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GRADUATE COLLEGE

I. THE CRYSTAL AND MOLECULAR STRUCTURE OF TRICYCLO-[4.4.2.0^{1,6}]DODECA-3,8-DIENE-11,12-DIONE

II. LONG-RANGE EFFECTS OF PI ELECTRONS ON $n\!\rightarrow\!\pi^*$

TRANSITIONS OF <u>CIS</u> *α*-DIKETONES

A DISSERTATION

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SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

ROBERT FINK Norman, Oklahoma

- I. THE CRYSTAL AND MOLECULAR STRUCTURE OF TRICYCLO-[4.4.2.0^{1,6}]DODECA-3,8-DIENE-11,12-DIONE
 - II. LONG-RANGE EFFECTS OF PI ELECTRONS ON $n \rightarrow \pi^*$ TRANSITIONS OF <u>CIS</u> α -DIKETONES

APPROVED BY

DISSERTATION COMMITTEE

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J. D. AND R. J.

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PART I

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRICYCLO-[4.4.2.0^{1,6}]DODECA-3,8-DIENE-11,12-DIONE

CHAPTER I

INTRODUCTION

Tricyclo [4.4.2.0^{1,6}]dodeca-3,8-diene-11,12-dione, $C_{12}H_{12}O_2$, is one of a series of tricyclic compounds synthesized by Bloomfield and co-workers.^{1,2} The visible and ultraviolet absorption spectra of this compound as well as its dihydro and tetrahydro derivatives have also been reported.³ The title compound and its dihydro derivative show absorption bands for electronic transitions at unusually long wavelengths, compared to other unsubstituted α -diketones.⁴⁻⁶ To investigate the cause for this red shift, as well as other interesting features of the low-energy absorptions of these tricyclic diketone systems in greater detail, it was deemed necessary to obtain more information about their molecular conformations. The crystal structure of the title compound was therefore determined to yield possible clues about the molecular conformations in solution.

CHAPTER II

EXPERIMENT'AL

A sample of tricyclo $[4.4.2.0^{1,6}]$ dodeca-3,8-diene-11,12-dione, henceforth to be called 2DB, with a 1°C melting point range was supplied by Bloomfield.⁷ Crystals were obtained by slowly cooling a solution of 2DB in redistilled n-hexane from 25°C to 0°C over a period of two days. Plate-like crystals were obtained in this manner. They showed narrow, symmetric diffraction peaks and were judged suitable for data collection.

Special care had to be taken with this compound due to its relative instability. The pink crystals of 2DB showed a white, powdery deposit on the edges after one day's exposure to an open atmosphere at room temperature. A solution of 2DB will completely decolorize within a day at room temperature when exposed to light. This decomposition is due to decarbonylation and is accelerated by light.^{7,8} When protected from light and stored in a freezer, crystals and solutions of 2DB have remained stable for extended periods of time. Consequently, crystals were stored at low temperatures and only used in subdued light as much as possible.

A method was sought which would retard the crystal decomposition and allow data taking at room temperature. For this purpose, intensities of several reflections were monitored as a function of time. For crystals

kept at room temperature in subdued light, and only intermittently exposed to x-rays, an average intensity loss of about 1% per hour was obtained. This intensity loss was only slightly greater when crystals were kept in the x-ray beam continuously. For better protection against light, a new crystal was completely coated with India ink and placed in the x-ray beam for seven hours. The average intensity loss of five reflections was 0.7% per hour, still far too rapid for satisfactory data taking. Crystals sealed in an ink-coated glass capillary tube showed an average intensity loss of 0.6% per hour during thirteen hours of continuous x-ray exposure.

A new crystal of 2DB was mounted on a goniometer and coated with a thin layer of hair spray. During eleven hours of continuous x-ray exposure, fifteen reflections were monitored. An average intensity decrease of only 0.03% per hour was obtained. This seemed to be a satisfactory way to preserve the crystal at room temperature and was consequently used with the data crystal.

All diffraction work was done with the General Electric XRD-5 diffractometer, using CuK_{α} radiation and nickel filters. The diffraction pattern of 2DB showed that the crystal belongs to the monoclinic system with the approximate unit cell dimensions a = 7.38 Å, b = 11.49 Å, c = 12.92 Å, and $\beta = 115.52^{\circ}$. Systematic absences were found in the hOg zone for those reflections where g is odd and for OkO reflections with k odd. This indicated that the space group is $P2_1/c$. The crystal density was measured by the flotation method using an aqueous potassium iodide solution. The experimental value of 1.251 g/cc agreed reasonably well with the calculated density of 1.264 g/cc, based on the approximate unit

cell parameters and four molecules of $C_{12}H_{12}O_2$ per unit cell.

The two-theta values of 38 reciprocal lattice points were accurately measured, using a 1° take-off angle, and used in a least-squares cell refinement program. (A list of all programs used is presented in Appendix A.) The improved unit cell parameters and calculated crystal density are hown in Table 1.

The diffraction intensities of h \bar{k} ℓ and h \bar{k} $\bar{\ell}$ reflections with $2\theta \leq 140^{\circ}$ were measured as integrated intensities using a theta-two theta scan at a 2° take-off angle. This encompassed 1870 independent reflections, excluding the systematic absences. Each diffraction intensity was corrected for background radiation by measuring the intensity at each side of the peak for half of the scanning time and subtracting this quantity from the total peak intensity to yield a net diffraction intensity. Of the 1870 intensities measured, 131 were considered too weak to be observed. They showed a net diffraction count of seven or less and a value of seven was assigned as their net diffraction intensity.

Two crystals were required to measure all diffraction intensities. They were of similar shape, irregular flat plates, and of slightly different size. The first crystal measured 0.69 by 0.55 by 0.19 mm while the dimensions of the second crystal were 0.69 by 0.52 by 0.29 mm. Each crystal was coated with a thin layer of hair spray at the start and kept in subdued light at all times. The intensities of 987 reflections were measured on the first crystal and 883 on the second crystal. The intensity of one reflection was measured after approximately each hour of x-ray exposure and used to scale the intensities to correct for crystal decom-

TABLE 1

UNIT-CELL DATA

Space Group $P2_1/c$ 4 Molecules in the Unit Cell Unit-Cell Dimensions $a = 7.438 \pm 0.003A$ $b = 11.539 \pm 0.005$ $c = 12.935 \pm 0.005$ $\beta = 116.22 \pm 0.02^{\circ}$ Reciprocal Unit-Cell Dimensions $a^* = 0.14987 \pm 0.00004 (A)^{-1}$ $b* = 0.08666 \pm 0.00004$ $c* = 0.08618 \pm 0.00002$ $\beta * = 63.78 \pm 0.02^{\circ}$ Crystal density Measured = 1.251g/ccCalculated = 1.255Unit-Cell Volume = $995.9(\text{\AA})^3$ F(0,0,0) = 400Equivalent Positions $(x,y,z), (-x,y+\frac{1}{2},\frac{1}{2}-z),$ $(-x, -y, -z), (x, \frac{1}{2}-y, \frac{1}{2}+z)$

position. In addition, the intensities of ten reflections, on or near the reciprocal crystal axes, were measured after every four hours of x-ray exposure. Only a small, general decrease in diffraction intensities was obtained for these reflections with x-ray exposure time. This decrease was more pronounced for the second data crystal, approximately 10% when the crystal was discarded. Crystal decomposition, evidenced by a white, powdery deposit on the crystal edges, was also more pronounced for the second crystal. Each crystal was exposed to x-rays for approximately 80 hours. The mosaic spread was similar for both crystals and was checked at the beginning and close to the end of data taking. A change in ϕ (ω for OkO reflections) of 0.45 degrees from one base of a peak to the other for a new crystal increased to 0.75 degrees after nearly 80 hours of x-ray exposure. These values were nearly identical in the directions of the three reciprocal axes. The first data crystal was discarded after about 80 hours of x-ray exposure due to the marked increase in mosaic spread. This resulted in quite broad diffraction peaks and slowed the data collection process considerably.

Thirty-one common reflections were measured on both crystals to allow the two data sets to be scaled to a common base. The intensities of most reflections were measured with a common tube current and nickel filter. However, the very high intensities of a few reflections necessitated the use of thicker filters and/or a lower tube current. Appropriate current-filter factors were obtained by measuring the integrated intensities of three suitable reflections, five times each, for each pair of currents and/or filters. The average value of every 15 ratios thus obtained was used as a current-filter factor.

Diffraction data are generally subjected to a series of corrections before being used for further analyses. A data reduction-absorption correction program was used for this purpose. Each integrated intensity was first diminished by the measured background count. This value was then multiplied by the appropriate current-filter factor, when applicable. To correct for the slow decomposition of the crystal, as evidenced by the decreasing intensity of the hourly monitor with x-ray exposure time, each group of reflections measured between two monitor reading was multiplied by the factor M_i/M_t , where M_i is the background corrected intensity of the one-hour monitor as first determined on the new crystal and M_t is the arithmetic average of the monitor's values before and after the group of reflections were measured.

Another modification of the data is to correct each diffraction intensity for the absorption of x-rays by the crystal. When a beam of x-rays passes through a crystal, it may suffer a significant decrease in intensity due to absorption. This intensity decrease may be described by an equation common to absorption processes;¹⁰ I = $I_0 e^{-\mu \tau}$, where I_0 is the intensity of the incident beam, I is the intensity of the beam after it has traveled $\tau_{\rm CM}$ through the crystal, and μ is the linear absorption coefficient expressed in reciprocal centimeters. This coefficient is calculated by¹¹ $\mu = \frac{n}{V} \sum_{i} (\mu_a)_i$, where n is the number of asymmetric units per unit cell, V is the volume of the unit cell, and the terms $(\mu_a)_i$ are the atomic absorption coefficients of all atoms in one asymmetric unit. These path-dependent absorption corrections are most important for crystal shapes which are far from spherical and where the molecule has one or more heavy atoms. Here the large atomic absorption coefficients

of the heavy atoms can cause significant differences in the ratios I/I_0 for reflections where the x-ray beam must traverse different thicknesses of crystalline material.

Two other corrections are routinely made on diffraction intensity data, the Lorentz and polarization corrections. The Lorentz factor (L) arises due to the manner in which intensity data are collected, namely, not all diffraction points are kept under diffraction conditions for the same length of time. For diffractometer data using a theta-two theta scan, the crystal is rotated at a constant angular velocity. The time required for a reciprocal lattice point to pass through the sphere of reflection is proportional to the inverse of sin 2θ , where θ is the diffraction angle. The Lorentz factor, $L = (\sin 2\theta)^{-1}$, is thus employed for diffractometer data. The second correction accounts for a phenomenon that is common to reflection and diffraction processes of electromagnetic radiation, partial or total polarization of the radiation beam after interacting with the reflection or diffraction planes. The electric vectors of an incident, unpolarized beam of x-ray photons can be resolved into two components, one which is parallel to the reflecting surface and another which is perpendicular to the first. Waves with their electric vector parallel to the reflecting surface are reflected to an extent that is proportional to the electron density in the plane. The intensity of the reflected waves associated with the other component of the electric vector depends on the electron density in the plane and the angle of incidence, varying as $\cos^2 2\theta$. The intensity decrease of the overall beam, due to polarization, is given by the polarization factor $p = 1/2 (1 + \cos^2 2\theta)$. Since the Lorentz and polarization effects are both only functions of the

diffraction angle, intensity corrections can conveniently be made for both effects by dividing the diffraction intensities by the Lorentzpolarization factor, Lp = $(1 + \cos^2 2\theta)/(2 \sin 2\theta)$.

Absorption corrections were made on the diffraction intensities in a manner described above. Each crystal face was identified by the indices of the crystallographic plane most nearly parallel to it and the perpendicular distance from each face to a common internal point was determined. From this, the average distance the x-ray beam traveled inside the crystal was calculated for each diffraction intensity by a Gaussian interpolation method. Values for atomic absorption coefficients applicable to Cu K_a radiation were taken from the International Tables for X-ray Crystallography¹¹ as 0.073 x 10⁻²³, 9.17 x 10⁻²³, and 30.5 x 10^{-23} cm² for hydrogen, carbon, and oxygen, respectively. This gave a linear absorption coefficient of 6.905 cm⁻¹.

