(2)
C11	58(3)	50(2)	93(3)	30(2)	26(2)	25(2)
C12	53(2)	43(2)	73(3)	11(2)	20(2)	15(2)
C13	60(3)	76(3)	115(4)	22(3)	35(3)	24(2)
C14	70(3)	93(3)	106(4)	17(3)	37(3)	38(3)
C15	84(4)	74(3)	119(4)	13(3)	26(3)	37(3)
C16	161(6)	105(4)	192(7)	59(5)	29(6)	48(4)
C17	182(7)	84(4)	177(6)	-8(4)	55(5)	19(4)
C18	67(3)	74(3)	88(3)	-3(3)	0(3)	5(3)
C19	87(4)	64(3)	87(3)	2(2)	6(3)	8(3)
C20	147(5)	63(3)	98(4)	5(3)	14(4)	7(4)
C21	207(8)	82(4)	139(5)	6(4)	25(5)	25(5)
C22	173(7)	96(5)	225(8)	-24(5)	67(6)	-46(5)
N2	86(3)	58(3)	129(4)	45(3)	41(3)	33(2)
O1	133(3)	88(2)	162(3)	78(2)	41(3)	50(2)
O2	182(4)	53(2)	145(3)	28(2)	51(3)	51(2)

The anisotropic displacement exponent takes the form:$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE 75

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIV)

N1-C2	1.372(5)	C2-N1-C6	123.8(3)
N1-C6	1.391(4)	C3-C2-N1	119.2(3)
C2-C3	1.342(5)	C3-C2-C2'	126.8(4)
C2-C2'	1.515(5)	N1-C2-C2'	114.0(3)
C3-C3'	1.470(5)	C2-C3-C3'	121.2(3)
C3-C4	1.514(4)	C2-C3-C4	120.2(4)
C3'-O3'	1.201(4)	C3'-C3-C4	118.7(3)
C3'-O3"	1.350(4)	O3'-C3'-O3"	121.2(4)
O3"-C13	1.434(4)	O3'-C3'-C3	128.4(4)
C4-C5	1.512(5)	O3"-C3'-C3	110.4(3)
C4-C7	1.514(4)	C3'-O3"-C13	116.8(3)
C5-C6	1.361(5)	C5-C4-C7	111.0(3)
C5-C5'	1.465(5)	C5-C4-C3	110.7(3)
C5'-O5'	1.12(7)	C7-C4-C3	112.1(3)
C5'-O5'A	1.24(4)	C6-C5-C5'	120.0(4)
C5'-O5"	1.344(5)	C6-C5-C4	120.7(3)
O5"-C18	1.447(4)	C5'-C5-C4	119.3(3)
C6-C6'	1.473(5)	O5'-C5'-O5"	127(2)
C7-C8	1.388(5)	O5'-C5'-C5	121(3)
C7-C12	1.392(4)	O5'A-C5'-C5	129.9(13)
C8-C9	1.376(5)	O5"-C5'-C5	110.3(4)
C9-C10	1.382(5)	C5'-O5"-C18	117.2(4)
C10-C11	1.369(5)	C5-C6-N1	117.3(4)
C11-C12	1.374(5)	C5-C6-C6'	128.7(4)
C11-N2	1.483(5)	N1-C6-C6'	113.9(3)
C13-C14	1.501(5)	C8-C7-C12	117.5(4)
C14-C15	1.493(6)	C8-C7-C4	122.0(3)
C15-C17	1.489(5)	C12-C7-C4	120.5(3)
C15-C16	1.503(6)	C9-C8-C7	121.7(4)
C18-C19	1.497(6)	C8-C9-C10	121.1(4)
C19-C20	1.481(5)	C11-C10-C9	116.7(4)
C20-C22	1.443(7)	C10-C11-C12	123.7(4)
C20-C21	1.494(7)	C10-C11-N2	118.9(4)
N2-O2	1.207(4)	C12-C11-N2	117.4(4)
N2-O1	1.207(4)	C11-C12-C7	119.4(4)
		O3"-C13-C14	107.0(3)
		C15-C14-C13	116.3(4)
		C17-C15-C14	112.3(4)
		C17-C15-C16	110.0(5)

TABLE 75 (Continued)

	C14-C15-C16	111.9(4)
	O5"-C18-C19	106.1(4)
	C20-C19-C18	114.7(4)
	C22-C20-C19	115.1(5)
	C22-C20-C21	110.3(5)
	C19-C20-C21	111.4(5)
	O2-N2-O1	123.0(4)
	O2-N2-C11	118.7(4)
	O1-N2-C11	118.3(5)

TABLE 76

TORSION ANGLES (°) FOR

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIV)

C6-N1-C2-C3	17.01(0.56)	C8-C7-C12-C11	-0.24(0.51)
C6-N1-C2-C2'	-164.11(0.34)	C4-C7-C12-C11	-178.55(0.33)
N1-C2-C3-C3'	-173.87(0.34)	C3'-O3"-C13-C14	172.04(0.34)
C2'-C2-C3-C3'	7.41(0.59)	O3"-C13-C14-C15	54.37(0.54)
N1-C2-C3-C4	6.27(0.53)	C13-C14-C15-C17	178.11(0.43)
C2'-C2-C3-C4	-172.45(0.34)	C13-C14-C15-C16	53.83(0.58)
C2-C3-C3'-O3'	-7.21(0.65)	C5'-O5"-C18-C19	171.10(0.36)
C4-C3-C3'-O3'	172.65(0.39)	O5"-C18-C19-C20	174.38(0.38)
C2-C3-C3'-O3"	173.04(0.32)	C18-C19-C20-C22	62.29(0.69)
C4-C3-C3'-O3"	-7.10(0.47)	C18-C19-C20-C21	-171.20(0.45)
O3'-C3'-O3"-C13	1.12(0.57)	C10-C11-N2-O2	-177.13(0.43)
C3-C3'-O3"-C13	-179.11(0.33)	C12-C11-N2-O2	3.72(0.60)
C2-C3-C4-C5	-26.61(0.46)	C10-C11-N2-O1	2.94(0.58)
C3'-C3-C4-C5	153.53(0.32)	C12-C11-N2-O1	-176.21(0.39)
C2-C3-C4-C7	97.91(0.39)	C8-C9-C10-C11	0.55(0.61)
C3'-C3-C4-C7	-81.95(0.39)	C9-C10-C11-C12	0.48(0.61)
C7-C4-C5-C6	-97.24(0.38)	C9-C10-C11-N2	-178.61(0.36)
C3-C4-C5-C6	27.87(0.46)	C10-C11-C12-C7	-0.63(0.58)
C7-C4-C5-C5'	82.68(0.39)	N2-C11-C12-C7	178.47(0.33)
C3-C4-C5-C5'	-152.21(0.33)	C7-C8-C9-C10	-1.44(0.62)
C6-C5-C5'-O5'	-15.04(4.96)	C12-C7-C8-C9	1.25(0.55)
C4-C5-C5'-O5'	165.04(4.93)	C4-C7-C8-C9	179.53(0.34)
C6-C5-C5'-O5'A	6.99(3.61)	C3-C4-C7-C12	132.19(0.35)
C4-C5-C5'-O5'A	-172.93(3.56)	C5-C4-C7-C12	-103.50(0.36)
C6-C5-C5'-O5"	-179.48(0.33)		
C4-C5-C5'-O5"	0.60(0.49)		
O5'-C5'-O5"-C18	14.78(5.85)		
C5-C5'-O5"-C18	177.99(0.32)		
C5'-C5-C6-N1	171.40(0.33)		
C4-C5-C6-N1	-8.68(0.52)		
C5'-C5-C6-C6'	-5.41(0.62)		
C4-C5-C6-C6'	174.51(0.36)		
C2-N1-C6-C5	-15.65(0.55)		
C2-N1-C6-C6'	161.62(0.35)		
C5-C4-C7-C8	78.27(0.41)		
C3-C4-C7-C8	-46.05(0.45)		

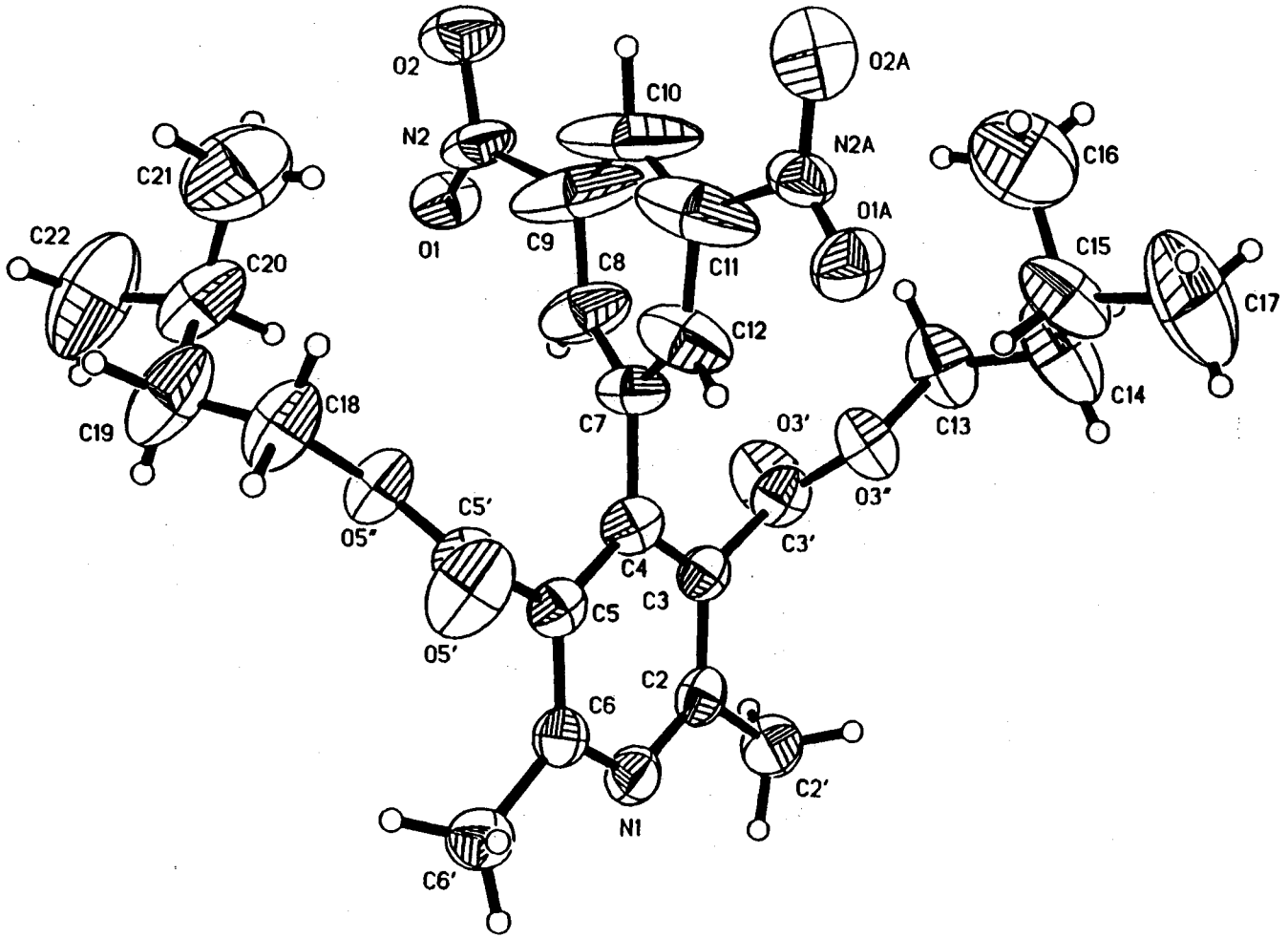

Figure 45: Projection view of Isopentyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine(XV)

TABLE 77

CRYSTAL DATA FOR

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate(XV)

Formula	$C_{25}H_{32}N_2O_6$
M. W.	456.53 g $mole^{-1}$
a	13.329(2) Å
b	13.331(3) Å
c	14.493(4) Å
α	90.00 °
β	90.00 °
γ	90.00 °
V	2575.2(10) $Å^3$
F(000)	976
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.18 g/cm^3
Z	4
Meas refl	3293
Obs refl	1469
R	6.95 %
R_w	13.38 %
G. O. F.	0.947
Space Group	$P2_12_12_1$
Octants meas	$-1 \leq h \leq 15$, $-1 \leq k \leq 15$, $-17 \leq l \leq 1$

TABLE 78

POSITIONAL PARAMETERS FOR

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XV)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.8728(4)	0.3768(4)	0.8749(4)
C2	0.8553(5)	0.2894(6)	0.8321(4)
C2'	0.7555(5)	0.2760(6)	0.7876(6)
H2'A	0.7167(5)	0.3361(6)	0.7950(6)
H2'B	0.7210(5)	0.2208(6)	0.8161(6)
H2'C	0.7645(5)	0.2623(6)	0.7231(6)
C3	0.9276(5)	0.2138(5)	0.8332(4)
C3'	0.9041(5)	0.1162(6)	0.7883(5)
O3'	0.8884(6)	0.1037(5)	0.7075(3)
O3"	0.9029(4)	0.0410(3)	0.8480(3)
C4	1.0199(5)	0.2294(5)	0.8754(4)
C5	1.0361(5)	0.3216(5)	0.9178(4)
C5'	1.1335(6)	0.3440(5)	0.9624(5)
O5'	1.1456(4)	0.3609(6)	1.0427(3)
O5"	1.2081(3)	0.3459(4)	0.9025(3)
C6	0.9599(5)	0.3944(5)	0.9167(4)
C6'	0.9726(6)	0.4947(5)	0.9623(6)
H6'A	0.9117(6)	0.5327(5)	0.9562(6)
H6'B	1.0267(6)	0.5304(5)	0.9334(6)
H6'C	0.9874(6)	0.4853(5)	1.0265(6)
C7	1.0982(5)	0.1496(5)	0.8763(5)
C8	1.1463(6)	0.1212(8)	0.7968(6)
H8A	1.1257(6)	0.1506(8)	0.7418(6)
C9	1.2203(9)	0.0546(12)	0.7932(12)
C10	1.2426(10)	0.0056(11)	0.8738(18)
H10A	1.2936(10)	-0.0420(11)	0.8733(18)
C11	1.1887(11)	0.0253(8)	0.9628(11)
C12	1.1234(8)	0.1018(6)	0.9573(7)
H12A	1.0934(8)	0.1239(6)	1.0115(7)
C13	0.8847(8)	-0.0579(6)	0.8134(5)
H13A	0.9457(8)	-0.0858(6)	0.7875(5)
H13B	0.8339(8)	-0.0562(6)	0.7656(5)
C14	0.8494(11)	-0.1205(8)	0.8942(7)
H14A	0.8317(11)	-0.1862(8)	0.8704(7)
H14B	0.7881(11)	-0.0904(8)	0.9172(7)
C15	0.9154(10)	-0.1355(7)	0.9721(7)
H15A	0.9371(10)	-0.0691(7)	0.9933(7)

TABLE 78 (Continued)

C16	1.0098(12)	-0.1947(11)	0.9451(11)
H16A	1.0431(12)	-0.1613(11)	0.8950(11)
H16B	0.9911(12)	-0.2611(11)	0.9262(11)
H16C	1.0543(12)	-0.1986(11)	0.9970(11)
C17	0.8701(15)	-0.1874(10)	1.0516(8)
H17A	0.8117(15)	-0.1514(10)	1.0716(8)
H17B	0.9179(15)	-0.1904(10)	1.1012(8)
H17C	0.8514(15)	-0.2542(10)	1.0339(8)
C18	1.3082(6)	0.3631(9)	0.9374(5)
H18A	1.3369(6)	0.3011(9)	0.9605(5)
H18B	1.3069(6)	0.4117(9)	0.9872(5)
C19	1.3688(7)	0.4025(11)	0.8570(8)
H19A	1.3358(7)	0.4618(11)	0.8330(8)
H19B	1.4342(7)	0.4228(11)	0.8796(8)
C20	1.3839(6)	0.3286(10)	0.7780(6)
H20A	1.3175(6)	0.3078(10)	0.7561(6)
C21	1.4397(11)	0.2374(12)	0.8047(11)
H21A	1.4472(11)	0.1946(12)	0.7520(11)
H21B	1.4033(11)	0.2025(12)	0.8521(11)
H21C	1.5047(11)	0.2560(12)	0.8276(11)
C22	1.4353(10)	0.3828(16)	0.7005(9)
H22A	1.4458(10)	0.3373(16)	0.6500(9)
H22B	1.4988(10)	0.4079(16)	0.7215(9)
H22C	1.3942(10)	0.4377(16)	0.6804(9)
N2	1.2797(10)	0.0681(12)	0.6803(12)
N2A	1.1807(10)	-0.0289(10)	1.0679(11)
O1	1.2500(12)	0.1134(15)	0.6121(10)
O1A	1.1330(17)	0.0045(18)	1.1348(11)
O2	1.3527(21)	0.0123(21)	0.6773(16)
O2A	1.2371(18)	-0.1005(20)	1.0662(11)

TABLE 79

ANISOTROPIC THERMAL PARAMETERS FOR

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XV)

ATOM	U11	U22	U33	U23	U13	U12
N1	59(3)	75(4)	79(3)	6(3)	3(3)	0(3)
C2	59(4)	79(4)	54(3)	10(4)	6(3)	-7(4)
C2'	70(4)	90(5)	97(5)	6(5)	-16(4)	1(4)
C3	62(4)	70(4)	48(3)	3(3)	5(3)	-1(4)
C3'	80(5)	92(5)	53(4)	-10(4)	6(4)	-4(4)
O3'	195(6)	109(4)	59(3)	-10(3)	-19(4)	-14(5)
O3"	126(4)	68(3)	52(2)	0(2)	-19(3)	-16(3)
C4	70(4)	83(4)	41(3)	-2(3)	0(3)	6(4)
C5	66(4)	76(4)	46(3)	6(3)	4(3)	3(4)
C5'	83(5)	88(5)	55(4)	-2(4)	-7(4)	4(5)
O5'	99(4)	199(6)	59(3)	-18(4)	-6(3)	-18(5)
O5"	63(3)	132(4)	56(3)	-18(3)	-2(2)	-12(3)
C6	74(4)	67(4)	57(4)	12(3)	14(4)	0(4)
C6'	83(5)	81(5)	98(6)	-18(4)	8(4)	3(4)
C7	68(4)	73(4)	88(4)	-21(4)	-19(4)	22(4)
C8	83(5)	150(8)	113(6)	-74(6)	-10(5)	31(6)
C9	107(8)	251(16)	238(16)	-64(14)	-91(10)	102(10)
C10	139(10)	167(12)	402(25)	-182(15)	-172(15)	111(9)
C11	192(13)	92(7)	219(15)	-59(9)	-134(12)	59(8)
C12	139(7)	80(5)	112(6)	-14(5)	-71(6)	25(6)
C13	171(9)	89(6)	69(5)	-23(4)	-18(6)	-35(6)
C14	275(15)	92(6)	111(7)	11(6)	-49(10)	-52(9)
C15	214(12)	72(5)	95(6)	-6(5)	-33(7)	9(7)
C16	245(17)	161(11)	208(15)	-28(12)	-9(15)	11(13)
C17	411(26)	156(10)	107(8)	41(8)	-20(13)	-77(15)
C18	75(5)	184(9)	69(4)	-16(6)	-12(4)	-21(6)
C19	76(5)	260(14)	136(8)	-40(10)	-3(6)	-31(8)
C20	71(5)	210(11)	081(5)	-40(7)	-4(5)	9(7)
C21	149(11)	256(18)	215(16)	13(15)	-31(12)	34(12)
C22	149(10)	384(24)	137(10)	23(15)	37(9)	-62(15)
O2	111(12)	118(12)	150(20)	-38(16)	12(16)	40(10)
O1	92(9)	110(11)	061(8)	31(10)	2(8)	30(8)
N2	70(8)	105(10)	114(12)	-29(10)	15(9)	33(8)
N2A	66(7)	57(7)	97(11)	6(8)	-21(8)	11(6)
O1A	91(11)	112(13)	71(10)	19(9)	24(10)	14(10)
O2A	131(13)	131(13)	82(11)	0(13)	-22(12)	-11(12)

The anisotropic displacement exponent takes the form:$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE 80

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XV)

