ULTRAVIOLET SPECTRAL STUDIES OF CONJUGATIVE

EFFECTS BETWEEN ADJACENT UNSATURATED

GROUPS AND PHOSPHORYL FUNCTIONS

By

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CHAPTER I

INTRODUCTION

Delocalization of electrons between phosphoryl groups and α, β - unsaturated linkages had not been examined previously in detail by means of ultraviolet spectroscopy. Compounds containing adjacent $C=O$, $C=N$, and $C=C$ seemed attractive as functional groups capable of electronic interaction with the phosphoryl function. It was anticipated that by examination of the acylphosphonates and their corresponding (2,4-dinitrophenyl)-hydrazone (DNP) derivatives some insight could be gained concerning the ground state geometric requirements with respect to the dihedral angle between the plane of the phosphoryl group and the plane of the P-C=X atoms.

CHAPTER II

HISTORICAL

Ultraviolet Spectroscopy

When a molecule absorbs ultraviolet light, an electron is excited to one of the unoccupied, antibonding orbitals of the molecule. A loosely held electron in a π orbital may easily be excited to an antibonding π (π^*) orbital having higher energy.
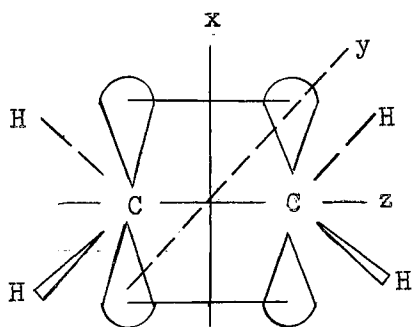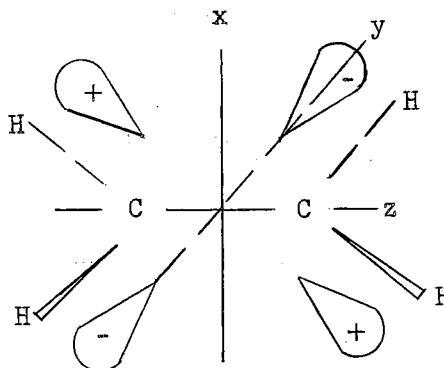
π orbital π^* orbital

Usually $\pi \longrightarrow \pi^*$ transitions are very intense as demonstrated by large molar absorptivities (ϵmax.$>$10,000). The bands produced by $\pi \longrightarrow \pi^*$ transitions within the near-ultraviolet are called K-bands. Conjugation of double

bonds, such as in butadiene and in acetophenone, shifts $\pi \longrightarrow \pi^*$ bands to longer wavelengths and increases their number and intensity. Further extension of a conjugated system produces regular shifts to longer wavelengths (12, 29).

Because of the symmetry of aromatic systems, the transition to a homopolar excited state is "forbidden" and can occur only with low intensity (ϵmax. = 250-3,000).

$\psi(E_1)$ $\psi(B)$
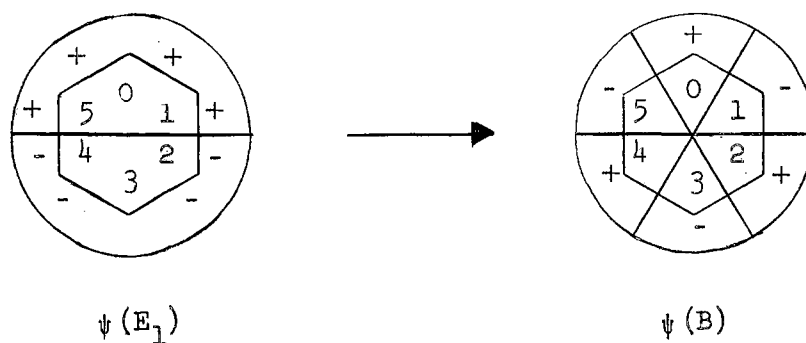
The band produced by the above transition is called the B-band. Transitions to various vibrational energy levels impart fine structure to the B-band. In a conjugated system of a hydrocarbon the excited state resulting from a $\pi \longrightarrow \pi^*$ transition is said to be more "polar" than the ground state due to the increased separation of the electrons from the nuclei to which they are bound (12, 21, 27, 29).

Electron-donor substituents are known as auxochromes, and they effect a bathochromic shift upon $\pi \longrightarrow \pi^*$ transitions. Electron-accepting substituents oppose the vacating of a low-energy π orbital. Consequently, more energy is required for the transition, and a hypsochromic shift is observed (12).

Transition of a nonbonding(n) electron to π^* ($n \longrightarrow \pi^*$) may be illustrated by the transition of a nonbonding electron of the oxygen atom in a carbonyl group to a π^* orbital of the carbonyl group.

$$\diagdown \text{C} :: \text{O} \qquad \longrightarrow \qquad \diagdown \text{C} :: \text{O}$$

n π^*
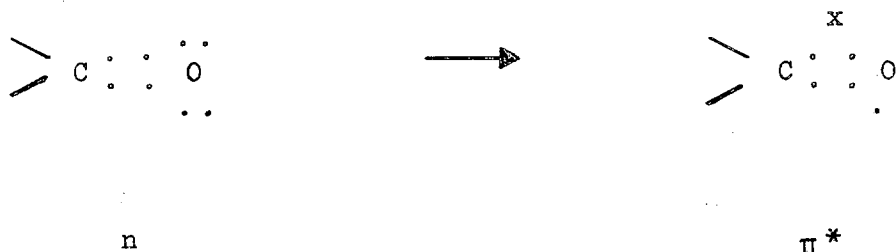
A $n \longrightarrow \pi^*$ transition produces a band called the R-band (ϵ max. <100) (12, 29).

Steric hindrance to coplanarity of a conjugated group usually raises the energy of the excited state more than the energy of the ground state. The required higher transition energy produces a hypsochromic shift which increases as the steric hindrance to coplanarity increases. For even a slight hindrance to coplanarity, a large hypochromic shift is often observed (12).

Ultraviolet Absorption of Ketones, Aldehydes, and Certain Derivatives

Isolated ketone groups absorb in the near ultraviolet at 270-285 mμ (ϵ max. <100) while isolated aldehyde groups absorb in the region of 280-300 mμ (29). Donation of electrons from the methyl group by resonance interaction raises the energy of the π^* orbital relative to that of an n electron; consequently in cyclohexane, acetone has maximum absorption (λ max.)

at 277.5 mμ(logεmax. = 1.11) while λmax. for acetaldehyde is 290 mμ(log εmax. = 1.23) (21). The absorption maxima of isolated ketones, R-bands, exhibit a hypsochromic shift with increasing polarity of solvent (19).

Unsaturated groups in conjugation with an ethylenic linkage display a strong K-band in the region of 215-250 mμ(εmax. = 10,000-20,000). Also a weak R-band appears in the region of 300-350 mμ. The two bands are shifted toward one another as the polarity of the solvent increases (29).

$$C = C \longleftarrow C = O \longrightarrow \overset{+}{C} - C = C - \overset{-}{O}$$

$$\pi \qquad\qquad\qquad \pi^*$$
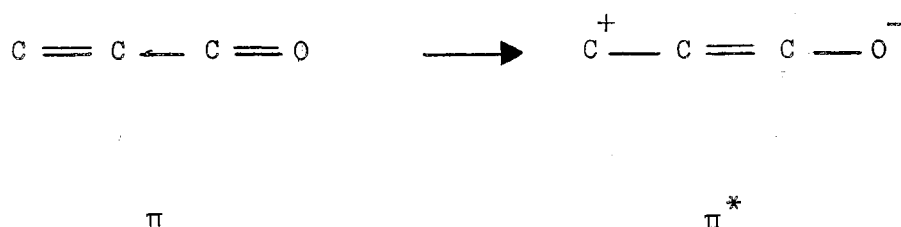
Benzaldehyde has K-, B-, and R-bands at approximately 248 mμ, 280 mμ, and 328 mμ, respectively (10). Benzophenone in ethanol has K- and R-bands at approximately 252 mμ(εmax. = 20,000) and 325 mμ(εmax. = 180), respectively (29). The R-bands of aryl ketones are found at longer wavelengths than those of aliphatic carbonyl compounds (12).

No K-band ($\pi \longrightarrow \pi^*$) is observed for α-diketones such as 2,3-butanedione. Besides the expected R-band ($n \longrightarrow \pi^*$) at 286 mμ(log εmax. = 1.39) in ethanol, 2,3-butanedione displays a series of bands in the region of 420-450 mμ(εmax. ~ 20) (27, 29). However, benzil in ethanol has the expected K-band at 250 mμ (log εmax. = 4.20) and the expected R-band at 370 mμ(log εmax. = 1.89) (17).

Compared to the K- and R-bands of benzophenone in ethanol, the corresponding R-band of benzil has undergone a bathochromic shift.

$$\pi \qquad\qquad \pi^*$$
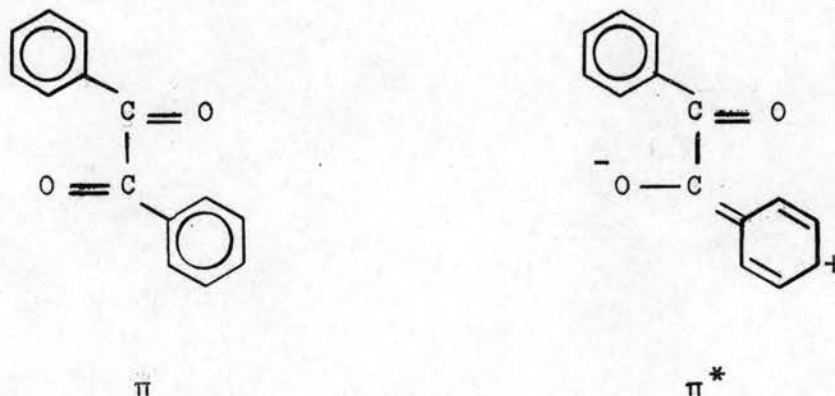
Leonard and Mader (24) studied the influence of steric configuration on the ultraviolet absorption of alicyclic 1,2-diketones having different ring sizes. The position of the R-bands of these diketones was found to vary in a regular fashion with the dihedral angle between the plane defined by one carbonyl carbon and its substituents and the plane defined by the next carbonyl carbon with its substituents. As the angle became larger or smaller than 90°, the band experienced a bathochromic shift. Overlap of p orbitals between the two carbonyl groups was greatest when the angle was 0° or 180°. The dihedral angle in benzil was postulated to be 90° (27). However, three of the cyclic ketones having dihedral angles greater than 90° displayed wavelength maxima lower than 370 mμ (27).

Barany and co-workers (3) reported that the monooxime and the mono-hydrazone of 2,3-butanedione in ethanol had λ max. at 229 mμ(ϵmax. = 13,000)

and at 275 mμ(ϵ max. = 12,500), respectively. These K-bands must involve
an imine bond since the parent compounds have no K-bands.

Although the position of the λ max. of (2,4-dinitrophenyl)hydrazones
varies slightly with alkyl substitution of the parent carbonyl group,
approximate assignments for the (2,4-dinitrophenyl)hydrazones of saturated
and α,β-unsaturated carbonyl compounds list λ_{max}. = 360 mμ(ϵ max. = 20,000)
and λ max. = 380 mμ(ϵ max. = 25,000), respectively (27). The DNP from
propionaldehyde has an approximate λ max. = 340 mμ(log ϵ max. = 4.35) (25).
The DNP derivative of acetophenone in ethanol has λ max. = 376 mμ(log
ϵ max. = 4.38).

## Ultraviolet Absorption of Some Phosphorus Compounds

Involvement of d orbitals of phosphorus in π bonds may be divided
into two classes: (a) formation of such π bonds between a phosphorus atom
and another atom or group, such as oxygen, an unsaturated group, or an
aromatic group, and (b) the conjugation of two chromophoric groups through
a phosphorus atom. Evidence appears to show that formation of dπ bonds by
expansion of the valence shell of phosphorus does occur when, and only when,
the phosphorus atom, without multiple bonds, would be positively charged.
The energy required to remove a π electron from a substituent in tetra-
substituted phosphorus compounds approximately equals the energy released
by placing the electron into one of the 3d orbitals of the positive
phosphorus atom. The positive charge on phosphorus not only increases the
energy required to remove a d electron from phosphorus (its orbital energy)
but also increases the overlap integral by pulling an electron in this
orbital closer to it. Consequently, pπ-dπ bonding is the most probable inter-
action by which the formal charge of phosphorus can be neutralized (21).

The π bonds around a tetrasubstituted phosphorus atom do not couple very much with the π bonds of phenyl groups (10, 20, 31). The benzenoid spectra of the various mono-, di-, and triphenyl derivatives of tetra-substituted phosphorus compounds in which phosphorus is part of a phosphoryl group are only mildly perturbed. It is sometimes possible to recognize the B-band as the one with closely spaced, discrete peaks. The slight conjugation between a phenyl ring and a phosphoryl group is recognized by the bathochromic and hyperchromic effects on the B-band, and particularly by the bathochromic effect on the primary band of benzene, normally at about 200 mμ. The B-band in triphenylphosphine oxide displays a λ max. and ε max. of 265.5 mμ and 2,420, respectively, while the corresponding values for benzene are 254.5 mμ and 180. The corresponding values for diphenyl-phosphonic acid are 265.0 mμ and 1,200. Additivity of the effects on molar absorptivity of several phenyl groups bound to the phosphorus atom indicates the lack of interaction between them (21).

The electronic spectra of phosphoryl compounds having a vinyl group bonded to phosphorus but lacking aromatic groups, display maxima in the same wavelength region and with approximately the same molar absorptivity as do simple olefins. For example 1-hexene has λ max. = 180 mμ (ε max. = 11,000). The corresponding values for a series of phosphoryl compounds having a vinyl group bonded to phosphorus are as follows: bis-(N,N-di-methylamido)vinylphosphonate [174 mμ(16,400)], di-n-butyl vinylphosphonate [177 mμ(13,400)], and di-(n-butyl)vinylphosphine oxide [179 mμ(14,600)]. The absorption maxima of the latter three compounds either remain unchanged or are slightly shifted to shorter wavelengths (no more than 6 mμ). From the values given, it is apparent that ε max. differs only slightly (22). The maximum for bis-(2-chloroethyl)vinylphosphine oxide in tetrahydrofuran

is at 215 mμ(εmax. = 19). The wavelength position of this band, with very low intensity, is significantly removed from that of the series of the three vinyl compounds above. However, the spectrum of this compound was not recorded below 210 mμ (11). At present chemical evidence argues in favor of conjugation between vinyl and phosphoryl groups, but spectral evidence for conjugation is inconclusive (22).