The absorption corrected intensities of the 31 common reflections measured on both crystals were compared to obtain a crystal scaling factor. Based on these values the average intensity ratio I(crystal 1)/ I(crystal 2) = 0.77 ± 0.03 was obtained. Thus, all intensities measured on the second data crystal were multiplied by 0.77 and the two data sets combined at this point. Lorentz-polarization corrections were then made to calculate relative structure factor amplitudes from the intensities as $|F(hkk)|_r^2 = I(hkk)/Lp$.

CHAPTER III

SOLUTION OF THE CRYSTAL STRUCTURE

Patterson Analysis

The atomic coordinates of the unit cell content may be inferred from the electron density variations within the unit cell. Electron density functions can be expressed by means of Fourier series as shown in equations 1a and 1b,

$$\rho(\mathbf{x},\mathbf{y},\mathbf{z}) = \frac{1}{V} \frac{\Sigma}{h} \frac{\Sigma}{k} \frac{\Sigma}{k} F(hk\ell) \exp[-2\pi i (hx+ky+\ell z)]$$
(1a)

$$\sigma(\mathbf{x},\mathbf{y},\mathbf{z}) = \frac{1}{V} \frac{\Sigma}{h} \frac{\Sigma}{k} \frac{\Sigma}{k} |F(hkl)| \cos[2\pi (hx+ky+lz)-\alpha(hkl)], \qquad (1b)$$

where V = volume of the unit cell, x,y, and z are fractional coordinates, $\rho(x,y,z)$ is the electron density at a point (x,y,z), F(hkl) is the structure factor for reflection hkl, and $\alpha(hkl)$ is the phase angle of F(hkl) relative to a specified origin. The indices hkl range from minus to plus infinity. The equations above can generally not be used directly to calculate the electron density functions since only the structure factor amplitudes, |F(hkl)|, can be obtained from experimental diffraction intensities and not the phase angle $\alpha(hkl)$ or the true form of the structure factor F(hkl) required in equation 1a. The structure factor of a reflection hkl is given by

$$F(hkl) = \sum_{j=1}^{N} f_j \exp[2\pi i (hx_j + ky_j + lz_j)]$$
(2)

where j sums over the N atoms in the unit cell, x_j, y_j , and z_j are the fractional atomic coordinates, and f_j is the scattering factor for atom j. A more explicit form of the scattering factor is $f_j = f_{o,j} e^{-BS^2}$ where $f_{o,j}$ is the scattering factor for an atom j at rest, $S = (\sin \theta)/\lambda$ and B is the temperature factor of atom j. It is thus seen that the calculation of electron densities requires data which can not be directly obtained from diffraction intensities. A less direct method, the Patterson method, ¹² is often useful for finding atomic coordinates.

The Patterson function may be defined by 13

$$P(u,v,w) = \frac{1}{V} \int_{0}^{1} \int_{0}^{1} \int_{0}^{1} \rho(x,y,z) \rho(x+u,y+v,z+w) dx dy dz$$
(3)

where x,y,z and u,v,w are fractional coordinates, (x,y,z) and $\rho(x+u, y+v, z+w)$ are electron densities at the points (x,y,z) and (x+u, y+v, z+w). Any two or more points of significant electron density within the unit cell, which may be connected by a vector with components (u,v,w), will give a significant contribution to a Patterson peak, P(u,v,w). Additional peaks, generated by the Patterson symmetry of the space group will also be revealed. Thus, a three dimensional Patterson calculation yields peaks which represent the endpoints of vectors connecting volume elements of high electron density. The distance from the origin to a Patterson peak represents the distance between the atom pairs which are revealed by this peak and the magnitude of the peak is proportional to the product of the electron densities connected by this vector. This method is most useful when a heavy atom is present, thus yielding very prominent heavy-heavy atom peaks and also prominent heavylight atom peaks. When no heavy atoms are present in the molecule the interpretation of Patterson maps becomes more difficult. For such molecules, a large number of Patterson peaks with similar magnitudes are obtained. Any peaks of prominent magnitudes are merely the results of overlapping peaks. It is therefore almost impossible to associate a calculated peak with a specific pair of atoms. Because of the small size of the molecule in question, it was still thought useful to seek the trial structure by the Patterson method, although symbolic addition procedures were also started.

A usable form for the Patterson function may be obtained by replacing the electron density functions by their Fourier expansions, Eq. 1. Integration yields

$$P(u,v,w) = \frac{1}{V} \sum_{k=1}^{\infty} \sum_{k=1}^{\infty} |F(hkl)|^2 \cos[2\pi(hu + kv + lw)].$$
(4)

Since $|F(hkl)|^2$ is obtainable from the diffraction intensities, P(u,v,w) can be calculated for any point (u,v,w) desired.

A Patterson calculation was made for one-fourth of the unit cell. This encompasses a total asymmetric unit for the space group $P2_1/c$. For convenience, the asymmetric unit was chosen as u = 0 to 1, v = 0 to $\frac{1}{2}$, and w = 0 to $\frac{1}{2}$, and P(u,v,w) was evaluated at 0.26 Å increments over this range of u,v, and w. The Patterson peaks were sharpened by using $|F(hkl)|^2$ M(S) as coefficients in equation 4 instead of $|F(hkl)|^2$. The sharpening functions M(S) = $(\sum_{i=1}^{2} \frac{2}{i}/\sum f_{o,i}^2)e^{i}w$ was used for this purpose. Here Z_i is the atomic number of atom 1, S = $(\sin \theta)/\lambda$, and the summations extend over all atoms in the unit cell. The magnitudes of the peaks were scaled to yield the arbitrary value of 5000 for the origin peak. This represents the sum of all vectors between every atom and itself. To obtain the trial structure from the Patterson, it was proposed to first find the orientations of the molecules in the unit cell by looking at prominent short vectors and then finding atomic coordinates by looking at the Harker sections.¹⁴ Certain features of the molecules suggested that this is feasible as can be seen from Figure 1. The rigidity of the four-membered ring was expected to keep the two six-membered rings nearly in the boat form. The four atom pairs C(1)-C(6), C(3)-C(4), C(8)-C(9), and C(11)-C(12) should thus be nearly parallel and their interatomic vectors revealed as one Patterson vector with a very prominent magnitude. Parallel to this vector, but of greater lengths, should be two other vectors, one for the atom pairs C(2)-C(5) and C(7)-C(10), and another for O(1)-O(2). These vectors were sought first in the Patterson map.

A program was written to calculate the lengths of each vector, the angle between the vector and the a-c plane (γ , measured in the direction of the b axis), and the angle between the projection of the vector on the a-c plane and the c axis (δ , measured in the direction of the positive a axis).

Six prominent short vectors were found in the a-c plane as shown in Table 2. Vector V_1 represents the largest peak in the Patterson map. Its length of 1.47 Å and magnitude of 1138 agree well with the expected values for a Patterson vector for the atom pairs C(1)-C(6), C(3)-C(4), C(8)-C(9) and C(11)-C(12) if these atoms are arranged such that their bonds are parallel or nearly parallel to each other. V_1 was therefore assigned to represent these four atom pairs. A vector approximately 2.8 Å in length for the atom pairs C(2)-C(5) and C(7)-C(10) and another



FIGURE 1. Atom-numbering scheme in the molecule.

TABLE 2

Vector	Length (Å)	Peak height	γ (⁰)	δ ([°])
vı	1.47	1138	0	-19
v ₂	3.00	630	0	-20
v ₃	1.53	397	0	101
V ₄	1.50	445	0	44
v ₅	2.50	487	0	13
v ₆	2.58	342	0	-51

PATTERSON VECTORS IN THE a-c PLANE

vector of length 3.2 Å for O(1)-O(2) were expected parallel to V_1 . Although two distinct peaks were not found, vector V_2 may well represent the resultant of two closely spaced overlapping peaks, thus V_2 was assigned to these atom pairs. This peak indeed appeared to be unsymmetric. A major part of determining the molecular orientation in the unit cell had thus been achieved with this interpretation. The C(1)-C(6) bond, and all others expected to be parallel to it, as mentioned above, are parallel to the a-c plane and are oriented 19-20° from the c axis toward the negative a axis. The remaining vectors in Table 2 were of great interest. Such vectors can arise by placing four atoms of a six-membered ring parallel to the a-c plane as shown in Figures 2 and 3. The magnitudes of these peaks suggested that each of the vectors, V_3 to V_6 , represents two C-C vectors. This is possible when at least one six-membered ring is in a "wing up" conformation. Possible atom pairs which could yield vectors V_3 to V_6 are given in Table 3.



FIGURE 2. Possible atomic arrangements for Patterson peaks in the a-c plane.



FIGURE 3. Alternant atomic arrangements for Patterson peaks in the a-c plane.

TABLE 3

ATOM PAIRS PARALLEL TO THE a-c PLANE

Vector	Atom Pairs	Alternant Atom Pairs
v ₃	C(4)-C(5), C(6)-C(7)	C(1)-C(2), C(9)-C(10)
v ₄	C(2)-C(3), C(1)-C(10)	C(5)-C(6), C(7)-C(8)
v ₅	C(2)-C(4), C(6)-C(10)	C(1)-C(5), C(7)-C(9)
v ₆	C(3)-C(5), C(1)-C(7)	C(2)-C(6), C(8)-C(10)

Two of the most prominent Patterson peaks which were not in the a-c plane were considered next. These are shown in Table 4.

TABLE 4

PROMINENT PATTERSON VECTORS NOT PARALLEL TO THE a-c PLANE

Vector	Length (Å)	Peak height	γ (⁰)	δ(⁰)
v ₇	2.52 A	717	23	71
v ₈	5.48	531	23	62

Vector V_7 appeared to be of special significance. It is perpendicular to V_1 , it has the proper length to connect two atoms of a six-membered ring which are separated by one atom, and the value of 23° for γ is exactly that expected for a vector connecting two atoms such as C(1) and C(3) when atoms C(2), C(3), C(4) and C(5) have equal y coordinates. The magnitude and width of this peak suggested that V_7 connects more than two atom pairs and that the molecule therefore possesses approximately mm symmetry with both wings folded up. Such a symmetry assignment would yield the long vector V_8 for the atom pairs C(3)-C(9) and C(4)-C(8), although this could well be an intermolecular vector.

With the eight vectors assigned so far, a tentative conformation and orientation within the unit cell were chosen as shown in Figure 4. The molecular fragments C(2)-C(3)-C(4)-C(5) and C(10)-C(1)-C(6)-C(7)each lie in planes which are parallel to the a-c plane. Possible additional peaks which should be obtained for this orientation were found for several atom pairs to further confirm this orientation.

For the space group $P2_1/c$, the symmetry of the Patterson is P2/m. The orientation represented in Figure 4 is therefore only one of four possible orientations which would yield the same Patterson peaks. A second orientation may be obtained by rotating the molecule 180° in the a-c plane and two further orientations are obtained by reflecting the two previous orientations through the a-c plane.

Possible coordinates were now sought in the Harker sections. The presence of two-fold screw axes in this space group yields the symmetry-related coordinates x,y,z, and $-x,\frac{1}{2} + y, \frac{1}{2}-z$. By taking the difference between these coordinates, 2x, $\frac{1}{2}$, $2z + \frac{1}{2}$ is obtained. Thus for two molecules related by a two-fold screw axis, a Patterson peak should be found in the Harker plane, $v = \frac{1}{2}$, for each symmetry related pair of atoms. A projection of the molecule onto the a-c plane should, therefore, be seen in this larker plane at twice its size, from which x and z coordinates can be obtained. The atomic positions of a given atom in two molecules related by the c-glide plane are x,y,z and x, $\frac{1}{2}-y$, $\frac{1}{2} + z$. The difference between these coordinates is 0, $\frac{1}{2} + 2y$, $\frac{1}{2}$. A Harker line therefore exists at u = 0, $w = \frac{1}{2}$ to yield information about the atomic y coordinates.