C2'-C2	1.488(9)	C2-C3-C4	120.6(6)
C3-C2	1.394(9)	C2-C3-C3'	118.8(6)
C3-C4	1.390(9)	C4-C3-C3'	120.6(6)
C3-C3'	1.488(10)	O3'-C3'-O3"	122.0(7)
C3'-O3'	1.201(7)	O3'-C3'-C3	125.8(7)
C3'-O3"	1.324(8)	O3"-C3'-C3	112.3(5)
O3"-C13	1.431(9)	C3'-O3"-C13	118.1(5)
C4-C5	1.390(9)	C5-C4-C3	117.7(6)
C4-C7	1.491(8)	C5-C4-C7	121.2(6)
C5-C6	1.406(9)	C3-C4-C7	121.1(6)
C5-C5'	1.481(9)	C4-C5-C6	119.5(6)
C5'-O5'	1.196(8)	C4-C5-C5'	120.5(6)
C5'-O5"	1.321(8)	C6-C5-C5'	119.9(6)
O5"-C18	1.445(8)	O5'-C5'-O5"	122.4(7)
C6-N1	1.330(8)	O5'-C5'-C5	125.5(7)
C6-C6'	1.501(10)	O5"-C5'-C5	112.1(5)
C7-C8	1.372(11)	C5'-O5"-C18	117.9(5)
C7-C12	1.377(11)	N1-C6-C5	120.9(6)
C8-C9	1.328(14)	N1-C6-C6'	117.1(6)
C9-C10	1.37(3)	C5-C6-C6'	121.9(6)
C9-N2	1.83(2)	C8-C7-C12	118.3(7)
C10-C11	1.50(2)	C8-C7-C4	121.1(7)
C11-C12	1.342(13)	C12-C7-C4	120.6(7)
C11-N2A	1.69(2)	C9-C8-C7	124.4(11)
C13-C14	1.513(12)	C10-C9-C8	116.5(13)
C14-C15	1.446(14)	C10-C9-N2	135.7(12)
C15-C17	1.473(15)	C8-C9-N2	106.9(14)
C15-C16	1.54(2)	C9-C10-C11	123.0(9)
C18-C19	1.513(13)	C10-C11-C12	113.1(12)
C19-C20	1.524(14)	C10-C11-N2A	136.9(12)
C20-C21	1.48(2)	C12-C11-N2A	109.7(14)
C20-C22	1.500(15)	C11-C12-C7	124.1(11)
N1-C2	1.341(8)	O3"-C13-C14	106.9(7)
O2-N2	1.23(3)	C13-C14-C15	119.4(11)
O1-N2	1.22(2)	C17-C15-C16	107.1(11)
N2A-O1A	1.24(3)	C17-C15-C14	115.3(12)
N2A-O2A	1.22(3)	C16-C15-C14	111.7(10)
		O5"-C18-C19	106.1(6)
		C20-C19-C18	115.2(11)
		C19-C20-C21	113.6(10)
		C19-C20-C22	108.2(12)

TABLE 80 (Continued)

C21-C20-C22	111.3(11)
C6-N1-C2	121.1(6)
N1-C2-C3	120.1(6)
N1-C2-C2'	117.4(6)
C3-C2-C2'	122.4(6)
O1-N2-O2	121.8(17)
O1-N2-C9	129.2(13)
O2-N2-C9	108.5(19)
O1A-N2A-O2A	127.8(16)
O1A-N2A-C11	125.7(15)
O2A-N2A-C11	106.2(16)

TABLE 81

TORSION ANGLES FOR (°)

Di-isopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XV)

C2-C3-C3'-O3'	63.89(1.03)	C5'-O5"-C18-C19	-157.81(0.82)
C4-C3-C3'-O3'	-116.02(0.92)	O5"-C18-C19-C20	-65.36(1.15)
C2-C3-C3'-O3"	-116.60(0.64)	C18-C19-C20-C21	-61.98(1.20)
C4-C3-C3'-O3"	63.49(0.79)	C18-C19-C20-C22	173.94(0.91)
O3'-C3'-O3"-C13	1.68(1.15)	C5-C6-N1-C2	-0.50(0.90)
C3-C3'-O3"-C13	-177.85(0.71)	C6'-C6-N1-C2	179.67(0.57)
C2-C3-C4-C5	1.45(0.88)	C6-N1-C2-C3	2.08(0.90)
C3'-C3-C4-C5	-178.65(0.55)	C6-N1-C2-C2'	179.72(0.57)
C2-C3-C4-C7	-179.46(0.60)	C4-C3-C2-N1	-2.58(0.88)
C3'-C3-C4-C7	0.45(0.91)	C3'-C3-C2-N1	177.52(0.56)
C3-C4-C5-C6	0.11(0.87)	C4-C3-C2-C2'	179.90(0.63)
C7-C4-C5-C6	-178.99(0.60)	C3'-C3-C2-C2'	0.00(0.89)
C3-C4-C5-C5'	-178.83(0.55)	C10-C9-N2-O1	178.22(1.91)
C7-C4-C5-C5'	2.08(0.92)	C8-C9-N2-O1	-13.20(2.13)
C4-C5-C5'-O5'	-117.37(0.90)	C10-C9-N2-O2	6.87(2.49)
C6-C5-C5'-O5'	63.70(1.04)	C8-C9-N2-O2	175.46(1.62)
C4-C5-C5'-O5"	64.23(0.83)	C10-C11-N2A-O1A	176.35(1.81)
C6-C5-C5'-O5"	-114.70(0.66)	C12-C11-N2A-O1A -	9.57(1.97)
O5'-C5'-O5"-C18	3.95(1.16)	C10-C11-N2A-O2A	2.10(2.11)
C5-C5'-O5"-C18	-177.59(0.73)	C12-C11-N2A-O2A	176.18(1.36)
C4-C5-C6-N1	-0.61(0.88)	C4-C7-C12-C11	175.91(0.89)
C5'-C5-C6-N1	178.33(0.57)	C3'-O3"-C13-C14	-159.44(0.83)
C4-C5-C6-C6'	179.21(0.62)	O3"-C13-C14-C15	-61.92(1.31)
C5'-C5-C6-C6'	-1.85(0.91)	C13-C14-C15-C17	173.19(1.03)
C5-C4-C7-C8	-112.02(0.80)	C13-C14-C15-C16	-64.34(1.29)
C3-C4-C7-C8	68.92(0.94)		
C5-C4-C7-C12	68.52(0.93)		
C3-C4-C7-C12	-110.55(0.79)		
C12-C7-C8-C9	-4.22(1.41)		
C4-C7-C8-C9	176.30(0.99)		
C7-C8-C9-C10	5.94(1.83)		
C7-C8-C9-N2	-165.18(0.88)		
C8-C9-C10-C11	-0.68(2.14)		
N2-C9-C10-C11	167.10(1.25)		
C9-C10-C11-C12	-5.89(1.95)		
C9-C10-C11-N2A	168.05(1.31)		
C10-C11-C12-C7	7.91(1.52)		
N2A-C11-C12-C7	-167.70(0.84)		
C8-C7-C12-C11	-3.57(1.35)		

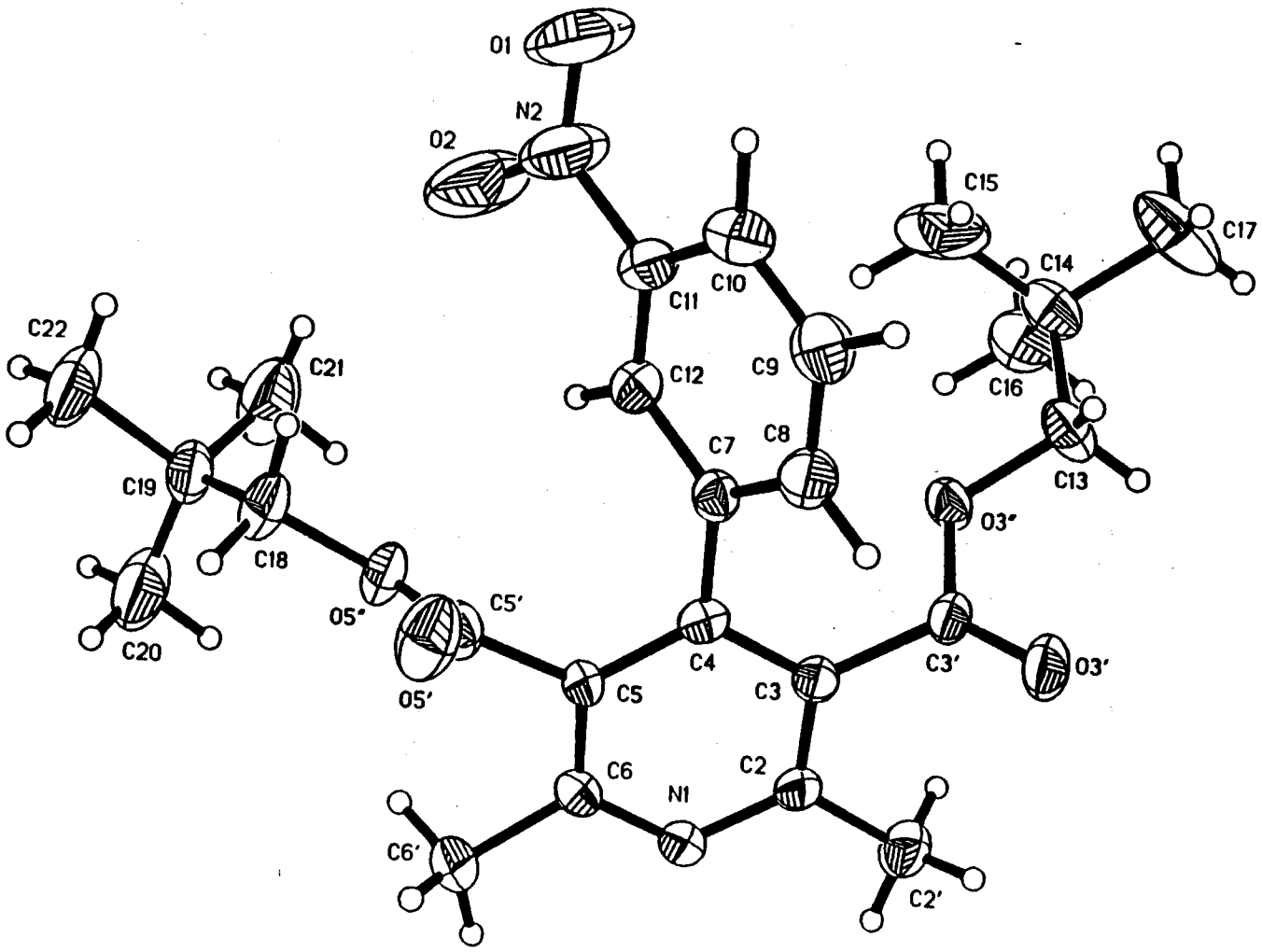

Figure 46: Projection view of Neopentyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine(XVI)

TABLE 82

CRYSTAL DATA FOR

Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XVI)

Formula	$C_{25}H_{32}N_2O_6$
M. W.	456.50 g mole^{-1}
a	17.736(3) Å
b	6.139(1) Å
c	24.756(4) Å
α	90.0 °
β	108.460(0) °
γ	90.0 °
V	2556.38(9) Å^3
F(000)	976
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.186 g/cm^3
Z	4
Meas refl	5973
Obs refl	1495
R	5.86 %
R_w	6.67 %
G. O. F.	1.29
Space Group	$P2_1/c$
Octants meas	$-1 \leq h \leq 21, -1 \leq k \leq 7, -29 \leq l \leq 28$

TABLE 83

POSITIONAL PARAMETERS FOR

Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XVI)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	-0.4538(3)	-0.7465(10)	-0.0410(2)
C2	-0.4123(4)	-0.6527(13)	0.0085(3)
C2'	-0.4280(4)	-0.7496(12)	0.0606(2)
C3	-0.3556(3)	-0.4933(12)	0.0126(2)
C3'	-0.3080(4)	-0.4039(12)	0.0695(2)
O3'	-0.3347(3)	-0.3027(11)	0.1000(2)
O3"	-0.2318(2)	-0.4534(8)	0.0816(2)
C4	-0.3413(3)	-0.4193(12)	-0.0376(2)
C5	-0.3865(3)	-0.5164(12)	-0.0886(2)
C5'	-0.3776(4)	-0.4328(15)	-0.1436(3)
O5'	-0.4000(3)	-0.2602(10)	-0.1633(2)
O5"	-0.3409(2)	-0.5788(8)	-0.1658(2)
C6	-0.4412(3)	-0.6751(13)	-0.0889(2)
C6'	-0.4923(3)	-0.7860(12)	-0.1428(2)
C7	-0.2803(3)	-0.2548(13)	-0.0354(2)
C8	-0.2791(4)	-0.0551(14)	-0.0097(3)
C9	-0.2209(4)	0.0976(14)	-0.0072(3)
C10	-0.1619(4)	0.0540(14)	-0.0309(3)
C11	-0.1651(4)	-0.1434(15)	-0.0574(3)
C12	-0.2208(4)	-0.3004(12)	-0.0600(2)
C13	-0.1794(3)	-0.3571(13)	0.1334(3)
C14	-0.0952(4)	-0.4319(16)	0.1419(3)
C15	-0.0709(4)	-0.3628(16)	0.0907(3)
C16	-0.0086(4)	-0.6705(16)	0.1479(3)
C17	-0.0427(4)	-0.3180(16)	0.1950(3)
C18	-0.3221(4)	-0.5040(13)	-0.2165(3)
C19	-0.2935(4)	-0.6969(15)	-0.2421(3)
C20	-0.3604(5)	-0.8531(16)	-0.2662(3)
C21	-0.2261(5)	-0.8108(16)	-0.2000(3)
C22	-0.2661(5)	-0.6024(14)	-0.2908(3)
N2	-0.021(5)	-0.1910(18)	-0.0836(4)
O1	-0.0500(4)	-0.0654(13)	-0.0779(3)
O2	-0.1134(4)	-0.3444(16)	-0.1145(4)
H2'A	-0.4690	-0.8577	0.0483
H2'B	-0.3805	-0.8158	0.0851
H2'C	-0.4451	-0.6366	0.0809
H2'D*	-0.4997	-0.7354	0.0506

TABLE 83 (Continued)

H2'E*	-0.4155	-0.9369	0.0586
H2'F*	-0.3937	-0.6399	0.0986
H6'A	-0.5262	-0.8936	-0.1345
H6'B	-0.5241	-0.6776	-0.1677
H6'C	-0.4581	-0.8546	-0.1611
H6'D*	-0.4758	-0.6699	-0.1795
H6'E*	-0.4703	-0.9905	-0.1438
H6'F*	-0.5564	-0.7791	-0.1445
H8A	-0.3196	-0.0237	0.0073
H9A	-0.2210	0.2339	0.0118
H10A	-0.1211	0.1575	-0.0303
H12A	-0.2198	-0.4371	-0.0786
H13A	-0.1954	-0.4015	0.1653
H13B	-0.1820	-0.2011	0.1306
H15A	-0.1022	-0.4360	0.0567
H15B	-0.0793	-0.2085	0.0861
H15C	-0.0157	-0.3947	0.0975
H16A	-0.1209	-0.7388	0.1134
H16B	-0.0343	-0.7159	0.1558
H16C	-0.1072	-0.7123	0.1788
H17A	-0.0578	-0.3661	0.2271
H17B	0.0125	-0.3500	0.2016
H17C	-0.0511	-0.1638	0.1902
H18A	-0.2813	-0.3948	-0.2060
H18B	-0.3685	-0.4430	-0.2438
H20A	-0.3769	-0.9158	-0.2362
H20B	-0.4038	-0.7739	-0.2917
H20C	-0.3441	-0.9669	-0.2867
H21A	-0.2437	-0.8707	-0.1702
H21B	-0.2065	-0.9257	-0.2182
H21C	-0.1844	-0.7073	-0.1841
H22A	-0.2223	-0.5047	-0.2752
H22B	-0.2501	-0.7169	-0.3112
H22C	-0.3099	-0.5240	-0.3162

*Disorder of methyl hydrogens on C2' and C6'

TABLE 84

ANISOTROPIC THERMAL PARAMETERS FOR

Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XVI)

ATOM	U11	U22	U33	U23	U13	U12
N1	36(3)	81(5)	41(3)	-3(3)	9(3)	-1(3)
C2	32(3)	75(6)	42(4)	8(4)	13(3)	-1(4)
C2'	64(4)	90(7)	46(4)	4(5)	23(3)	11(4)
C3	34(4)	71(6)	37(4)	10(4)	9(3)	-1(4)
C3'	45(4)	77(6)	36(4)	9(4)	15(3)	-9(4)
O3'	60(3)	164(6)	52(3)	23(4)	15(2)	-36(3)
O3"	37(2)	88(4)	41(2)	13(3)	0(2)	-16(3)
C4	38(4)	60(6)	46(4)	-3(4)	17(3)	-1(4)
C5	37(4)	62(6)	30(4)	0(4)	7(3)	-2(4)
C5'	52(4)	65(6)	43(4)	12(5)	9(3)	0(5)
O5'	116(5)	87(5)	66(3)	30(4)	40(3)	24(4)
O5"	73(3)	74(4)	40(2)	15(3)	31(2)	7(3)
C6	36(4)	74(6)	38(4)	4(4)	4(3)	2(4)
C6'	58(4)	91(7)	45(4)	-18(5)	12(3)	-16(4)
C7	43(4)	52(6)	35(3)	4(4)	9(3)	1(4)
C8	54(4)	64(6)	53(4)	9(5)	15(3)	1(4)
C9	76(5)	58(7)	64(5)	-1(5)	18(4)	-7(4)
C10	53(5)	65(7)	74(5)	-8(5)	14(4)	2(5)
C11	50(4)	68(7)	64(5)	-6(5)	26(4)	-8(5)
C12	49(4)	62(6)	50(4)	2(5)	19(3)	-6(4)
C13	57(5)	73(6)	56(4)	1(5)	-6(4)	-17(4)
C14	58(5)	74(7)	60(5)	-2(5)	-7(4)	5(5)
C15	44(5)	175(12)	130(7)	-3(6)	3(5)	39(8)
C16	63(5)	110(9)	78(5)	17(6)	4(4)	10(6)
C17	89(6)	122(9)	124(7)	-3(7)	-45(5)	-20(7)
C18	88(5)	78(7)	49(4)	10(5)	37(4)	14(4)
C19	76(5)	78(7)	42(4)	1(5)	23(4)	1(4)
C20	152(9)	129(9)	75(5)	-14(8)	64(6)	-15(6)
C21	124(7)	161(10)	81(5)	64(8)	49(6)	23(6)
C22	126(7)	145(10)	65(5)	6(7)	58(5)	-1(6)
N2	83(6)	126(9)	159(8)	-36(6)	78(6)	-42(6)
O1	117(5)	164(8)	231(8)	-69(6)	120(6)	-54(6)
O2	126(6)	185(9)	240(9)	-48(6)	133(6)	-97(7)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE 85

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XVI)

N1-C2	1.342 (8)	C2-N1-C6	117.8(6)
N1-C6	1.348 (9)	N1-C2-C2'	114.1(6)
C2-C2'	1.525 (10)	N1-C2-C3	123.2(6)
C2-C3	1.384 (10)	C2'-C2-C3	122.5(5)
C3-C3'	1.498 (8)	C2-C3-C3'	120.6(6)
C3-C4	1.419 (9)	C2-C3-C4	119.2(5)
C3'-O3'	1.184 (9)	C3'-C3-C4	120.2(6)
C3'-O3"	1.324 (8)	C3-C3'-O3'	124.8(6)
O3"-C13	1.450 (7)	C3-C3'-O3"	111.0(6)
C4-C5	1.398 (8)	O3'-C3'-O3"	124.2(5)
C4-C7	1.468 (10)	C3'-O3"-C13	115.4(5)
C5-C5'	1.510 (10)	C3-C4-C5	116.4(6)
C5-C6	1.374 (10)	C3-C4-C7	121.4(5)
C5'-O5'	1.181 (11)	C5-C4-C7	122.1(6)
C5'-O5"	1.325 (10)	C4-C5-C5'	118.5(6)
O5"-C18	1.469 (8)	C4-C5-C6	120.6(6)
C6-C6'	1.517 (8)	C5'-C5-C6	120.8(5)
C7-C8	1.378 (11)	C5-C5'-O5'	123.9(8)
C7-C12	1.405 (10)	C5-C5'-O5"	110.5(7)
C8-C9	1.380 (11)	O5'-C5'-O5"	125.6(7)
C9-C10	1.380 (12)	C5'-O5"-C18	114.6(6)
C10-C11	1.371 (12)	N1-C6-C5	122.7(5)
C11-C12	1.367 (11)	N1-C6-C6'	114.2(6)
C11-N2	1.487 (13)	C5-C6-C6'	123.1(6)
C13-C14	1.513 (10)	C4-C7-C8	122.2(6)
C14-C15	1.522 (12)	C4-C7-C12	119.6(7)
C14-C16	1.474 (14)	C8-C7-C12	118.2(7)
C14-C17	1.521 (10)	C7-C8-C9	121.9(7)
C18-C19	1.506 (12)	C8-C9-C10	120.4(8)
C19-C20	1.495 (12)	C9-C10-C11	117.0(7)
C19-C21	1.488 (10)	C10-C11-C12	124.4(7)
C19-C22	1.547 (12)	C10-C11-N2	117.4(8)
N2-O1	1.178 (12)	C12-C11-N2	118.2(8)
N2-O2	1.189 (14)	C7-C12-C11	118.1(7)
		O3"-C13-C14	109.1(6)
		C13-C14-C15	109.1(6)
		C13-C14-C16	111.0(7)
		C15-C14-C16	109.1(7)
		C13-C14-C17	106.7(7)
		C15-C14-C17	109.6(7)
		C16-C14-C17	111.3(6)

TABLE 85 (Continued)

	O5"-C18-C19	108.2(6)
	C18-C19-C20	109.9(7)
	C18-C19-C21	112.2(6)
	C20-C19-C21	109.7(7)
	C18-C19-C22	105.3(7)
	C20-C19-C22	109.6(6)
	C21-C19-C22	110.0(7)
	C11-N2-O1	119.2(10)
	C11-N2-O2	116.0(9)
	O1-N2-O2	124.21(1)

TABLE 86

TORSION ANGLES (°) FOR

Dineopentyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate (XVI)