Jaffe and Orchin (21) proposed that if oxygen is considered as lying on the z-axis of the central phosphorus atom, and if its two π orbitals interact with d_{xz} and d_{yz} orbitals of the phosphorus atom, then the axes of the remaining d orbitals of phosphorus also become fixed in position relative to oxygen.


$d_{xz} -\pi_x$ $d_{yz} -\pi_y$
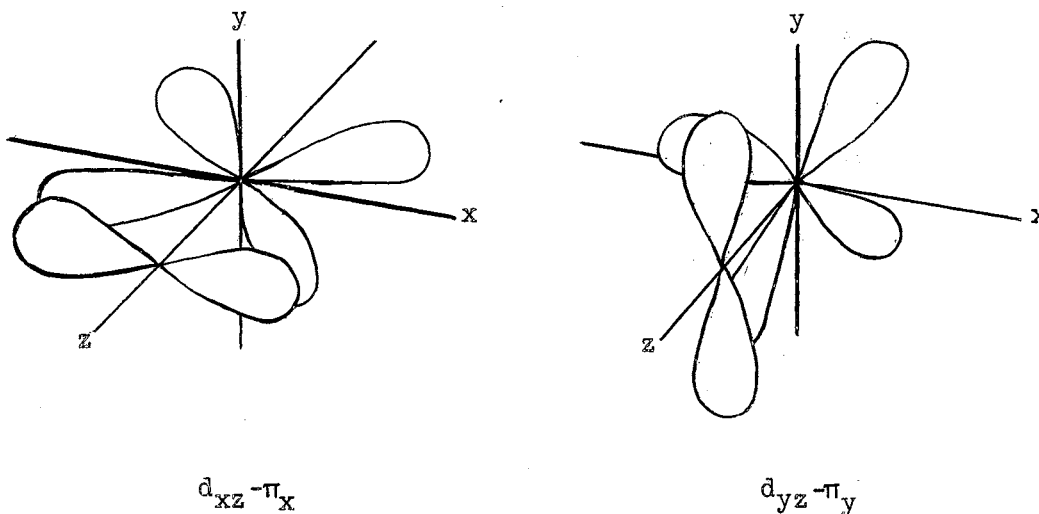
Consequently, owing to the fixed position of the d orbitals, the π orbitals of the three chromophoric substituents on phosphorus may not be properly oriented with respect to any of the five d orbitals of phosphorus for optimum overlap. However, some interaction of d orbitals of phosphorus

with π orbitals of the chromophoric substituents is possible whatever
the orientation of the chromophore plane with respect to the rest of the
molecule.

Conjugated sulfone groups are similar in many respects to conjugated
phosphoryl groups. When the normally transparent sulfone group is con-
jugated with a multiple bond, as in ethyl vinyl sulfone and in divinyl
sulfone, the molar absorptivities at 210 mμ are approximately 450 and 2,200,
respectively. The effect of the sulfonyl group on the spectrum of benzene
in phenyl methyl sulfone is to shift the primary and secondary absorption
maxima to about 217 mμ and 264 mμ, respectively. Also, log ε max. for the
corresponding maxima are increased to 3.83 and 2.99, respectively. In
diphenyl sulfone the primary absorption maximum is shifted to 235 mμ (log
ε max. = 4.2). This band is thought to represent the excitation of the
benzene sulfonyl group with interchange with the other phenyl group. Since
the two benzene rings are known to be non-coplanar, the two p orbitals on
the aromatic carbons attached to sulfur may overlap with lobes of the
proper sign of the same 3d orbital on sulfur (26).

Griffin and Polsky (19) reported evidence for strong conjugative
effects in tri-2-pyrrylphosphine oxides. While the weak absorption of
pyrrole and of N-methylpyrrole drops smoothly from 225 mμ to 300 mμ, in-
tense bands appear at 237.5 mμ (log ε = 4.06) and at 248 mμ (log ε = 4.11) in
95% ethanol for tri-2-pyrrylphosphine oxide (XVIII) and the N-methyl
analog (XIX), respectively. The appearance of the new, intense band for
XVIII and XIX is indicative of conjugative interaction between the
phosphoryl group and the π electrons of the pyrrole ring.
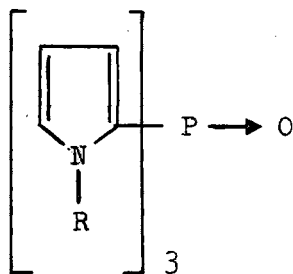
XVIII. R=H

XIX. R=CH$_3$

Pyrroles substituted in the 2-position with carbonyl or phenyl groups display two intense bands, designated X and Y, at 228-252 mμ(log ϵ = 3.57-3.70) and 263-289.5 mμ(log ϵ = 4.10-4.22). The single intense band in the spectra of XVIII and XIX is probably related to the Y-band. The hypsochromic shift displayed by XVIII and XIX relative to the 2-carbonyl substituted pyrroles indicates the degree of conjugation to be much weaker. However, the intense band in both XVIII and XIX indicates conjugation of the pyrrole ring with the phosphoryl group to be much more pronounced than that of a phenyl ring with the phosphoryl group.

Griffin and Brown (18) reported that the ultraviolet absorption spectrum of 2,5-diphenyl-3-furylphosphonic acid (XX) is similar to that of 2,5-diphenylfuran (XXI).
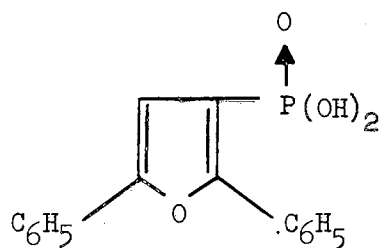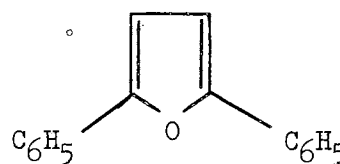
XX   XXI

For XX the absorption maxima are 225 mμ(ϵmax. = 30,200) and 318 mμ(ϵmax. = 36,400), while the corresponding maxima for XXI are 226 mμ(ϵmax. = 16,200) and 324 mμ(ϵmax. = 29,200). The hyperchromic shift for XX relative to XXI is consistent with the effect of a number of arylphosphonic acids and indicative of a weak resonance interaction between the phosphono group and the furan ring. The very weak hypochromic shift observed may be due to interference of the phosphono group with planarity of the 1,4-diphenyl-butadiene system which is the main chromophore. Ortho phosphono groupings in the biphenylylphosphonic acids cause a similar disruption of planarity leading to a comparable effect on the absorption spectra.

Cotton and Schunn (11) have studied the ultraviolet absorption of salts of dialkoxyphosphonylacetylmethanide ions (XXII) and of tetraalkoxy-diphosphonylmethanide ions (XXIII) in tetrahydrofuran. The former compounds displayed much greater near-ultraviolet absorption than did the compounds containing single chromophores analogous to those in the separate canonical forms.

$$\left[(RO)_2P(O)CHC(O)CH_3\right]^- \qquad \left\{\left[(RO)_2P(O)\right]_2CH\right\}^-$$
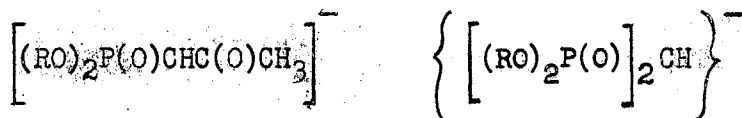
XXII XXIII

Consequently, the entire chromophoric chain $\left[>P(O)CHC(O)-\right]^-$ must be responsible for the intense absorption. The maxima for $\left[>P(O)CHP(O)-\right]^-$, $\left[>P(O)CHC(O)-\right]^-$, and $\left[-C(O)CHC(O)-\right]^-$ are given as 225 mμ(ϵ) 2,000), $\sim$ 240 mμ($\epsilon \geq$ 8,000), and $\sim$ 280 mμ($\epsilon \simeq$ 20,000), respectively. The above data for the three linkages illustrate the much greater conjugative ability of carbonyl groups as compared to phosphoryl groups.

Arbuzov and co-workers (2) have shown that the ultraviolet absorption spectrum of diethyl 2-cyclopentanon-1-ylphosphonate (XXIV) in sodium methoxide-methanol displays a maximum at 245 mμ. This wavelength is given as evidence for the enol form, and the value compares favorably with λ max. for the $\left[>P(O)CHC(O)-\right]^-$ linkage given above.
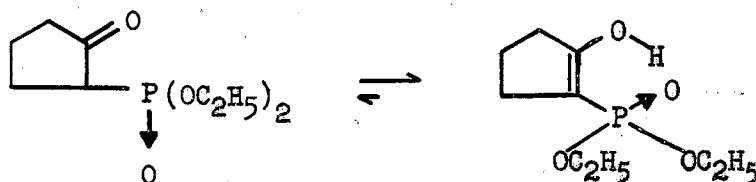
XXIV

One would not expect XXIV to be in the keto form in inert solvents because diethoxyphosphonylacetylmethane (XXV) has λ max. at 285 mμ (ϵ max. = 38) as expected for isolated ketones (11).

$$(C_2H_5O)_2 \overset{\overset{O}{\uparrow}}{P} CH_2 \overset{\overset{O}{\parallel}}{C} CH_3$$
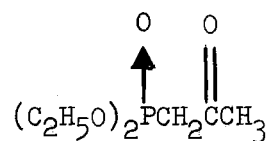
XXV

Ackerman and co-workers (1) in 1956 reported ultraviolet absorption data for two acylphosphonates, diethyl octanoylphosphonate and diethyl palmitoylphosphonate. In isooctane as solvent both phosphonates showed a double peak at 333 and 341 mμ. The molar absorptivities were 59.04 and 62.81 for the C_8 and C_{16} derivatives, respectively. An extensive study of the ultraviolet absorption spectra of acylphosphonates was not made.

CHAPTER III

DISCUSSION OF RESULTS AND CONCLUSIONS

The ultraviolet spectra of some substituted acylphosphonates, their 2,4-dinitrophenylhydrazones, and two phosphine oxides were recorded. The object of this research was to examine conjugative effects of the phosphoryl group with three types of adjacent double bonds. The double bonds were $>C=O$, $>C=N-$, and $>C=C<$.
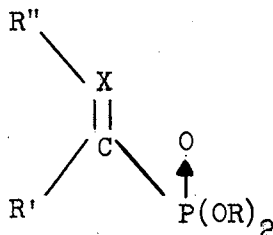
The acylphosphonates examined were as follows: diethyl acetylphosphonate (I), diethyl propionylphosphonate (II), diethyl cyclopentoylphosphonate (III), diethyl cyclohexoylphosphonate (IV), diethyl benzoylphosphonate (V), diethyl (p-tert-butylbenzoyl)phosphonate (VI), diethyl p-chlorobenzoylphosphonate (VII), and dimethyl p-anisoylphosphonate (VIII).

$$\begin{array}{c} O \\ \parallel \\ R \diagdown \overset{\displaystyle C}{} \diagup P(OR')_2 \\ \downarrow \\ O \end{array}$$
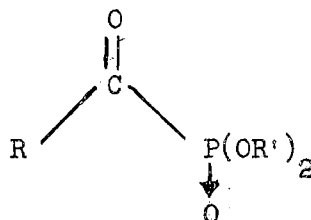
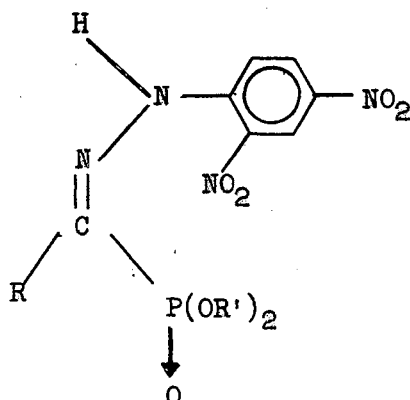|	R	R'
I.	CH_3	C_2H_5
II.	C_2H_5	C_2H_5
III.	Cyclopentyl	C_2H_5
IV.	Cyclohexyl	C_2H_5
V.	C_6H_5	C_2H_5
VI.	p-(t-C_4H_9)C_6H_4	C_2H_5
VII.	p-ClC_6H_4	C_2H_5
VIII.	p-$CH_3OC_6H_4$	CH_3

The 2,4-dinitrophenylhydrazones examined were as follows: diethyl acetylphosphonate (2,4-dinitrophenyl)hydrazone (IX), diethyl propionyl-phosphonate (2,4-dinitrophenyl)hydrazone (X), diethyl cyclohexoylphos-phonate (2,4-dinitrophenyl)hydrazone (XI), dimethyl benzoylphosphonate (2,4-dinitrophenyl)hydrazone (XII), dimethyl (p-tert-butylbenzoyl)phos-phonate (2,4-dinitrophenyl)hydrazone (XIII), dimethyl p-anisoylphosphonate (2,4-dinitrophenyl)hydrazone (XIV), and diethyl p-anisoylphosphonate (2,4-dinitrophenyl)hydrazone (XV).

	R	R'
IX.	CH_3	C_2H_5
X.	C_2H_5	C_2H_5
XI.	Cyclopentyl	C_2H_5
XII.	C_6H_5	CH_3
XIII.	p-(t-C_4H_9)C_6H_4	CH_3
XIV.	p-$CH_3OC_6H_4$	CH_3
XV.	p-$CH_3OC_6H_4$	C_2H_5

The phosphine oxides examined were diphenylvinylphosphine oxide (XVI) and diphenylpropenylphosphine oxide (XVII).

$$(C_6H_5)_2\overset{O}{\underset{\uparrow}{P}}CH{=}CH_2$$

XVI

$$(C_6H_5)_2\overset{O}{\underset{\uparrow}{P}}CH{=}CHCH_3$$

XVII
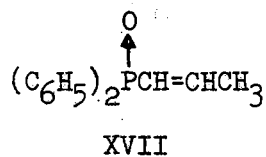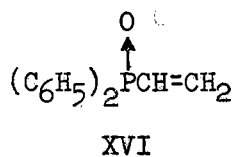
The acylphosphonates were obtained by methods developed in this laboratory (5, 6, 7, 8). Repeated distillation and/or fractional crystallization was used to purify all compounds needed. Thin layer chromatography on silica gel with anhydrous acetone-chloroform was employed to check purity on all the acylphosphonates immediately before dilution with cyclohexane. The DNP derivatives in which the carbonyl group was bonded to a benzene nucleus were dissolved in methanol owing to their low solubility in cyclohexane. All compounds studied were carefully weighed to the nearest 0.0001 gram. The absorbance of the compounds was recorded within the wavelength region of 210 mμ to 400 mμ.