FIGURE 4. Trial orientation.

A scale drawing was made of the Harker plane, $v = \frac{1}{2}$, to attempt to find possible x and z coordinates. Although many prominent peaks existed in this plane, unique molecular projections were not apparent. From the partial orientation established by vectors V_1 to V_8 , it was clear that atom pairs, or groups of four atoms per molecule, had similar y coordinates. The Harker plane, therefore, contained peaks which not only represented vectors between symmetry-related atoms but also vectors between all combinations of atoms having similar y-coordinates. Indeed, larger Patterson peaks are obtained in the Harker plane for two atoms not symmetry related than for two symmetry-related atoms. The Harker line at u = 0, $w = \frac{1}{2}$ contained prominent, but very broad peaks from which no clear information was discernible. Several possible projections onto the Harker plane and line were used to assign atomic coordinates. From these, intra- and intermolecular vectors were calculated for atom pairs not yet identified by Patterson peaks and the expected peaks were sought in Patterson map. None of the coordinate sets chosen were satisfactory in this search. Although this approach may be expected to yield a trial structure eventually, the symbolic addition procedure was pursued more actively at this point as a source for the trial structure.

Introduction to the Symbolic Addition Method

A number of methods have been proposed for the direct determination of structure factor phases. Many of these methods, including the symbolic addition procedure, have been reviewed by Woolfson¹⁵ in a recent book. Only a brief discussion of pertinent relationships will therefore be given here.

Structure factor phases can be obtained more readily for crystals

belonging to centrosymmetric space groups than noncentrosymmetric space groups. For such space groups, F(hkl) as given in Eq. 2 may be expressed as:

$$F(hk\ell) = \sum_{j=1}^{N/2} f_{j} \{ \exp[2\pi i (hx_{j} + ky_{j} + \ell z_{j})] + \exp[-2\pi i (hx_{j} + ky_{j} + \ell z_{j})] \}, \quad (5)$$

or

$$F(hkl) = 2 \sum_{j=1}^{N/2} f_{j} \cos[2\pi (hx_{j} + ky_{j} + lz_{j})].$$
(6)

The structure factor is, therefore, a real number for centrosymmetric space groups. Since |F(hkl)| can readily be obtained from the experimental diffraction intensities, only two values are possible for the correct expression of F(hkl).

$$\mathbf{F}(\mathbf{hkl}) = (+1) \left[\mathbf{F}(\mathbf{hkl}) \right] \tag{7}$$

or
$$F(hkl) = (-1) |F(hkl)|$$
 (8)

The phase problem has thus been simplified considerably since only two phases (signs) are possible. Earliest investigations have only been concerned with centrosymmetric crystals due to this simplicity; however, more recently J, Karle and I. L. Karle¹⁶⁻¹⁸ have also successfully applied direct methods to noncentrosymmetric cases.

For brevity, the following notation will be used in this discussion:

$$H = h_{i}, k_{j}, \ell_{i}$$

$$K = h_{j}, k_{j}, \ell_{j}$$

$$H-K = h_{i}-h_{j}, k_{i}-k_{j}, \ell_{i}-\ell_{j}$$

$$S(H) = sign of structure factor F(H)$$

$$HX_{i} = hx_{i} + ky_{i} + \ell z_{i}$$
The possibility of obtaining structure factor phases from their amplitudes can be seen by considering the Harker-Kasper inequalities.¹⁹ Two obvious relationships are

$$|F(0,0,0)| > 0$$
 (9)

and
$$|F(H)| < F(0,0,0)$$
 (10)

For a centrosymmetric space group, another useful inequality can be obtained. (Derivations of some of the inequalities given here may be found in Appendix B.)

$$\left(\frac{F(H)}{F(0,0,0)}\right)^{2} \leq \frac{1}{2} + \frac{1}{2}\left(\frac{F(2H)}{F(0,0,0)}\right)$$
(11)

If |F(H)| and |F(2H)| are both reasonably large, this inequality may demand that S(2H) = +. Application of this, as well as other Harker-Kasper inequalities, to the determination of signs requires that many relatively large structure factors are available. Ordinary structure factors are not suitable for such calculations. Their magnitudes decrease rapidly with an increase in the diffraction angle since atomic scattering factors decrease for higher order reflections. To circumvent this difficulty, the unitary structure factor, U(H), has been introduced. If all atoms in the unit cell are considered to be point atoms at rest, then they will have scattering factors which are equal to their atomic number, Z_i , independent of the diffraction angle. The structure factors for such a set of atoms, $F(H)_{pt}$, are related to the real structure factors by

$$F(H)_{pt} = F(H) \left[\sum_{i=1}^{N} Z_{i} \right] \left[e^{-BS^{2}} \sum_{i=1}^{N} f_{o,i} \right], \qquad (12)$$

where B is the overall temperature factor, $S = (\sin \theta)/\lambda$, and $f_{0,i}$ is the atom-at-rest scattering factor for atom i. Unitary structure factors employ this point-atom-at-rest model, but express each structure factor in the fractional form F(H)_{pt}/F(0,0,0). Thus

$$U(H) = F(H) \left[e^{-BS^2} \sum_{i=1}^{N} f_{o,i} \right] .$$
 (13)

From Eq. 13 it can be seen that U(H) and F(H) differ only in magnitude and that unitary structure factors will not show the rapid decrease in magnitude with increasing diffraction angles. From its definition, it can also be seen that the range of U(H) is -1 to +1.

Some Harker-Kasper inequalities, for space groups containing a center of symmetry, can now be conveniently expressed as:

$$U(0,0,0) = 1$$
 (14)

$$U(H) \leq U(0,0,0)$$
 (15)

$$U(H)^2 \leq \frac{1}{2}[1 + U(2H)]$$
 (16)

$$[U(H) + U(K)]^{2} \leq [1 + U(H + K)][1 + U(H-K)]$$
(17)

$$[U(H)-U(K)]^{2} \leq [1-U(H+K)][1-U(H-K)]$$
(18)

Equations 17 and 18 may be combined and rewritten in a slightly different form by expressing each structure factor as the product of its sign and magnitude. Considering both cases, S(H)S(K) = + and S(H)S(K) = -, the following relationships can be obtained:

$$(|U(H)| + |U(K)|)^{2} \le (1 + S(H)S(K)S(H + K)|U(H + K)|)$$

x $(1 + S(H)S(K)S(K-K)|U(H-k)|)$ (19)

$$(|U(H)| - |U(K)|)^{2} \le (1-S(H)S(K)S(H + K)|U(H + K)|)$$

 $\times (1-S(H)S(K)S(H-K)|U(H-k)|).$ (20)

If only sufficiently large |U|'s are involved, Eq. 19 may demand that one or both of the following equations be satisfied:

$$S(H)S(K)S(H + K) = +$$
 (21)

$$S(H)S(K)S(H-K) = +$$
 (22)

Thus, if S(H) and S(K) are known, one or two additional structure factor signs can be calculated. For two structure factors U(H) and U(K) with known signs but significantly different magnitudes, Eq. 20 can also place restrictions on S(H+K) and S(H-K) if |U(H + K)| and |U(H-K)| are sufficiently large.

A major difficulty encountered when employing inequalities is that generally not enough large unitary structure factors are obtained in a data set to generate a sufficient number of unambiguous signs. A representative electron density map of a structure can generally be calculated if about 15% of the structure factors, consisting primarily of the largest amplitudes, are correctly signed. It is often not possible to obtain this many signs, particularly for larger molecules. For a structure of N similar atoms in the unit cell, the root-mean-square value of U is approximately equal to $N^{-\frac{1}{2}}$.¹⁰ Thus, as the molecular size increases, the number of large U's and consequently the number of signs which can be calculated decreases.

Shortly after the appearance of the Harker-Kasper inequalities Sayre, 20 and Karle and Hauptmann^{21,22} derived equations which are not as

restrictive as the inequalities, but also not as exact. These equations express a probable relationship between structure factor signs. The Sayre equation was derived in terms of ordinary structure factors and may be expressed as (See Appendix C):

$$F(H) \sim \phi \sum_{K} F(K) F(H-K)$$
(23)

where ϕ is a scaling factor. When applied to centrosymmetric crystals, where the phase can only be +1 or -1, equation 23 yields the sign relationship

$$S(H) \sim S[\sum_{K} F(K) F(H-K)].$$
 (24)

Application of Eq. 24 requires a knowledge of many structure factor signs before one additional sign, S(H), can be calculated. However, Sayre showed that if |F(H)| is large, a tendency exists for all terms of the series to have the same sign. In particular, terms with both |F(K)|and |F(H-K)| large will have the same sign as F(H). Thus, a probable sign relationship can be established as

$$S(H) \sim S(K) S(H-K)$$
. (25)

It may be noted that this equation is very similar to Eq. 22. However, Eq. 25 is applied more liberally, namely, even if |U|'s in Eq. 19 are not large enough to place definite restrictions on the signs, Eq. 25 states that the relationship is still probably true if |F(H)|, |F(K)|, and |F(H-K)| are reasonably large.

Equation 25 still requires that two signs are known before an additional sign can be calculated. These starting signs can always be

obtained. For most space groups the origin of the unit cell may be placed at one of several positions. Moving the origin from one allowable position to another will change the signs of all structure factors of one class of reflections. Another choice of origin would change all signs of another class of structure factors. Conversely, by arbitrarily specifying the signs of some structure factors, the origin of the unit cell will be fixed. A study of which structure factors may arbitrarily be signed for the various space groups has been made by Hauptman and Karle^{22,23} and shows the following results. For all primitive centrosymmetric space groups in the triclinic, monoclinic, and orthorhombic systems, the sign of one structure factor in each class of reflections which are not structure invariants may be specified. Thus three signs may be arbitrarily chosen subject to the following conditions: (a) the crystallographic indices of the three structure factors must belong to different parity groups, (b) the indices of none of the chosen structure factors may belong to the parity group eee, and (c) the parity of linear combination of any two sets of indices may not be identical with the parity of the remaining set.

Mathematically equivalent results of the Sayre equation had been derived earlier by Karle and Hauptman²¹ and led to the development of the Sigma-2 equation,²²

$$S(H) \sim S[\sum_{K} E(K)E(H-K)].$$
(26)

The normalized structure factors, E, used here are related to the ordinary structure factors by

$$E(H) = F(H) / (\varepsilon \sum_{j=1}^{N} f_{j}^{2})^{\frac{1}{2}}, \qquad (27)$$

where f_j is the temperature-corrected scattering factor, $f_j = f_{o,j} e^{-BS^2}$. It may be noted that the three types of structure factors introduced so far, F, U, and E, differ only in magnitude but not in sign. The denominator in Eq. 27 again serves to increase the amplitudes of higher order structure factors and thus yield more relatively large E's in a data set. The factor ε corrects for space group extinctions, thereby reducing all E's to a common base.

Probability equations, which show the certainty of a calculated sign, have been derived and are most conveniently applied in the form given by Woolfson,²⁴ and Cochran and Woolfson.²⁵ In terms of normalized structure factors

$$P_{+}$$
 (H) $\simeq \frac{1}{2} + \frac{1}{2} \tanh[\sigma_{3}\sigma_{2}^{-3/2} | E(H) | \sum_{K} E(K)E(H-K)],$ (28)

where $\sigma_n = \sum_{i=1}^{N} Z_i^n$. A value of P_+ (H) \approx 1 indicates a high probability that S(H) = +, while P_+ (H) \approx 0 indicates a high probability that S(H) = -.