C6-N1-C2-C2'	-177.8(0.6)	C10-C11-C12-C7	2.0(0.9)
C6-N1-C2-C3	-2.5(1.0)	N2-C11-C12-C7	-179.8(0.6)
C2-N1-C6-C5	1.9(1.0)	C10-C11-N2-O1	4.3(1.1)
C2-N1-C6-C6'	-178.5(0.6)	C10-C11-N2-O2	-167.5(0.8)
N1-C2-C3-C3'	-176.6(0.6)	C12-C11-N2-O1	-174.0(0.8)
N1-C2-C3-C4	1.7(1.1)	C12-C11-N2-O2	14.2(1.2)
C2'-C2-C3-C3'	-1.6(1.1)	O3"-C13-C14-C15	59.1(0.9)
C2'-C2-C3-C4	176.6(0.6)	O3"-C13-C14-C16	-61.1(0.7)
C2-C3-C3'-O3'	-64.9(1.1)	O3"-C13-C14-C17	177.4(0.6)
C2-C3-C3'-O3"	114.9(0.7)	O5"-C18-C19-C20	68.1(0.6)
C4-C3-C3'-O3'	116.8(0.8)	O5"-C18-C19-C21	-54.3(0.8)
C4-C3-C3'-O3"	-63.3(0.8)	O5"-C18-C19-C22	-173.9(0.5)
C2-C3-C4-C5	-0.3(1.0)	C8-C7-C12-C11	-0.4(0.8)
C2-C3-C4-C7	-178.3(0.6)	C7-C8-C9-C10	0.3(1.0)
C3'-C3-C4-C5	178.0(0.6)	C8-C9-C10-C11	1.1(0.9)
C3'-C3-C4-C7	-0.1(1.0)	C9-C10-C11-C12	-2.4(1.0)
C3-C3'-O3"-C13	174.5(0.6)	C9-C10-C11-N2	179.4(0.6)
O3'-C3'-O3"-C13	-5.6(1.0)		
C3'-O3"-C13-C14	178.9(0.6)		
C3-C4-C5-C5'	175.9(0.6)		
C3-C4-C5-C6	-0.3(1.0)		
C7-C4-C5-C5'	-6.0(1.0)		
C7-C4-C5-C6	177.8(0.6)		
C3-C4-C7-C8	-54.8(0.9)		
C3-C4-C7-C12	125.0(0.7)		
C5-C4-C7-C8	127.2(0.7)		
C5-C4-C7-C12	-52.9(0.9)		
C4-C5-C5'-O5'	-69.5(0.9)		
C4-C5-C5'-O5"	109.8(0.7)		
C6-C5-C5'-O5'	106.6(0.9)		
C6-C5-C5'-O5"	-74.0(0.8)		
C4-C5-C6-N1	-0.6(1.1)		
C4-C5-C6-C6'	179.8(0.6)		
C5'-C5-C6-N1	-176.7(0.7)		
C5'-C5-C6-C6'	3.7(1.1)		
C5-C5'-O5"-C18	-174.1(0.5)		
O5'-C5'-O5"-C18	5.3(0.9)		
C5'-O5"-C18-C19	-170.7(0.5)		
C4-C7-C8-C9	179.1(0.6)		
C12-C7-C8-C9	-0.7(0.9)		
C4-C7-C12-C11	179.8(0.5)		

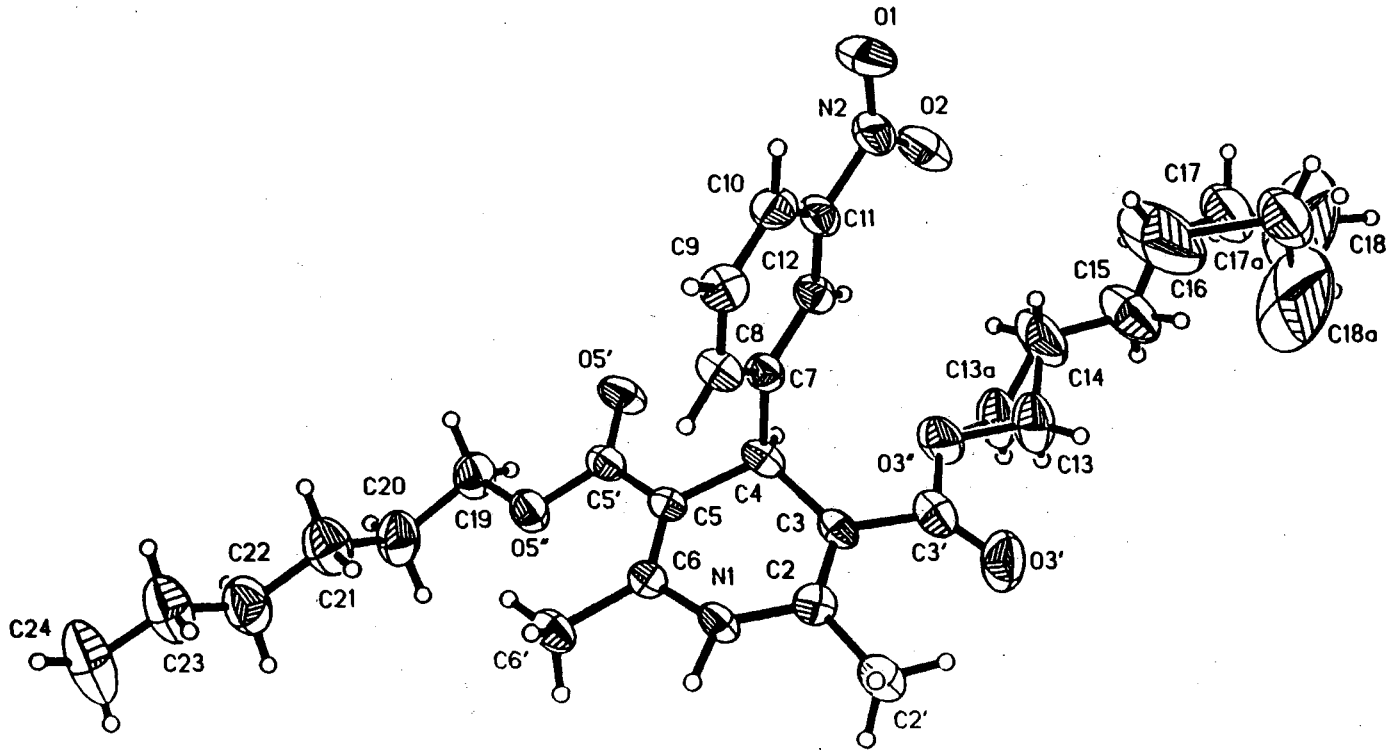

Figure 47: Projection view of Hexyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine(XVII)

TABLE 87

CRYSTAL DATA FOR

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XVII)

Formula	$C_{27}H_{39}N_2O_6$
M. W.	487.6 g mole^{-1}
a	13.782(5) Å
b	16.259(6) Å
c	13.027(5) Å
α	90.0 °
β	104.48(1) °
γ	90.0 °
V	2826(2) Å^3
F(000)	1052
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.146 g/cm^3
Z	4
Meas refl	6130
Obs refl	1656
R	6.81 %
R_w	7.88 %
G. O. F.	1.59
Space Group	$P2_1/c$
Octants meas	$-16 \leq h \leq 16, -19 \leq k \leq 1, -1 \leq l \leq 15$

TABLE 88

POSITIONAL PARAMETERS FOR

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XVII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.3912(4)	0.3320(3)	0.3390(4)
N2	0.5137(6)	0.4095(5)	-0.1720(6)
O1	0.4821(5)	0.4535(4)	-0.2494(5)
O2	0.5923(5)	0.3688(4)	-0.1555(5)
C2	0.4908(5)	0.3471(4)	0.3401(5)
C2'	0.5464(5)	0.3941(4)	0.4362(6)
C3	0.5277(5)	0.3183(4)	0.2594(5)
C3'	0.6368(6)	0.3261(5)	0.2635(8)
O3'	0.7006(4)	0.3586(4)	0.3333(5)
O3"	0.6584(3)	0.2921(3)	0.1773(4)
C4	0.4571(5)	0.2788(4)	0.1607(5)
C5	0.3646(4)	0.2416(4)	0.1899(5)
C5'	0.3180(5)	0.1726(4)	0.1226(6)
O5'	0.3418(3)	0.1506(3)	0.0426(4)
O5"	0.2464(3)	0.1313(3)	0.1583(3)
C6	0.3335(5)	0.2732(4)	0. 2734(5)
C6'	0.2390(5)	0.2514(4)	0.3097(5)
C7	0.4286(5)	0.3426(4)	0.0705(5)
C8	0.3536(5)	0.4017(4)	0.0675(6)
C9	0.3305(5)	0.4612(4)	-0.0125(6)
C10	0.3807(6)	0.4631(5)	-0.0923(6)
C11	0.4557(6)	0.4058(5)	-0.0878(6)
C12	0.4809(5)	0.3449(4)	-0.0100(5)
C13	0.7645(10)	0.3028(13)	0.1769(13)
C13A	0.7491(35)	0.2494(44)	0.1592(47)
C14	0.7799(6)	0.2905(7)	0.0769(8)
C15	0.8894(7)	0.2912(7)	0.0663(9)
C16	0.9135(9)	0.3150(14)	-0.0167(12)
C17	1.0185(15)	0.2800(11)	-0.0405(16)
C17A	1.0253(43)	0.3847(38)	-0.0053(44)
C18	1.0763(12)	0.3381(40)	-0.0067(23)
C18A	1.2709(358)	0.3344(821)	0.0877(722)
C19	0.2051(5)	0.0569(5)	0.0968(6)
C20	0.1331(6)	0.0156(5)	0.1520(7)
C21	0.0406(6)	0.0597(5)	0.1508(7)
C22	-0.0355(7)	0.0113(5)	0.1982(8)
C23	-0.1332(8)	0.0551(6)	0.1890(9)

TABLE 88 (Continued)

C24	-0.2085(7)	0.0126(6)	0.2298(10)
H1A	0.3595	0.3447	0.3988
H2'A	0.6144	0.4023	0.4325
H2'B	0.5148	0.4466	0.4380
H2'C	0.5456	0.3637	0.4991
H2'D*	0.5781	0.4441	0.4030
H2'E*	0.5004	0.4057	0.4913
H4A	0.4936	0.2255	0.1309
H6'A	0.2015	0.2111	0.2621
H6'B	0.2583	0.2290	0.3801
H6'C	0.1983	0.2994	0.3095
H6'D*	0.2604	0.2013	0.3286
H6'E*	0.1776	0.2600	0.2399
H6'F*	0.2149	0.2831	0.3794
H8A	0.3187	0.4008	0.1226
H9A	0.2790	0.5010	-0.0127
H10A	0.3651	0.5022	-0.1494
H12A	0.5320	0.3051	-0.0112
H13A	0.7999	0.2584	0.2185
H13B	0.7936	0.3538	0.2070
H13C	0.7812	0.2041	0.2016
H13D	0.7739	0.3010	0.1908
H14A	0.7473	0.3366	0.0365
H14B	0.7469	0.2412	0.0459
H15A	0.9243	0.2484	0.1115
H15B	0.9211	0.3426	0.0910
H16A	0.8585	0.3431	-0.0633
H16B	0.9036	0.2572	-0.0307
H17A	0.10123	0.2908	-0.1143
H17B	0.10392	0.2239	-0.0261
H17C	0.10334	0.4232	-0.0584
H17D	0.10316	0.3312	-0.0341
H18A	0.11837	0.3143	-0.0007
H18B	0.10979	0.3801	-0.0225
H18C	0.11229	0.3306	0.0841
H18D	0.11135	0.3248	-0.0006
H18E	0.10077	0.3518	-0.0685
H18F	0.10314	0.3541	0.0556
H19A	0.2588	0.0203	0.0930
H19B	0.1696	0.0719	0.0261
H20A	0.1678	0.0088	0.2252
H20B	0.1151	-0.0381	0.1227
H21A	0.0078	0.0713	0.0782
H21B	0.0564	0.1109	0.1880
H22A	-0.0049	0.0029	0.2722

TABLE 88 (Continued)

H22B	-0.0478	-0.0414	0.1642
H23A	-0.1626	0.0638	0.1148
H23B	-0.1199	0.1079	0.2226
H24A	-0.2698	0.0430	0.2205
H24B	-0.2222	-0.0399	0.1955
H24C	-0.1791	0.0046	0.3041

*Disorder of methyl hydrogens on C2' and C6'

TABLE 89

ANISOTROPIC THERMAL PARAMETERS FOR

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XVII)

ATOM	U11	U22	U33	U23	U13	U12
N1	61(4)	61(4)	63(4)	-4(3)	36(3)	-2(3)
N2	98(6)	85(6)	74(6)	-43(5)	25(5)	5(5)
O1	153(6)	146(6)	76(4)	-37(5)	33(4)	39(4)
O2	127(5)	101(5)	90(4)	-16(4)	64(4)	7(4)
C2	65(5)	45(4)	61(5)	2(4)	17(4)	-1(4)
C2'	86(5)	75(5)	85(6)	-8(4)	45(5)	-1(5)
C3	54(5)	47(4)	64(5)	6(4)	28(4)	15(4)
C3'	67(6)	69(6)	91(7)	6(5)	36(5)	14(5)
O3')	64(4)	152(6)	133(6)	-15(4)	31(4)	-34(5)
O3"	59(3)	135(5)	96(4)	16(3)	42(3)	7(4)
C4	68(5)	49(4)	61(5)	3(4)	37(4)	2(4)
C5	52(4)	52(4)	44(4)	1(4)	20(4)	-1(4)
C5'	58(5)	66(5)	54(5)	6(4)	25(4)	6(4)
O5'	100(4)	84(4)	65(3)	-10(3)	48(3)	-7(3)
O5"	66(3)	73(3)	73(3)	-13(3)	32(3)	-14(3)
C6	55(4)	54(5)	52(5)	-3(4)	17(4)	4(4)
C6'	63(5)	85(6)	77(5)	7(4)	40(4)	-1(4)
C7	55(4)	57(5)	54(5)	-3(4)	22(4)	-5(4)
C8	73(5)	64(5)	69(5)	4(4)	33(4)	7(5)
C9	75(5)	61(5)	77(6)	7(4)	18(5)	3(5)
C10	81(6)	61(5)	66(6)	-11(5)	5(5)	19(4)
C11	76(5)	66(6)	63(5)	-26(5)	28(5)	-5(5)
C12	68(5)	46(4)	62(5)	-7(4)	23(4)	0(4)
C13	65(8)	105(13)	144(11)	-3(9)	43(7)	-24(11)
C13A	65(8)	105(13)	144(11)	-3(9)	43(7)	-24(11)
C14	86(7)	186(10)	156(10)	9(7)	76(7)	38(8)
C15	123(9)	165(9)	170(11)	13(7)	92(8)	44(8)
C16	98(10)	880(59)	332(24)	68(20)	87(14)	333(32)
C17	114(15)	204(15)	173(15)	-18(12)	51(12)	58(15)
C17A	114(15)	204(15)	173(15)	-18(12)	51(12)	58(15)
C18	72(12)	767(63)	398(29)	9(27)	47(15)	-100(36)
C18A	72(12)	767(63)	398(29)	9(27)	47(15)	-100(36)
C19	79(5)	84(6)	84(6)	-17(5)	25(5)	-30(5)
C20	81(6)	91(6)	122(7)	-21(5)	26(5)	-26(6)
C21	105(7)	92(6)	135(8)	-14(6)	47(6)	-12(6)
C22	112(7)	116(8)	137(8)	-37(7)	50(6)	-18(7)

TABLE 89 (Continued)

C23	113(7)	119(8)	186(10)	-31(7)	73(8)	-26(8)
C24	133(8)	153(10)	286(15)	-37(8)	126(10)	-37(10)

The anisotropic displacement exponent takes the form:$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE 90

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XVII)

N1-C2	1.392 (9)	C2-N1-C6	122.6(6)
N1-C6	1.391 (8)	O1-N2-O2	124.7(9)
N2-O1	1.225 (10)	O1-N2-C11	118.6(8)
N2-O2	1.242 (11)	O2-N2-C11	116.7(7)
N2-C11	1.510 (13)	N1-C2-C2'	113.3(6)
C2-C2'	1.502 (9)	N1-C2-C3	119.3(6)
C2-C3	1.360 (11)	C2'-C2-C3	127.4(6)
C3-C3'	1.497 (11)	C2-C3-C3'	120.7(6)
C3-C4	1.545 (9)	C2-C3-C4	120.5(6)
C3'-O3'	1.216 (10)	C3'-C3-C4	118.9(7)
C3'-O3"	1.350 (12)	C3-C3'-O3'	126.5(9)
O3"-C13	1.474 (15)	C3-C3'-O3"	111.3(6)
O3"-C13A	1.499 (59)	O3'-C3'-O3"	122.2(8)
C4-C5	1.543 (10)	C3'-O3"-C13	112.2(8)
C4-C7	1.543 (9)	C3'-O3"-C13A	133.3(21)
C5-C5'	1.470 (9)	C3-C4-C5	110.2(6)
C5-C6	1.366 (10)	C3-C4-C7	110.0(5)
C5'-O5'	1.222 (9)	C5-C4-C7	112.5(5)
C5'-O5"	1.366 (9)	C4-C5-C5'	114.7(6)
O5"-C19	1.483 (9)	C4-C5-C6	119.5(6)
C6-C6'	1.533 (10)	C5'-C5-C6	125.8(6)
C7-C8	1.404 (10)	C5-C5'-O5'	124.2(7)
C7-C12	1.413 (10)	C5-C5'-O5"	114.6(6)
C8-C9	1.399 (10)	O5'-C5'-O5"	121.1(6)
C9-C10	1.386 (12)	C5'-O5"-C19	115.4(6)
C10-C11	1.383 (12)	N1-C6-C5	120.1(6)
C11-C12	1.397 (10)	N1-C6-C6'	111.6(6)
C13-C14	1.387 (21)	C5-C6-C6'	128.2(6)
C13A-C14	1.416 (67)	C4-C7-C8	121.8(6)
C14-C15	1.549 (14)	C4-C7-C12	120.2(6)
C15-C16	1.268 (21)	C8-C7-C12	118.0(6)
C16-C17	1.655 (27)	C7-C8-C9	121.5(7)
C16-C17A	1.889 (62)	C8-C9-C10	120.7(7)
C17-C18	1.243 (53)	C9-C10-C11	117.5(7)
C17A-C18	1.037 (79)	N2-C11-C10	117.9(7)
C19-C20	1.520 (12)	N2-C11-C12	118.4(7)
C20-C21	1.461 (12)	C10-C11-C12	123.7(8)
C21-C22	1.557 (14)	C7-C12-C11	118.5(6)
C22-C23	1.502 (14)	O3"-C13-C14	111.8(10)
C23-C24	1.453 (16)	O3"-C13A-C14	108.7(41)

TABLE 90 (Continued)

	C13-C14-C15	117.7(9)
	C13A-C14-C15	123.7(21)
	C14-C15-C16	123.2(10)
	C15-C16-C17	118.9(14)
	C15-C16-C17A	119.9(20)
	C16-C17-C18	100.6(23)
	C16-C17A-C18	95.9(48)
	O5"-C19-C20	108.2(6)
	C19-C20-C21	116.7(7)
	C20-C21-C22	114.8(7)
	C21-C22-C23	114.0(8)
	C22-C23-C24	116.9(8)

TABLE 91

TORSION ANGLES (°) FOR

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XVII)

C6-N1-C2-C2'	-163.5(0.6)	C5'-C5-C6-C6'	-6.7(1.1)
C6-N1-C2-C3	15.4(0.9)	C4-C7-C12-C11	-177.3(0.6)
C2-N1-C6-C5	-15.6(0.9)	C8-C7-C12-C11	0.2(0.9)
C2-N1-C6-C6'	163.5(0.6)	C7-C8-C9-C10	0.6(1.0)
O1-N2-C11-C10	-11.5(1.1)	C8-C9-C10-C11	-1.9(1.0)
O1-N2-C11-C12	168.4(0.7)	C9-C10-C11-N2	-177.6(0.7)
O2-N2-C11-C10	166.5(0.7)	C9-C10-C11-C12	2.4(1.1)
O2-N2-C11-C12	-13.5(1.0)	N2-C11-C12-C7	178.4(0.6)
N1-C2-C3-C3'	-173.8(0.6)	C10-C11-C12-C7	-1.6(1.0)
N1-C2-C3-C4	7.6(0.9)	O3"-C13-C14-C15	-174.0(1.1)
C2'-C2-C3-C3'	4.9(1.0)	O3"-C13A-C14-C15	152.9(1.8)
C2'-C2-C3-C4	-173.7(0.6)	C13-C14-C15-C16	-149.4(1.8)
C2-C3-C3'-O3'	-1.8(1.2)	C13A-C14-C15-C16	166.8(3.6)
C2-C3-C3'-O3"	178.5(0.6)	C14-C15-C16-C17	-155.4(1.2)
C4-C3-C3'-O3'	176.8(0.7)	C14-C15-C16-C17A	135.6(2.4)
C4-C3-C3'-O3"	-2.9(0.9)	C15-C16-C17-C18	-98.1(2.6)
C2-C3-C4-C5	-26.7(0.8)	O5"-C19-C20-C21	67.9(0.8)
C2-C3-C4-C7	97.9(0.7)	C19-C20-C21-C22	174.1(0.7)
C3'-C3-C4-C5	154.6(0.6)	C20-C21-C22-C23	-175.7(0.8)
C3'-C3-C4-C7	-80.8(0.7)	C21-C22-C23-C24	178.9(0.9)
C3-C3'-O3"-C13	177.0(1.0)	C12-C7-C8-C9	0.2(0.9)
C3-C3'-O3"-C13A	-148.2(3.7)	C5'-C5-C6-N1	172.1(0.6)
O3'-C3'-O3"-C13	-2.7(1.3)	C5-C5'-O5"-C19	-174.7(0.5)
O3'-C3'-O3"-C13A	32.1(3.8)	O5'-C5'-O5"-C19	3.2(0.8)
C3'-O3"-C13-C14	-162.1(1.2)	C5'-O5"-C19-C20	175.7(0.5)
C3'-O3"-C13A C14	-124.0(2.8)	C4-C7-C8-C9	177.7(0.6)
C3-C4-C5-C5'	-153.1(0.5)		
C3-C4-C5-C6	26.4(0.8)		
C7-C4-C5-C5'	83.7(0.7)		
C7-C4-C5-C6	-96.7(0.7)		
C3-C4-C7-C8	-80.2(0.8)		
C3-C4-C7-C12	97.2(0.7)		
C5-C4-C7-C8	43.1(0.8)		
C5-C4-C7-C12	-139.5(0.6)		
C4-C5-C5'-O5'	-7.7(0.9)		
C4-C5-C5'-O5"	170.2(0.5)		
C6-C5-C5'-O5'	172.9(0.6)		
C6-C5-C5'-O5"	-9.3(0.9)		
C4-C5-C6-N1	-7.4(0.9)		
C4-C5-C6-C6'	173.8(0.6)		