In the compounds studied there is strong ultraviolet spectroscopic evidence for conjugation involving adjacent phosphoryl and carbonyl groups. The R-band (n$\longrightarrow$$\pi$*) of the carbonyl group in the corresponding aliphatic aldehydes (observed in cyclohexane and isooctane) at 290-292.5 mμ appeared at 334-345 mμ in the acylphosphonates. A high-intensity absorbance, probably due to the bathochromic shift from approximately 188 mμ of the K-band of the carbonyl group being conjugated with the phosphoryl group, begins to sharply increase at about 220 mμ for I, II, III, and IV. This region is just outside of the range of the Cary Model 14 and the exact location of the band cannot be established.

The K-band ($\pi$$\longrightarrow$$\pi$*) of the corresponding benzaldehydes (observed in cyclohexane or hexane) was observed at longer wavelengths ($\Delta\lambda$max. of 17 to 40 mμ) in the acylphosphonates, V, VII, and VIII, than in the substituted benzaldehydes. The expected increase in bathochromic shift with increasing mesomeric effect of a p-substituent on the K-band was observed as follows: p-H$\langle$p-Cl$\langle$ p-(t-C$_4$H$_9$) $\langle$ p-CH$_3$O. A high-intensity band, probably due to the bathochromic shift of the 198 mμ band in benzene, appears at

increasingly higher wavelengths in the series following: VII $\langle$ VI $\langle$ VIII.
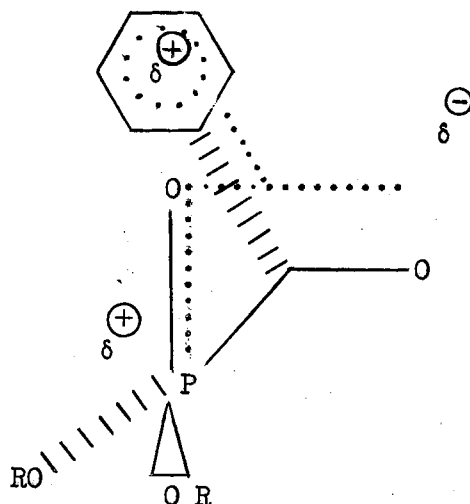
In the series of (2,4-dinitrophenyl)hydrazones the conclusions concerning conjugative effects between the phosphoryl and the imine group were not as evident as with the acylphosphonates. The DNP derivatives of I, II, and IV displayed intense bands in the region of 333 to 347.5 mμ., very similar in wavelength position and molar absorptivity to certain bands in the corresponding aliphatic aldehydes. The compound XII in methanol displayed an intense band at 360 mμ(ϵmax. = 25,000) while the λ max. for the DNP derivative of benzaldehyde in methanol was at 377 mμ(ϵmax. = 21,900). The direction and magnitude of wavelength change and band intensity, respectively, were not perfectly duplicated, but the general direction of change is consistent.

In the two phosphine oxides studied, conclusive evidence for conjugation of the phosphoryl group with an ethylenic double bond is lacking. In both compounds the position of the original 198 mμ band of benzene is moved toward longer wavelengths and the molar absorptivities of the maxima at 222 and 223 mμ are more than twice the molar absorptivities of the same bands in benzene. In addition the characteristic fine structure of the B-band is observed in the region of 254 mμ to 272 mμ for both phosphine oxides. A slightly greater intensity of both bands is found in the spectrum of XVII relative to XVI. Any conjugative effect between the vinyl group and the phosphoryl group would probably be obscured by the bands due to the benzene nucleus.

The four humps and/or shoulders on the bands at 334 mμ(ϵmax. = 52.3) and 340 mμ(ϵmax. = 71.5) for both I and II, respectively, closely resembled those in acetaldehyde (290 mμ, ϵmax. = 17.0) and propionaldehyde (292.5 mμ, ϵmax. = 18.6) (23). In I, II, III, and IV the λ max. of the R-band displayed

a bathochromic shift of approximately 44 mμ in comparison with the alde-
hydes mentioned above.   This shift is comparable in magnitude to that ob-
served for acrolein with respect to propionaldehyde, approximately equal
to 37.5 (29).

The postulated perpendicular orientation of the plane of the P → O
bond to the plane defined by the carbon atom of the carbonyl group and
its two substituents (7) is supported by the bathochromic ultraviolet
shift observed with the acylphosphonates.

The situation is more favorable when the shifts are compared with the
bathochromic shift and hyperchromic effect of an axial α-halogen upon
the n → π* transition of an unsubstituted cyclohexanone.   The direction
of the inductive effect of a halogen and/or the P → O group would oppose
the flow of electrons into the carbonyl function.   This effect should be
greater for the P → O group than the halogen atom.   The inductive effect

of an α-equatorial halogen upon the $n \rightarrow \pi^*$ transition lowers the energy
of the ground state (27). The result is a hypsochromic shift of the R-
band, approximately 5 mμ (21). An α-axial halogen appears to have little
inductive effect on the carbonyl group, probably because the inductive
effect is overshadowed by the electronic interaction. Overlap of the
orbital of the carbonyl group and a σ orbital of the α-halogen is greater
for an axial substituent (15). It must be admitted that the angle between
the C-X bond and the C=O bond in axial α-halocyclohexanones is approxi-
mately 109°, whereas the postulated angle between the P$\rightarrow$O plane and the
plane defined by the carbonyl group and its two substituents is 90°. The
larger bathochromic shift upon the R-band by the phosphoryl group in com-
parison to that produced by an axial halogen in an α-halocyclohexanone is
very likely related to the greater overlap of a nonbonding orbital from
the phosphoryl oxygen with a π orbital of the carbon atom of the carbonyl
group in comparison to the overlap of a nonbonding orbital from the
halogen atom with a similar π orbital.

The acylphosphonates containing a benzene nucleus on the carbonyl
group displayed bathochromic shifts in the K-band ($\pi \rightarrow \pi^*$) relative to
the corresponding benzaldehydes. In these compounds, V, VI, VII, and VIII,
the B-band apparently was obscured by the higher-intensity K-band. Chromo-
phoric substituents in the benzene nucleus often produce K-bands in the
region usually associated with B-bands (approximately 240-260 mμ) (17).

An examination of molecular models of I and V revealed that when
the plane of the phosphoryl group was perpendicular to the plane defined
by the carbon atom of the carbonyl group and its two substituents, less
overlap of van der Waal radii was observed than in any other orientation
of the carbonyl group with respect to the phosphoryl function.

Examination of a molecular model of a DNP derivative XI indicated that when the phosphorus-carbon bond was rotated until all nonbonding interactions were at a minimum, the phosphoryl group was _trans_ and coplanar with respect to the imine bond. In this conformation overlap between an sp^2-hybrid, nonbonding orbital of the oxygen atom in the phosphoryl group with a π-orbital of the carbon atom in the imine group would be difficult.

In the comparison of the spectra of the DNP derivatives with those of the acylphosphonates, the change in wavelength from the K-band of the carbonyl compound to the highest intensity band of the corresponding DNP derivative was significantly less than the 150 mμ shift observed for most α,β-unsaturated carbonyl compounds. Perhaps the _trans_, coplanar conformation of the imine and phosphoryl groups does not permit as extensive delocalization of electrons through the two groups. In analogy, it is thought that α-diketones resist $\pi \rightarrow \pi^*$ transitions because both terminal oxygen atoms resist polarization in which one of them acquires a positive charge (10).

Conjugative effects between ethylenic and phosphoryl bonds have been postulated from chemical data in that nucleophiles attack in a 1,4-fashion, but direct spectroscopic evidence for an α,β-conjugated system is lacking (22). In triphenylphosphine oxide the ϵmax. at 224 mμ is 21,300 and the ϵmax. at 265.5 mμ is 2,420 (20). A strong hyperchromic effect on benzene bands, originally at about 200 mμ (primary) and 255 mμ (B-band), in triphenylphosphine oxide may be due to resonance between the phosphoryl group and the benzene nucleus, although it is doubtful since the hyperchromic effect due to addition of benzene rings is additive (20). The molar absorptivity of XVII at 222 mμ (ϵmax. = 22,900) is approximately equal to

that of triphenylphosphine oxide while that of XVI at 223 mμ (ϵmax. = 17,400)

is more than the molar absorptivity of diphenylphosphinic acid at 224 mμ

(ϵmax. = 13,000) (20). Apparently the propenyl group does slightly affect

the primary and the B-band of benzene. A small bathochromic shift (about

7 mμ) from the λmax. of the B-band in XVI is observed. The λmax. of XVI

for the B-band is essentially the same as that for triphenylphosphine oxide.

The slight perturbations due to the vinyl and propenyl groups upon the B-band

of benzene may take place by way of conjugation with the d orbitals of

phosphorus.

In conclusion, strong ultraviolet spectroscopic evidence has been

found for delocalization of electrons between adjacent phosphoryl and

carbonyl groups. By comparison of the ultraviolet absorption effects of

the acylphosphonates with those of axial α-halocyclohexanones upon the

R-band of a carbonyl group and by examination of molecular models of the

acylphosphonates, support has been found for a perpendicular

orientation of the P$\rightarrow$O plane with respect to the plane defined by the

carbon atom of the carbonyl group and its two substituents. It seems

quite likely that a similar type of delocalization of electrons does occur

in the system >P(O)-C=N. However, geometric requirements of the ground

state for DNP derivatives may be important since syn and anti forms are

possible and could change the degree of overlap between the phosphoryl and

the imine groupings. The phosphine oxides studied did not allow good

interpretation of any delocalization of electrons between adjacent phos-

phoryl and ethylenic bonds owing to the phenyl groups.

TABLE I

ULTRAVIOLET SPECTRAL DATA FOR THE DIALKYL ACYLPHOSPHONATES

Compound	Solvent	Concentration (moles/liter x 10^{-5})	λmax. (mμ)	εmax. x 10^{-1}	log εmax.
I	cyclohexane	948.0	345	4.89	1.689
			334	5.23	1.718
			322.5(s)	4.37	1.640
II	cyclohexane	1020.0	352.5	4.98	1.697
			340	7.15	1.854
			330	7.07	1.849
			318.5	5.49	1.739
III	cyclohexane	787.0	340	6.17	1.790
			280(s)	2.57	1.410
IV	cyclohexane	1840.0	345	5.34	1.727
			279	4.01	1.603
V	cyclohexane	8.93	258	926.0	3.966
VI	cyclohexane	18.7	271	217.0	3.336
			219	361.0	3.557
VII	cyclohexane	4.89	270	1500.0	4.176
			217.5(s)	971.0	3.987
VIII	cyclohexane	8.85	295	433.0	3.518
			228	205.0	3.312

TABLE II

ULTRAVIOLET SPECTRAL DATA FOR THE DNP DERIVATIVES

Compound	Solvent	Concentration (moles/liter x 10^{-5})	λmax. (mμ)	ϵmax. x 10^{-3}	log ϵmax.
IX	cyclohexane	2.56	333	19.4	4.288
			274	28.2	4.450
			227.5	13.7	4.137
X	cyclohexane	1.92	345	41.8	4.621
			252.5	21.7	4.336
			225	21.6	4.334
XI	cyclohexane	2.81	347.5	23.9	4.378
			255	12.2	4.104
XII	methanol	2.52	360	25.0	4.398
			260	14.1	4.149
			222.5	17.8	4.250
XIII	methanol	2.64	385	26.5	4.423
			266	24.8	4.396
			231	20.9	4.320
XIV	methanol	1.49	395	24.7	4.392
			268	40.9	4.612
XV	methanol	3.53	395	26.2	4.418
			297	8.5	3.929
			234	17.3	4.238

TABLE III

ULTRAVIOLET SPECTRAL DATA FOR THE PHOSPHINE OXIDES

Compound	Solvent	Concentration (moles/liter x 10^{-5})		λmax. (mμ)	ϵmax. x 10^{-2}	log ϵmax.
XVI	cyclohexane	A	73.2	272	10.7	3.029
				265	12.3	3.090
				259	9.29	2.968
				254	6.82	2.833
		B	5.86	223	174.0	4.240
XVII	cyclohexane	A	12.7	272	27.8	3.444
				265	27.0	3.431
				260	22.2	3.346
				254	17.3	3.238
		B	2.54	222	229.0	4.360

CHAPTER IV

EXPERIMENTAL

Ultraviolet Spectrophotometer. The ultraviolet spectra were obtained
on a Cary Model 14 recording spectrophotometer using quartz cells. The
rate of change in wavelength was 0.25 mμ per second and the chart speed
was two inches per minute.

Spectral Determinations; General Information. Spectral-grade cy-
clohexane was the solvent used for all compounds except the dialkyl acyl-
phosphonate (2,4-dinitrophenyl)hydrazones in which the carbonyl group was
bonded to a benzene nucleus. The concentration of the maximum amount of
the latter compounds in cyclohexane was too low to give good absorbance.
Consequently, the (2,4-dinitrophenyl)hydrazone derivatives were dissolved
in Baker analyzed reagent grade methanol (99.8 per cent purity) containing
only 0.0003 per cent acetone.

Thin Layer Chromatography Determinations; General Information. Thin
layer chromatography (t.l.c.) on a 0.25 mm. thickness of silica gel with
acetone-chloroform in the volume ratio of 1:9 showed only one spot after
development with iodine vapor for each of the compounds examined. A micro-
liter pipet was used to apply the dialkyl acylphosphonate dissolved in
methylene chloride. R_f values were recorded for each of the above compounds.