The importance of using only large structure factors in the sign determining process is again brought out. In the early stages, when only a few signs are known, a structure factor, E(H), might only be related to one pair of signed structure factors, E(K) and E(H-K). The Sigma-2 equation is then applied as $S(H) \sim S[E(K)E(H-K)]$, identical to Eq. 25. The summation in Eq. 28 will also contain only one term. This requires rather large |E|'s to yield P_+ (H) near 0 or 1. As more signs become available, the summation over K may include several terms. The signs of smaller structure factors, E(H), can then be determined with a high probability of being correct. The necessity of having large E's in the early stages specifies that the origin defining structure factors, in addition to satisfying the parity requirements, should be chosen from the largest few amplitudes in the data set. However, they should also be involved in as many triplets, of the type H, K, H-K, as possible so that several new signs can be calculated. Once a sign has been obtained, the signs of all symmetry related structure factors will automatically be given and can also be used to generate additional signs. For the space group $P2_1/c$, for example, the structure factor relationships are summarized by the following equations:²⁶

$$F(hkl) = F(hkl) \neq F(hkl), F(hkl) = F(hkl)$$
 for k+1 even, (29)

$$F(hkl) = -F(hkl) \neq F(hkl), F(hkl) = -F(hkl) \text{ for } k+1 \text{ odd}, \quad (30)$$

$$F(hkl) = F(hkl)$$
 for general reflections. (31)

The number of signs which can be calculated by Eqs. 25 or 26 is rather limited, however, when attempting to sign all large structure factors first. It is generally found that after a few signs have been calculated, no additional triplets of the type H, K, H-K exist where two of the indices are those of signed E's and the remaining index belongs to an unsigned structure factor. This often occurs after only a small fraction of the largest E's have been signed. A symbol sign, e.g. A, may be given to a new, unsigned structure factor at this point. By properly choosing this structure factor, a significant number of additional signs can be calculated in terms of ±A. After all possible signs have again been calculated, a new symbol sign, e.g. B, can be given to another unsigned E and signs in terms of ±B and ±AB can be calculated. This process may be repeated a few times, as needed. Alternatively, a few symbol signs may be assigned at the very beginning, along with the origin-defining signs. The proper choice of structure factors for these assignments allows the calculation of signs for most of the larger structure factors. Again, many of the signs will be in terms of symbols or combinations of symbols. After a sufficient number of signs have been calculated, the symbols can be evaluated. Most of the signed structure factors will be involved in several triplets. For a given structure factor, E(H), Eq. 25 may show S(H) to be equal to several symbols can be established. By looking at the signs of many structure factors, several independent relationships can be obtained. Similarly, the symbols may be evaluated in terms of + or -. Although discrepancies will occur when evaluating the symbols, most often a significantly larger number of equations will show a symbol to be equal to one sign instead of the other.

The symbolic addition method can easily be carried out by hand calculations once the normalized structure factors and triplet combinations have been obtained. In this case, the probability equation, Eq. 28 is too cumbersome to use. Eq. 25 is used directly, and any sign calculated by this equation is accepted as long as |E(H)|, |E(K)|, and |E(H-K)|are large. The choice of minimum values of |E|'s to be used is somewhat arbitrary, although in practice only |E|'s \geq 2.0 are often used in the early stages and |E|'s \geq 1.5 are allowed in later stages. When a computer is employed to calculate structure factor signs by this method, the probability equation can be conveniently applied in conjunction with Eq. 26. Criteria may be set to allow a sign to become accepted only when the

probability that it is correct exceeds a specified minimum. These acceptance limits are also somewhat arbitrary. It is very important that the first few signs are calculated correctly since most of the remaining signs will be obtained in terms of these signs. Thus, probabilities very close to 1.0 must be obtained in the early stages. As the process continues, the limits to be exceeded can gradually be lowered.

After a sufficient number of structure factors have been signed, 10-15% of the data, electron density maps (E-maps) are calculated which may yield the trial structure for the compound.

Application of the Symbolic Addition Method

The series of five computer programs, written by S. R. Hall²⁷ and revised by F. R. Ahmed,²⁸ were used for the structure factor sign determination of this structure. These programs employ the symbolic addition method in the manner described by Karle and Karle,¹⁸ using normalized structure factors and the Sigma-2 equation.

An overall isotropic temperature factor, B, and scale factor, K, were first calculated by means of a Wilson plot.²⁹ This yielded B = 4.63and K = 0.1437. Normalized structure factor amplitudes were then calculated for all reflections by Eq. 32,

$$|E(H)| = \frac{K e^{BS^2}}{(\epsilon \sum_{i=1}^{N} f_{0,i}^2)} |F(H)|. \qquad (32)$$

The experimental structure factor amplitudes, |F(H)|, are placed on an absolute scale by means of K. All |E|'s \geq 1.50 were retained for use in

the sign determination. This yielded 230 independent structure factors, about 12% of the total data.

In principle, the distribution of |E|'s in a data set is independent of the unit cell content and depends only on the presence or absence of a center of symmetry. Such a distribution can, therefore, serve as a statistical method to test for a center of symmetry. The |E| statistics were calculated for this structure and are compared with theoretical distributions³⁰ in Table 5. Good agreement is found with the theoretical distribution for centrosymmetric structures.

TABLE 5

	Theore	Theoretical			
	Centro- Symmetric	Noncentro- Symmetric			
< E >	0.798	0.886	0.782		
< E ² >	1.000	1.000	0.975		
< E ² -1>	0.968	0.736	0.961		
E > 3	0.3%	0.01%	0.21%		
E > 2	5.0%	1.8%	4.6%		
E > 1	32.0%	37.0%	30.0%		

E STATISTICS

The 230 independent |E|'s and their symmetry-related structure factors were used to calculate the triplet combinations E(H), E(K), and E(H-K). Triplets were calculated for all $|E(H)| \ge 1.50$ but using only |E(K)| and $|E(H-K)| \ge 1.80$. For each triplet, the value of $\sigma_3 \sigma_2^{-3/2} \ge 1.80$. |E(H)E(K)E(H-K)| was also calculated for use in the probability equation, Eq. 28.

The fourth program of this series initiated the sign determination. Using |E(K)| and $|E(H-K)| \ge 1.80$, signs were sought only for $|E(H)| \ge 1.80$ in this step. This involved only the 137 largest independent |E|'s and their symmetry-related amplitudes. The three origin-defining structure factors were picked from the 15 largest amplitudes available and assigned the phase + 1. These signed structure factors were then used as E(K) and E(H-K) to sign new structure factors, E(H), by means of S(H) = S(K)S(H-K)and the value of $\sigma_3 \sigma_2^{-3/2} |E(H)|E(K)E(H-K)$ was stored. For any structure factor, E(H), involved in more than one triplet, the accumulated sum

SUM(H) =
$$\sum_{K} \sigma_{3} \sigma_{2}^{-3/2} | E(H) | E(K) E(H-K)$$
 (33)

was stored. Up to four independent symbol signs were allowed in this program. Thus, every structure factor accrued 16 different sums as indicators of S(H) being \pm , \pm A, \pm B, \pm AB, \pm C, \pm AC, \pm BC, \pm ABC, \pm D, \pm AD, \pm BD, \pm ABD, \pm CD, \pm ACD, \pm BCD, and \pm ABCD.

A calculated structure factor sign was not used to calculate additional signs until its probability of being correct, as calculated by Eq. 28, exceeded specified acceptance limits. The limits used for this calculation are given in Table 6. Signs calculated from the origindefining signs were tested against limits 1-3, consecutively, and only accepted if their accumulated value of SUM(H) exceeded the specified limits. When no additional signs could be calculated, the symbol A was chosen as the sign of one of the ten largest remaining unsigned structure

TABLE 6)
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ACCEPTANCE LIMITS FOR STRUCTURE FACTOR SIGNS

Limit	SUM(H)	P ₊ (H)	· · · · ·
	. 8.0	- 1.00000	· .
2	7.5	1.00000	
3	7.0	1.00000	
4	6.5	1.00000	
5	6.0	0.99999	
6	5.5	0.99999	
7	5.0	0.99996	
8	4.5	0.99987	
9	4.0	0.99967	
10	3.5	0.99909	
11	3.0	0.99752	
12	2.5	0.99330	
13	2.4	0.99183	
14	2.2	0.98787	
15	2.0	0.98201	
16	2.0	0.98201	

factors and limits 4-6 were made acceptance limits. This process was repeated by assigning the symbol signs B, C, and D, as needed, and adding three limits of Table 6 as acceptance limits after each symbol was assigned. Any structure factor which had accumulated appreciable values of SUM(H) in more than one counter was given that sign which corresponded to its largest value of SUM(H). After all possible signs were calculated, all counters were compared with limit 16 (identical to limit 15 for this calculation). Of the 137 |E|'s \geq 1.80, only four signs were left undetermined, 17 were accepted as + or -, and the remaining 116 were in terms of symbols and combinations of symbols. Symbol signs were evaluated by comparing all appropriate counters having SUM(H) \geq 2.0 (limit 16). A symbol was considered evaluated if at least three equations were obtained for it and at least two-thirds of these indicated that it was + or -. These results are shown in Table 7. In practice, a structure factor sign is never accepted if its probability of being correct, as given by equation 28, is below 0.97. In the early stages, this value must be much closer to 1.00. The acceptance limits shown in Table 6 reflect this trend. They were chosen somewhat arbitrarily, since no fixed criteria exist for making these choices, and also somewhat higher than usual with limit 16 corresponding to $P_{\perp}(H) = 0.982$. The data presented here represents the first application of the symbolic addition method to this structure. Had the process been totally unfruitful, subsequent calculations would have been made with less stringent acceptance limits.

Seven of the fifteen symbol signs were evaluated by the procedure discussed above, yielding 70 definite structure factor signs for |E|'s \geq 1.80. In addition, the relationship B = C = -D was also clearly

Symbol	Number of Equations for Symbol = +	Number of Equations for Symbol = -	Accepted Sign for Symbol
Δ		4	
B	0		T.
AB	0	0	
С	0	0	
AC	0	0	
BC	27	0	+
ABC	22	3	+
D	0	0	
AD	0	1	
BD	0	5	_
ABD	1	3	-
CD	0	9	-
ACD	1	2	-
BCD	0	0	
ARCD	0	0	

EVALUATED SYMBOL SIGNS

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revealed. Comparison of these results with the most consistent set of signs calculated by hand⁹ showed excellent agreement (only 4 discrepancies for the 70 signs) and in addition indicated the relationship B = C = -D = +. If the specification that SUM(H) for a structure factor may not be less than 2.0 in at least two counters before a symbol-identifying equation could be established had been lowered to 1.7 (corresponding to $P_+(H) = 0.967$), the same relationship would have been obtained and all symbols would have been evaluated. However, the fact that not a single erroneous sign was obtained by the method employed may be a justification for using such high acceptance limits.

The 70 structure factors for which definite signs had been obtained in the previous stage were then used to calculate signs of |E|'s in the range $1.5 \leq |E| < 1.80$ by direct application of the Sigma-2 equation. All calculated signs with a probability of being correct greater than 0.970 were accepted. This produced 30 additional signs. The 100 signed E's thus obtained (referred to as Calculation I in Table 8) were then used to calculate an E-map. Since this calculation employed only 5.3% of the total data, many superfluous peaks were obtained. However, 14 of the 32 largest peaks clearly revealed the positions of all carbon and oxygen atoms as a trial structure which refined readily. This trial structure was in excellent agreement with one of the possible molecular orientations deduced from the Patterson analysis.