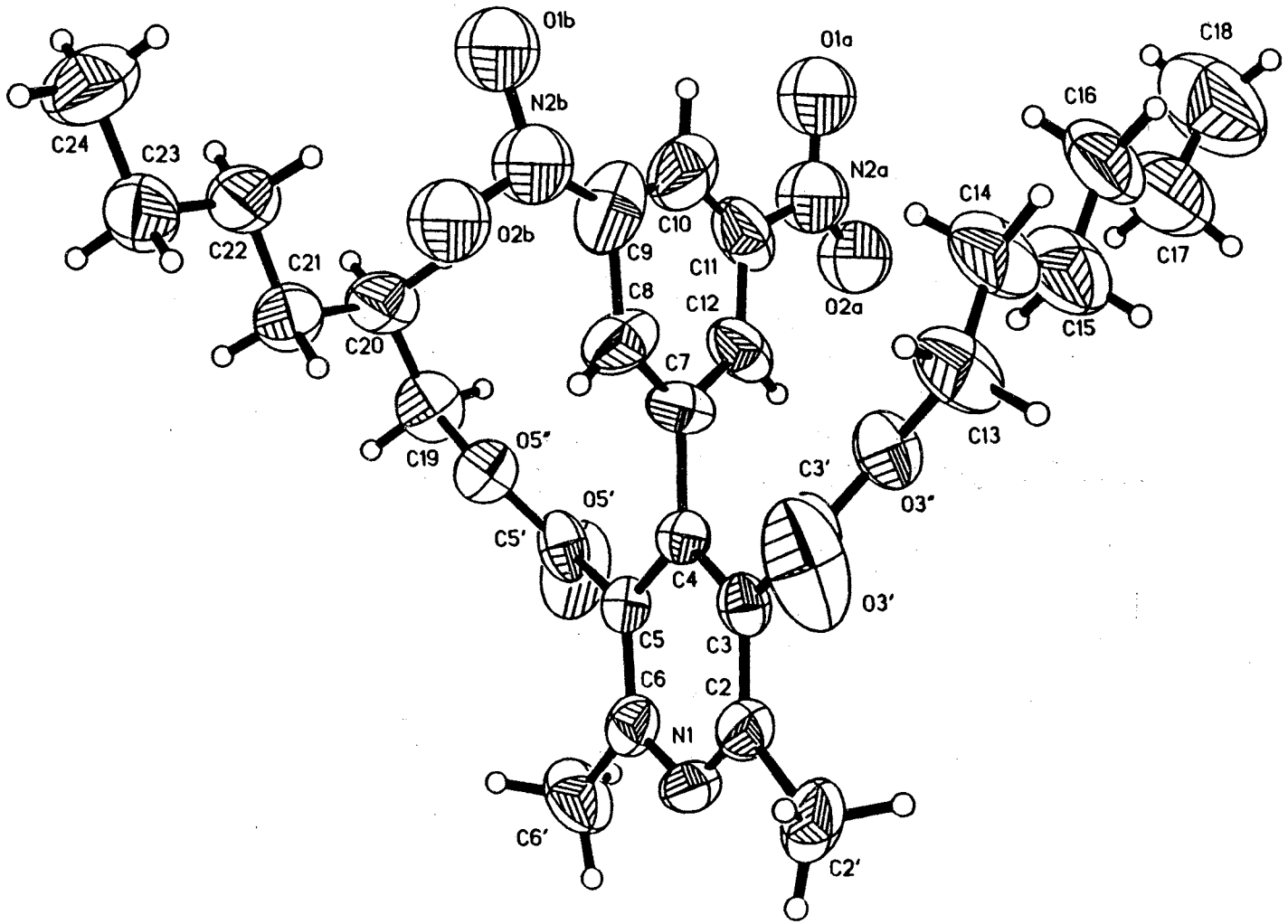

Figure 48: Projection view of Hexyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine(XVIII)

TABLE 92

CRYSTAL DATA FOR

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XVIII)

Formula	$C_{27}H_{36}N_2O_6$
M. W.	484.58 g $mole^{-1}$
a	8.089(2) Å
b	11.495(2) Å
c	15.707(5) Å
α	69.29(2) °
β	88.12(2) °
γ	87.03(2) °
V	1364.2(6) $Å^3$
F(000)	520
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.18 g/cm^3
Z	2
Meas refl	9318
Obs refl	769
R	6.05 %
R_w	13.12 %
G. O. F.	0.537
Space Group	P-1
Octants meas	$-1 \leq h \leq 11$, $-15 \leq k \leq 15$, $-20 \leq l \leq 22$

TABLE 93

POSITIONAL PARAMETERS FOR

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XVIII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.7484(12)	0.5015(13)	0.5650(7)
H1A	0.7463(12)	0.5115(13)	0.6168(7)
C2	0.6967(14)	0.5977(12)	0.4903(10)
C2'	0.6446(14)	0.7115(9)	0.5105(8)
H2'A	0.6470(14)	0.6933(9)	0.5750(8)
H2'B	0.5343(14)	0.7381(9)	0.4891(8)
H2'C	0.7190(14)	0.7765(9)	0.4804(8)
C3	0.7104(11)	0.5848(10)	0.4088(8)
C3'	0.6557(17)	0.6938(11)	0.3270(10)
O3'	0.5320(12)	0.7562(8)	0.3242(7)
O3"	0.7690(10)	0.7202(6)	0.2606(5)
C4	0.7652(11)	0.4739(10)	0.3972(7)
C5	0.8111(11)	0.3737(9)	0.4788(8)
C5'	0.8696(16)	0.2503(11)	0.4752(8)
O5'	0.9887(11)	0.1929(7)	0.5131(6)
O5"	0.7643(9)	0.2077(6)	0.4308(4)
C6	0.8025(14)	0.3920(12)	0.5608(8)
C6'	0.8506(14)	0.2916(11)	0.6490(6)
H6'A	0.8351(14)	0.3231(11)	0.6979(6)
H6'B	0.9648(14)	0.2661(11)	0.6456(6)
H6'C	0.7827(14)	0.2216(11)	0.6599(6)
C7	0.7767(19)	0.4586(8)	0.3088(8)
C8	0.6391(19)	0.4625(9)	0.2622(10)
H8A	0.5389(19)	0.4744(9)	0.2893(10)
C9	0.6314(26)	0.4499(13)	0.1725(13)
C10	0.7980(36)	0.4398(14)	0.1446(12)
H10A	0.8088(36)	0.4359(14)	0.0865(12)
C11	0.9473(23)	0.4346(12)	0.1857(13)
C12	0.9303(18)	0.4446(8)	0.2693(9)
H12A	1.0255(18)	0.4419(8)	0.3018(9)
C13	0.7245(19)	0.8214(11)	0.1768(9)
H13A	0.7428(19)	0.9011(11)	0.1824(9)
H13B	0.6087(19)	0.8189(11)	0.1636(9)
C14	0.8328(28)	0.8038(15)	0.1024(10)
H14A	0.8056(28)	0.7257(15)	0.0968(10)
H14B	0.8015(28)	0.8693(15)	0.0459(10)
C15	1.0117(27)	0.8028(16)	0.1091(12)

TABLE 93 (Continued)

H15A	1.0442(27)	0.7331(16)	0.1630(12)
H15B	1.0385(27)	0.8780(16)	0.1195(12)
C16	1.1174(30)	0.7948(15)	0.0316(11)
H16A	1.0939(30)	0.7196(15)	0.0205(11)
H16B	1.0897(30)	0.8653(15)	-0.0227(11)
C17	1.2934(33)	0.7937(19)	0.0490(13)
H17A	1.3124(33)	0.8640(19)	0.0674(13)
H17B	1.3210(33)	0.7188(19)	0.1002(13)
C18	1.4016(25)	0.7984(19)	-0.0216(13)
H18A	1.5133(25)	0.7967(19)	-0.0021(13)
H18B	1.3796(25)	0.8738(19)	-0.0723(13)
H18C	1.3874(25)	0.7281(19)	-0.0397(13)
C19	0.8121(15)	0.0922(10)	0.4162(8)
H19A	0.7900(15)	0.0215(10)	0.4708(8)
H19B	0.9296(15)	0.0900(10)	0.4020(8)
C20	0.7153(20)	0.0859(10)	0.3396(8)
H20A	0.7519(20)	0.0115(10)	0.3274(8)
H20B	0.7402(20)	0.1570(10)	0.2857(8)
C21	0.5314(20)	0.0842(11)	0.3543(9)
H21A	0.4946(20)	0.1553(11)	0.3706(9)
H21B	0.5046(20)	0.0095(11)	0.4049(9)
C22	0.4370(21)	0.0878(10)	0.2699(9)
H22A	0.4637(21)	0.1623(10)	0.2191(9)
H22B	0.4728(21)	0.0164(10)	0.2537(9)
C23	0.2550(20)	0.0867(12)	0.2858(9)
H23A	0.2184(20)	0.1599(12)	0.2995(9)
H23B	0.2285(20)	0.0139(12)	0.3380(9)
C24	0.1632(19)	0.0850(14)	0.2031(9)
H24A	0.0463(19)	0.0840(14)	0.2157(9)
H24B	0.1982(19)	0.0121(14)	0.1899(9)
H24C	0.1873(19)	0.1580(14)	0.1517(9)
N2A	1.1227(20)	0.4275(14)	0.1546(12)
O1A	1.1507(16)	0.4143(11)	0.0816(9)
O2A	1.2480(22)	0.4196(15)	0.1996(10)
N2B	0.4541(27)	0.4631(28)	0.1454(25)
O1B	0.3962(35)	0.4535(24)	0.0753(20)
O2B	0.2869(44)	0.4728(31)	0.1852(21)

TABLE 94

ANISOTROPIC THERMAL PARAMETERS FOR

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XVIII)

ATOM	U11	U22	U33	U23	U13	U12
N1	95(8)	148(10)	92(8)	-79(8)	28(7)	-53(8)
C2	87(9)	85(10)	95(10)	-49(8)	18(9)	-20(8)
C2'	117(10)	88(9)	186(12)	-85(9)	46(9)	-26(8)
C3	53(7)	64(8)	78(8)	-20(7)	7(6)	-4(6)
C3'	71(10)	62(8)	139(12)	-16(9)	18(10)	6(7)
O3'	118(8)	92(7)	255(11)	13(6)	37(8)	40(6)
O3"	98(7)	72(5)	97(6)	-1(5)	-8(5)	10(5)
C4	43(6)	72(7)	64(7)	-25(6)	-7(6)	-1(6)
C5	59(7)	56(7)	71(8)	-19(6)	-4(6)	-6(6)
C5'	50(8)	72(9)	100(10	-3(7)	2(7)	-3(7)
O5'	94(7)	92(6)	230(10)	-32(6)	-55(7)	23(5)
O5"	81(6)	62(5)	101(6)	-32(4)	-7(4)	20(4)
C6	68(8)	87(9)	86(10)	-33(8)	-8(7)	-19(7)
C6'	129(12)	141(11)	77(8)	5(8)	-12(8)	-31(9)
C7	124(11)	52(6)	57(8)	-15(6)	4(9)	20(7)
C8	175(15)	71(8)	83(10)	-16(7)	-59(10)	0(8)
C9	143(21)	81(9)	156(15)	1(9)	-85(14)	-10(13)
C10	208(29)	73(10)	118(13)	-12(8)	-52(17)	-24(17)
C11	154(18)	86(9)	122(13)	-40(9)	72(13)	-24(11)
C12	143(14)	68(8)	89(9)	-22(6)	46(9)	0(8)
C13	178(15)	104(9)	90(9)	23(9)	-12(11)	28(9)
C14	232(23)	153(14)	85(11)	39(10)	-38(15)	-17(15)
C15	179(20)	182(16)	111(14)	16(11)	-33(16)	-20(15)
C16	204(23)	170(14)	95(12)	22(10)	-3(16)	-39(16)
C17	218(25)	256(22)	129(17	-29(15)	10(19)	-51(21)
C18	220(24)	348(29)	196(19)	-52(19)	79(18)	-59(20)
C19	112(11)	68(8)	131(10)	-36(7)	14(9)	24(7)
C20	156(15)	79(8)	104(10)	-45(7)	15(11)	8(9)
C21	132(13)	104(10)	134(12)	-71(8)	31(11)	-15(9)
C22	173(16)	90(9)	113(11)	-54(8)	24(11)	-20(10)
C23	136(15)	140(12)	143(13)	-75(10)	39(12)	-25(10)
C24	170(16)	256(19)	157(13)	-103(13)	-40(12)	-23(13)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE 95

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XVIII)

N1-C6	1.335(12)	C6-N1-C2	122.2(11)
N1-C2	1.357(12)	C3-C2-N1	118.8(11)
C2-C3	1.340(12)	C3-C2-C2'	127.9(13)
C2-C2'	1.489(13)	N1-C2-C2'	113.0(12)
C3-C4	1.397(11)	C2-C3-C4	123.3(10)
C3-C3'	1.503(14)	C2-C3-C3'	117.6(12)
C3'-O3'	1.193(11)	C4-C3-C3'	119.0(11)
C3'-O3"	1.327(11)	O3'-C3'-O3"	123.4(12)
O3"-C13	1.456(11)	O3'-C3'-C3	124.4(13)
C4-C5	1.432(11)	O3"-C3'-C3	111.9(11)
C4-C7	1.459(12)	C3'-O3"-C13	116.0(10)
C5-C6	1.375(12)	C3-C4-C5	115.5(9)
C5-C5'	1.491(13)	C3-C4-C7	123.5(10)
C5'-O5'	1.189(11)	C5-C4-C7	121.0(10)
C5'-O5"	1.332(12)	C6-C5-C4	119.6(10)
O5"-C19	1.456(10)	C6-C5-C5'	119.9(11)
C6-C6'	1.504(12)	C4-C5-C5'	120.4(10)
C7-C8	1.342(14)	O5'-C5'-O5"	124.0(12)
C7-C12	1.398(14)	O5'-C5'-C5	124.1(13)
C8-C9	1.47(2)	O5"-C5'-C5	111.7(10)
C9-C10	1.42(2)	C5'-O5"-C19	117.5(9)
C9-N2B	1.494(6)	N1-C6-C5	120.5(11)
C10-C11	1.38(2)	N1-C6-C6'	116.9(13)
C11-C12	1.360(15)	C5-C6-C6'	122.6(12)
C11-N2A	1.493(5)	C8-C7-C12	118.6(11)
C13-C14	1.50(2)	C8-C7-C4	120.3(13)
C14-C15	1.45(2)	C12-C7-C4	121.1(13)
C15-C16	1.49(2)	C7-C8-C9	126.4(15)
C16-C17	1.46(2)	C10-C9-C8	105.6(17)
C17-C18	1.38(2)	C10-C9-N2B	145.8(26)
C19-C20	1.482(13)	C8-C9-N2B	108.3(23)
C20-C21	1.498(15)	C9-C10-C11	133.2(20)
C21-C22	1.538(14)	C12-C11-C10	113.0(15)
C22-C23	1.485(15)	C12-C11-N2A	114.2(19)
C23-C24	1.523(14)	C10-C11-N2A	132.8(20)
O2A-N2A	1.24(2)	C11-C12-C7	123.1(13)
O1A-N2A	1.221(15)	O3"-C13-C14	106.8(11)
O1B-N2B	1.25(3)	C15-C14-C13	119.5(18)
N2B-O2B	1.49(4)	C14-C15-C16	119.0(19)
		C17-C16-C15	112.4(19)
		C18-C17-C16	117.0(22)

TABLE 95 (Continued)

	O5"-C19-C20	108.5(9)
	C19-C20-C21	115.3(12)
	C20-C21-C22	112.9(12)
	C23-C22-C21	112.0(12)
	C22-C23-C24	111.6(13)
	O1A-N2A-O2A	113.8(17)
	O1A-N2A-C11	119.0(17)
	O2A-N2A-C11	126.7(20)
	O1B-N2B-O2B	92.8(24)
	O1B-N2B-C9	127.6(31)
	O2B-N2B-C9	139.1(33)

TABLE 96

TORSION-ANGLES-(°)-FOR

Dihexyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (XVIII)

C6-N1-C2-C3	-4.4(17)	N2B-C9-C10-C11	175.8(26)
C6-N1-C2-C2'	-179.0(10)	C9-C10-C11-C12	-2.1(27)
N1-C2-C3-C4	4.5(16)	C9-C10-C11-N2A	-178.0(17)
C2'-C2-C3-C4	178.1(10)	C10-C11-C12-C7	0.0(17)
N1-C2-C3-C3'	-178.6(10)	N2A-C11-C12-C7	176.8(11)
C2'-C2-C3-C3'	-5.0(17)	C8-C7-C12-C11	0.0(15)
C2-C3-C3'-O3'	-43.3(18)	C4-C7-C12-C11	-177.5(10)
C4-C3-C3'-O3'	133.7(13)	C3'-O3"-C13-C14	-158.5(12)
C2-C3-C3'-O3"	130.7(11)	O3"-C13-C14-C15	-59.2(19)
C4-C3-C3'-O3"	-52.3(13)	C13-C14-C15-C16	-175.5(12)
O3'-C3'-O3"-C13	-8.3(18)	C14-C15-C16-C17	-179.5(17)
C3-C3'-O3"-C13	177.6(10)	C15-C16-C17-C18	-174.0(17)
C2-C3-C4-C5	-1.6(14)	C5'-O5"-C19-C20	-159.2(10)
C3'-C3-C4-C5	-178.5(9)	O5"-C19-C20-C21	-61.6(13)
C2-C3-C4-C7	178.5(11)	C19-C20-C21-C22	175.6(9)
C3'-C3-C4-C7	1.7(15)	C20-C21-C22-C23	-179.7(10)
C3-C4-C5-C6	-1.3(13)	C21-C22-C23-C24	-177.7(9)
C7-C4-C5-C6	178.5(11)	C12-C11-N2A-O1A	177.7(13)
C3-C4-C5-C5'	179.2(9)	C10-C11-N2A-O1A	-6.4(26)
C7-C4-C5-C5'	-0.9(15)	C12-C11-N2A-O2A	6.3(24)
C6-C5-C5'-O5'	-46.1(16)	C10-C11-N2A-O2A	-177.7(19)
C4-C5-C5'-O5'	133.3(12)	C10-C9-N2B-O1B	10.4(56)
C6-C5-C5'-O5"	128.6(10)	C8-C9-N2B-O1B	-177.2(30)
C4-C5-C5'-O5"	-52.0(12)	C8-C9-N2B-O2B	-7.6(46)
O5'-C5'-O5"C19	-9.9(16)	C10-C9-N2B-O2B	-179.9(33)
C5-C5'-O5"-C19	175.5(8)		
C2-N1-C6-C5	1.5(17)		
C2-N1-C6-C6'	-177.9(10)		
C4-C5-C6-N1	1.4(15)		
C5'-C5-C6-N1	-179.2(10)		
C4-C5-C6-C6'	-179.2(10)		
C5'-C5-C6-C6'	0.2(15)		
C3-C4-C7-C8	-66.4(14)		
C5-C4-C7-C8	113.8(11)		
C3-C4-C7-C12	111.1(11)		
C5-C4-C7-C12	-68.8(13)		
C12-C7-C8-C9	1.9(17)		
C4-C7-C8-C9	179.4(10)		
C7-C8-C9-C10	-3.1(19)		
C7-C8-C9-N2B	-178.6(16)		
C8-C9-C10-C11	3.4(26)		