Compounds Examined. The following compounds were obtained by methods
developed in this laboratory (5, 6, 7, 8): diethyl acetylphosphonate (I),
diethyl propionylphosphonate (II), diethyl cyclopentoylphosphonate (III),

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diethyl cyclohexoylphosphonate (IV), diethyl benzoylphosphonate (V), diethyl (p-tert-butylbenzoyl)phosphonate (VI), diethyl (p-chlorobenzoyl)-phosphonate (VII), dimethyl p-anisoylphosphonate (VIII), diethyl acetyl-phosphonate (2,4-dinitrophenyl)hydrazone (IX), diethyl propionylphosphonate (2,4-dinitrophenyl)hydrazone (X), diethyl cyclohexoylphosphonate (2,4-di-nitrophenyl)hydrazone (XI), dimethyl benzoylphosphonate (2,4-dinitrophenyl)-hydrazone (XII), dimethyl (p-tert-butylbenzoyl)phosphonate (2,4-dinitro-phenyl)hydrazone (XIII), dimethyl p-anisoylphosphonate (2,4-dinitrophenyl)-hydrazone (XIV), diethyl p-anisoylphosphonate (2,4-dinitrophenyl)hydrazone (XV), diphenylvinylphosphine oxide (XVI), and diphenylpropenylphosphine oxide (XVII). The compounds listed gave the corresponding R_f values on t.l.c. chromatograms with acetone-chloroform (1:9 ratio by volume): I (.39), II (.36), III (.42), IV (.38), V (.40), VI (.38), VII (.39) and VIII (.34).

Plate I

Wavelength (mμ)

$CH_3C(O)P(O)(OC_2H_5)_2(I)$; 9.48×10^{-3} (cyclohexane) molar

Plate II

$C_2H_5C(O)P(O)(OC_2H_5)_2$ (II); 1.02×10^{-2} (cyclohexane)
molar

Plate III

Wavelength (mµ)

$\triangleright$C(O)P(O)(OC$_2$H$_5$)$_2$(III); 7.87 x 10^{-3} (cyclohexane)
molar

Plate IV

Wavelength (mμ)

⬡C(O)P(O)(C$_2$H$_5$)$_2$(IV); 1.84 x 10^{-2} (cyclohexane)
molar

33

Plate V

Wavelength (mμ)

Absorbance

$C_6H_5C(O)P(O)(OC_2H_5)_2(V)$; 8.93 x 10^{-5} (cyclohexane) molar

Plate VI

$$\underline{p}\text{-}(\underline{t}\text{-}C_4H_9)C_6H_4C(O)P(O)(OC_2H_5)_2 \text{ (VI)}; \ 1.87 \times 10^{-4} \text{ (cyclohexane)}$$
molar

Plate VII

Absorbance

Wavelength (mμ)

p-ClC$_6$H$_4$C(O)P(O)(OC$_2$H$_5$)$_2$(VII); 4.89 x 10^{-5} (cyclohexane) molar

Plate VIII

Wavelength (mμ)