For comparison, the last stage of the phase determining process was repeated three times. The 70 signed E's and the 65 remaining structure factors with symbol signs and $|E| \ge 1.80$ were used twice to calculate signs for $|E| \ge 1.50$. The first time the assignment B = C = -D = + was

Calculation	I	II	III	IV	
Starting signs					
Definite	70	70	70	122	
Symbol	0	65	65	0	
Symbol Assignment		B=C=-D=+	B=C=-D=-		
Signs calculated	30	90	88	78	
Total number of signed E's	100	225	223	200	
Peak heights at atomic positions*	8.0-15.0	18.8-27.5	-1.37-11.0	12.8-27.5	
Largest superfluous peak	15.0	9.5	35.0	11.7	
Incorrect signs**	0	0	114	19	

FINAL SIGNS AND E-MAP RESULTS

TABLE 8

*Using coordinates of trial structure obtained from Calculation I. **Compared with calculated structure factors after 14 refinements. made, the relationship expected to be correct, and for the second calculation B = C = -D = - was used. The final calculation used 122 signs for |E|'s \geq 1.80 calculated by hand⁹ as starting signs. These three calculations are referred to as Calculation II, III, and IV, respectively in Table 8. Each set of signs obtained was used in an E-map calculation and the results are shown in Table 8. E-maps of calculations I, II, and IV, yielded identical trial structures while the E-map based on Calculation III yielded peaks which did not correspond to a meaningful molecular structure. Of special interest are the results of calculations II and IV. Only about 11% of the structure factor signs have been determined here, yet the smallest peak at an atomic position is larger than the largest superfluous peak. Finding a trial structure from such a map is trivial.

CHAPTER IV

REFINEMENT OF THE CRYSTAL STRUCTURE

Coordinates of the twelve carbon and two oxygen atoms, taken from the E-maps, were refined by three-dimensional block-diagonal leastsquares using the weighting scheme

> $\sqrt{w} = |Fo|/P \text{ if } |Fo| \leq P$ $\sqrt{w} = P/|Fo| \text{ if } |Fo| > P$

or

with P = 16.0. The atomic scattering factors used for the calculation of structure factors (F_c) were interpolated from the values of Table 9. Six refinements were first carried out using the carbon and oxygen coordinates and isotropic temperature factors as parameters. During these refinements, the residual index

$$R = \frac{||Fo| - |F_c||}{\Sigma |kFo|}$$

dropped from as initial value of 0.316 to 0.169. At this point, anisotropic thermal parameters were introduced and further refinements carried out. A difference Fourier was calculated after R had dropped to 0.134. Twelve of the 19 most prominent peaks obtained showed the expected positions of all hydrogen atoms. Further refinements added the coordinates and isotropic temperature factors of all hydrogens as parameters.

TABLE	9
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$\frac{\sin \theta}{\lambda}$ (Å ⁰⁻¹)	f _{o,0} (e)	f _{o,C} (e)	f _{o,H} (e)
0.00	8.000	6.000	1.000
0.05	7.796	5.760	0.992
0.10	7.250	5.126	0.854
0.15	6.482	4.358	0.712
0.20	5.634	3.581	0.566
0.25	4.814	2.976	0.439
0.30	4.094	2.506	0.330
0.35	3.492	2.165	0.248
0.40	3.010	1.950	0.184
0.50	2.338	1.685	0.104
0.60	1.944	1.536	0.060
0.70	1.714	1.426	0.038
0.80	1.566	1.322	0.020
0.90	1.462	1.218	0.013
1.00	1.374	1.114	0.010
1.10	1.296	1.012	0.007
1.20	1.220	0.916	0.005
1.30	1.144	0.821	0.003

ATOMIC SCATTERING FACTORS

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Significant shifts were initially obtained for the hydrogen parameters. Least-squares refinement was continued until the shifts in all parameters were less than 1/7 of their estimated standard deviations. At this point R had dropped to 0.057 when including all reflections and R = 0.052 when using observed reflections only. A final difference Fourier map, using the refined coordinates of all atoms, showed no peaks (positive or negative) greater than 0.19 $e/(A^{0})^{3}$. A final Fourier map was calculated and yielded electron densities at the atomic positions as shown in Table 10.

TABLE 10

ELECTRON DENSITIES AT THE ATOMIC POSITIONS

Atom	(e/Å ³)	Atom	(e/Å ³)
C(1)	7.4	H(1)	0.8
C(2)	6.5	H(2)	0.9
C(3)	6.5	H(3)	0.8
C(4)	6.1	H(4)	0.7
C(5)	6.2	н(5)	0.8
C(6)	.7.0	H(6)	0.8
C(7)	6.4	H(7)	0.9
C(8)	6.3	H(8)	0.9
C(9)	6.1	н(9)	0.8
C(10)	6.5	H(10)	0.7
C(11)	6.4	H(11)	0.8
C(12)	7.3	H(12)	0.8
0(1)	7.1		
0(2)	8.0		

CHAPTER V

RESULTS AND DISCUSSION OF THE CRYSTAL STRUCTURE ANALYSIS

The accuracy of a crystal structure may be assessed by the agreement between observed and calculated structure factors at the conclusion of least squares refinement, the magnitude of residual peaks in the final difference Fourier map, the standard deviation of atomic coordinates, bond lengths, and bond angles, and the agreement between calculated bond lengths and bond angles with those previously determined for similar structures. The overall R value of 0.057 at the end of refinement shows that an acceptable agreement between observed and calculated structure factors had been obtained. The flatness of the final difference Fourier (largest peaks are -0.19 and +0.18) shows that the entire unit cell content is accounted for by four molecules of $C_{12}H_{12}O_2$. By collecting intensity data out to 140° in 20, quite small standard deviations were obtained for the atomic coordinates, bond lengths, and bond The very small shifts in atomic parameters at the end of reangles. finement show that these values have probably been determined as accurately as possible with the present data.

The final atomic coordinates and their estimated standard deviations are given in Table 11. The standard deviations of carbon and oxygen coordinates are ± 0.002 Å while those of hydrogen atoms are ± 0.03 Å

FRACTIONAL ATOMIC COORDINATES (x10⁴)

(Estimated Standard Deviations are in Parentheses)

Atom	x/a	y/b	z/c
C(1)	1295(2)	3860(2)	2293(2)
C(2)	2896(3)	2942(2)	2493(2)
C(3)	4342(3)	2839(2)	3748(2)
C(4)	3720(3)	2911 (2)	4555(2)
C(5)	1566(3)	3096(2)	4261(2)
C(6)	530(2)	3937(2)	3246(2)
C(7)	~1747(3)	3958(2)	2794(2)
C(8)	-2746(3)	4660(2)	1712(2)
C(9)	-2112(3)	4602(2)	914(2)
C(10)	- 390(3)	3836(2)	1050(2)
C(11)	2192(3)	5978(2)	2623(2)
C(12)	1413(3)	5158(2)	3553(2)
0(1)	3094(2)	5703(1)	2283(1)
0(2)	1399(2)	5884(1)	4203(1)
H (1)	3515(27)	3160(16)	1983(17)
H(2)	2208(22)	2149(14)	2208(14)
H(3)	5860(21)	2648(14)	3942(14)
H(4)	4814(27)	2823(18)	5470(18)
H(5)	1487(26)	3422(15)	4937(15)
H(6)	686(24)	2341(17)	4023(16)
H(7)	~1966(24)	4311(15)	3470(15)
н(8)	~2153(26)	3090(16)	2641(16)
H(9)	-3907(26)	5133(16)	1657(16)
H(10)	-2836(25)	5071(16)	166(15)
11(11)	179(26)	4106(16)	486(15)
H(12)	- 881(23)	2977(15)	849(15)

or less. Anisotropic temperature factors of carbon and oxygen atoms and isotropic factors of hydrogen atoms are given in Tables 12 and 13, respectively. The lengths and direction cosines of the vibrational ellipsoids of the anisotropic atoms are given in Table 14. As expected, the two bridgehead carbons, C(1) and C(6), show the least thermal motion. All bond lengths and angles are given in Tables 15-18.

The molecular conformation may be described as a nearly planar cyclobutadione system with the two cyclohexene rings in the boat form, folded toward the four-membered ring. The molecular symmetry is very nearly two-fold (C_2), or even mm (C_{2v}) although significant deviations from both of these symmetries exist as can be seen by examining the calculated bond distances and angles (Tables 15-18). For the purpose of discussing and relating bond lengths and angles, mm symmetry will be assumed and average values of sets of bond lengths and angles, related by this assumed symmetry, are given in Tables 19 and 20, respectively.

The four bonds connected to the cyclobutane ring range from 1.528(3) to 1.541(3) \mathring{A} in length and have an average value of 1.534 \mathring{A} , in good agreement with the average length of a normal C-C single bond reported by Sutton³¹ as 1.537 ± 0.005 \mathring{A} . The four bonds in the cyclohexene rings which are adjacent to the double bonds show the expected shortening from a single bond length. They range from 1.490(3) to 1.505(3) \mathring{A} and have an average length of 1.499 \mathring{A} . The two double bonds in the cyclohexene rings, with lengths of 1.318(3) and 1.313(3) \mathring{A} , are identical within experimental error, but slightly shorter than the average value of carbon-carbon double bonds of 1.335 ± 0.005 A.³¹ The cyclobutane ring shows a small increase in some bond lengths, compared to a normal C-C single bond in

ANISOTROPIC THERMAL PARAMETERS OF CARBON AND OXYGEN ATOMS ($\times 10^4$)

(Standard deviation of last digit in parentheses)

Atom	^b 11	^b 22	^b 33	^b 12	^b 13	^b 23
C(1)	203(4)	57(2)	63(2)	-11(5)	118(4)	-88(3)
C(2)	241(5)	81(2)	92(2)	35(6)	154(5)	- 1(3)
C(3)	218(5)	91(2)	101(2)	41(6)	103(5)	32(4)
C(4)	271(6)	98(2)	86(2)	30(6)	80(5)	43(4)
C(5)	324(6)	105(2)	76(2)	31(6)	176(6)	34(4)
C(6)	205(7)	63(2)	67(2)	8(5)	129(5)	3(3)
C(7)	210(5)	96(2)	103(2)	-31(6)	168(5)	-17(4)
C(8)	187(5)	92(2)	114(2)	6(5)	90(5)	-14(4)
C(9)	247(6)	88(2)	85(2)	1(6)	55(5)	6(3)
C(10)	285(6)	86(2)	66(2)	32(6)	103(5)	6(3)
C(11)	213(5)	71(2)	89(2)	-23(5)	135(5)	18(3)
C(12)	206(5)	76(2)	74(2)	24(5)	79(5)	-28(3)
0(1)	453(5)	103(2)	173(2)	-117(5)	358(5)	20(3)
0(2)	366(4)	110(2)	124(2)	-34(5)	1 9 2(4)	-100(3)

Temperature	factor	=	exp	-(h ² b ₁₁	+	^{к²ь} 22	+	² 433
				+ hkb 12	+	hlb 13	+	klb ₂₃)

TABLE	13
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ISOTROPIC TEMPERATURE FACTORS OF HYDROGEN ATOMS

(Standard deviation of last digit in parentheses)

Atom	B(A ²)
H(1)	7.4(5)
H(2)	5.3(4)
H(3)	4.9(4)
H(4)	8.4(6)
H(5)	5.9(5)
H(6)	7.2(5)
H(7)	5.8(4)
H(8)	6.7(5)
H(9)	6.4(5)
H(10)	6.2(5)
H(11)	6.9(5)
H(12)	6.1(5)

LENGTHS AND DIRECTION COSINES WITH RESPECT TO THE UNIT CELL AXES

Atom	Β ₁ (Α) ²	\$1(x10 ³)	٤ ₂ (x10 ³)	ل ₃ (x10 ³)
C(1)	3.758	648	-220	369
	2.951	-622	-637	647
C(2)	4,998	325	241	677
- ()	4.717	-494	-781	560
	3.434	-807	575	477
C(3)	6.249	-338	440	896
	4.914	639	756	-408
	3.498	691	-484	176
C(4)	6.601	-641	501	805
	5.463	706	683	-141
	3.502	302	-532	576
C(5)	6.340	498	699	240
	5.300	-754	641	206
	3.243	-428	-316	949
C(6)	3.901	571	-079	481
	3.410	-242	9 35 ·	340
	2.841	-785	-346	808
C(7)	5.866	117	-548	691
	4.832	-091	824	541
	3.076	989	141	-479
C(8)	7.031	-456	-208	979
	4.813	-051	977	209
	3.321	888	-050	017
C(9)	6.531	-825	080	866
	4.686	126	991	-016
	3.689	550	-107	500
C(10)	5.645	911	411	-366
	4.414	-412	895	336
	3,542	034	-173	868

OF THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS

TA	BLE	14

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Atom	B _i (A) ²	¹ (x10 ³)	^k 2(x10 ³)	l ₃ (x10 ³)
		····		<u></u>
C(11)	5.047	-209	433	879
•	4.124	-659	600	-116
	3.006	723	672	-463
C(12)	5.493	-593	-607	736
	3.483	737	-145	267
	3.219	-324	781	622
0(1)	10.038	437	-114	608
	7.750	-609	693	616
	3.182	662	712	-502
0(2)	9.055	-177	-654	738
	6.488	966	028	-197
	3.427	-188	756	646

C-C AND C-O BOND LENGTHS

(Standard deviation of last digit in parentheses)

Length (Å)*
1.528(3)
1.572(3)
1.541(3)
1.534(3)
1.505(3)
1.318(3)
1.490(3)
1.538(3)
1.528(3)
1.531(3)
1.500(3)
1.313(3)
1.501(3)
1.551(3)
1.193(2)
1.190(2)

*Not corrected for thermal motion.