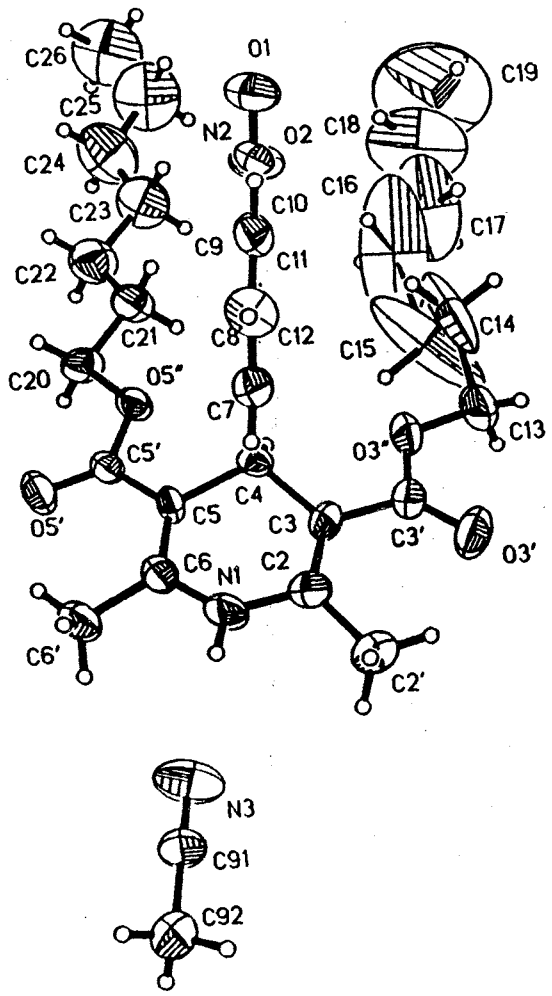

Figure 49: Projection view of [Heptyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine] • CH_3CN (XVIV)

TABLE 97

CRYSTAL DATA FOR

Diheptyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIX)

Formula	$C_{31}H_{45}N_3O_6$
M. W.	555.7 g $mole^{-1}$
a	9.632(2) Å
b	12.361(1) Å
c	15.127(2) Å
α	105.96(1) °
β	99.75(1) °
γ	103.07(1) °
V	1634.3(4) $Å^3$
F(000)	600
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	Mg/m^3
Z	2
Meas refl	5642
Obs refl	1347
R	7.41 %
R_w	8.65 %
G. O. F.	1.84
Space Group	P-1
Octants meas	$-1 \leq h \leq 11, -13 \leq k \leq 13, -17 \leq l \leq 17$

TABLE 98

POSITIONAL PARAMETERS FOR

Diheptyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIX)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.3482(10)	0.7545(9)	0.1059(5)
C2	0.4595(13)	0.8577(11)	0.1514(9)
C2'	0.4805(12)	0.9388(9)	0.938(7)
C3	0.5311(11)	0.8797(8)	0.2406(7)
C3'	0.6408(12)	0.9930(10)	0.2982(9)
O3'	0.6869(9)	1.0736(7)	0.2704(5)
O3"	0.6909(8)	0.9951(6)	0.3849(6)
C4	0.5062(10)	0.7854(7)	0.2892(6)
C5	0.3570(10)	0.6931(7)	0.2390(6)
C5'	0.2951(12)	0.6238(9)	0.2954(7)
O5'	0.1784(8)	0.5479(6)	0.2684(4)
O5"	0.3799(6)	0.6559(5)	0.3822(5)
C6	0.2902(11)	0.6800(9)	0.1503(8)
C6'	0.488(10)	0.5905(8)	0.0921(6)
C7	0.6296(11)	0.7298(9)	0.2930(9)
C8	0.6721(14)	0.6802(10)	0.2111(9)
C9	0.7831(16)	0.6261(11)	0.2138(9)
C10	0.8565(12)	0.6203(10)	0.2973(12)
C11	0.8142(13)	0.6680(10)	0.3762(9)
C12	0.7056(12)	0.7217(8)	0.3766(7)
C13	0.7941(16)	1.0995(11)	0.4499(10)
C14	0.8549(19)	1.0567(16)	0.5547(19)
C15	0.7671(23)	1.0654(23)	0.5711(15)
C16	0.8157(39)	1.0159(25)	0.6770(21)
C17	0.9040(35)	1.0561(23)	0.7396(18)
C18	0.9501(33)	1.0506(29)	0.8372(17)
C19	1.0336(33)	1.0594(30)	0.8946(17)
C20	0.3317(11)	0.6007(9)	0.4485(7)
C21	0.4488(12)	0.6629(10)	0.5406(8)
C22	0.4184(13)	0.6219(11)	0.6167(10)
C23	0.5364(16)	0.6863(12)	0.7088(9)
C24	0.5258(18)	0.6429(15)	0.7864(12)
C25	0.6359(23)	0.6907(17)	0.8695(11)
C26	0.6164(20)	0.6411(14)	0.9418(11)
N2	0.8853(11)	0.6586(10)	0.4672(8)
N3	0.1781(11)	0.7110(9)	-0.0961(6)

TABLE 98 (Continued)

O1	0.9811(10)	0.6114(8)	0.4696(7)
O2	0.8468(10)	0.7022(8)	0.5383(6)
C92	0.0542(12)	0.6969(9)	-0.2631(7)
C91	0.1230(12)	0.7053(9)	-0.1686(7)

TABLE 99

ANISOTROPIC THERMAL PARAMETERS FOR

Diheptyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIX)

ATOM	U11	U22	U33	U23	U13	U12
N1	75(7)	102(8)	55(6)	7(6)	-11(6)	34(6)
C2	69(9)	90(10)	95(10)	24(8)	11(7)	48(9)
C2'	125(11)	109(10)	116(10)	13(9)	-7(9)	67(9)
C3	72(8)	66(7)	72(8)	5(6)	18(7)	41(7)
C3'	64(8)	68(8)	107(11)	5(7)	13(8)	43(8)
O3'	150(8)	89(6)	117(7)	-22(6)	-3(6)	62(6)
O3"	78(6)	66(5)	91(6)	-17(5)	-12(5)	24(5)
C4	46(7)	49(7)	51(7)	23(6)	6(5)	9(6)
C5	49(7)	49(6)	40(6)	-7(6)	6(5)	9(5)
C5'	43(7)	67(8)	59(8)	9(6)	6(6)	25(6)
O5'	66(5)	89(5)	80(5)	-16(5)	-5(4)	26(4)
O5"	51(4)	86(5)	60(5)	8(4)	5(4)	37(4)
C6	55(8)	71(8)	67(8)	8(6)	7(7)	24(7)
C6'	75(9)	104(9)	72(8)	3(7)	-11(6)	29(7)
C7	47(8)	51(7)	67(8)	1(6)	16(7)	21(7)
C8	66(10)	75(9)	92(12)	17(7)	19(8)	34(8)
C9	88(11)	112(11)	64(10)	35(9)	35(8)	16(8)
C10	56(9)	75(9)	116(12	12(7)	17(10)	29(10)
C11	47(8)	54(8)	79(10)	13(6)	11(7)	33(7)
C12	42(7)	48(7)	66(9)	3(6)	6(6)	16(6)
C13	85(11)	68(9)	166(15)	-2(9)	-18(10)	21(11)
C14	58(15)	115(15)	460(53)	-3(11)	6(20)	-109(20)
C15	137(22)	591(59)	169(24)	132(28)	-54(18)	-289(35)
C16	709(94)	312(39)	309(49)	-151(45)	430(61)	-190(37)
C17	371(39)	251(34)	177(31)	-23(30)	156(32)	-91(27)
C18	388(45)	480(45)	134(24)	232(40)	114(33)	63(30)
C19	646(98)	901(98)	284(52)	215(80)	111(51)	334(63)
C20	69(8)	113(9)	81(9)	30(7)	28(8)	62(8)
C21	73(9)	154(12)	106(10)	2(8)	8(8)	100(10)
C22	88(11)	149(13)	142(13)	37(10)	37(10)	67(12)
C23	158(15)	147(14)	84(12)	35(12)	15(12)	21(11)
C24	175(18)	223(20)	116(15)	33(16)	18(15)	21(16)
C25	282(26)	259(23)	71(13)	46(20)	42(16)	51(15)
C26	264(23)	241(22)	153(18)	106(19)	52(17)	-2(17)

TABLE 99 (Continued)

N2	46(8)	92(9)	100(10)	10(6)	-6(8)	47(8)
N3	156(10)	214(11)	76(7)	65(9)	-10(7)	56(7)
O1	83(7)	155(9)	167(9)	48(6)	11(6)	86(7)
O2	103(7)	142(8)	83(7)	45(6)	-1(6)	49(6)
C92	110(10)	99(9)	103(10)	12(8)	15(8)	52(8)
C91	105(10)	109(9)	68(8)	12(8)	-6(7)	47(7)

The anisotropic displacement exponent takes the form:$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE 100

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Diheptyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIX)

N1-C2	1.378 (13)	C2-N1-C6	124.0(9)
N1-C6	1.358 (16)	N1-C2-C2'	114.2(10)
C2-C2'	1.501 (19)	N1-C2-C3	119.4(13)
C2-C3	1.330 (17)	C2'-C2-C3	126.4(9)
C3-C4	1.537 (16)	C2-C3-C4	121.0(8)
C3-C3'	1.478 (12)	C2-C3-C3'	123.1(12)
C4-C5	1.534 (11)	C4-C3-C3'	115.9(9)
C4-C7	1.502 (16)	C3-C4-C5	110.1(8)
C5-C6	1.335 (15)	C3-C4-C7	111.5(9)
C5-C5'	1.470 (16)	C5-C4-C7	111.5(7)
C6-C6'	1.494 (12)	C4-C5-C6	120.7(9)
C7-C8	1.396 (19)	C4-C5-C5'	115.6(8)
C7-C12	1.391 (17)	C6-C5-C5'	123.7(8)
C8-C9	1.384 (21)	N1-C6-C5	120.1(8)
C9-C10	1.369 (22)	N1-C6-C6'	113.8(9)
C10-C11	1.351 (21)	C5-C6-C6'	126.0(10)
C11-C12	1.360 (18)	C4-C7-C8	121.2(11)
C11-N2	1.477 (19)	C4-C7-C12	122.8(11)
N2-O1	1.199 (16)	C8-C7-C12	116.0(11)
N2-O2	1.221 (15)	C7-C8-C9	121.5(13)
N3-C91	1.111 (14)	C8-C9-C10	121.1(13)
C92-C91	1.436 (15)	C9-C10-C11	117.1(13)
C13-C14	1.849 (33)	C10-C11-C12	123.7(13)
C13-C15	2.036 (30)	C10-C11-N2	118.9(12)
C13-O3"	1.418 (12)	C12-C11-N2	117.4(12)
C14-C15	0.942 (33)	C7-C12-C11	120.7(11)
C15-C16	1.890 (44)	C11-N2-O1	119.3(12)
C16-C17	1.070 (38)	C11-N2-O2	118.6(12)
C17-C18	1.493 (40)	O1-N2-O2	122.1(12)
C18-C19	1.041 (40)	N3-C91-C92	178.8(13)
C3'-O3'	1.209 (16)	C14-C13-C15	27.5(10)
C3'-O3"	1.309 (16)	C14-C13-O3"	103.7(10)
C5'-O5'	1.212 (11)	C15-C13-O3"	97.3(10)
C5'-O5"	1.324 (12)	C13-C14-C15	87.3(24)
O5"-C20	1.443 (14)	C13-C15-C14	65.1(23)
C20-C21	1.513 (13)	C13-C15-C16	155.5(19)
C21-C22	1.426 (21)	C14-C15-C16	90.42(8)
C22-C23	1.520 (16)	C15-C16-C17	130.4(30)
C23-C24	1.428 (26)	C16-C17-C18	140.8(34)

TABLE 100 (Continued)

C24-C25	1.382 (21)	C17-C18-C19	149.4(36)
C25-C26	1.412 (28)	C3-C3'-O3'	126.0(12)
		C3-C3'-O3"	111.6(11)
		O3'-C3'-O3"	122.2(9)
		C13-O3"-C3'	118.4(10)
		C5-C5'-O5'	125.3(9)
		C5-C5'-O5"	112.2(8)
		O5'-C5'-O5"	122.5(11)
		C5'-O5"-C20	119.4(7)
		O5"-C20-C21	105.2(8)
		C20-C21-C22	113.69)
		C21-C22-C23	112.8(11)
		C22-C23-C24	117.3(12)
		C23-C24-C25	120.4(15)
		C24-C25-C26	116.2(17)

TABLE 101

TORSION ANGLES (°) FOR

Diheptyl 2,6-Dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XIX)

C6-N1-C2-C2'	-166.0(1.1)	O3"-C13-C14-C15	-79.4(1.9)
C6-N1-C2-C3	10.4(2.0)	C14-C13-C15-C16	-5.8(2.9)
C2-N1-C6-C5	-12.1(1.9)	O3"-C13-C15-C14	105.7(1.8)
C2-N1-C6-C6'	166.0(1.1)	O3"-C13-C15-C16	100.0(3.6)
N1-C2-C3-C4	8.3(1.9)	C14-C13-O3"-C3'	-171.6(1.1)
N1-C2-C3-C3'	-173.4(1.2)	C15-C13-O3"-C3'	161.1(1.2)
C2'-C2-C3-C4	-175.8(1.1)	C13-C14-C15-C16	177.6(1.2)
C2'-C2-C3-C3'	2.5(2.1)	C13-C15-C16-C17	70.3(5.8)
C2-C3-C4-C5	-22.0(1.5)	C14-C15-C16-C17	65.1(4.7)
C2-C3-C4-C7	102.3(1.2)	C15-C16-C17-C18	164.2(3.9)
C3'-C3-C4-C5	159.6(0.9)	C16-C17-C18-C19	148.4(7.2)
C3'-C3-C4-C7	-76.1(1.1)	C3-C3'-O3"-C13	-178.1(1.1)
C2-C3-C3'-O3'	-6.3(2.1)	O3'-C3'-O3"-C13	5.1(1.8)
C2-C3-C3'-O3"	177.1(1.2)	C5-C5'-O5"-C20	176.9(0.9)
C4-C3-C3'-O3'	172.1(1.2)	O5'-C5'-O5"-C20	-1.2(1.6)
C4-C3-C3'-O3"	-4.5(1.5)	C5'-O5"-C20-C21	-176.6(0.9)
C3-C4-C5-C6	20.3(1.3)	O5"-C20-C21-C22	178.5(1.0)
C3-C4-C5-C5'	-158.9(0.9)	C21-C22-C23-C24	-172.7(1.4)
C7-C4-C5-C6	-104.0(1.2)	C22-C23-C24-C25	174.4(1.7)
C7-C4-C5-C5'	76.8(1.2)	C23-C24-C25-C26	-179.3(1.8)
C3-C4-C7-C8	-54.1(1.1)	C10-C11-N2-O1	1.8(1.6)
C3-C4-C7-C12	127.6(1.0)	C10-C11-N2-O2	179.8(1.0)
C5-C4-C7-C8	69.4(1.3)	C12-C11-N2-O1	179.7(1.0)
C5-C4-C7-C12	-108.9(1.0)	C12-C11-N2-O2	-2.3(1.5)
C4-C5-C6-N1	-5.1(1.6)	N2-C11-C12-C7	-177.5(0.9)
C4-C5-C6-C6'	177.1(1.0)	C10-C11-C12-C7	0.3(1.7)
C5'-C5-C6-N1	174.1(1.1)		
C5'-C5-C6-C6'	-3.7(1.8)		
C4-C5-C5'-O5'	179.3(1.1)		
C4-C5-C5'-O5"	1.3(1.3)		
C6-C5-C5'-O5'	0.1(1.9)		
C6-C5-C5'-O5"	-177.9(1.0)		
C4-C7-C8-C9	-178.2(1.0)		
C12-C7-C8-C9	0.2(1.6)		
C4-C7-C12-C11	178.4(0.9)		
C8-C7-C12-C11	0.0(1.5)		
C7-C8-C9-C10	-0.7(1.8)		
C8-C9-C10-C11	1.0(1.7)		
C9-C10-C11-C12	-0.8(1.7)		
C9-C10-C11-N2	177.0(1.0)		

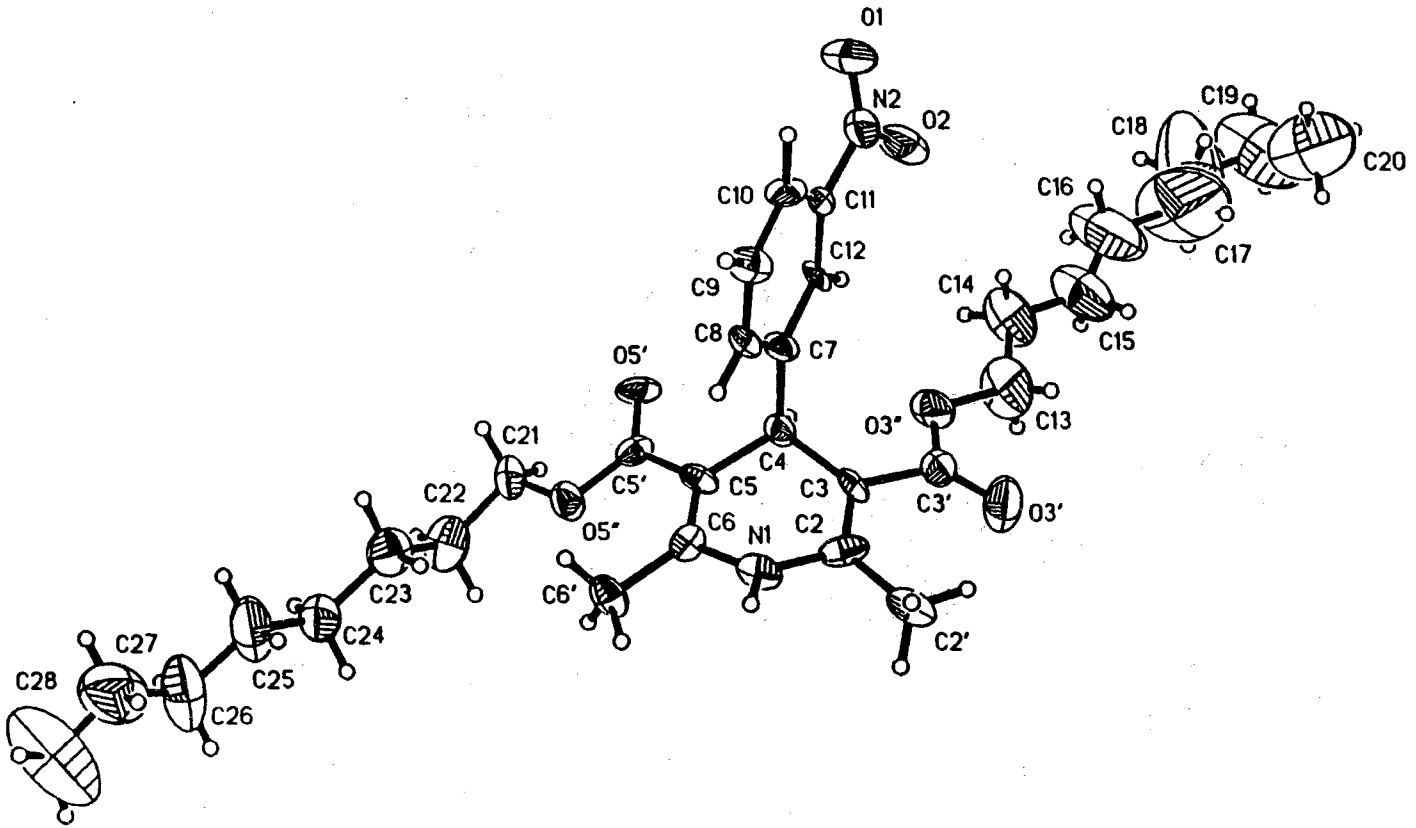

Figure 50: Projection view of Octyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine(XX)

TABLE 102

CRYSTAL DATA FOR

Dioctyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XX)

Formula	$C_{31}H_{46}N_2O_6$
M. W.	542.7 g mole^{-1}
a	15.983(2) Å
b	15.916(2) Å
c	12.856(3) Å
α	90.0 °
β	106.32(1) °
γ	90.0 °
V	3139.1(9) Å^3
F(000)	1176
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.13 g/cm^3
Z	4
Meas refl	6810
Obs refl	1027
R	7.53 %
R_w	7.85 %
G. O. F.	1.50
Space Group	$P2_1/c$
Octants meas	$-19 \leq h \leq 18, -18 \leq k \leq 1, -1 \leq l \leq 15$

TABLE 103

POSITIONAL PARAMETERS FOR

Dioctyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XX)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.967(8)	0.3309(8)	0.1690(9)
C2	0.91(11)	0.3445(10)	0.1637(11)
C2'	-0.0365(8)	0.3958(8)	0.0662(11)
C3	-0.0201(8)	0.3178(8)	0.2438(13)
C3'	-0.1160(10)	0.3256(11)	0.2339(15)
O3'	-0.1700(7)	0.3569(8)	0.1621(10)
O3"	-0.1342(6)	0.2885(8)	0.3166(9)
C4	0.0391(8)	0.2774(9)	0.3444(12)
C5	0.1163(9)	0.2387(8)	0.3171(10)
C5'	0.1582(10)	0.1718(8)	0.3866(11)
O5'	0.1406(6)	0.1489(6)	0.4678(7)
O5"	0.2190(7)	0.1287(7)	0.3532(7)
C6	0.1462(9)	0.2703(9)	0.2370(12)
C6'	0.2262(7)	0.2491(8)	0.2019(10)
C7	0.0615(10)	0.3413(10)	0.4363(12)
C8	0.1277(9)	0.3993(10)	0.4422(12)
C9	0.1450(10)	0.4607(10)	0.5200(13)
C10	0.1021(11)	0.4630(9)	0.5991(12)
C11	0.0360(9)	0.4063(10)	0.5921(11)
C12	0.0179(8)	0.3460(8)	0.5140(11)
C13	-0.2227(10)	0.2919(15)	0.3170(15)
C14	-0.2407(11)	0.2811(14)	0.4104(16)
C15	-0.3332(17)	0.2816(17)	0.4168(21)
C16	-0.3596(18)	0.3020(24)	0.4854(24)
C17	-0.4573(31)	0.3045(33)	0.4970(33)
C18	-0.4886(37)	0.2755(30)	0.5404(42)
C19	-0.5744(26)	0.2916(34)	0.5478(41)
C20	-0.6248(25)	0.3167(25)	0.5313(26)
C21	0.2549(10)	0.0563(11)	0.4160(13)
C22	0.3128(12)	0.0103(11)	0.3606(15)
C23	0.3912(12)	0.0542(10)	0.3625(13)
C24	0.4531(12)	0.0038(12)	0.3105(14)
C25	0.5371(14)	0.0431(12)	0.3148(16)
C26	0.5972(13)	-0.0022(16)	0.2661(21)
C27	0.6820(19)	0.0459(16)	0.2835(20)
C28	0.7353(16)	0.0100(13)	0.2345(22)