Absorbance

$\underline{p}$-$CH_3$$OC_6$$H_4$$C(O)P(O)(OCH_3)_2$(VIII); 8.85×10^{-5} (cyclohexane)
molar
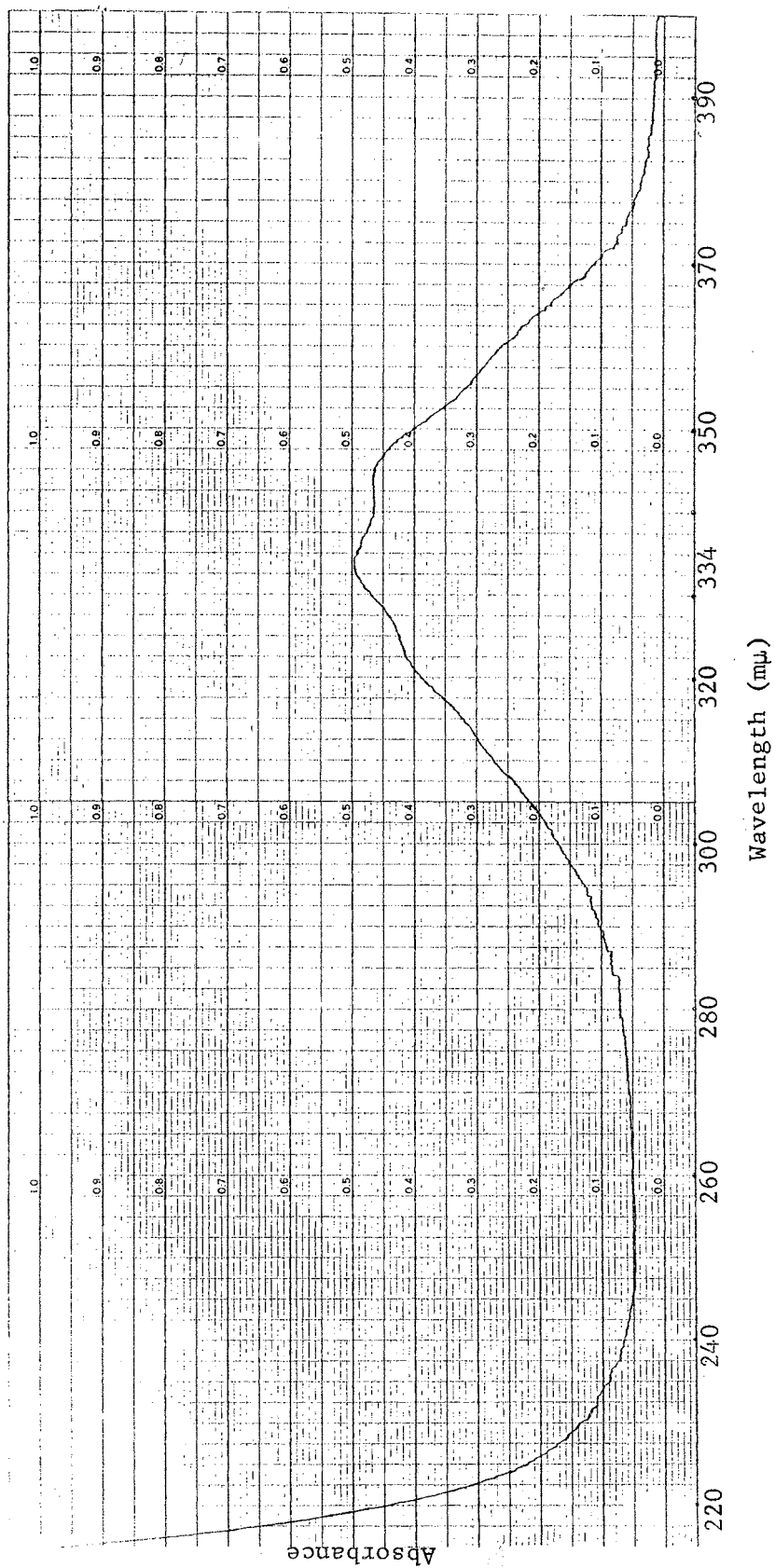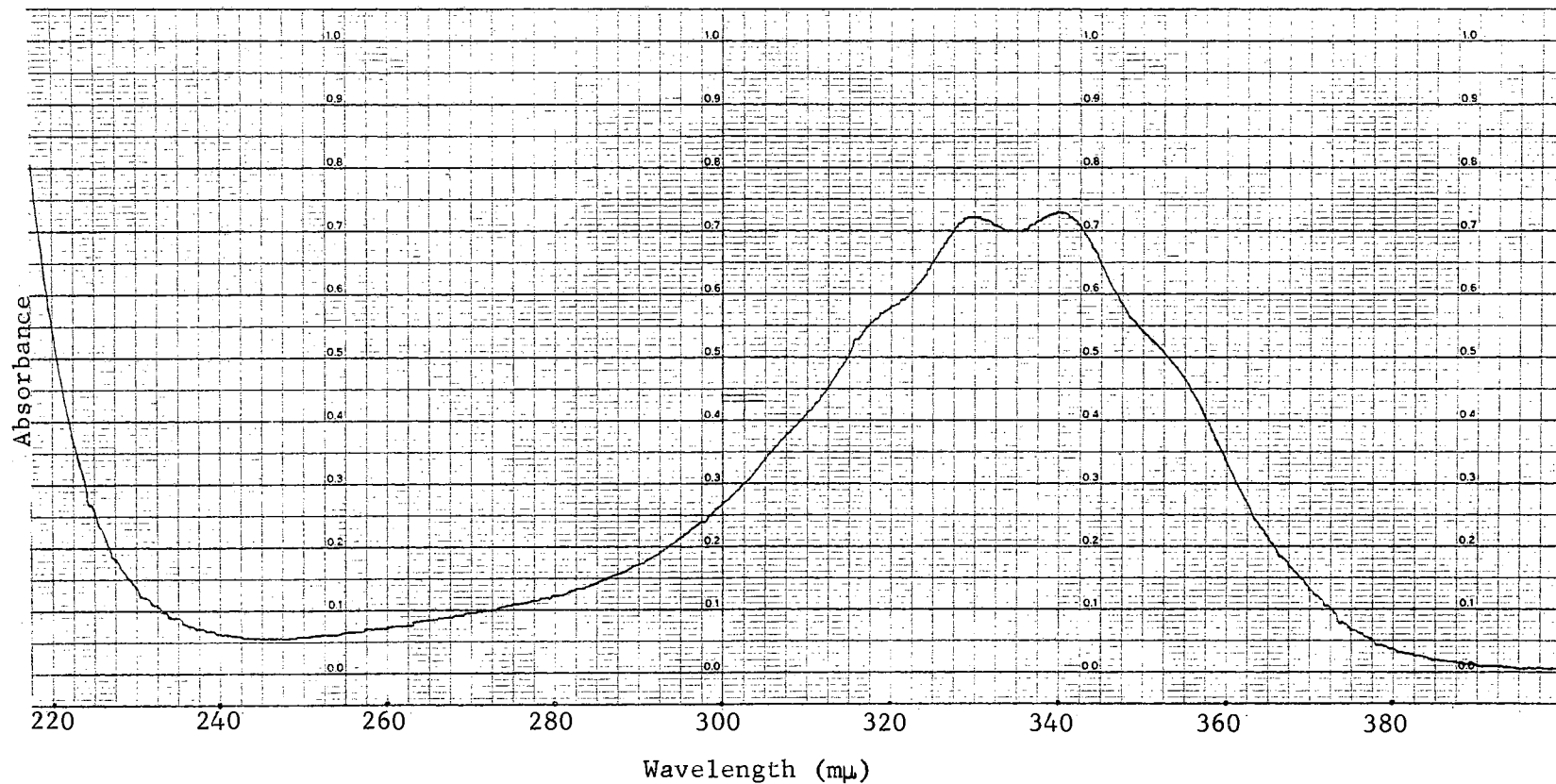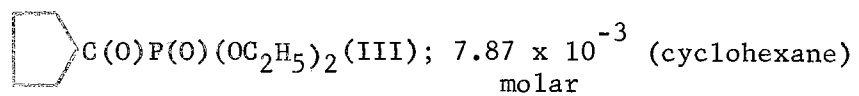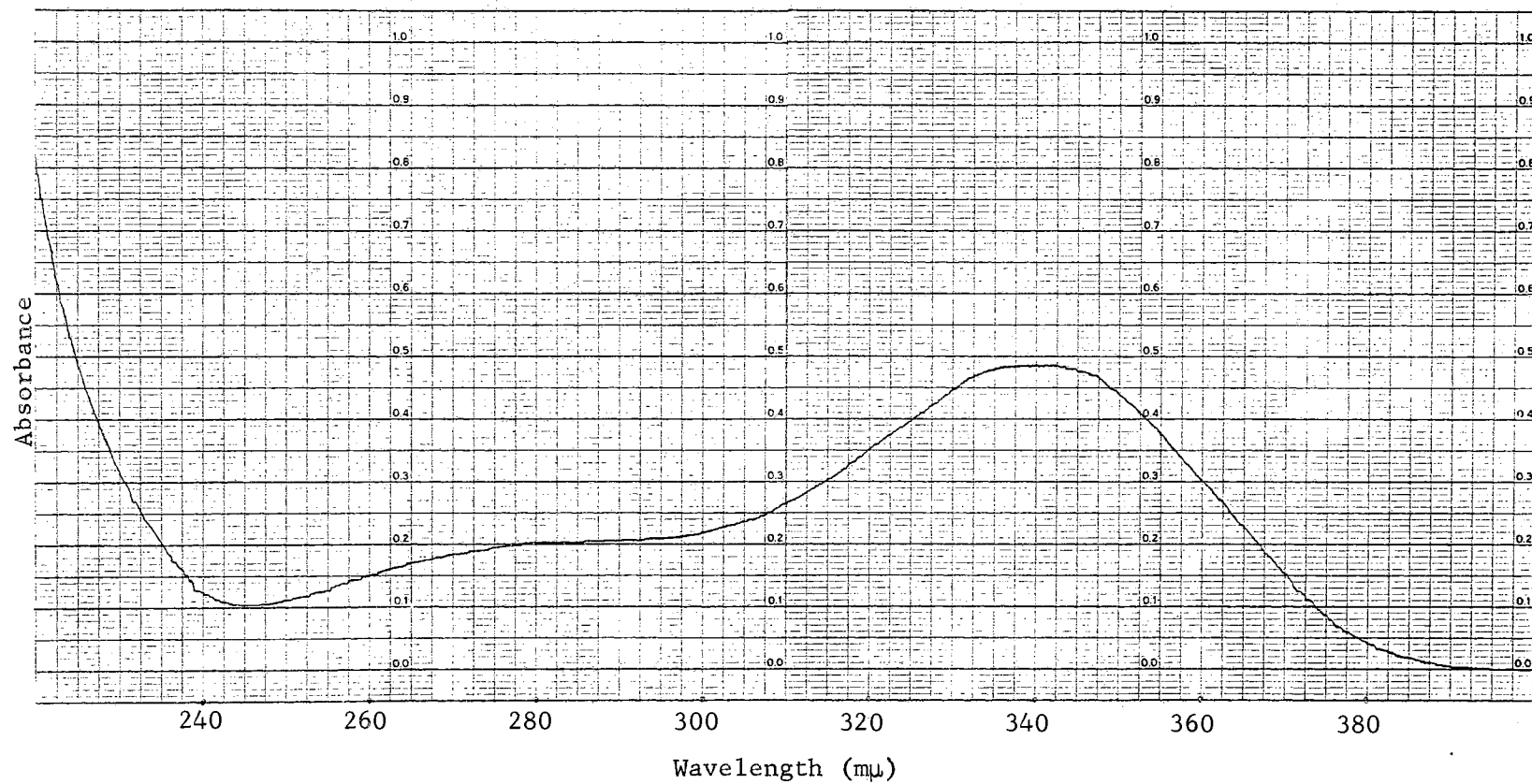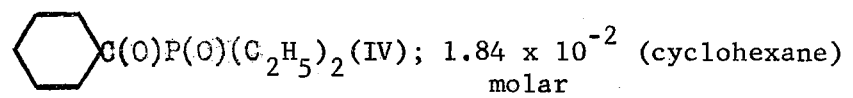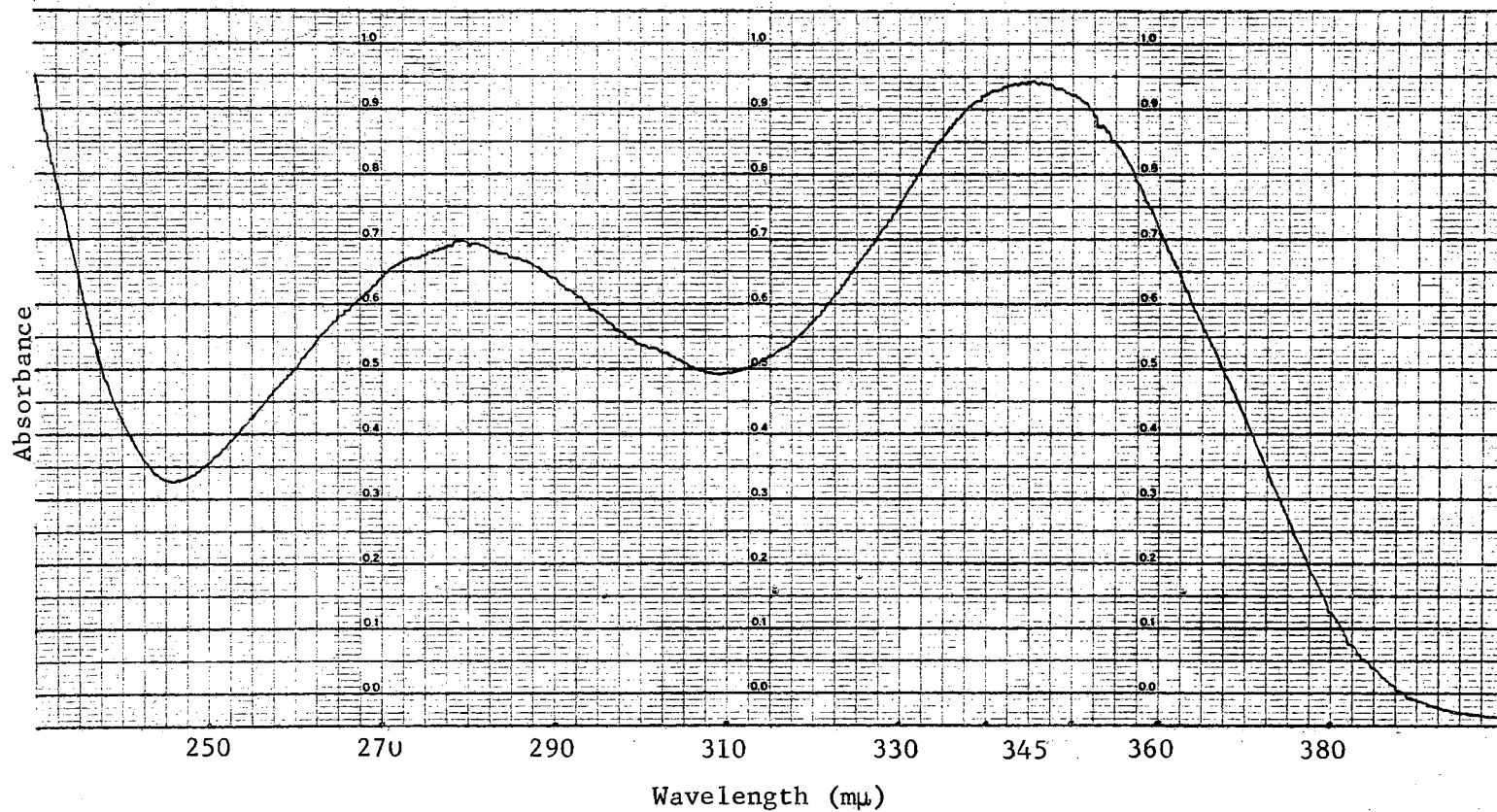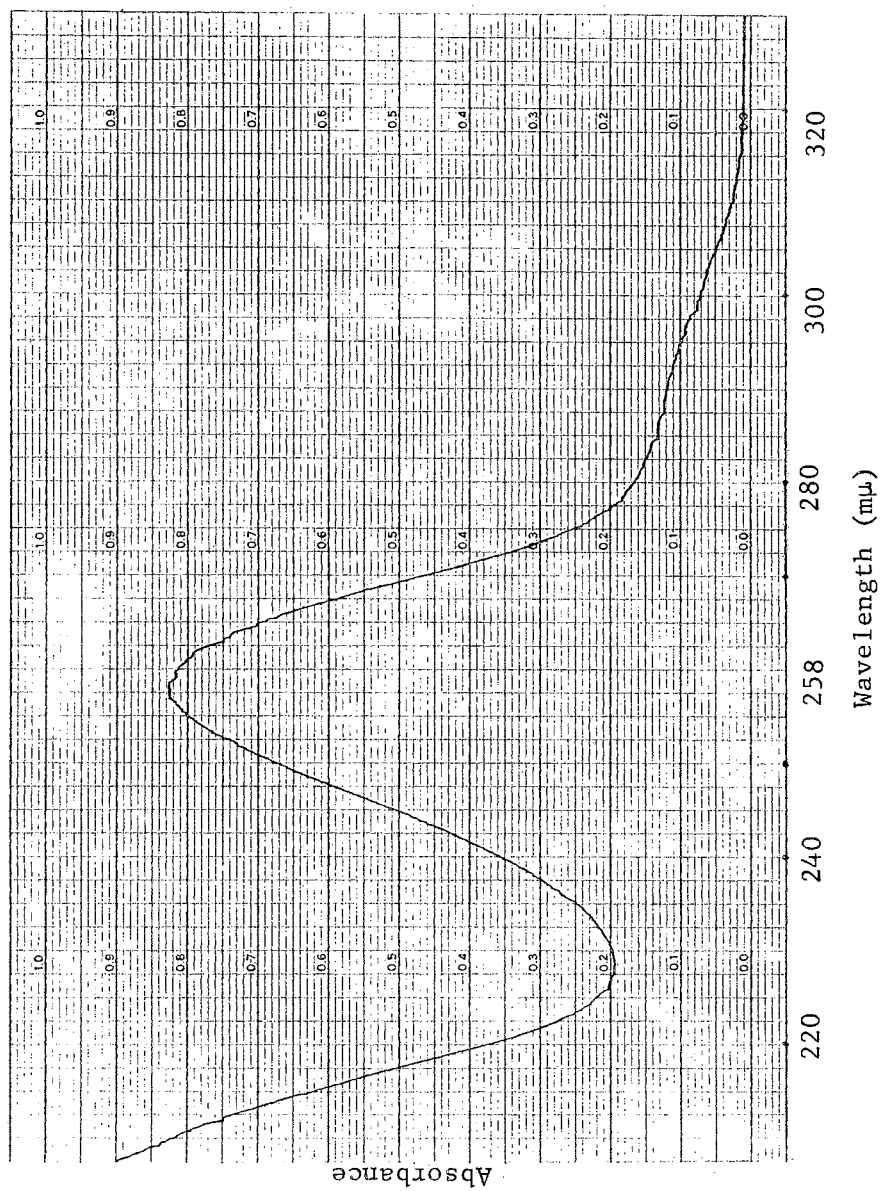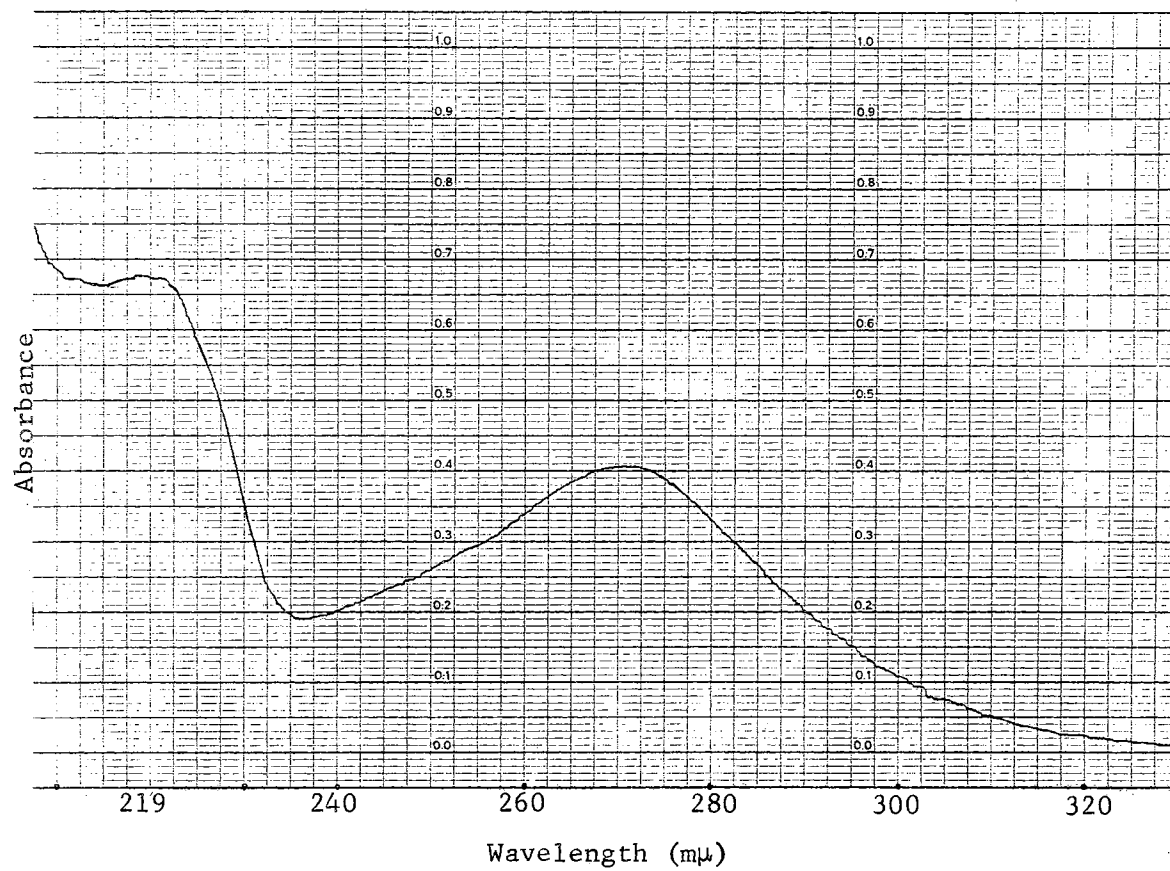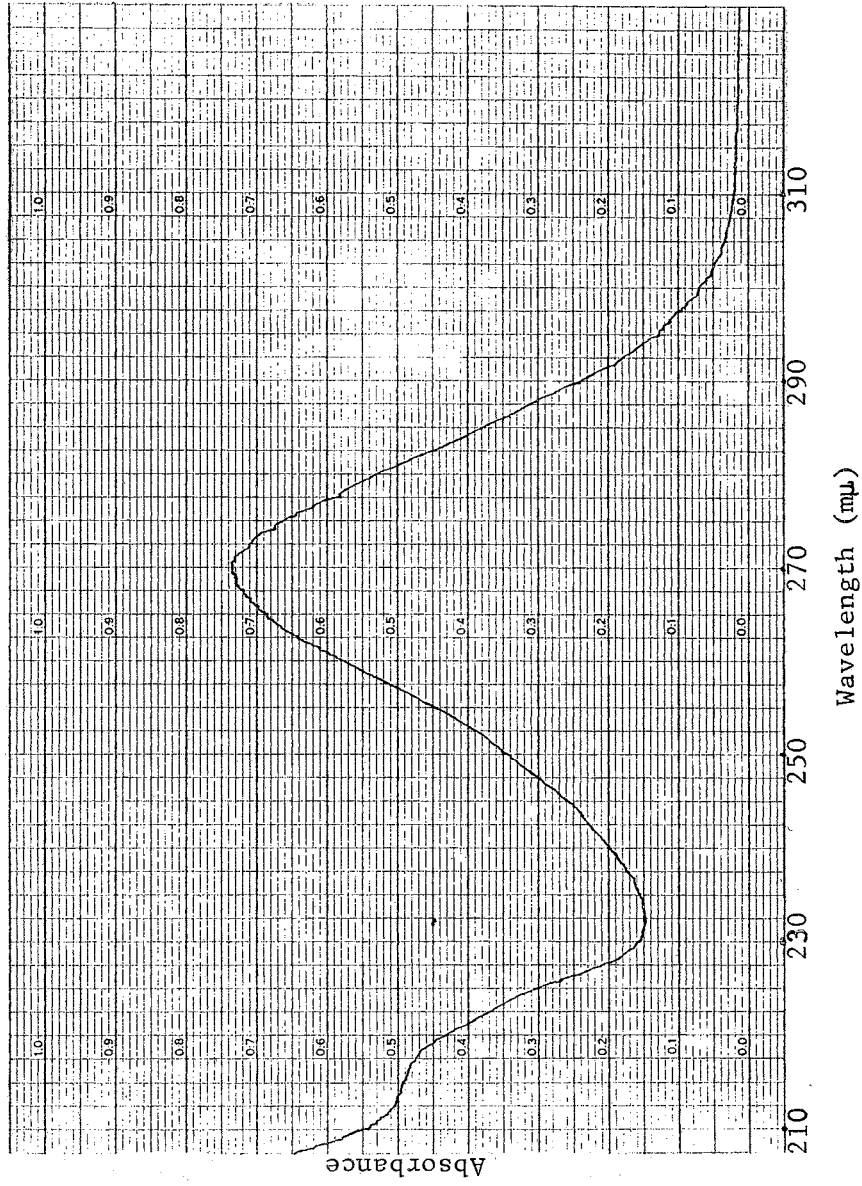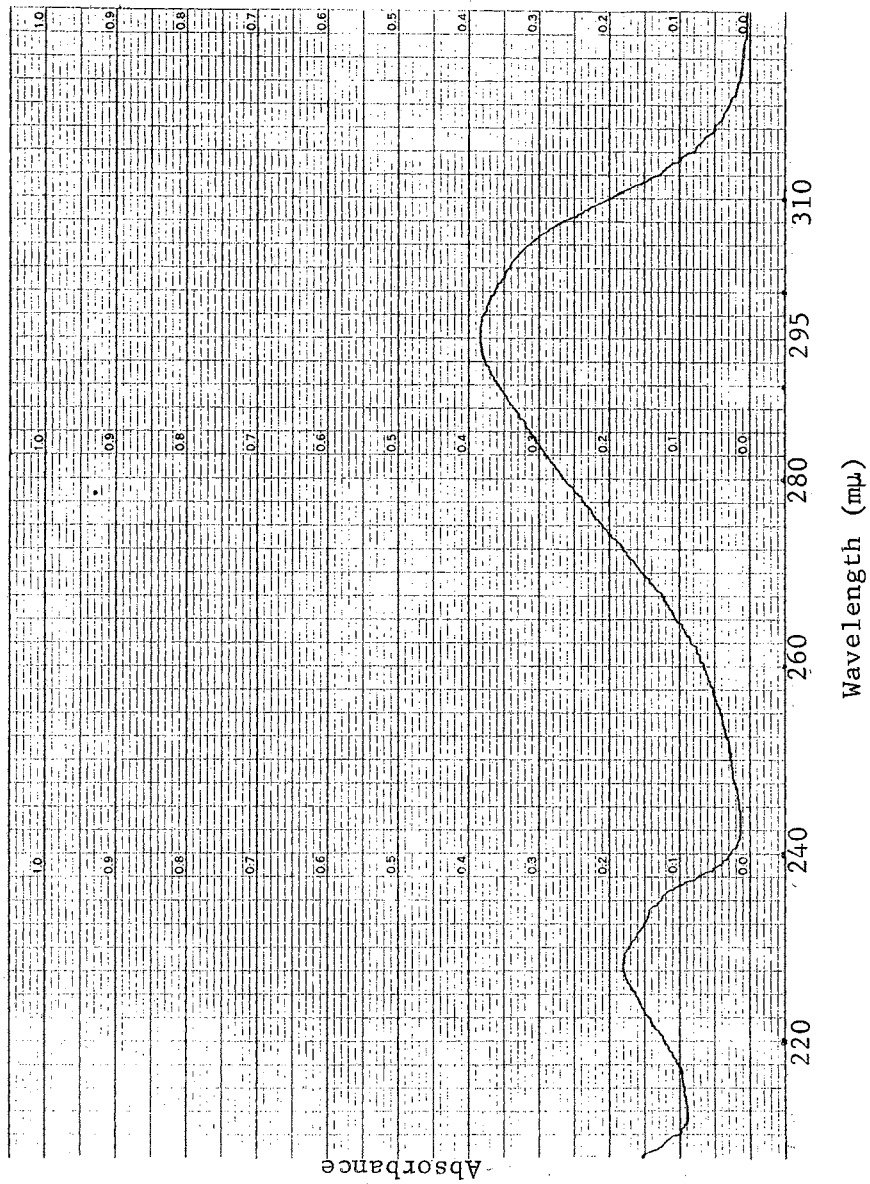
Plate IX
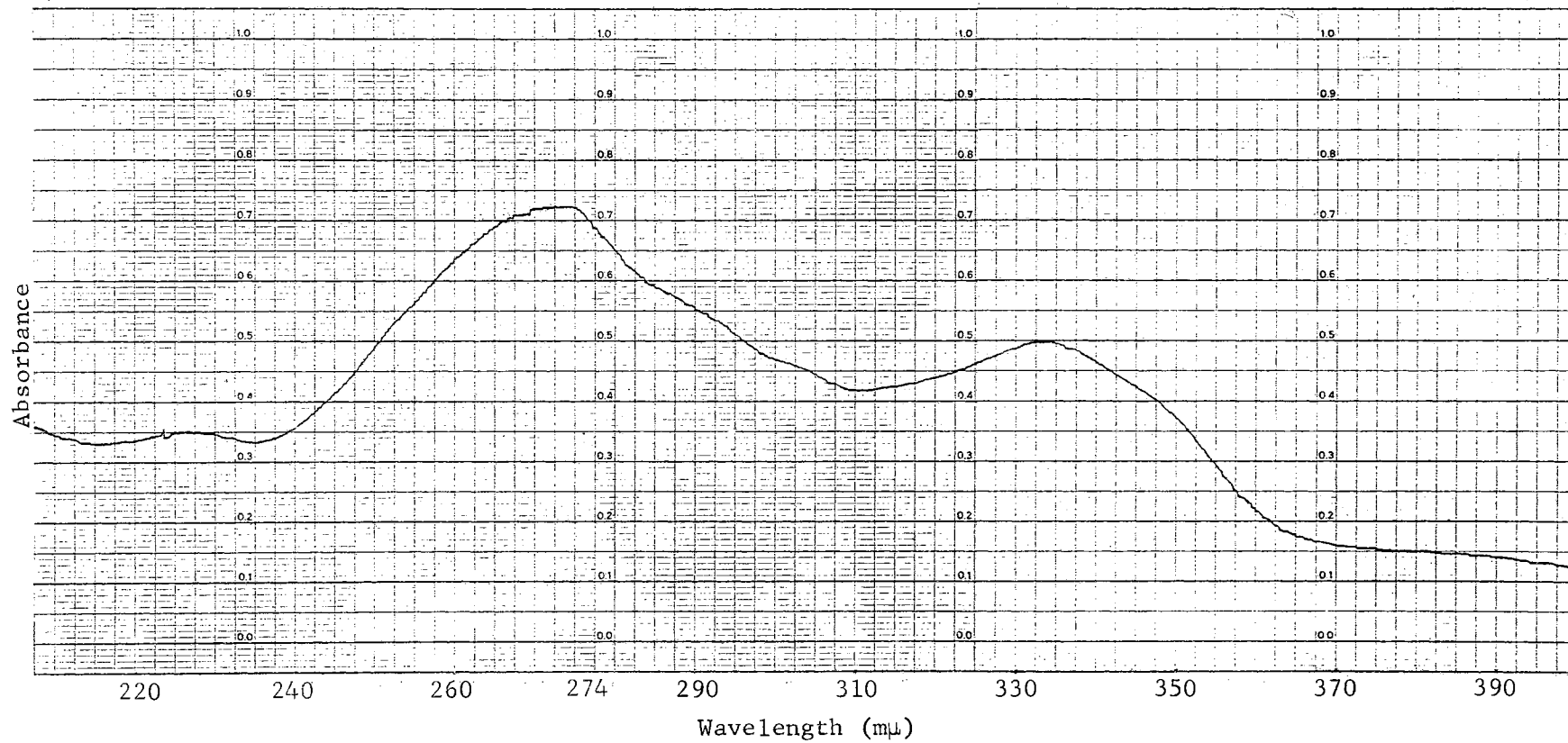
DNP of $CH_3C(O)P(O)(OC_2H_5)_2$ (IX); 2.56×10^{-5} (cyclohexane) molar
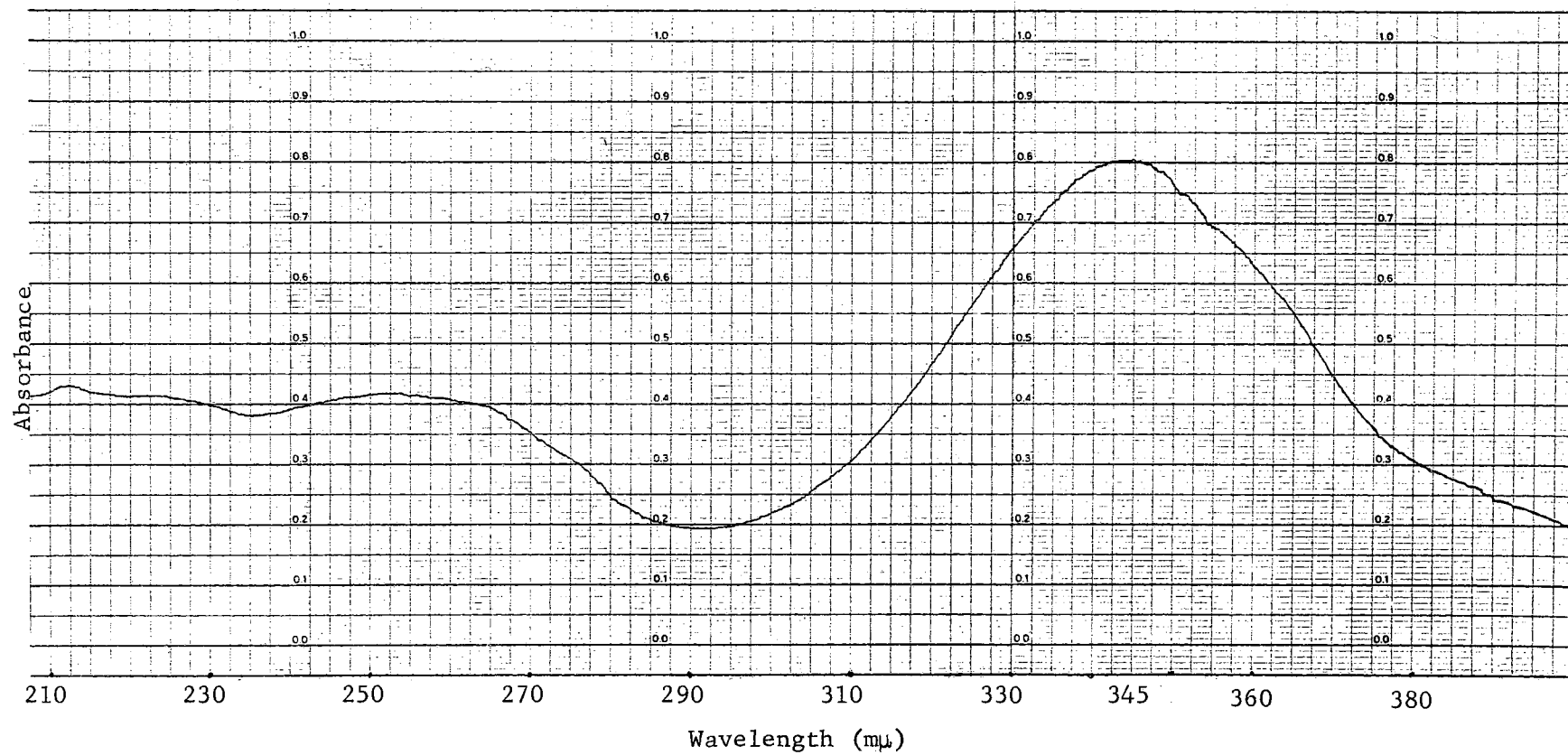
Plate X