C - H BOND LENGTHS

(Standard deviation of last digit in parentheses)

Bond	Length (A)
C(2) - H(1)	0.99(2)
C(2) - H(2)	1.03(2)
C(3) - H(3)	1.07(2)
C(4) - H(4)	1.10(2)
C(5) - H(5)	0.98(2)
C(5) - H(6)	1.05(2)
C(7) - H(7)	1.04(2)
C(7) - H(8)	1.04(2)
C(8) - H(9)	1.00(2)
C(9) - H(10)	1.03(2)
C(10) - H(11)	1.04(2)
C(10) - H(12)	1.05(2)



FIGURE 5. C-C and C-O bond lengths.

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C-C-C AND C-C-O BOND ANGLES

(Standard deviation of last digit in parentheses)

Atoms	Angle (⁰)
C(2) - C(1) - C(6) C(2) - C(1) - C(10) C(2) - C(1) - C(11) C(6) - C(1) - C(10)	115.6(2) 112.2(2) 112.2(2) 114.2(1)
$\begin{array}{c} C(6) - C(1) - C(11) \\ C(10) - C(1) - C(11) \\ C(1) - C(2) - C(3) \end{array}$	89.6(1) 111.1(2) 111.7(2)
$\begin{array}{r} C(2) - C(3) - C(4) \\ C(3) - C(4) - C(5) \\ C(4) - C(5) - C(6) \\ \end{array}$	121.1(2) 121.4(2) 112.6(2)
C(1) - C(6) - C(5) C(1) - C(6) - C(7) C(1) - C(6) - C(12) C(5) - C(6) - C(7)	114.6(2) 115.1(2) 89.6(1) 112.9(2)
C(5) - C(6) - C(12) C(7) - C(6) - C(12) C(6) - C(7) - C(8)	111.3(2) 111.1(2) 112.0(2)
C(7) - C(8) - C(9) C(8) - C(9) - C(10) C(1) - C(10) - C(9) C(1) - C(11) - C(12)	120.3(2) 121.4(2) 111.8(2)
$\begin{array}{c} c(1) - c(11) - c(12) \\ c(1) - c(11) - o(1) \\ c(12) - c(11) - o(1) \\ c(6) - c(12) - c(11) \end{array}$	134.2(2) 135.5(2) 90.5(1)
C(6) - C(12)- O(2) C(11)- C(12)- O(2)	134.0(2) 135.4(2)

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C-C-H AND H-C-H BOND ANGLES

(Standard deviation of last digit in parentheses)

Atoms	Angle (⁰)
C(1) - C(2) - H(1) $C(1) - C(2) - H(2)$ $C(3) - C(2) - H(2)$ $H(1) - C(2) - H(2)$ $H(1) - C(2) - H(2)$ $H(1) - C(2) - H(2)$ $C(2) - C(3) - H(3)$ $C(4) - C(3) - H(3)$ $C(3) - C(4) - H(4)$ $C(5) - C(4) - H(4)$ $C(5) - C(4) - H(4)$ $C(4) - C(5) - H(5)$ $C(4) - C(5) - H(5)$ $C(6) - C(5) - H(6)$ $H(5) - C(5) - H(6)$ $H(5) - C(5) - H(6)$ $C(6) - C(7) - H(7)$ $C(6) - C(7) - H(7)$ $C(6) - C(7) - H(8)$ $H(7) - C(8) - H(9)$ $C(9) - C(8) - H(9)$ $C(10) - C(9) - H(10)$ $C(10) - C(9) - H(11)$	Angle () 106(1) 109(1) 115(1) 109(1) 107(2) 117(1) 122(1) 119(1) 108(1) 108(1) 108(1) 108(1) 108(2) 104(1) 108(2) 104(1) 112(1) 111(1) 113(1) 125(1) 120(1) 109(1)
C(1) - C(10) - H(12) C(9) - C(10) - H(11) C(9) - C(10) - H(12) H(11) - C(10) - H(12)	108(1) 109(1) 110(1) 108(1)



FIGURE 6. Selected C-C-C and C-C-O bond angles.

AVERAGE VALUES AND RANGES OF BOND LENGTHS RELATED

BY ASSUMED mm SYMMETRY

< **.**.

(Standard deviation of last digit in parentheses)

Bonds*	Average Length $(\overset{O}{A})$	Range (Å)
C(1) - C(2)	1.534(3)	1.528(3) - 1.541(3)
C(2) - C(3)	1.499(3)	1.490(3) - 1.505(3)
C(3) - C(4)	1.316(3)	1.313(3) - 1.318(3)
C(1) - C(11)	1.532(3)	1.531(3) - 1.534(3)
C(11)- O(1)	1.192(2)	1.190(2) - 1.193(2)
C(2) - H(1)	1.01 (2)	0.98 (2) - 1.04 (2)
C(2) - H(2)	1.04 (2)	1.03 (2) - 1.05 (2)
C(3) - H(3)	1.05 (2)	1.00 (2) - 1.10 (2)

*Each bond shown is one of the symmetry-related set.

AVERAGE VALUES AND RANGES OF BOND ANGLES RELATED

BY ASSUMED mm SYMMETRY

(Standard deviation of last digit in parentheses)

Atoms*	Average Angle (⁰)	Range (⁰)
C(2) - C(1) - C(6)	114.9(2)	114.2(1) - 115.6(2)
C(2) - C(1) - C(10)	112.6(2)	112.2(2) - 112.9(2)
C(2) - C(1) - C(11)	111.4(2)	111.1(2) - 112.2(2)
C(6) - C(1) - C(11)	89.6(1)	89.6(1) - 89.6(1)
C(1) - C(2) - C(3)	112.0(2)	111.7(2) - 112.6(2)
C(2) - C(3) - C(4)	121.0(2)	120.3(2) - 121.4(2)
C(1) - C(11)- C(12)	90.4(1)	90.3(1) - 90.5(1)
C(1) - C(11) - O(1)	134.1(2)	134.0(2) - 134.2(2)
C(12)- C(11)- O(1)	135.3(2)	135.4(2) - 135.5(2)
C(1) - C(2) - H(1)	107 (1)	104 (1) - 109 (1)
C(1) - C(2) - H(2)	106 (1)	104 (1) - 109 (1)
C(3) - C(2) - H(1)	111 (1)	108 (1) - 115 (1)
C(3) - C(2) - H(2)	111 (1)	109 (1) - 115 (1)
C(2) - C(3) - H(3)	118 (1)	115 (1) - 119 (1)
C(4) - C(3) - H(3)	122 (1)	119 (1) - 125 (1)
H(1) - C(2) - H(2)	109 (2)	107 (2) - 113 (1)

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this ring connects the bridgehead carbon atoms, C(1) and C(6), and has a value of 1.572(3) Å. The bond connecting the carbonyl carbons is shortened to 1.551(3) Å. This shortening is expected through π -electron interaction. The shortest two bonds in the cyclobutane ring, however, are the C(1) - C(11) and C(6) - C(12) bonds with values of 1.534(3) and 1.531(3) Å, respectively. Interactions between the π -electrons of the carbonyl carbons and the bridgehead bonds of the cyclohexene rings may help to keep these bonds close to the normal single bond distance. Further evidence of such interactions will be given in a later section.

The long bond lengths in the cyclobutane ring are not unusual. They have been found in various cyclobutane rings for both planar and puckered rings. Greenberg and Post³² report bond lengths of 1.547(3) and 1.561(3) Å in the planar ring of tetracyanocyclobutane. Dunitz³³ has reported bond lengths of 1.555 and 1.585(0.020) for the planar ring tetraphenylcyclobutane. The puckered ring of <u>trans</u> -1.2- cyclobutanedicarboxylic acid has bond lengths ranging from 1.517 to 1.553 Å,³⁴ while values of 1.552 and 1.567(6) Å are reported for the planar ring of <u>trans</u>-1,3-cyclobutanedicarboxylic acid.³⁵ The puckered four-membered ring in <u>trans</u>-Bicyclo 4.2.0 octyl-1-3,5-Dinitrobenzoate has bond lengths ranging from 1.532(4) to 1.556(4) Å, as reported by Barnett and Davis.³⁶

The carbonyl bond lengths of 1.193(2) and 1.190(2) Å are identical within experimental error. This value is slightly smaller than the average carbonyl bond length reported by Sutton as 1.215 \pm 0.005 Å, but in agreement with the carbonyl bond lengths of the α -diketones glyoxal and diacetyl, 1.20 \pm 0.01 and 1.20 \pm 0.02 Å, respectively.³¹ All C-H bond lengths fall in the range 0.98-1.10 Å, with standard deviations of 0.02 Å. These values are obtained by using the refined hydrogen co-
ordinates, and are in good agreement with C-H bond lengths reported by various authors.

Geometry of the Molecule

The deviation of the molecular symmetry from mm symmetry can be seen from the three least-squares planes in Table 21. Plane 1 was fitted to the carbon atoms in the four-membered ring. Plane 2 was fitted to C(1), C(6), and the ethylene portions of the two six-membered rings. Plane 3 was fitted to the midpoints of the atom pairs C(1) - C(6), C(2) - C(5), C(3) - C(4), C(7) - C(10), C(8) - C(9), C(11) - C(12), and O(1) - O(2). For mm symmetry, these three planes should be mutually perpendicular. The calculated planes show that planes 2 and 3 meet at 90.0° , but the angles between planes 1 and 2 and planes 1 and 3 are 89.2° and 89.1° , respectively. The double bond C(8) - C(9) is slightly closer to the carbonyl carbons than the C(3) - C(4) bond and the two cyclohexene rings are twisted from mm symmetry by 0.9° about a line bisecting the C(1) - C(6) and C(11) - C(12) bonds.