TABLE 103 (Continued)

N2	-0.0153(10)	0.04094(11)	0.6719(14)
O1	0.0147(8)	0.4525(9)	0.7528(9)
O2	-0.0818(9)	0.3701(8)	0.6503(11)

TABLE 104

ANISOTROPIC THERMAL PARAMETERS FOR

Dioctyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XX)

ATOM	U11	U22	U33	U23	U13	U12
N1	61(9)	65(10)	64(9)	-27(8)	44(8)	0(8)
C2	83(14)	65(13)	38(11)	-36(11)	19(11)	0(10)
C2'	93(12)	68(12)	81(13)	-4(10)	54(11)	-14(11)
C3	53(10)	17(9)	63(10)	11(8)	32(10)	-7(9)
C3'	62(13)	75(15)	60(14)	14(11)	23(12)	10(12)
O3'	67(9)	137(12)	119(12)	21(8)	22(8)	37(10)
O3"	54(8)	134(11)	83(9)	-19(8)	34(7)	-25(8)
C4	42(10)	59(11)	51(11)	7(10)	25(10)	8(11)
C5	61(10)	45(11)	51(9)	-5(8)	40(9)	-1(9)
C5'	72(13)	35(11)	38(10)	6(9)	1(10)	-4(9)
O5'	101(9)	75(8)	31(6)	3(7)	27(6)	8(6)
O5"	70(8)	73(9)	68(8)	30(6)	29(7)	21(7)
C6	51(11)	30(10)	51(11)	-7(9)	7(10)	5(9)
C6'	54(9)	72(12)	84(12)	-3(9)	46(9)	8(9)
C7	49(11)	51(11)	50(11)	-3(9)	17(10)	-22(10)
C8	55(12)	64(12)	56(12)	22(10)	15(10)	-23(11)
C9	85(13)	62(14)	62(12)	3(10)	28(11)	-6(11)
C10	86(14)	37(12)	43(11)	8(10)	1(11)	-20(9)
C11	53(11)	31(9)	43(10)	25(9)	-1(9)	-18(9)
C12	61(10)	33(10)	48(10)	32(9)	29(9)	6(9)
C13	62(15)	248(28)	177(26)	-26(18)	70(16)	25(21)
C14	84(17)	216(24)	188(26)	-9(18)	98(19)	5(20)
C15	175(29)	207(27)	209(34)	3(23)	119(25)	-45(23)
C16	152(30)	560(63)	301(50)	-22(37)	77(31)	-278(47)
C17	248(55)	711(109	274(46)	-74(65)	168(45)	-1(54)
C18	257(73)	214(43)	957(179	33(44)	50(99)	-89(70)
C19	127(61)	939(154	559(90)	-36(60)	16(48)	-557(110)
C20	108(42)	890(127	239(38)	-53(51)	90(34)	-97(54)
C21	58(13)	97(16)	86(14)	32(11)	15(11)	10(13)
C22	79(14)	87(17)	133(18)	-25(14)	11(14)	8(15)
C23	109(18)	75(16)	102(16)	20(14)	23(15)	9(12)

TABLE 104 (Continued)

C24	87(14)	139(18)	97(15)	29(16)	26(13)	19(14)
C25	86(17)	182(25)	178(22)	41(19)	52(17)	58(19)
C26	88(19)	189(31)	251(32)	23(20)	60(21)	35(26)
C27	246(36)	181(34)	168(24)	78(29)	79(27)	14(23)
C28	361(44)	79(22)	511(58)	-32(24)	318(43)	-3(26)
N2	84(14)	90(16)	65(11)	39(12)	20(13)	7(11)
O1	152(12)	141(12)	68(8)	22(9)	35(9)	-32(9)
O2	127(12)	105(12)	85(10)	15(10)	71(11)	3(8)

The anisotropic displacement exponent takes the form:$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE 105

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Dioctyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XX)

N1-C2	1.399 (22)	C2-N1-C6	121.5(13)
N1-C6	1.390 (18)	N1-C2-C2'	111.7(14)
C2-C2'	1.503 (19)	N1-C2-C3	118.9(12)
C2-C3	1.316 (24)	C2'-C2-C3	129.2(15)
C3-C4	1.514 (19)	C2-C3-C4	122.1(13)
C3-C3'	1.506 (22)	C2-C3-C3'	119.0(14)
C4-C5	1.506 (21)	C4-C3-C3'	118.9(14)
C4-C7	1.524 (21)	C3-C4-C5	109.3(13)
C5-C6	1.347 (22)	C3-C4-C7	109.5(11)
C5-C5'	1.430 (18)	C5-C4-C7	115.1(11)
C6-C6'	1.509 (21)	C4-C5-C6	121.0(12)
C7-C8	1.390 (22)	C4-C5-C5'	115.4(13)
C7-C12	1.372 (23)	C6-C5-C5'	123.4(14)
C8-C9	1.370 (22)	N1-C6-C5	118.6(14)
C9-C10	1.377 (25)	N1-C6-C6'	110.3(13)
C10-C11	1.373 (22)	C5-C6-C6'	131.1(12)
C11-C12	1.360 (20)	C4-C7-C8	119.6(15)
C11-N2	1.484 (25)	C4-C7-C12	123.0(13)
C13-C14	1.322 (30)	C8-C7-C12	117.4(13)
C13-O3"	1.416 (21)	C7-C8-C9	120.4(16)
C14-C15	1.505 (35)	C8-C9-C10	121.2(15)
C15-C16	1.127 (45)	C9-C10-C11	117.9(13)
C16-C17	1.611 (60)	C10-C11-C12	120.8(15)
C3'-O3'	1.183 (19)	C10-C11-N2	119.9(14)
C3'-O3"	1.318 (23)	C12-C11-N2	119.3(14)
C5'-O5'	1.212 (19)	C7-C12-C11	122.0(13)
C5'-O5"	1.353 (20)	C14-C13-O3"	118.1(14)
O5"-C21	1.432 (19)	C13-C14-C15	121.1(17)
C17-C18	0.965 (80)	C14-C15-C16	129.3(24)
C18-C19	1.424 (77)	C15-C16-C17	131.6(28)
C19-C20	0.871 (59)	C3-C3'-O3'	127.1(18)
C21-C22	1.506 (27)	C3-C3'-O3"	110.2(13)
C22-C23	1.430 (27)	O3'-C3'-O3"	122.7(16)
C23-C24	1.562 (28)	C13-O3"-C3'	115.7(13)
C24-C25	1.468 (29)	C5-C5'-O5'	125.5(15)
C25-C26	1.474 (35)	C5-C5'-O5"	115.6(13)
C26-C27	1.518 (36)	O5'-C5'-O5"	118.8(12)
C27-C28	1.323 (42)	C5'-O5"-C21	116.1(12)
N2-O1	1.227 (20)	C16-C17-C18	135.7(51)
N2-O2	1.196 (21)	C17-C18-C19	128.1(56)
		C18-C19-C20	155.5(65)

TABLE 105 (Continued)

	O5"-C21-C22	109.1(14)
	C21-C22-C23	114.0(15)
	C22-C23-C24	113.6(14)
	C23-C24-C25	116.6(16)
	C24-C25-C26	118.3(17)
	C25-C26-C27	110.6(21)
	C26-C27-C28	112.4(22)
	C11-N2-O1	116.4(15)
	C11-N2-O2	116.7(15)
	O1-N2-O2	126.9(19)

TABLE 106

TORSION ANGLES (°) FOR

Dioctyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XX)

C6-N1-C2-C2'	-165.3(1.2)	O3"-C13-C14-C15	-178.3(2.0)
C6-N1-C2-C3	19.5(2.0)	C14-C13-O3"-C3'	-158.7(2.0)
C2-N1-C6-C5	-16.2(2.0)	C13-C14-C15-C16	-149.5(3.6)
C2-N1-C6-C6'	161.6(1.2)	C14-C15-C16-C17	179.7(3.5)
N1-C2-C3-C4	3.6(2.1)	C15-C16-C17-C18	113.4(7.5)
N1-C2-C3-C3'	-174.8(1.3)	C3-C3'-O3"-C13	179.6(1.4)
C2'-C2-C3-C4	-170.7(1.3)	O3'-C3'-O3"-C13	-2.9(2.5)
C2'-C2-C3-C3'	10.9(2.3)	C5-C5'-O5"-C21	-173.8(1.1)
C2-C3-C4-C5	-25.6(1.8)	O5'-C5'-O5"-C21	2.5(1.8)
C2-C3-C4-C7	101.3(1.7)	C5'-O5"-C21-C22	173.3(1.2)
C3'-C3-C4-C5	152.8(1.2)	C16-C17-C18-C19	173.1(4.9)
C3'-C3-C4-C7	-80.3(1.6)	C17-C18-C19-C20	3.7(***)
C2-C3-C3'-O3'	-3.3(2.5)	O5"-C21-C22-C23	69.2(1.6)
C2-C3-C3'-O3"	174.0(1.4)	C21-C22-C23-C24	176.8(1.3)
C4-C3-C3'-O3'	178.2(1.6)	C22-C23-C24-C25	-176.8(1.5)
C4-C3-C3'-O3"	-4.5(1.9)	C23-C24-C25-C26	-179.6(1.7)
C3-C4-C5-C6	28.6(1.6)	C24-C25-C26-C27	-177.1(1.8)
C3-C4-C5-C5'	-155.9(1.1)	C25-C26-C27-C28	-175.7(2.1)
C7-C4-C5-C6	-95.1(1.5)	C12-C11-N2-O2	-15.2(2.1)
C7-C4-C5-C5'	80.4(1.5)	N2-C11-C12-C7	178.2(1.3)
C3-C4-C7-C8	-81.8(1.6)	C10-C11-N2-O1	-13.5(2.1)
C3-C4-C7-C12	96.7(1.6)	C10-C11-N2-O2	166.0(1.5)
C5-C4-C7-C8	41.8(1.8)	C12-C11-N2-O1	165.3(1.4)
C5-C4-C7-C12	-139.6(1.4)		
C4-C5-C6-N1	-9.7(1.9)		
C4-C5-C6-C6'	173.0(1.3)		
C5'-C5-C6-N1	175.2(1.2)		
C5'-C5-C6-C6'	-2.1(2.3)		
C4-C5-C5'-O5'	-5.5(1.9)		
C4-C5-C5'-O5"	170.5(1.1)		
C6-C5-C5'-O5'	169.8(1.3)		
C6-C5-C5'-O5"	-14.1(1.9)		
C4-C7-C8-C9	175.7(1.3)		
C12-C7-C8-C9	-3.0(2.1)		
C4-C7-C12-C11	-176.6(1.2)		
C8-C7-C12-C11	2.0(2.0)		
C7-C8-C9-C10	4.9(2.2)		
C8-C9-C10-C11	-5.7(2.1)		
C9-C10-C11-C12	4.7(2.1)		
C9-C10-C11-N2	-176.6(1.3)		
C10-C11-C12-C7	-3.0(2.1)		

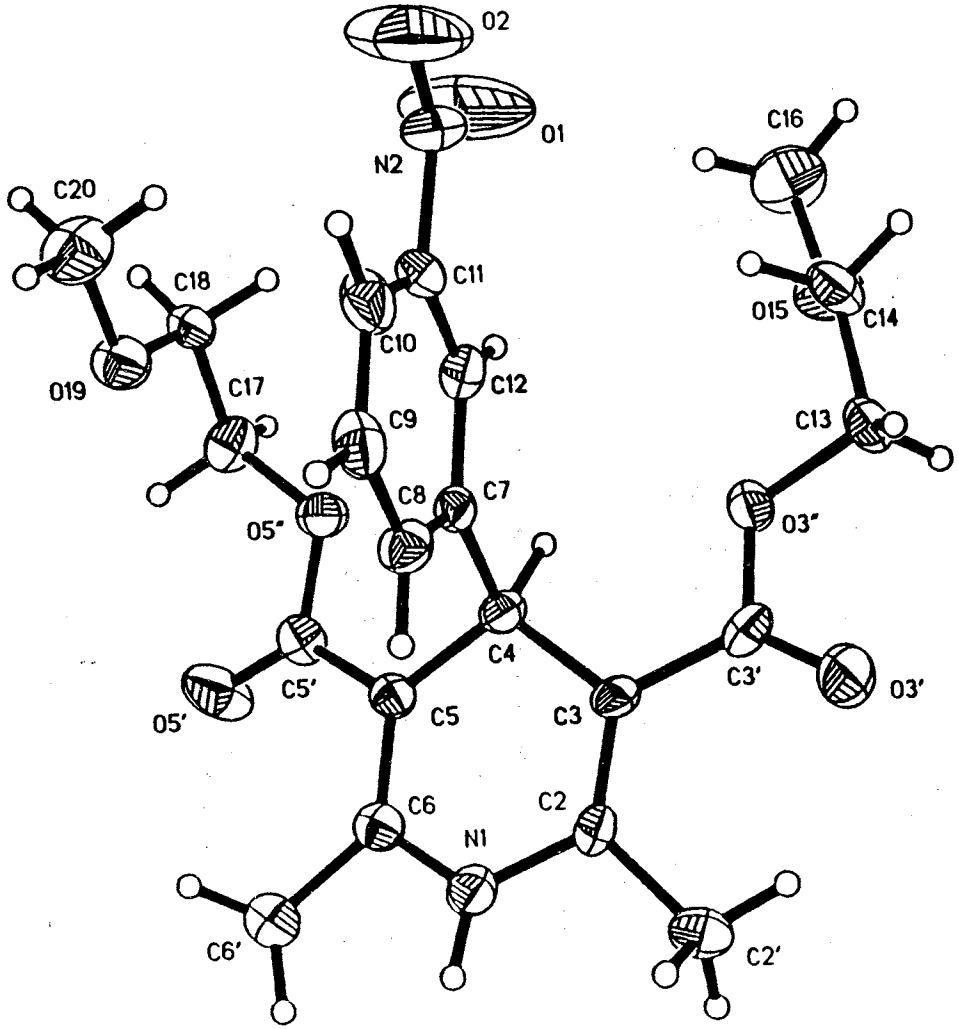

Figure 51: Projection view of 2-Methoxy ethyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-1,4-dihydropyridine(XXI)

TABLE 107

CRYSTAL DATA FOR

Di-(2-methoxyethyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XXI)

Formula	$C_{21}H_{26}N_2O_8$
M. W.	434.2g $mole^{-1}$
a	15.3210(10) Å
b	51.520(4) Å
c	10.8740(10) Å
α	90.0 °
β	90.0 °
γ	90.0 °
V	8582.9(12) $Å^3$
F(000)	3680
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.345 g/cm^3
Z	20
Meas refl	2036
Obs refl	1403
R	5.75%
R_w	5.71%
G. O. F.	1.02
Space Group	Fdd2
Octants meas	$-1 \leq h \leq 17, -1 \leq k \leq 49, -1 \leq l \leq 12$

TABLE 108

POSITIONAL PARAMETERS FOR

Di-(2-methoxyethyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XXI)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))	
N1	-0.1031(3)	0.2489(1)	0.8578(8)	0.049(2)
C2	-0.0904(4)	0.2302(1)	0.9489(8)	0.039(2)
C2'	-0.1132(4)	0.2397(1)	0.10774(9)	0.053(3)
C3	-0.0655(4)	0.2060(1)	0.9158(8)	0.039(2)
C3'	-0.0539(4)	0.1856(1)	0.10097(9)	0.042(3)
O3'	-0.0570(4)	0.1884(1)	0.11204(8)	0.077(2)
O3"	-0.0341(3)	0.1625(1)	0.9604(7)	0.052(2)
C4	-0.0399(4)	0.1996(1)	0.7832(?)	0.039(2)
C5	-0.0746(4)	0.2196(1)	0.6933(8)	0.037(2)
C5'	-0.0755(4)	0.2140(1)	0.5642(9)	0.043(2)
O5'	-0.1035(4)	0.2275(1)	0.4816(8)	0.088(2)
O5"	-0.0385(3)	0.1910(1)	0.5400(7)	0.049(2)
C6	-0.1002(4)	0.2436(1)	0.7358(9)	0.042(3)
C6'	-0.1298(5)	0.2663(1)	0.6596(9)	0.062(3)
C7	0.0592(4)	0.1963(1)	0.7770(9)	0.037(2)
C8	0.1149(4)	0.2157(1)	0.8148(9)	0.047(2)
C9	0.2046(4)	0.2124(1)	0.8106(9)	0.056(3)
C10	0.2406(5)	0.1895(2)	0.7713(10)	0.067(3)
C11	0.1841(5)	0.1703(1)	0.7349(9)	0.054(3)
C12	0.0946(4)	0.1729(1)	0.7360(8)	0.050(3)
C13	-0.0137(5)	0.1415(1)	0.10431(9)	0.055(3)
C14	0.0245(5)	0.1201(1)	0.9685(10)	0.064(3)
O15	-0.0424(4)	0.1081(1)	0.9011(9)	0.077(2)
C16	-0.0126(6)	0.0892(2)	0.8188(12)	0.099(4)
C17	-0.0221(4)	0.1837(1)	0.4123(9)	0.053(3)
C18	0.0706(4)	0.1750(1)	0.3982(9)	0.048(2)
O19	0.1259(3)	0.1967(1)	0.4241(8)	0.059(2)
C20	0.2151(4)	0.1903(2)	0.4163(11)	0.080(3)
O1	0.1729(6)	0.1287(1)	0.6539(12)	0.183(6)
O2	0.2938(5)	0.1414(1)	0.7000(14)	0.223(7)
N2	0.2194(6)	0.1451(1)	0.6933(10)	0.91(4)
H1A	-0.1119	0.2655	0.8808	0.080
H2'A	-0.1043	0.2259	1.1351	0.080
H2'B	-0.0756	0.2540	1.0979	0.080
H2'C	-0.1729	0.2453	1.0806	0.080
H4A	-0.0691	0.1780	0.7518	0.050

TABLE 108 (Continued)

H6'A	-0.1455	0.2809	0.7096	0.080
H6'B	-0.0822	0.2709	0.6067	0.080
H6'C	-0.1790	0.2611	0.6106	0.080
H8A	0.0905	0.2317	0.8441	0.080
H9A	0.2418	0.2265	0.8345	0.080
H10A	0.3026	0.1868	0.7714	0.080
H12A	0.0578	0.1589	0.7092	0.080
H13A	-0.0649	0.1354	1.0848	0.080
H13B	0.0277	0.1476	1.1027	0.080
H14A	0.0537	0.1075	1.0188	0.080
H14B	0.0 667	0.1276	0.9137	0.080
H16A	-0.0606	0.0817	0.7747	0.080
H16B	0.0267	0.0973	0.7616	0.080
H16C	0.0177	0.0760	0.8635	0.080
H17A	-0.0296	0.1989	0.3620	0.080
H17B	-0.0629	0.1707	0.3862	0.080
H18A	0.0823	0.1687	0.3168	0.080
H18B	0.0805	0.1612	0.4559	0.080
H20A	0.02505	0.2051	0.4351	0.080
H20B	0.2278	0.1766	0.4734	0.080
H20C	0.2276	0.1845	0.3342	0.080

TABLE 109

ANISOTROPIC THERMAL PARAMETERS FOR

Di-(2-methoxyethyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XXI)

ATOM	U11	U22	U33	U12	U13	U23
N1	38(3)	68(4)	78(4)	-9(4)	-4(3)	-1(3)
N1	54(4)	43(3)	51(4)	-4(3)	14(3)	-3(3)
C2	39(4)	45(4)	33(4)	-4(3)	8(3)	2(3)
C2'	64(5)	36(4)	61(5)	-2(3)	-3(4)	-13(4)
C3	28(3)	43(4)	46(4)	5(3)	9(3)	-1(3)
C3'	41(4)	52(5)	34(4)	-8(3)	8(3)	-11(4)
O3'	131(5)	59(4)	40(3)	13(3)	7(3)	-4(3)
O3"	78(3)	40(2)	38(3)	7(2)	6(3)	4(2)
C4	38(4)	38(4)	42(4)	1(3)	9(3)	-3(3)
C5	30(4)	39(4)	43(4)	1(3)	-1(3)	3(3)
C5'	50(4)	40(4)	41(4)	-4(3)	-7(4)	-1(4)
O5'	160(6)	61(3)	44(3)	38(4)	-26(4)	-5(3)
O5"	55(3)	50(3)	43(3)	13(2)	0(2)	-1(2)
C6	34(4)	41(4)	50(5)	-1(3)	-1(3)	0(3)
C6'	73(5)	52(4)	61(5)	8(4)	7(4)	5(4)
C7	33(4)	44(4)	34(4)	7(3)	2(3)	11(3)
C8	38(4)	56(4)	47(4)	3(3)	2(4)	1(4)
C9	46(4)	63(5)	60(5)	-8(4)	-3(4)	21(4)
C10	43(4)	74(5)	83(6)	8(4)	4(5)	39(5)
C11	58(5)	53(5)	51(5)	22(4)	7(4)	21(4)
C12	50(5)	56(4)	44(4)	-1(4)	11(4)	8(4)
C13	84(5)	36(4)	44(5)	4(3)	-2(4)	7(4)
C14	75(6)	38(4)	79(6)	10(4)	2(5)	17(5)
O15	77(4)	73(4)	79(4)	9(3)	3(4)	-17(3)
C16	141(8)	78(5)	79(7)	7(6)	4(7)	-37(6)
C17	58(5)	61(5)	41(4)	-10(4)	-1(4)	-13(4)
C18	60(4)	36(4)	47(4)	9(4)	3(4)	3(3)
O19	43(3)	54(3)	81(4)	-2(2)	0(3)	0(3)
C20	52(5)	108(7)	80(6)	5(4)	-7(5)	0(6)
O1	146(7)	87(5)	315(15)	33(5)	-15(9)	-94(8)
O2	96(6)	101(5)	471(20)	47(4)	102(10)	37(9)
N2	84(6)	69(5)	118(7)	39(5)	50(6)	20(5)