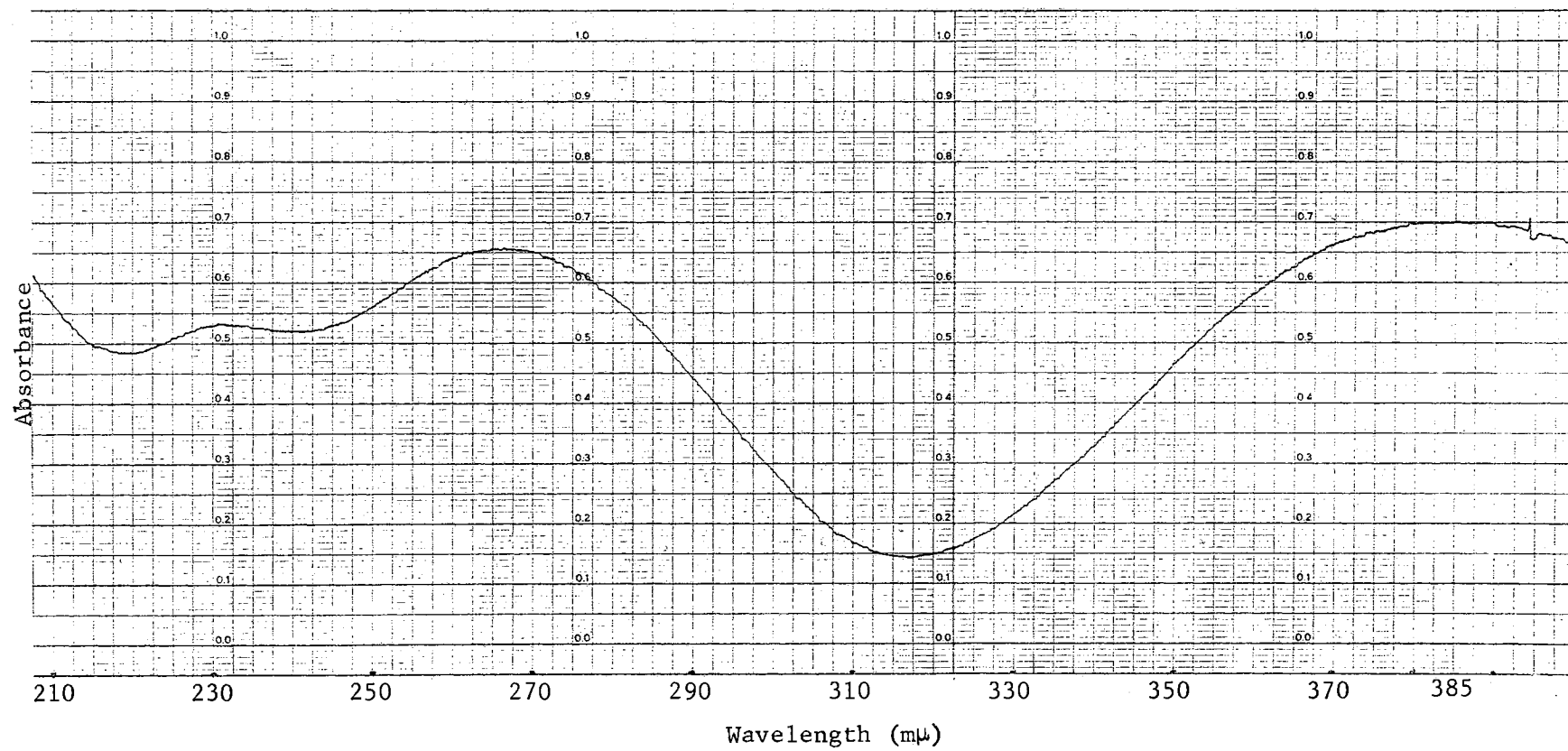DNP of $C_2H_5C(O)P(O)(OC_2H_5)_2$ (X); 1.92×10^{-5} (cyclohexane) molar
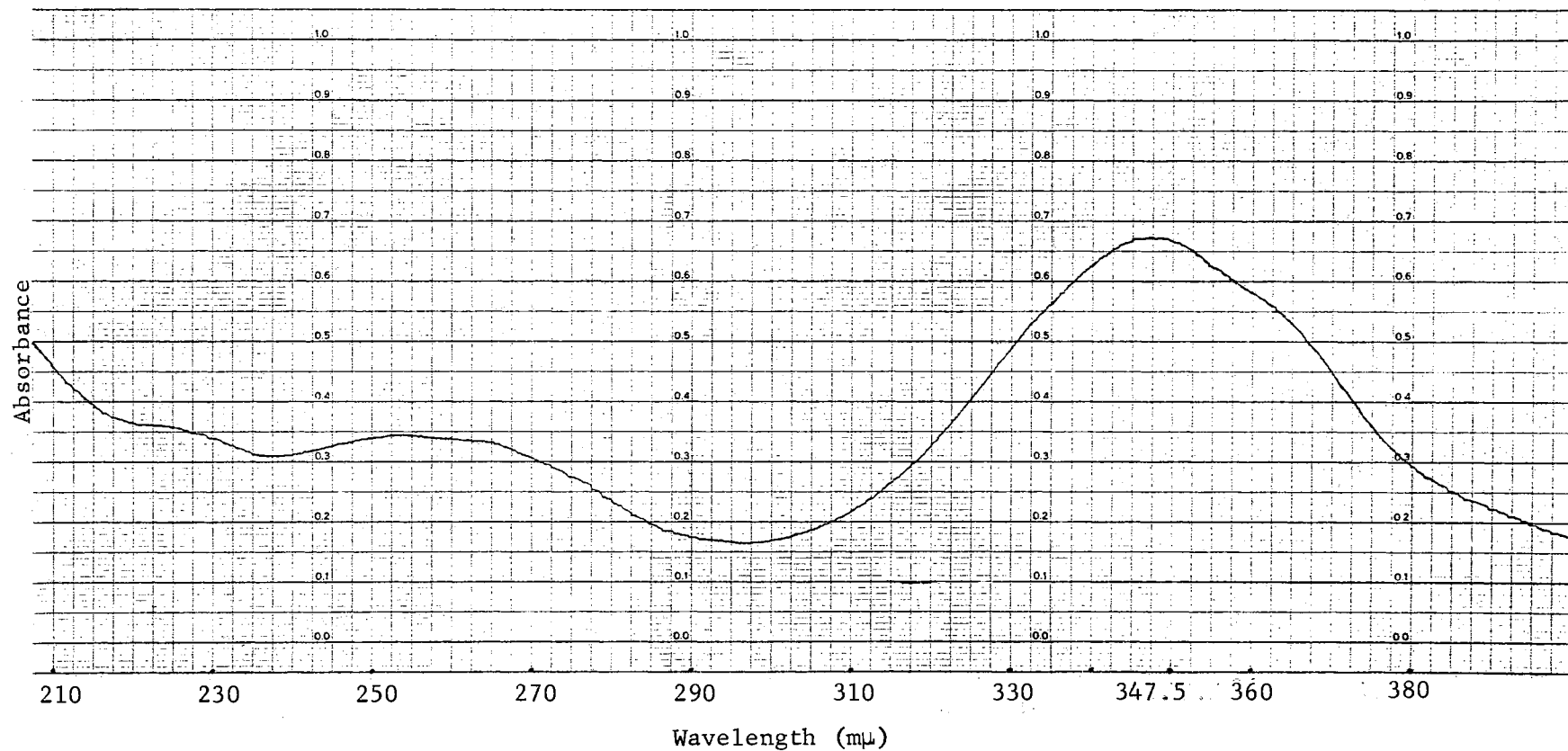
Plate XI