The molecule's deviation from mm symmetry can also be seen from Table 22 and Figures 7 and 8. For these illustrations, atomic coordinates were transformed to orthogonal Cartesian coordinates with distances measured in Angstroms. The midpoint of the C(1) - C(6) bond was placed at the origin of the coordinate system and the C(1) - C(6) bond was used to define the x-axis. A line from the origin to the midpoint of the C(11) - C(12) bond is perpendicular to the x-axis and was used to define the z-axis. The y-axis was generated perpendicular to the x and z axes. The coordinate axes thus define three mutually perpendicular planes through the molecule. The perpendicular distance from every carbon and oxygen

TABLE	21
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LEAST-SQUARES PLANES THROUGH THE MOLECULE

Plane	Atoms to which plane was fitted	Equation of Plane*
1	C(1),C(6),C(11),C(12)	-0.629x+0.391y-0.672z = 0.166
2	C(1),C(3),C(4),C(6),C(8),C(9)	-0.323x-0.913y-0.250z =-4.495
3	Midpoints of C(1) - C(6),	0.702x-0.053y-0.710z =-3.156
	C(2) - C(5),C(3) - C(4),C(3)	7) - C(10),
	C(8) - C(9),C(11) - C(12),C	0(1) - 0(2)

Deviation from

Atom	Plane l(Å)	Plane 2(Å)	Plane 3(Å)	
C(1)	0.004	-0.123	0.787	
C(2)	-1.242	0.438	1.434	
C(3)	-2.493	0.067	0.658	
C(4)	-2.510	0.055	-0.660	
C(5)	-1.295	0.408	-1.436	
C(6)	-0.004	-0.121	-0.785	
C(7)	1.260	0.451	-1.421	
C(8)	2.499	0.065	-0.661	
C(9)	2.512	0.057	0.652	
C(10)	1.305	0.436	1.431	
C(11)	-0.004	-1.658	0.775	
C(12)	0.004	-1.652	-0.775	
0(1)	-0.002	-2.496	1.625	
0(2)	0.065	-2.483	-1.624	

*x, y, and z are given in A.

atom to each of these planes was calculated and the results are shown in Table 22. For ideal mm symmetry, the absolute values of all distances from any plane in each set of atoms shown should be identical.

The nature of the cyclobutadione system can be seen from the least-squares plane 1 in Table 21. The deviation of each of the cyclobutane carbons from this plane is 0.004 Å. This is twice the standard deviation of the coordinates and threfore very near the limits of a significant deviation from planarity. It may be noted that O(1) is removed by only 0.002 A from this plane while O(2) is 0.065 Å away. The latter distance is a very significant deviation, enough to destroy both mm and two-fold symmetry of the molecule. The distances of the remaining atoms from this plane also show significant deviations from mm and two-fold symmetry. The dihedral angle for the cyclobutane ring is 179.1° .

Least-squares planes through the carbonyl groups and bonded atoms are given in Table 23. The carbonyl carbon, C(11), exist in a virtually planar environment, deviating only 0.004 Å from the plane fitted to C(1), C(11), C(12), and O(1). The surroundings of the other carbonyl carbon, C(12), is significantly nonplanar, with C(12) about 0.023 Å removed from a plane containing C(6), C(11), and O(2). The non-planarity of this group can also be seen in Table 21 by noting the distance of O(2)from Plane 1. It is interesting to note that O(2) is bent out of the plane in the direction of the cyclohexene ring which is closest to the carbonyl groups.

The molecular packing in the unit cell is shown in Figure 10 and some intermolecular distances are given in Table 24. Of interest is the O(2) - H(12) distance between molecules related by two-fold screw axes.

DISTANCES OF ATOMS FROM IDEAL mm SYMMETRY PLANES

		Plane	Equation of Plane	
		I Lanc	nquation of fianc	
		4	x = 0	
		5	y = 0	
		6	z = 0	
			Distance from	
Set	Atom	Plane 4(Å)	Plane 5(Å)	Plane 6(Å)
1	C(1)	-0.786	0.000	0.000
	C(6)	0.786	0.000	0.000
2	C(2)	-1.445	1.250	-0.580
	C(15)	1.425	1.287	-0.547
	C(7)	1.435	-1.268	-0.554
	C(10)	-1.417	-1.297	-0.542
3	C(3)	-0.681	2.497	-0.225
	C(4)	0.637	2.506	-0.213
	C(8)	0.686	-2.503	-0.151
	C(9)	-0.627	-2.509	-0.145
4	C(11)	-0.775	0.009	1.534
	C(12)	0.775	-0.009	1.531
5	0(1)	-1.626	0.011	2.372
	0(2)	1.624	-0.074	2.364

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FIGURE 7. x-y Projection depicting distortion of the molecule from mm symmetry.



FIGURE 8. y-z Projection depicting distortion of the molecule from mm symmetry.



FIGURE 9. Stereoscopic view of the molecule with thermal ellipsoids.

Plane	Atoms to which pla was fitted	ane Equ	uation of Plane*
7	C(1),C(11)	-0.626x+0).3934y-0.673z = 0.174
	C(12),O(1)		
8	C(6),C(11),	-0.620x+0	0.371y-0.691z =-0.018
	C(12),0(2)		
Atom	Deviation from Plane 7 (Å)	Atom	Deviation from Plane 8 (Å)
C(1)	0.001	C(6)	0.005
C(11)	-0.004	C(11)	0.005
C(12)	0.001	C(12)	-0.018
0(1)	0.002	0(2)	0.008

TABLE 23

LEAST SQUARES PLANES THROUGH THE CARBONYL GROUPS

*x, y, and z are given in $\overset{O}{A}$.

.



FIGURE 10. Molecular packing

TABLE 24

ance (Å) C	ode**
0.001	
3.821	a
3.850	Ъ
3.472	a
3.437	с
3.541	c
3.686	b
2.854	a
2.887	a
2.441	a
2.858	d
2.768	Ъ
2.537	e
0 000	c
	2.887 2.441 2.858 2.768 2.537

INTERMOLECULAR DISTANCES*

*Distances are given for C - C < 3.90 Å, C - O < 3.70 Å, O - H < 2.90 Å, and H - H < 2.6 Å.

**Atom A is at (x,y,z) and atom B is located by the following codes: $a = (-x, \frac{1}{2} + y, \frac{1}{2}-z), b = (1 + x, y, z), c = (1-x, 1-y, 1-z), d = (-x, 1-y, 1-z),$ e = (-1-x, 1-y, -z), f = (-x, 1-y, -z). These atoms are separated by 2.441 Å, about 0.16 Å less than the sum of hydrogen and oxygen van der Waals radius.^{37,38} 0(2) is bent out of the plane of the four-membered ring in the direction which shortens this distance. A planar dione system, however, would only have increased the 0(2) - H(12) distance by 0.03 Å. Reports are found for other crystal structures where the distance between an alkyl hydrogen and an oxygen is considerably shorter than the sum of their van der Waals radii, and the possibility of a C - H----O hydrogen bond has been suggested.^{38,39} For molecules with a keto oxygen, a favorable geometry for such a hydrogen bond seems to have a H----O distance of 2.27 Å and a C - H----O angle of 164°.³⁸ Deviation from these values exist, of course. The 0(2)----H(12) separation of 2.441 Å found in this structure is considerably larger than the favorable hydrogen bond distance and the C - H----O angle of 136° is 28 degrees less than the most favorable bond angle. Any existing hydrogen bond interaction in this crystal would have to be considered as quite weak.

BIBLIOGRAPHY

- J. J. Bloomfield and J. R. S. Irelan, J. Org. Chem., <u>31</u>, 2017 (1966).
- 2. J. J. Bloomfield, Tetrahedron Letters, 587 (1968).
- J. J. Bloomfield and R. E. Moser, J. Am. Chem. Soc., <u>90</u>, 5625 (1968).
- 4. H. Birnbaum, R. C. Cookson, and N. Lewin, J. Chem. Soc., 1224 (1961).
- 5. N. J. Leonard and P. M. Mader, J. Am. Chem. Soc., 72, 5388 (1950).
- K. Alder, H. K. Schafer, H. Esser, H. Krieger, and R. Reubke, Ann. 593, 23 (1955).
- 7. J. J. Bloomfield, Central Research Department, Monsanto Company, St. Louis, Missouri 63166.
- 8. A. P. Marchand, The University of Oklahoma, Norman, Oklahoma 73069, personal communication.
- 9. D. van der Helm, Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73069.
- G. H. Stout and L. H. Jensen, <u>X-ray Structure Determination</u>, The Macmill Company, London, 1968, p. 67.
- 11. International Tables for x-Ray Crystallography, Vol. III, Kynoch Press, Birmingham (1962).
- 12. A. L. Patterson, Z. Krist., A90, 517 (1935).
- H. Lipson and W. Cocharan, <u>The Determination of Crystal Structures</u>, G. Bell, London, 1957.
- 14. D. Harker, J. Chem. Phys., <u>4</u>, 381 (1936).
- 15. M. M. Woolfson, <u>Direct Methods in Crystallography</u>, Oxford University Press, New York, 1961.

- 69
- 16. I. L. Karle and J. Karle, Acta Cryst., 17, 835 (1964).
- 17. I. L. Karle and J. Karle, Acta Cryst., <u>21</u>, 860 (1966).
- 18. J. Karle and I. L. Karle, Acta Cryst., 21, 849 (1966).
- 19. D. Harker and J. S. Kasper, Acta Cryst., <u>1</u>, 70 (1948).
- 20. D. Sayre, Acta Cryst., 5, 60 (1952).
- 21. J. Karle and H. Hamptman, Acta Cryst., <u>3</u>, 181 (1950).
- 22. H. Hamptman and J. Karle, <u>Solution of the Phase Problem. I.</u> <u>The Centrosymmetric Crystal</u>, A.C.A. Monograph No. 3 <u>Pittsburgh: Polycrystal Bookservice</u>, 1953.
- 23. H. Hamptman and J. Karle, Acta Cryst., 12, 93 (1959).
- 24. M. M. Woolfson, Acta Cryst., 7, 51 (1954).
- 25. W. Cochran and M. M. Woolfson, Acta Cryst., 8,1 (1955).
- International Tables for x-Ray Crystallography, Vol. I, Kynoch Press, Birmingham (1962).
- 27. S. R. Hall, Division of Pure Physics, National Research Council of Canada, Ottawa, Canada.
- 28. F. R. Ahmed, National Research Council of Canada, Ottawa, Canada.
- 29. A. J. C. Wilson, Nature, 150, 151 (1942).
- I. L. Karle, K. S. Dragonette, and S. A. Brenner, Acta Cryst., 19, 713 (1965).
- 31. L. E. Sutton, <u>Tables of Interatomic Distances and Configuration</u> in <u>Molecules and Ions</u>, <u>Supplement 1956-59</u>, The Chemical Society, London, 1965.
- 32. D. Greenberg and B. Post, Acta Cryst., <u>B24</u>, 918 (1968).
- 33. J. D. Dunitz, Acta Cryst., <u>2</u>, 1 (1949).
- 34. E. Benedetti, P. Corradini, and C. Pedone, Acta Cryst., <u>B26</u>, 493 (1970).
- 35. T. N. Margulis and M. S. Fischer, J. Am. Chem. Soc., 89, 223 (1967).
- 36. B. L. Barnett and R. E. Davis, Acta Cryst., B26, 326 (1970).
- L. Pauling, <u>The Nature of the Chemical Bond</u>, Cornell University Press, Ithaca, New York, 1940.

- W. C. Hamilton and J. A. Ibers, <u>Hydrogen Bonding in Solids</u>, W. A. Benjamin, Inc., New York, Amsterdam, 1968.
- 39. D. J. Sutor, Nature, 195, 68 (1962).