The anisotropic displacement exponent takes the form:$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE 110

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Di-(2-methoxyethyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XXI)

N1-C2	1.397 (11)	C2-N1-C6	123.5(6)
N1-C6	1.356 (13)	N1-C2-C2'	113.3(6)
C2-C2'	1.522 (13)	N1-C2-C3	119.2(8)
C2-C3	1.352 (9)	C2'-C2-C3	127.4(7)
C3-C3'	1.475 (11)	C2-C3-C3'	120.4(8)
C3-C4	1.531 (8)	C2-C3-C4	121.5(7)
C3'-O3'	1.214 (13)	C3'-C3-C4	117.8(6)
C3'-O3"	1.339 (9)	C3-C3'-O3'	126.7(7)
O3"-C13	1.440 (10)	C3-C3'-O3"	112.5(8)
C4-C5	1.518 (9)	O3'-C3'-O3"	120.7(7)
C4-C7	1.529 (8)	C3'-O3"-C13	117.7(8)
C5-C5'	1.433 (13)	C3-C4-C5	111.7(5)
C5-C6	1.378 (9)	C3-C4-C7	108.6(5)
C5'-O5'	1.214 (11)	C5-C4-C7	113.2(5)
C5'-O5"	1.342 (8)	C4-C5-C5'	119.8(5)
O5"-C17	1.460 (12)	C4-C5-C6	119.7(7)
C6-C6'	1.500 (11)	C5'-C5-C6	120.4(7)
C7-C8	1.376 (9)	C5-C5'-O5'	127.8(7)
C7-C12	1.398 (9)	C5-C5'-O5"	111.5(7)
C8-C9	1.385 (9)	O5'-C5'-O5"	120.7(9)
C9-C10	1.369 (11)	C5'-O5"-C17	119.0(7)
C10-C11	1.374 (11)	N1-C6-C5	121.2(7)
C11-C12	1.377 (10)	N1-C6-C6'	112.0(6)
C11-N2	1.479 (11)	C5-C6-C6'	126.8(8)
C13-C14	1.489 (11)	C5-C6-C6'	126.8(8)
C14-O15	1.404 (11)	C5-C6-C6'	126.8(8)
O15-C16	1.397 (13)	C5-C6-C6'	126.8(8)
C17-C18	1.498 (9)	C4-C7-C12	119.6(5)
C18-O19	1.430 (8)	C8-C7-C12	118.8(6)
O19-C20	1.408 (8)	C7-C8-C9	121.1(6)
O1-N2	1.184 (12)	C8-C9-C10	121.1(7)
O2-N2	1.157 (12)	C9-C10-C11	117.1(7)
		C10-C11-C12	123.8(7)
		C10-C11-N2	119.3(7)
		C12-C11-N2	116.9(7)
		C7-C12-C11	118.2(6)
		O3"-C13-C14	107.5(8)
		C13-C14-O15	108.9(6)
		C14-O15-C16	113.8(6)
		O5"-C17-C18	109.7(7)

TABLE 110 (Continued)

	C17-C18-O19	107.8(5)
	C18-O19-C20	112.4(5)
	C11-N2-O1	121.0(8)
	C11-N2-O2	119.1(8)
	O1-N2-O2	119.8(9)

TABLE 111

TORSION ANGLES (°) FOR

Di-(2-methoxyethyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (XXI)

C6-N1-C2-C2'	-169.3(0.5)	C10-C11-C12-C7	-0.2(1.5)
C6-N1-C2-C3	6.8(0.9)	N2-C11-C12-C7	178.9(0.9)
C2-N1-C6-C5	-7.5(0.9)	C10-C11-N2-O1	-175.2(1.2)
C2-N1-C6-C6'	171.0(0.5)	C10-C11-N2-O2	5.2(1.7)
N1-C2-C3-C3'	-178.3(0.5)	C12-C11-N2-O1	5.7(1.6)
N1-C2-C3-C4	7.8(0.9	C12-C11-N2-O2	-173.9(1.2)
C2'-C2-C3-C3'	-2.8(1.0)	O3"-C13-C14-O15	-73.9(0.8)
C2'-C2-C3-C4	-176.7(0.6)	C13-C14-O15-C16	174.2(0.8)
C2-C3-C3'-O3'	-6.9(1.0)	O5"-C17-C18-O19	-64.3(0.8)
C2-C3-C3'-O3"	176.4(0.5)	C17-C18-O19-C20	178.5(0.8)
C4-C3-C3'-O3'	167.2(0.6)	C8-C7-C12-C11	-0.4(1.3)
C4-C3-C3'-O3"	-9.5(0.8)	C7-C8-C9-C10	-1.5(1.5)
C2-C3-C4-C5	-19.3(0.8)	C8-C9-C10-C11	0.9(1.5)
C2-C3-C4-C7	106.2(0.6)	C9-C10-C11-C12	-0.1(1.5)
C3'-C3-C4-C5	166.6(0.5)	C9-C10-C11-N2	-179.1(0.9)
C3'-C3-C4-C7	-67.8(0.7)	C4-C7-C12-C11	-178.2(0.7)
C3-C3'-O3"-C13	174.7(0.5)		
O3'-C3'-O3"-C13	-2.2(0.9)		
C3'-O3"-C13-C14	-167.7(0.6)		
C3-C4-C5-C5'	-165.4(0.5)		
C3-C4-C5-C6	18.4(0.8)		
C7-C4-C5-C5'	71.6(0.7)		
C7-C4-C5-C6	-104.6(0.6)		
C3-C4-C7-C8	-56.4(0.9)		
C3-C4-C7-C12	121.3(0.8)		
C5-C4-C7-C8	68.3(0.9)		
C5-C4-C7-C12	-114.0(0.8)		
C4-C5-C5'-O5'	177.3(0.7)		
C4-C5-C5'-O5"	-3.8(0.8)		
C6-C5-C5'-O5'	-6.5(1.1)		
C6-C5-C5'-O5"	172.4(0.5)		
C4-C5-C6-N1	-6.4(0.9)		
C4-C5-C6-C6'	175.3(0.6)		
C5'-C5-C6-N1	177.4(0.6)		
C5'-C5-C6-C6'	-0.9(1.0)		
C5-C5'-O5"-C17	-171.1(0.5)		
O5'-C5'-O5"-C17	7.9(0.9)		
C5'-O5"-C17-C18	129.5(0.6)		
C4-C7-C8-C9	178.9(0.8)		
C12-C7-C8-C9	1.2(1.4)		

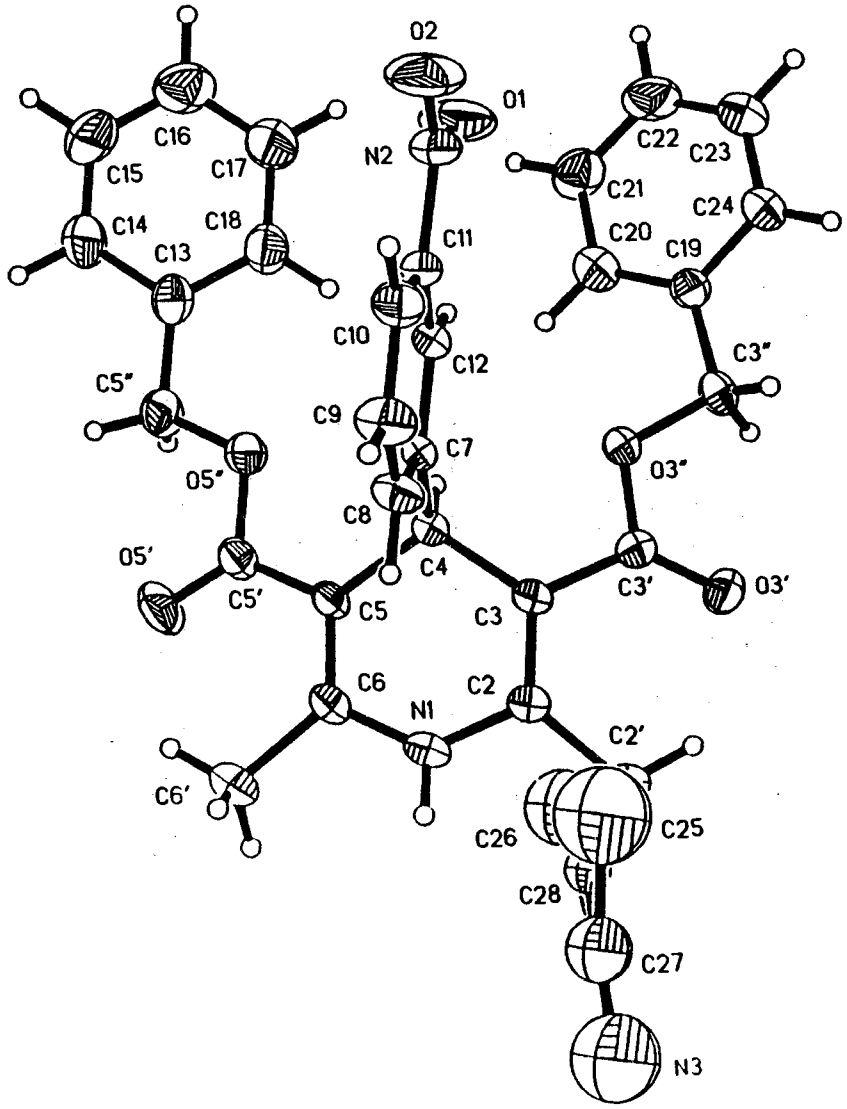

Figure 52: Projection view of (Benzyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) • 0.5 CH_3CN (XXII)

TABLE 112

CRYSTAL DATA FOR

(Dibenzyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) • 0.5 CH_3CN (XXII)

Formula	$C_{31}H_{29}N_2O_6$
M. W.	519.0 g $mole^{-1}$
a	9.499(1) Å
b	10.804(1) Å
c	13.174(2) Å
a	80.48(1) °
b	88.53(1) °
g	82.19(1) °
V	1320.2(3) $Å^3$
F(000)	544.5
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.306 Mg/m^3
Z	2
Meas refl	4209
Obs refl	2241
R	5.19 %
R_w	6.06 %
G. O. F.	1.26
Space Group	P-1
Octants meas	$-1 \leq h \leq 10, -11 \leq k \leq 11, -14 \leq l \leq 14$

TABLE 113

POSITIONAL PARAMETERS FOR

(Dibenzyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) • 0.5 CH_3CN (XXII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.1177(3)	0.4354(3)	0.1929(2)
N2	0.1450(4)	-0.2248(3)	0.1232(4)
N3	0.5476	0.6769	0.0000
O1	0.1060(4)	-0.2744(3)	0.2072(3)
O2	0.1821(4)	-0.2848(3)	0.0549(3)
C2	0.2110(4)	0.3557(3)	0.2606(3)
C2'	0.3344(4)	0.4164(3)	0.2889(3)
C3	0.1832(3)	0.2359(3)	0.2936(3)
C3'	0.2744(4)	0.1507(3)	0.3706(3)
C3"	0.3221(4)	-0.0594(3)	0.4601(3)
O3'	0.3757(3)	0.1739(2)	0.4131(2)
O3"	0.2333(2)	0.337(2)	0.3889(2)
C4	0.0583(3)	0.1870(3)	0.2506(3)
C5	-0.0555(4)	0.2973(3)	0.2111(2)
C5'	-0.2031(4)	0.2757(3)	0.2091(3)
C5"	-0.3641(4)	0.1242(3)	0.2369(3)
O5'	-0.3063(3)	0.3558(2)	0.1920(2)
O5"	-0.2186(2)	0.1507(2)	0.2307(2)
C6	-0.199(4)	0.4131(3)	0.1783(3)
C6'	-0.1118(5)	0.5282(3)	0.1231(3)
C7	0.1066(3)	0.1095(3)	0.1662(3)
C8	0.1036(3)	-0.0205(3)	0.1821(3)
C9	0.1485(4)	-0.0871(3)	0.1045(3)
C10	0.1960(4)	-0.0320(3)	0.0113(3)
C11	0.2003(4)	0.0963(4)	-0.0039(3)
C12	0.1563(4)	0.1651(3)	0.0730(3)
C13	-0.3662(4)	-0.0155(4)	0.2476(3)
C14	-0.4796(4)	-0.0586(4)	0.2092(4)
C15	-0.4887(5)	-0.1854(5)	0.2207(5)
C16	-0.3857(6)	-0.2716(5)	0.2697(4)
C17	-0.2718(6)	-0.2305(4)	0.3065(3)
C18	-0.2618(4)	-0.1035(4)	0.2963(3)
C19	0.2573(4)	-0.1792(3)	0.4804(3)
C20	0.1130(5)	-0.1821(4)	0.4814(3)
C21	0.0584(5)	-0.2962(4)	0.5060(3)
C22	0.1484(7)	-0.4060(4)	0.5303(4)

TABLE 113 (Continued)

C23	0.2914(6)	-0.4041(4)	0.5292(4)
C24	0.3457(5)	-0.2920(3)	0.5041(3)
C25	0.4434	0.4474	0.0262
C26	0.5156	0.4427	0.0000
C27	0.5177	0.5752	0.0014
C28	0.5000	0.5000	0.0000

TABLE 114

ANISOTROPIC THERMAL PARAMETERS FOR

(Dibenzyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) • 0.5 CH_3CN (XXII)

ATOM	U11	U22	U33	U23	U13	U12
N1	70(2)	28(2)	83(2)	-6(2)	20(2)	3(2)
N2	68(3)	39(2)	109(3)	-2(2)	-15(2)	-28(2)
O1	176(4)	41(2)	116(3)	-30(2)	-3(3)	-3(2)
O2	124(3)	60(2)	157(3)	-3(2)	22(2)	-62(2)
C2	52(2)	35(2)	61(2)	-5(2)	-8(2)	-9(2)
C2'	76(3)	41(2)	90(3)	-15(2)	-18(2)	-3(2)
C3	45(2)	30(2)	48(2)	-2(2)	-4(2)	-7(2)
C3'	46(2)	41(2)	51(2)	-9(2)	-6(2)	-5(2)
C3"	68(3)	47(2)	61(2)	-2(2)	-29(2)	10(2)
O3'	68(2)	57(2)	85(2)	-21(1)	-35(2)	6(1)
O3"	54(2)	38(1)	61(2)	-5(1)	-22(1)	3(1)
C4	41(2)	31(2)	48(2)	-4(2)	-7(2)	-2(2)
C5	48(2)	31(2)	46(2)	5(2)	-10(2)	-5(2)
C5'	49(3)	46(2)	56(2)	6(2)	-9(2)	-7(2)
C5"	37(2)	69(3)	76(3)	-5(2)	1(2)	-7(2)
O5'	50(2)	61(2)	113(2)	17(1)	-12(2)	3(2)
O5"	39(2)	50(2)	70(2)	-3(1)	-1(1)	-10(1)
C6	55(3)	35(2)	66(3)	6(2)	-14(2)	-6(2)
C6'	77(3)	40(2)	113(4)	5(2)	-27(3)	1(2)
C7	36(2)	30(2)	49(2)	-1(2)	-10(2)	-3(2)
C8	46(2)	32(2)	55(2)	-2(2)	-12(2)	-3(2)
C9	48(2)	32(2)	68(3)	-2(2)	-14(2)	-14(2)
C10	65(3)	53(3)	68(3)	1(2)	-4(2)	-22(2)
C11	86(3)	54(2)	53(2)	-9(2)	10(2)	-8(2)
C12	67(3)	35(2)	54(2)	-5(2)	2(2)	0(2)
C13	36(2)	73(3)	61(3)	-7(2)	4(2)	-9(2)
C14	51(3)	82(3)	121(4)	-3(3)	-20(3)	-13(3)
C15	66(4)	96(4)	166(5)	-28(3)	-22(4)	-33(4)
C16	88(4)	74(3)	119(4)	-32(3)	12(3)	-12(3)
C17	91(4)	68(3)	92(4)	-14(3)	-14(3)	6(3)
C18	60(3)	70(3)	73(3)	-14(2)	-11(2)	1(2)
C19	59(3)	43(2)	45(2)	-7(2)	-12(2)	1(2)
C20	65(3)	56(3)	64(3)	-2(2)	-2(2)	-6(2)
C21	74(3)	76(3)	80(3)	-30(3)	3(3)	-1(2)

TABLE 114 (Continued)

C22	127(5)	50(3)	96(4)	-33(3)	-19(3)	12(2)
C23	96(4)	45(3)	131(5)	-4(3)	-36(4)	0(3)
C24	69(3)	45(2)	89(3)	0(2)	-23(2)	1(2)

The anisotropic displacement exponent takes the form:$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE 115

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

(Dibenzyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) • 0.5 CH_3CN (XXII)

N1-C2	1.379 (4)	C2-N1-C6	123.1(3)
N1-C6	1.385 (5)	O1-N2-O2	122.4(3)
N2-O1	1.219 (6)	O1-N2-C9	118.7(4)
N2-O2	1.212 (6)	O2-N2-C9	118.9(4)
N2-C9	1.472 (5)	N3-C27-C28	176.5(1)
N3-C27	1.168 (1)	N3-C27-C26	166.7(1)
C26-C27	1.439 (1)	N1-C2-C2'	113.6(3)
C2-C2'	1.502 (6)	N1-C2-C3	118.6(3)
C2-C3	1.355 (4)	C2'-C2-C3	127.8(3)
C3-C3'	1.465 (4)	C2-C3-C3'	120.4(3)
C3-C4	1.520 (5)	C2-C3-C4	120.7(3)
C3'-O3'	1.200 (5)	C3'-C3-C4	118.9(3)
C3'-O3"	1.355 (4)	C3-C3'-O3'	127.6(3)
C3"-O3"	1.449 (4)	C3-C3'-O3"	111.1(3)
C3"-C19	1.489 (5)	O3'-C3'-O3"	121.2(3)
C4-C5	1.527 (4)	O3"-C3"-C19	109.3(3)
C4-C7	1.525 (5)	C3'-O3"-C3"	115.2(3)
C5-C5'	1.454 (5)	C3-C4-C5	110.2(3)
C5-C6	1.339 (5)	C3-C4-C7	111.1(3)
C5'-O5'	1.215 (4)	C5-C4-C7	111.1(3)
C5'-O5"	1.361 (4)	C4-C5-C5'	119.5(3)
C5"-O5"	1.447 (4)	C4-C5-C6	120.4(3)
C5"-C13	1.495 (6)	C5'-C5-C6	120.1(3)
C6-C6'	1.509 (5)	C5-C5'-O5'	126.8(3)
C7-C8	1.390 (4)	C5-C5'-O5"	112.6(3)
C7-C12	1.376 (5)	O5'-C5'-O5"	120.6(4)
C8-C9	1.372 (5)	O5"-C5"-C13	109.5(3)
C9-C10	1.366 (5)	C5'-O5"-C5"	114.9(3)
C10-C11	1.373 (5)	N1-C6-C5	119.1(3)
C11-C12	1.378 (6)	N1-C6-C6'	112.7(3)
C13-C14	1.370 (6)	C5-C6-C6'	128.1(4)
C13-C18	1.368 (5)	C4-C7-C8	120.7(3)
C14-C15	1.368 (8)	C4-C7-C12	121.4(3)
C15-C16	1.351 (7)	C8-C7-C12	117.9(3)
C16-C17	1.354 (8)	C7-C8-C9	118.9(3)
C17-C18	1.373 (6)	N2-C9-C8	117.9(3)
C19-C20	1.375 (6)	N2-C9-C10	118.7(4)
C19-C24	1.378 (5)	C8-C9-C10	123.3(3)
C20-C21	1.388 (6)	C9-C10-C11	117.7(4)

TABLE 115 (Continued)

C21-C22	1.362 (6)	C10-C11-C12	120.0(4)
C22-C23	1.361 (9)	C7-C12-C11	122.0(3)
C23-C24	1.368 (6)	C5"-C13-C14	118.8(3)
C25-C27	1.617 (1)	C14-C13-C18	117.8(4)
		C14-C15-C16	121.0(5)
		C15-C16-C17	118.8(5)
		C16-C17-C18	120.8(4)
		C3"-C19-C20	123.1(3)
		C13-C14-C15	120.8(4)
		C13-C18-C17	120.7(4)
		C3"-C19-C24	118.5(4)
		C20-C19-C24	118.4(4)
		C19-C20-C21	120.5(3)
		C20-C21-C22	119.7(5)
		C21-C22-C23	120.2(5)
		C22-C23-C24	120.3(4)
		C19-C24-C23	120.9(4)
		C5"-C13-C18	123.4(4)
		N3-C27-C25	163.9(1)