DNP of ⬡C(O)P(O)(OC$_2$H$_5$)$_2$(XI); 2.81 x 10^{-5} (cyclohexane) molar

Plate XII
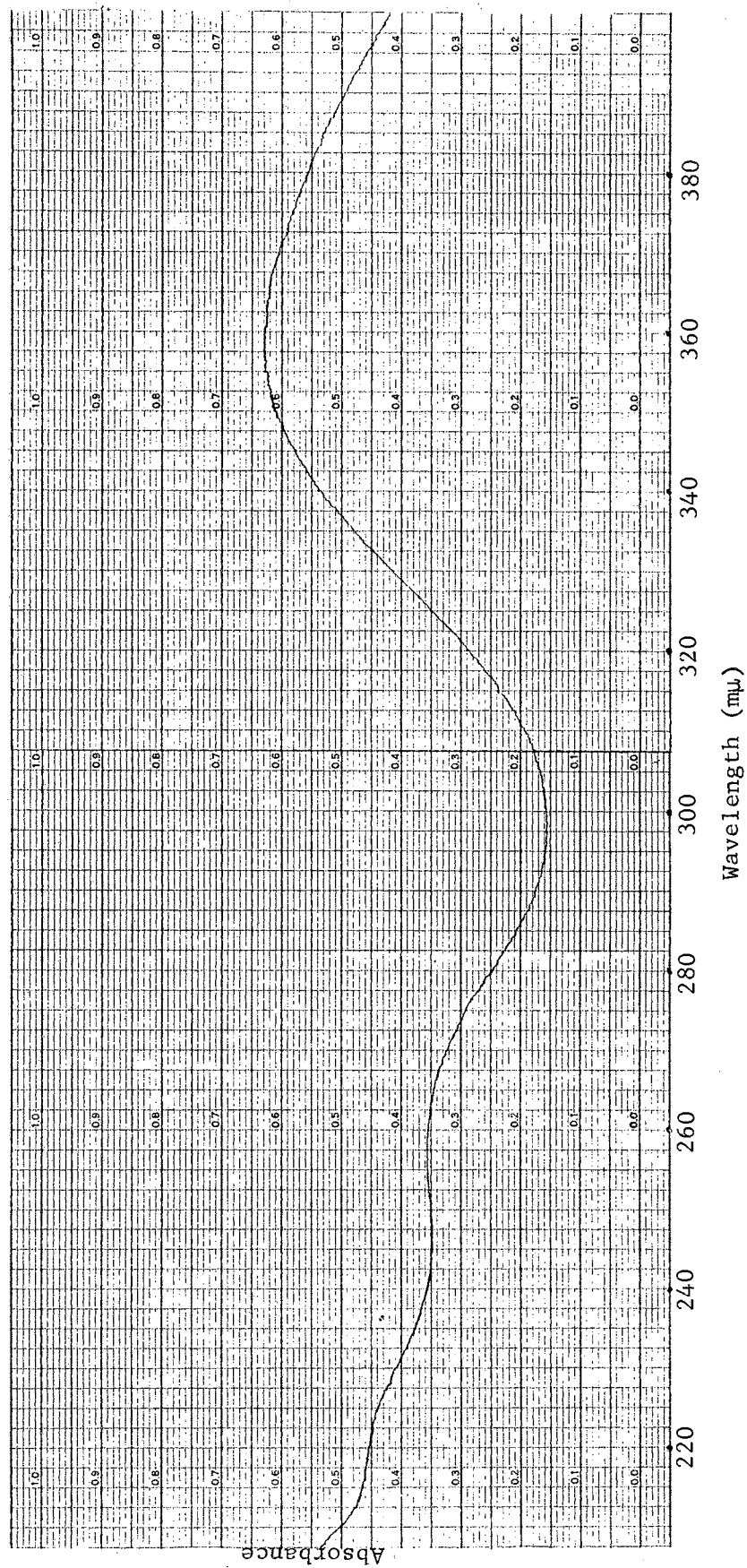
DNP of $C_6H_5C(O)P(O)(OCH_3)_2$ (XII); 2.52×10^{-5} (methanol) molar

Wavelength (mμ)

Absorbance

Plate XIII

DNP of p-(t-C$_4$H$_9$)C$_6$H$_4$C(O)P(O)(OCH$_3$)$_2$ (XIII); 2.64 x 10^{-5} (methanol)
molar

Plate XIV

Absorbance

Wavelength (mμ)
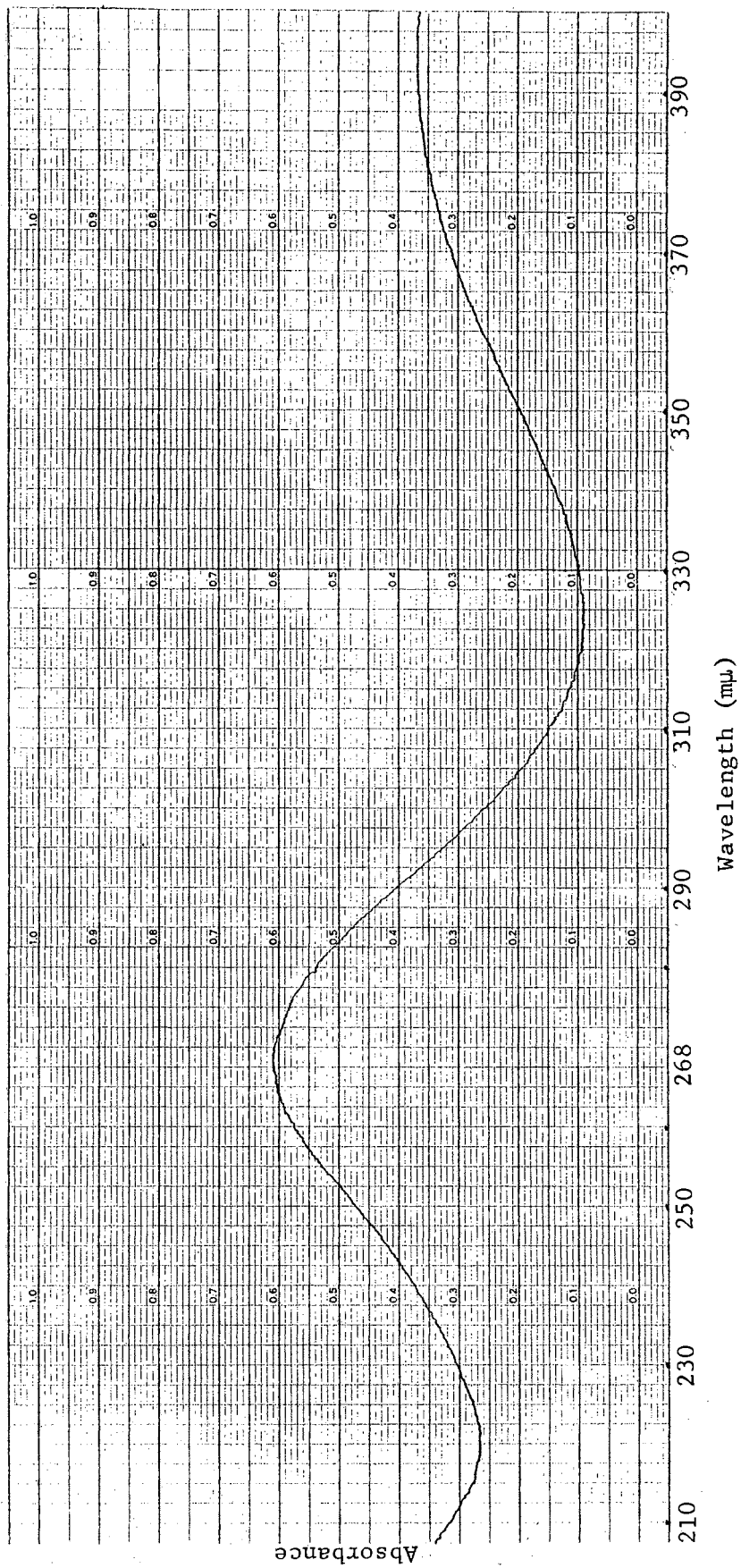
DNP of p-CH$_3$OC$_6$H$_4$C(O)P(O)(OCH$_3$)$_2$ (XIV); 1.49 x 10^{-5} (methanol) molar
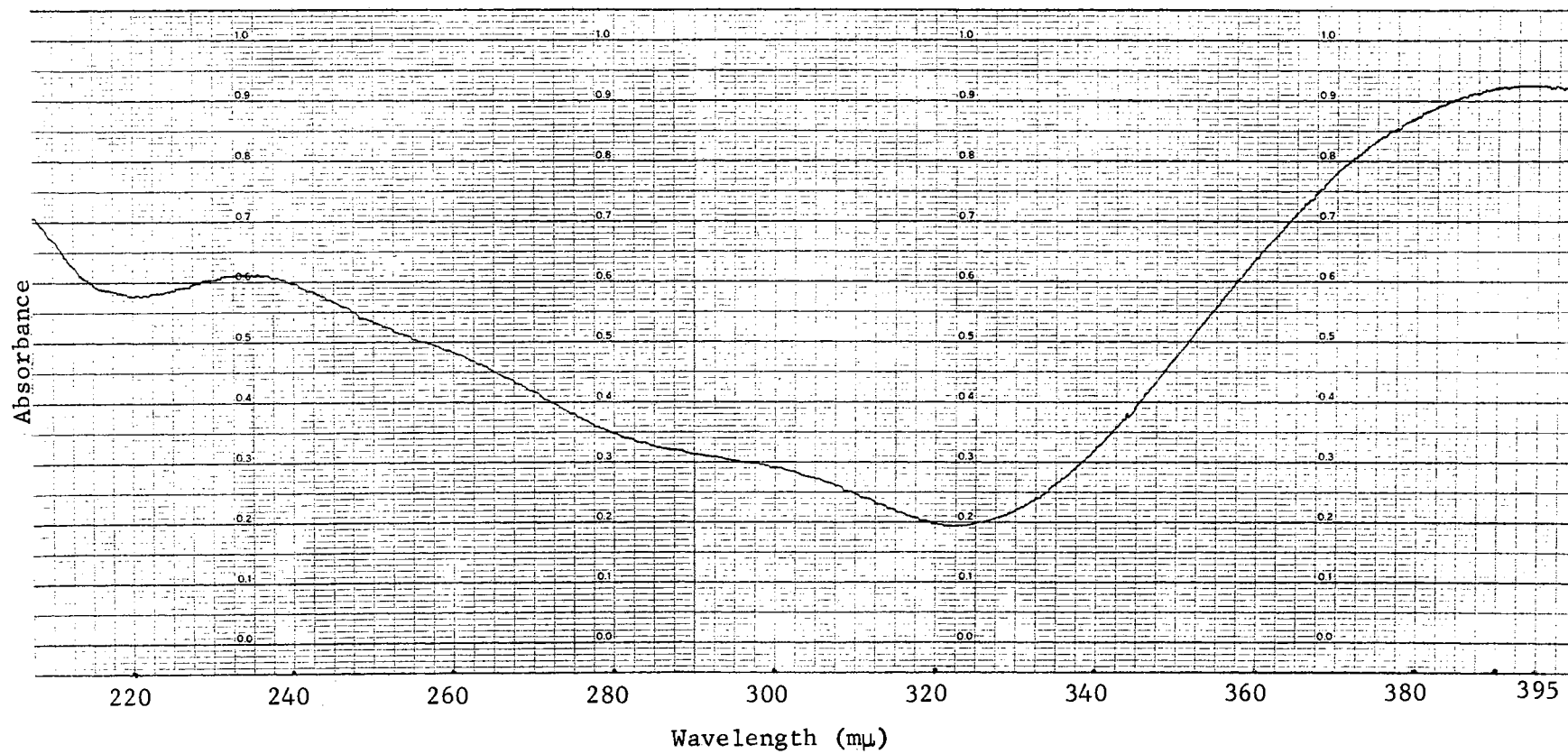
Plate XV