TABLE 116

TORSION ANGLES (°) FOR

(Dibenzyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) • 0.5 CH_3CN (XXII)

C6-N1-C2-C2'	-161.7(0.3)	O5"-C5"-C13-C14	-150.5(0.4)
C6-N1-C2-C3	18.3(0.5)	O5"-C5"-C13-C18	31.2(0.5)
C2-N1-C6-C5	-16.4(0.5)	C4-C7-C8-C9	-179.7(0.3)
C2-N1-C6-C6'	164.7(0.3)	C12-C7-C8-C9	-0.7(0.5)
O1-N2-C9-C8	-1.8(0.6)	C4-C7-C12-C11	180.0(0.3)
O1-N2-C9-C10	178.2(0.4)	C8-C7-C12-C11	1.0(0.5)
O2-N2-C9-C8	178.8(0.4)	C7-C8-C9-N2	179.8(0.3)
O2-N2-C9-C10	-1.1(0.6)	C7-C8-C9-C10	-0.2(0.5)
N1-C2-C3-C3'	-176.0(0.3)	N2-C9-C10-C11	-179.1(0.4)
N1-C2-C3-C4	4.6(0.5)	C8-C9-C10-C11	0.9(0.6)
C2'-C2-C3-C3'	4.0(0.6)	C9-C10-C11-C12	-0.6(0.6)
C2'-C2-C3-C4	-175.4(0.3)	C10-C11-C12-C7	-0.3(0.6)
C2-C3-C3'-O3'	1.5(0.6)	C5"-C13-C14-C15	-177.4(0.4)
C2-C3-C3'-O3"	-176.7(0.3)	C18-C13-C14-C15	1.0(0.7)
C4-C3-C3'-O3'	-179.1(0.3)	C5"-C13-C18-C17	177.9(0.4)
C4-C3-C3'-O3"	2.7(0.4)	C14-C13-C18-C17	-0.4(0.6)
C2-C3-C4-C5	-25.1(0.4)	C13-C14-C15-C16	-0.5(0.8)
C2-C3-C4-C7	98.4(0.3)	C14-C15-C16-C17	-0.6(0.8)
C3'-C3-C4-C5	155.5(0.3)	C15-C16-C17-C18	1.2(0.8)
C3'-C3-C4-C7	-81.0(0.4)	C16-C17-C18-C13	-0.7(0.7)
C3-C3'-O3"-C3"	176.8(0.3)	C3"-C19-C20-C21	-176.7(0.4)
O3'-C3'-O3"-C3"	-1.5(0.5)	C24-C19-C20-C21	0.1(0.6)
C19-C3"-O3"-C3'	174.7(0.3)	C3"-C19-C24-C23	176.2(0.4)
O3"-C3"-C19-C20	-32.6(0.5)	C20-C19-C24-C23	-0.8(0.6)
O3"-C3"-C19-C24	150.6(0.3)	C19-C20-C21-C22	0.6(0.6)
C3-C4-C5-C5'	-153.0(0.3)	C20-C21-C22-C23	-0.8(0.7)
C3-C4-C5-C6	27.0(0.4)	C21-C22-C23-C24	0.2(0.7)
C7-C4-C5-C5'	83.5(0.4)	C22-C23-C24-C19	0.6(0.7)
C7-C4-C5-C6	-96.5(0.4)	C13-C5"-O5"-C5'	172.9(0.3)
C3-C4-C7-C8	110.9(0.3)	C5-C5'-O5"-C5"	175.9(0.3)
C3-C4-C7-C12	-68.0(0.4)	O5'-C5'-O5"-C5"	-3.4(0.5)
C5-C4-C7-C8	-126.1(0.3)	C5'-C5-C6-C6'	-9.5(0.6)
C5-C4-C7-C12	55.0(0.4)		
C4-C5-C5'-O5'	170.4(0.4)		
C4-C5-C5'-O5"	-8.8(0.4)		
C6-C5-C5'-O5'	-9.7(0.6)		
C6-C5-C5'-O5"	171.1(0.3)		
C4-C5-C6-N1	-8.2(0.5)		
C4-C5-C6-C6'	170.4(0.4)		
C5'-C5-C6-N1	171.8(0.3)		

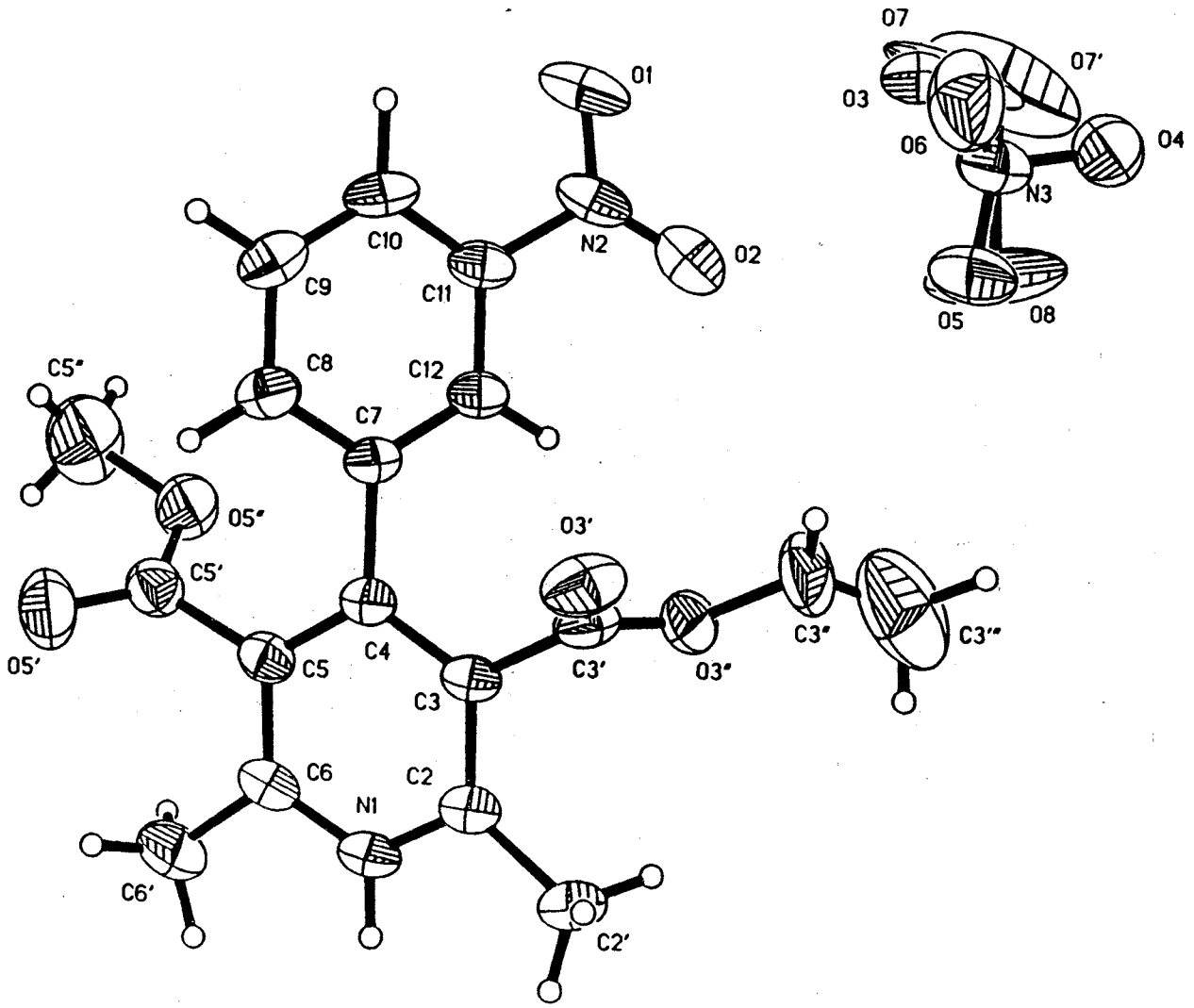

Figure 53: Projection view of [Methyl ethyl 2,6-dimethyl-3,5-dicarboxylate-4-(3-nitrophenyl)-pyridine] • NO_3 (XXIII)

TABLE 117

CRYSTAL DATA FOR

Ethyl methyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate • NO_3
(XXIII)

Formula	$C_{17}H_{17}N_2O_6$
M. W.	345.33 g $mole^{-1}$
a	9.034(1) Å
b	10.228(1) Å
c	12.392(2) Å
α	78.71(1) °
β	71.05(1) °
γ	69.40(1) °
V	1009.4(2) $Å^3$
F(000)	362
μMoKα	11.28 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.136 g/cm^3
Z	2
Meas refl	4289
Obs refl	Refined on F^2
R	6.6 %
R_w	16.47 %
G. O. F.	0.914
Space Group	P-1
Octants meas	$-1 \leq h \leq 10, -11 \leq k \leq 12, -14 \leq l \leq 14$

TABLE 118

POSITIONAL PARAMETERS FOR

Ethyl methyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate • NO_3
(XXIII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
N1	0.1657(5)	0.1143(5)	0.0479(3)
C2	0.1314(6)	0.1959(5)	0.1302(4)
C2'	0.0295(7)	0.3465(6)	0.1135(4)
C3	0.1957(6)	0.1393(5)	0.2227(4)
C3'	0.1615(8)	0.2338(5)	0.3133(4)
C3"	-0.0328(11)	0.3571(8)	0.4616(7)
C3"'	-0.2006(22)	0.4151(14)	0.4934(10)
O3'	0.2637(5)	0.2740(4)	0.3253(4)
O3"	0.0067(5)	0.2638(4)	0.3756(3)
C4	0.2971(6)	0.0010(5)	0.2274(4)
C5	0.3330(6)	-0.0795(5)	0.1381(4)
C5'	0.4437(8)	-0.2275(6)	0.1329(5)
C5"	0.4904(14)	-0.4641(8)	0.2156(8)
O5'	0.5687(6)	-0.2626(5)	0.0581(4)
O5"	0.3850(5)	-0.3110(4)	0.2181(3)
C6	0.2647(7)	-0.0212(6)	0.0469(4)
C6'	0.2920(8)	-0.0979(7)	-0.0531(5)
C7	0.3623(6)	-0.0605(5)	0.3301(4)
C8	0.5291(6)	-0.1316(5)	0.3155(4)
C9	0.5896(7)	-0.1870(6)	0.4103(5)
C10	0.4825(7)	-0.1737(5)	0.5195(5)
C11	0.3175(7)	-0.1024(5)	0.5315(4)
C12	0.2543(6)	-0.0444(5)	0.4386(4)
N2	0.2030(8)	-0.0838(6)	0.6458(4)
N3	-0.0051(9)	0.3072(7)	0.8267(5)
O1	0.2439(6)	-0.1623(6)	0.7259(3)
O2	0.0712(7)	0.0101(6)	0.6566(3)
O3	0.0936(17)	0.2047(15)	0.8494(10)
O4	-0.1377(11)	0.3603(9)	0.9046(9)
O5	0.0014(27)	0.3695(19)	0.7311(13)
O6	0.1292(22)	0.3174(27)	0.8269(18)
O7	-0.0129(159)	0.2016(76)	0.8934(56)
O7'	-0.0749(96)	0.2650(119)	0.9072(52)
O8	-0.0550(62)	0.3663(59)	0.7592(37)

TABLE 119

ANISOTROPIC THERMAL PARAMETERS FOR

Ethyl methyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate • NO_3 (XXIII)

ATOM	U11	U22	U33	U23	U13	U12
N1	70(3)	72(3)	50(2)	3(2)	-24(2)	-29(2)
C2	63(3)	63(3)	52(3)	3(2)	-24(2)	-25(3)
C2'	98(4)	71(4)	73(3)	11(3)	-47(3)	-7(3)
C3	63(3)	60(3)	47(2)	4(2)	-27(2)	-25(2)
C3'	79(4)	56(3)	62(3)	3(2)	-41(3)	-18(3)
C3"	114(6)	117(6)	104(5)	-66(4)	-35(5)	0(5)
C3"'	228(16)	203(11)	182(9)	-80(8)	5(11)	-112(12)
O3'	111(3)	75(2)	113(3)	1(2)	-77(3)	-39(2)
O3"	87(3)	72(2)	70(2)	-26(2)	-28(2)	-17(2)
C4	54(3)	59(3)	49(2)	4(2)	-21(2)	-22(2)
C5	62(3)	62(3)	46(3)	0(2)	-12(2)	-26(2)
C5'	82(4)	71(3)	63(3)	-11(3)	-16(3)	-23(3)
C5"	211(10)	62(5)	153(7)	2(4)	-6(7)	-21(6)
O5'	94(3)	97(3)	98(3)	-24(3)	7(3)	-8(3)
O5"	110(3)	59(2)	90(3)	2(2)	-18(2)	-19(2)
C6	73(3)	80(4)	45(3)	-1(2)	-17(2)	-39(3)
C6'	120(5)	105(4)	56(3)	-15(3)	-29(3)	-44(4)
C7	63(3)	55(3)	54(3)	4(2)	-27(2)	-22(2)
C8	63(3)	62(3)	77(3)	7(2)	-38(3)	-16(3)
C9	70(3)	76(3)	85(4)	5(3)	-37(3)	-21(3)
C10	89(4)	66(3)	88(4)	16(3)	-59(3)	-35(3)
C11	76(4)	67(3)	54(3)	5(2)	-34(3)	-33(3)
C12	67(3)	64(3)	47(3)	3(2)	-25(2)	-32(2)
N2	102(4)	108(4)	53(3)	-2(3)	-33(3)	-57(3)
N3	97(5)	98(4)	68(4)	4(3)	-41(4)	-34(5)
O1	158(4)	164(4)	55(2)	22(3)	-54(3)	-80(3)
O2	101(3)	120(4)	71(3)	-22(2)	-15(2)	-47(3)
O3	121(8)	109(9)	62(7)	-4(6)	-45(6)	17(9)
O4	86(5)	122(7)	98(6)	-26(5)	-29(5)	-11(5)
O5	158(14)	126(9)	52(6)	26(5)	-26(7)	-39(8)
O6	86(11)	148(17)	151(16)	-55(14)	-18(10)	-25(11)
O7	405(156)	106(51)	71(34)	83(31)	-134(62)	-180(79)
O7'	279(55)	711(126)	90(40)	54(57)	-15(38)	-433(76)
O8	242(35)	275(38)	185(39)	107(29)	-184(34)	-98(26)

The anisotropic displacement exponent takes the form:$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE 120

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

Ethyl methyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate • NO_3
(XXIII)

N1-C2	1.333(6)	C2-N1-C6	124.0(4)
N1-C6	1.360(6)	N1-C2-C3	118.7(4)
C2-C3	1.387(6)	N1-C2-C2'	117.0(4)
C2-C2'	1.505(7)	C3-C2-C2'	124.2(4)
C3-C4	1.391(6)	C4-C3-C2	120.2(4)
C3-C3'	1.510(7)	C4-C3-C3'	121.3(4)
C3'-O3'	1.193(6)	C2-C3-C3'	118.4(4)
C3'-O3"	1.317(6)	O3'-C3'-O3"	125.8(5)
C3"-C3'"	1.37(2)	O3'-C3'-C3	123.2(6)
C3"-O3"	1.444(7)	O3"-C3'-C3	111.0(4)
C4-C5	1.394(6)	C3'"-C3"-O3"	106.8(8)
C4-C7	1.508(6)	C3'-O3"-C3"	112.9(5)
C5-C6	1.394(6)	C3-C4-C5	119.2(4)
C5-C5'	1.492(7)	C3-C4-C7	119.6(4)
C5'-O5'	1.195(6)	C5-C4-C7	121.2(4)
C5'-O5"	1.315(7)	C6-C5-C4	119.7(4)
C5"-O5"	1.520(9)	C6-C5-C5'	116.7(4)
C6-C6'	1.503(7)	C4-C5-C5'	123.6(4)
C7-C12	1.382(6)	O5'-C5'-O5"	125.7(5)
C7-C8	1.391(7)	O5'-C5'-C5	122.5(5)
C8-C9	1.392(7)	O5"-C5'-C5	111.8(5)
C9-C10	1.383(8)	C5'-O5"-C5"	114.2(5)
C10-C11	1.382(7)	N1-C6-C5	118.2(4)
C11-C12	1.386(6)	N1-C6-C6'	117.2(4)
C11-N2	1.458(7)	C5-C6-C6'	124.6(5)
N2-O1	1.219(6)	C12-C7-C8	120.6(4)
N2-O2	1.225(6)	C12-C7-C4	119.1(4)
N3-O8	1.06(4)	C8-C7-C4	120.3(4)
N3-O7'	1.09(5)	C9-C8-C7	120.3(5)
N3-O3	1.168(11)	C10-C9-C8	119.8(5)
N3-O5	1.22(2)	C11-C10-C9	118.7(4)
N3-O7	1.23(5)	C10-C11-C12	122.7(5)
N3-O6	1.25(2)	C10-C11-N2	119.7(5)
N3-O4	1.287(10)	C12-C11-N2	117.6(5)
		C7-C12-C11	117.9(4)
		O1-N2-O2	123.3(6)
		O1-N2-C11	118.2(6)
		O2-N2-C11	118.5(5)
		O8-N3-O7'	124.9(52)

TABLE 120 (Continued)

O8-N3-O3	143.4(31)
O7'-N3-O3	77.7(58)
O8-N3-O5	25.2(36)
O7'-N3-O5	150.0(43)
O3-N3-O5	125.5(12)
O8-N3-O7	138.8(48)
O7'-N3-O7	34.3(85)
O3-N3-O7	46.4(59)
O5-N3-O7	150.4(27)
O8-N3-O6	116.4(32)
O7'-N3-O6	116.1(36)
O3-N3-O6	62.5(11)
O5-N3-O6	93.1(17)
O7-N3-O6	101.8(49)
O8-N3-O4	93.0(30)
O7'-N3-O4	45.7(61)
O3-N3-O4	120.0(9)
O5-N3-O4	114.4(11)
O7-N3-O4	79.9(57)
O6-N3-O4	120.0(10)

TABLE 121

TORSION ANGLES (°) FOR

Ethyl methyl 2,6-dimethyl-4-(3-nitrophenyl)-pyridine-3,5-dicarboxylate • NO_3
(XXIII)

C6-N1-C2-C3	-2.22(0.61)	C9-C10-C11-C12	1.12(0.66)
C6-N1-C2-C2'	175.72(0.41)	C9-C10-C11-N2	-177.72(0.42)
N1-C2-C3-C4	1.0(0.59)	C8-C7-C12-C11	-0.73(0.59)
C2'-C2-C3-C4	-176.77(0.42)	C4-C7-C12-C11	179.57(0.36)
N1-C2-C3-C3'	178.30(0.38)	C10-C11-C12-C7	0.30(0.63)
C2'-C2-C3-C3'	0.53(0.66)	N2-C11-C12-C7	179.15(0.37)
C2-C3-C3'-O3'	-108.30(0.48)	C10-C11-N2-O1	-20.07(0.62)
C4-C3-C3'-O3'	68.97(0.55)	C12-C11-N2-O1	161.04(0.42)
C2-C3-C3'-O3"	71.91(0.47)	C10-C11-N2-O2	159.4 (0.42)
C4-C3-C3'-O3"	-110.81(0.42)	C12-C11-N2-O2	-19.45(0.61)
O3'-C3'-O3"-C3"	2.22(0.62)	C8-C9-C10-C11	-2.09(0.68)
C3-C3'-O3"-C3"	-178.00(0.39)		
C3'"-C3"-O3"-C3'	161.56(0.75)		
C2-C3-C4-C5	0.77(0.58)		
C3'-C3-C4-C5	-176.45(0.39)		
C2-C3-C4-C7	-178.15(0.37)		
C3'-C3-C4-C7	4.63(0.59)		
C3-C4-C5-C6	-1.47(0.58)		
C7-C4-C5-C6	177.43(0.38)		
C3-C4-C5-C5'	177.79(0.40)		
C7-C4-C5-C5'	-3.32(0.61)		
C4-C5-C5'-O5'	-117.23(0.54)		
C6-C5-C5'-O5'	62.05(0.65)		
C4-C5-C5'-O5"	63.00(0.57)		
C6-C5-C5'-O5"	-117.73(0.46)		
O5'-C5'-O5"-C5"	-1.46(0.88)		
C5-C5'-O5"-C5"	178.30(0.57)		
C2-N1-C6-C5	1.52(0.62)		
C2-N1-C6-C6'	-179.47(0.42)		
C4-C5-C6-N1	0.40(0.59)		
C5'-C5-C6-N1	-178.90(0.38)		
C4-C5-C6-C6'	-178.53(0.44)		
C5'-C5-C6-C6'	2.16(0.66)		
C3-C4-C7-C12	49.82 0.54)		
C5-C4-C7-C12	-129.07(0.43)		
C3-C4-C7-C8	-129.88(0.42)		
C5-C4-C7-C8	51.23(0.56)		
C12-C7-C8-C9	-0.25(0.63)		
C4-C7-C8-C9	179.45(0.41)		
C7-C8-C9-C10	1.69(0.69)		

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