DNP of $\underline{p}$-CH$_3$OC$_6$H$_4$C(O)P(O)(OC$_2$H$_5$)$_2$ (XV); 3.53 x 10^{-5} (methanol)
molar

43

Plate XVI

Wavelength (mμ)

Absorbance
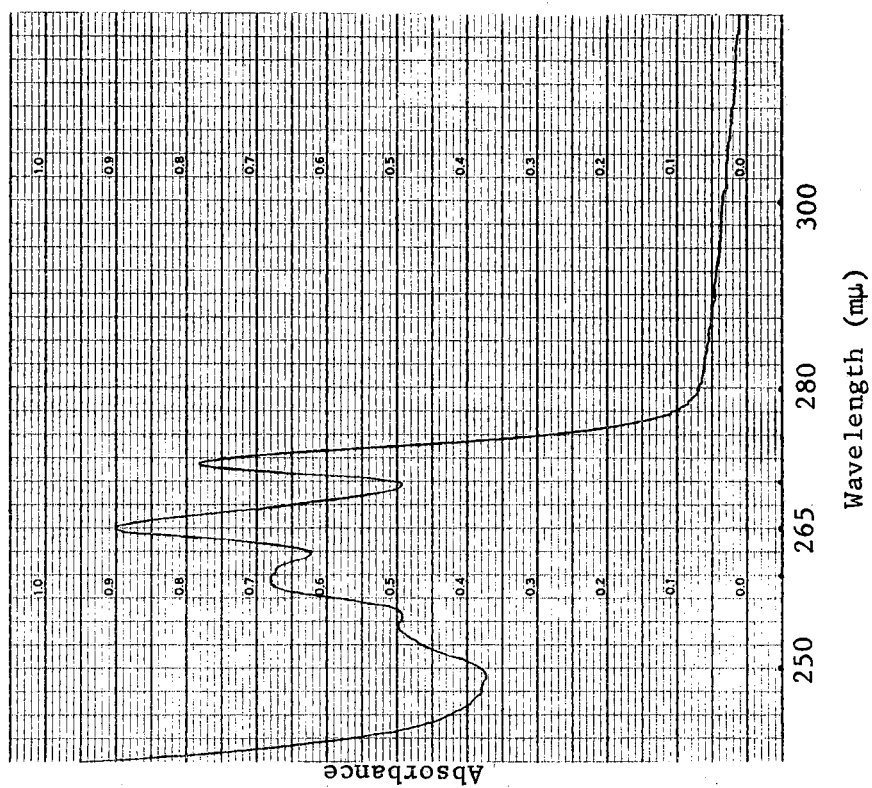
$(C_6H_5)_2P(O)CH=CH_2$ (XVI); 7.32×10^{-4} (cyclohexane) molar

Plate XVII

Wavelength (mμ)

Absorbance
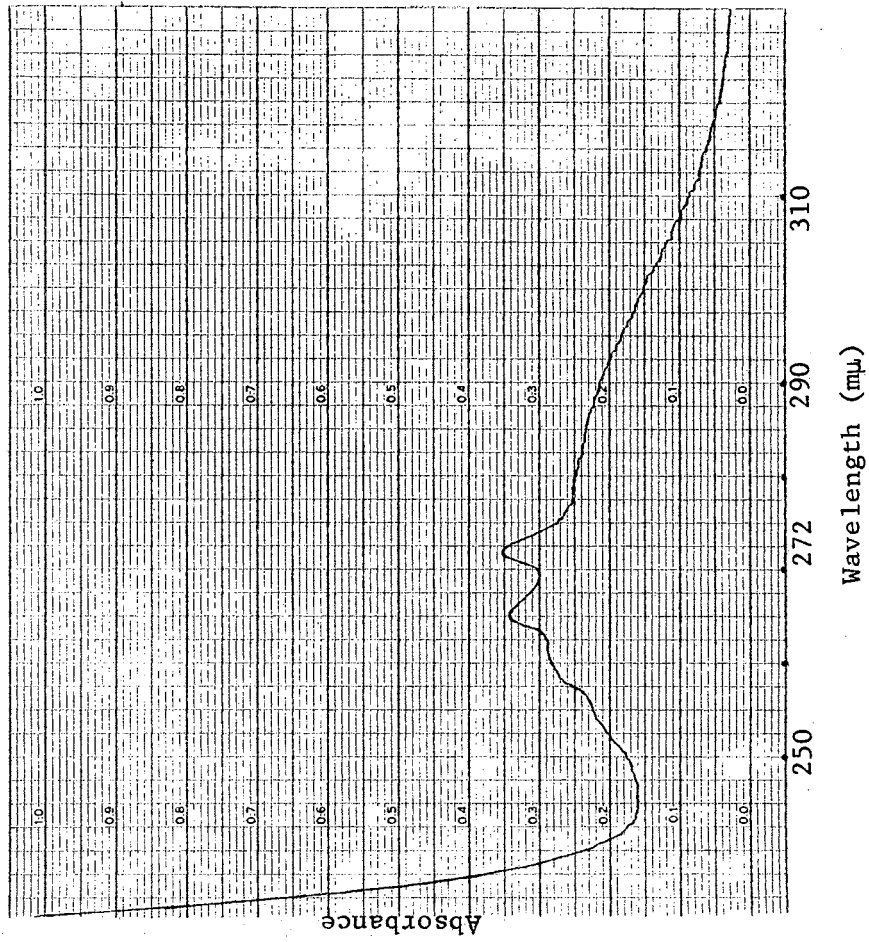
$(C_6H_5)_2P(O)CH=CHCH_3$ (XVII); 1.27×10^{-4} (cyclohexane) molar

Plate XVIII
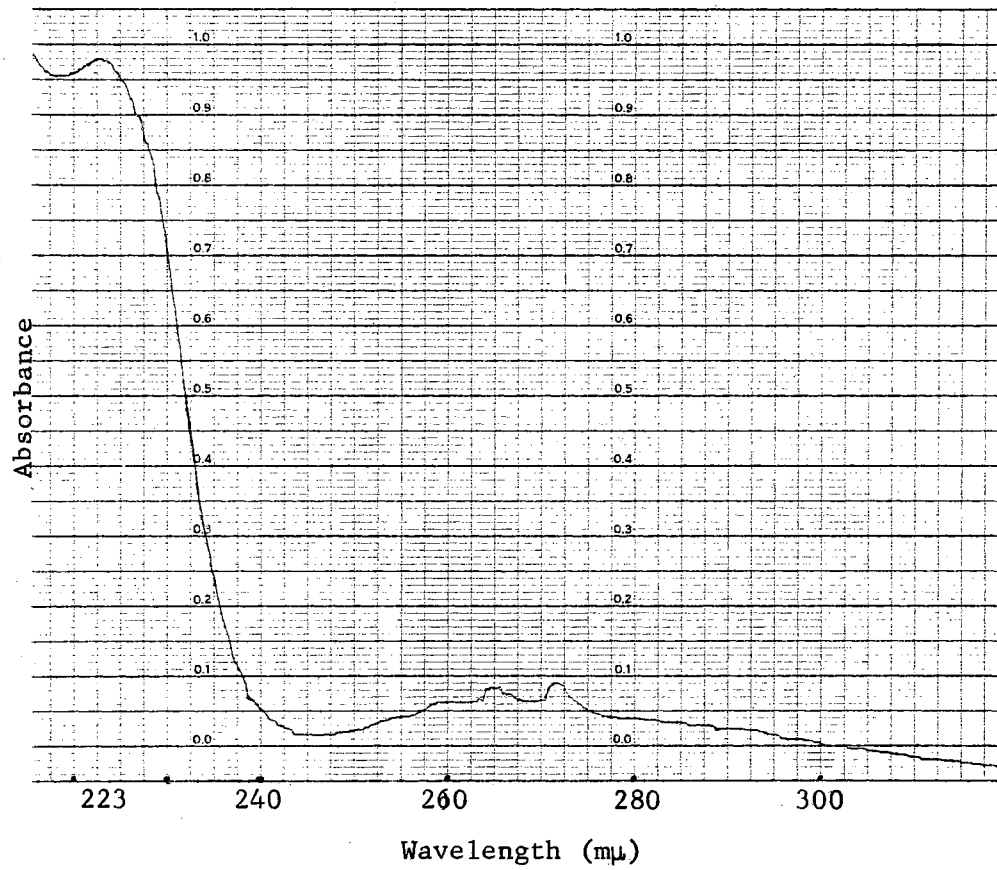
$(C_6H_5)_2P(O)CH=CH_2$ (XVI); 5.86×10^{-5} (cyclohexane)
molar

Plate XIX
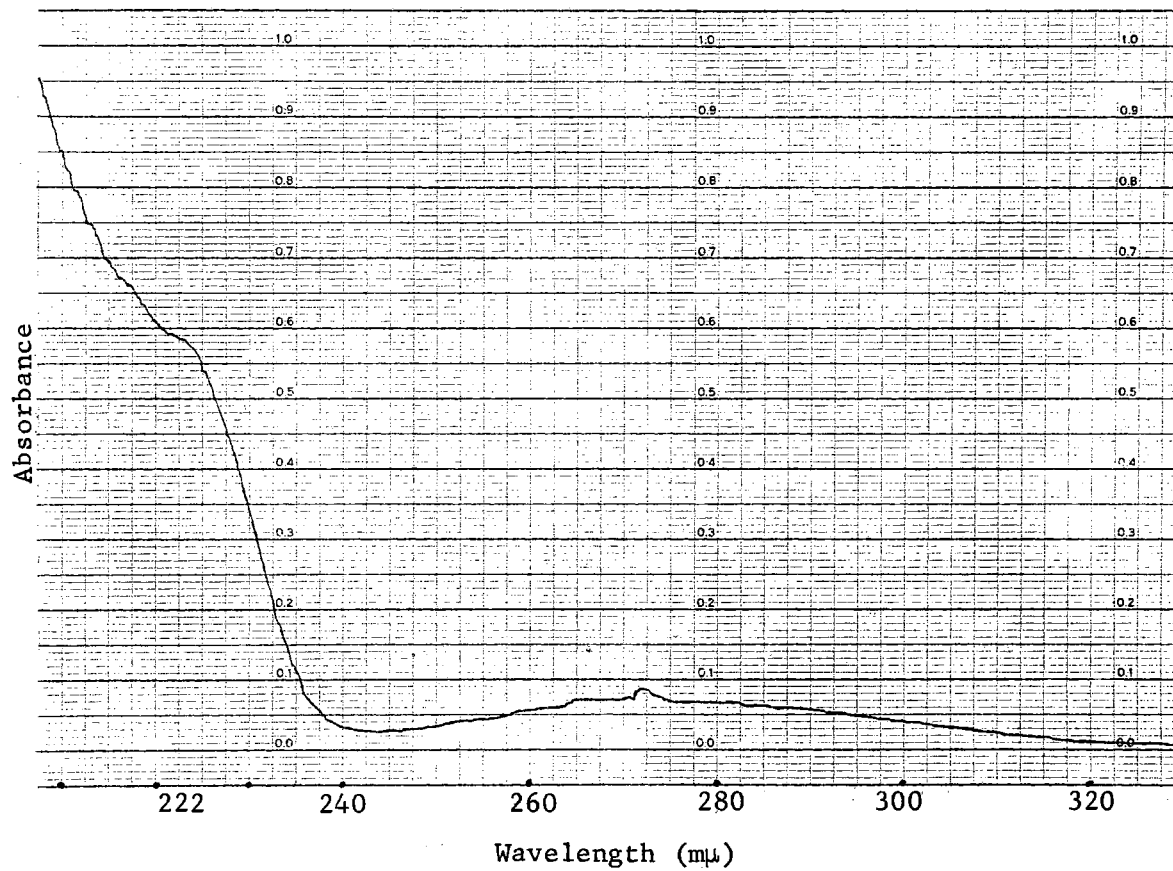
$(C_6H_5)_2P(O)CH=CHCH_3$ (XVII); 2.54 x 10^{-5} (cyclohexane)
molar

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