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APPENDIX A

COMPUTER PROGRAMS USED IN THE CRYSTAL STRUCTURE ANALYSIS

Type of Calculation		Αι	uthor
Goniostat Setting	Р.	J.	Shapiro
Absorption Corrections	Ρ.	J.	Shapiro
Least-Squares Unit Cell Dimensions	т.	v.	Willoughby
Least-Squares Planes	т.	ν.	Willoughby
Data Reduction	F.	R.	Ahmed
Tape Generation and Lorentz-Polarization Corrections	F.	R.	Ahmed
Fourier	F.	R.	Ahmed
Structure Factor Least Squares	F.	R.	Ahmed
Symbolic Addition	F.	R.	Ahmed
Bond Lengths and Angles	м.	B.	Hossain
Packing Distances	G.	She	epherd
Principal Axes of Thermal Ellipsoids	W.	Α.	Franks
Structure Factor Listing	Ε.	Env	vall
Stereoscopic Drawing	с.	к.	Johnson

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APPENDIX B

DERIVATIONS OF SOME STRUCTURE FACTOR INEQUALITIES¹⁵

The structure factor for a centrosymmetric crystal can be ex-

$$F(H) = \sum_{j=1}^{N} f_j \cos 2\pi HX_j$$

where H represents a set of crystallographic indices h,k,ℓ , $HX_j = hx_j + ky_j + \ell z_j$, and f is the temperature-corrected atomic scattering factor. The unitary structure factor is related to F(H) by

$$U(H) = \frac{F(H)}{\sum_{j} f_{j}}$$

Defining a unitary scattering factor

$$n_{j} = \frac{f_{j}}{\Sigma f_{j}}$$

U(H) can be conveniently expressed as

$$U(II) = \sum_{j=1}^{\infty} n_{j} \cos 2\pi HX_{j}.$$

It may also be noted that

$$\sum_{j=1}^{\Sigma n} \sum_{j=1}^{m}$$

Harker-Kasper inequalities can be obtained by using the Cauchy inequality

$$\left|\sum_{j=1}^{N} a_{j}b_{j}\right| \leq (\sum_{j=1}^{N} |a_{j}|^{2})(\sum_{j=1}^{N} |b_{j}|^{2})$$

where a_j and b_j may be real or complex numbers. With $a_j = \sqrt{n_j}$ and $b_j = \sqrt{n_j} \cos 2\pi H X_j$,

$$|\sum_{j} a_{j} b_{j}|^{2} = |\sum_{j} n_{j} \cos 2\pi HX_{j}|^{2} = |U(H)|^{2} = U(H)^{2}.$$

Also,

$$\sum_{j} |a_{j}|^{2} = \sum_{j} n_{j} = 1, \text{ and}$$

$$\sum_{j} |b_{j}|^{2} = \sum_{j} (\cos 2\pi H X_{j})^{2}$$

=
$$1/2 \sum_{j} n_{j} (1 + \cos 4\pi HX_{j})$$

= $1/2(\sum_{j} n_{j} + \sum_{j} n_{j} \cos [2\pi (2H)X_{j}])$
j j j

= 1/2[1 + U(2H)].

Therefore U(H) $^2 \leq 1/2$ 1 + U(2H) .

Equation 17 of Chapter 3 can be derived by applying the Cauchy inequality to the sum of two structure factors.

$$U(\mathbf{H}) + U(\mathbf{K}) = \sum_{j=1}^{n} (\cos 2\pi \mathbf{H} \mathbf{X}_{j} + \cos 2\pi \mathbf{K} \mathbf{X}_{j})$$
$$= \sum_{j=1}^{n} 2n_{j} \cos [\pi (\mathbf{H} + \mathbf{K}) \mathbf{X}_{j}] [\cos \pi (\mathbf{H} - \mathbf{K}) \mathbf{X}_{j}]$$

Defining

$$a_{j} = \sqrt{2n_{j}} \cos[\pi(H + K)X_{j}] \text{ and}$$

$$b_{j} = \sqrt{2n_{j}} \cos[\pi(H - K)X_{j}],$$

$$\left|\sum_{j}a_{j}b_{j}\right|^{2} = [U(H) + U(K)]^{2} \text{ and}$$

$$\sum_{j}|a_{j}|^{2} = \sum_{j}2n_{j} \cos^{2}[\pi(H + K)X_{j}]$$

$$= \sum_{j}n_{j}(1 + \cos[2\pi(H + K)X_{j}])$$

$$= 1 + U(H + K).$$
Similarly,

$$\sum_{j}|b_{j}|^{2} = 1 + U(H - K), \text{ yielding}$$

 $[U(H) + U(K)]^2 \leq [1 + U(H + K)][1 + U(H - K)].$

For Eq. 18, consider the difference between two unitary structure factors,

$$U(H) - U(K) = \sum_{j=1}^{n} (\cos 2\pi HX_{j} - \cos 2\pi KX_{j})$$

= $-\sum_{j=1}^{n} 2n_{j} \sin [\pi (H + K)X_{j}] \sin[\pi (H - K)X_{j}].$

With

$$a_j = \sqrt{2n_j} \sin[\pi(H + K)X_j]$$
 and

$$b_{j} = \sqrt{2n_{j}} \sin[\pi(H - K)X_{j}],$$

$$\left|\sum_{j} a_{j} b_{j}\right|^{2} = [U(H) - U(K)]^{2} \text{ and}$$

$$p_j = \sqrt{2n} \sin[\pi(H - 1)]$$

$$\sum_{j} |a_{j}|^{2} = \sum_{j} 2n_{j} \sin^{2}[\pi(H + K)X_{j}]$$

$$= \sum_{j} n_{j} (1 - \cos[2\pi(H + K)X_{j}])$$

$$= 1 - U(H + K).$$
Similarly,
$$\sum_{j} |b_{j}|^{2} = 1 - U(H - K).$$

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Thus from the Cauchy inequality,

$$[U(H) - U(K)]^2 \le [1 - U(H + K)][1 - U(H - K)]$$

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APPENDIX C

THE SAYRE EQUATION^{15,20}

The electron density in a crystal may be expressed by the Fourier series

$$\rho(X) = \frac{1}{V} \sum_{H} F(H) e^{-2\pi i H X}$$

The square of the electron density, $\rho^2(X)$, can be expressed by a similar equation but with different Fourier coefficients,

$$\rho^{2}(X) = \frac{1}{V} \sum_{H} G(H) e^{-2\pi i H X}$$

F(H) and G(H) are structure factors for the two cases,

$$F(H) = \sum_{j} f_{j} e^{2\pi i H X} j \text{ and}$$
$$G(H) = \sum_{j} g_{j} e^{2\pi i H X} j \cdot$$

For a hypothetical crystal consisting only of equal atoms with their electron densities completely resolved, all f_j 's are identical and all g_j 's are also identical. In addition, peaks of $\rho(X)$ and $\rho^2(X)$ would coincide so that one may equate X_j with X_j . For such a collection of atoms,

$$F(H) = f \Sigma e^{2\pi i H X} j$$
 and j

$$G(H) = g \Sigma e^{2\pi I H X} j .$$

$$j$$

$$F(H) = \frac{f}{g} G(H) .$$

Thus

Sayre pointed out the property of Fourier series that when a function and the square of that function are both expressed by a series, the Fourier coefficients of the two series are related. For the series of $\rho(X)$ and $\rho^2(X)$, F(H) and G(H) are related by

$$G(H) = A \sum_{K} F(K) F(H - K),$$

$$K$$

where A is a scaling constant. Thus

$$F(H) = \frac{fA}{g} \sum_{K} F(H) F(H - K).$$

This relationship between structure factor signs was first applied by Sayre to a hypothetical, one-dimensional array of eaual atoms with resolved electron densities. Although the equation is rigorous for a system of equal, resolved atoms, Sayre extended it to real crystals as a probable equation,

$$F(H) \simeq \phi \Sigma F(K) F(H - K),$$

$$K$$

where ϕ is a positive scaling constant when |F(H)| is reasonably large. For centrosymmetric crystals, where the structure factors are real numbers, this equation can be used to determine structure factor signs. Sayre showed that for a pair of structure factors F(K) and F(H - K) in the summation where both have reasonably large amplitudes, the product of these structure factors has the same sign as F(H). This yields the useful sign relationship between large structure factors, S(H) = S(K) S(H - K).

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APPENDIX D

The following table shows a comparison of the observed and calculated structure factors. The numbers shown were placed on the calculated structure factor scale then multiplied by 9.5. Unobserved reflections are followed by an asterisk. All k indices are shown as positive numbers although intensities were measured for reflections with negative k indices only.

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TABLE 25

STRUCTURE FACTOR LISTING

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PART II

LONG-RANGE EFFECTS OF PI ELECTRONS ON $n \rightarrow \pi *$ TRANSITIONS OF <u>CIS</u> α -DIKETONES

CHAPTER I

INTRODUCTION

Molecules which contain oxygen, nitrogen, or sulfur in an unsaturated group often possess low-intensity absorption bands with molar absorption coefficients, ε , in the range of 10-100.¹ These bands are generally observed at longer wavelengths than any other absorption bands for the molecule. They were first denoted as R-bands by Burawoy² but are now more commonly referred to as $n \rightarrow \pi^*$ bands, a notation introduced by Kasha.³

The low-intensity band for aliphatic ketones and aldehydes is found at approximately 300 mµ with $\varepsilon \sim 10$.¹ It was first suggested by Mulliken⁴ that this band is due to an electronic transition from a lone-pair, non-bonding orbital (n) centered on the oxygen atom, to a higher energy orbital. McMurry⁵ showed that the intensity of this band is far too low to be an allowed n+o* transition, and it is therefore concluded that the accepting orbital is the antibonding pi molecular orbital (MO) of the carbonyl group and that the transition is an n+π* transition. This absorption usually shows a distinct solvent dependence,

moving to shorter wavelengths with increasing solvent polarity. Particularly in hydroxylic solvents the lone pair orbital may participate in hydrogen bonding with the solvent and thereby be stabilized with respect to an isolated non-bonding orbital, thus resulting in a blue shifted $n \rightarrow \pi^*$ transition.

Other absorptions found for simple ketones include a very weak absorption band due to a triplet $n \rightarrow \pi^*$ transition, a reasonably intense band for the $n \rightarrow \sigma^*$ transition, and an intense band for the $\pi \rightarrow \pi^*$ transition. Typical wavelengths and intensities of these bands at the peak maxima are shown in Table 1.⁶

TABLE 1

Transition λ_{max} (mµ)IntensityTriplet $n \rightarrow \pi^*$ 400Very weak ($\varepsilon \sim 10^{-3}$)Singlet $n \rightarrow \pi^*$ 290Weak ($\varepsilon \sim 10$) $n \rightarrow \sigma^*$ 180Moderate - Strong $\pi \rightarrow \pi^*$ < 180</td>Strong

ABSORPTION BANDS IN ALIPHATIC KETONES

Conjugation of a carbonyl with a vinyl group extends the pi-electron structure over four atoms. Of the four resulting pi molecular orbitals, the highest occupied and lowest empty MO have energies which are respectively higher and lower than the energies of the corresponding MO's in the isolated carbonyl group. With no appreciable change in energies for the nonbonding and sigma orbitals upon conjugation, a red shift is predicted for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions and little change for the $n \rightarrow \sigma^*$ transition. Such a change is observed for α,β -unsaturated ketones.⁶ The singlet $n \rightarrow \pi^*$ band appears at approximately 300-330 mµ and the $\pi \rightarrow \pi^*$ band at about 230 mµ. The $n \rightarrow \sigma^*$ band can generally not be seen due to the new location of the intense $\pi \rightarrow \pi^*$ transition. The presence of the oxygen atom in the pi system also makes the $\pi \rightarrow \pi^*$ transition assume some charge transfer characteristics. The excitation involves the transferral of electron density from an MO centered primarily on the vinyl group to an antibonding MO predominantly centered on the carbonyl group.

When steric hindrance forces the vinyl and carbonyl groups to be non-planar, considerable overlap may occur between the lone-pair orbital of the oxygen and the pi system of the vinyl group. This results in an increase in intensity for the $n \rightarrow \pi *$ transition due to intensity borrowing from the $\pi \rightarrow \pi *$ transition. The oscillator strength for a forbidden transition, such as the $n \rightarrow \pi *$, may be related to the oscillator strength of the transition from which intensity borrowing occurs, the $\pi \rightarrow \pi *$ in this case, by $f_{n \rightarrow \pi *} = f_{\pi \rightarrow \pi *} (\frac{SP}{\Delta E})^2$, where ΔE is the difference between the two transition energies, S is the overlap integral between the non-bonding orbital and the vinyl pi system, and P is the mixing energy for unit overlap.⁷

Ketones which contain a vinyl group that is not formally conjugated with the carbonyl group show an absorption band which is not characteristic of either group. In α , β -unsaturated ketones this band appears in the 200-260 m μ region with variable intensity and considerable charge transfer, as evidenced by solvent effects.⁶ The spectrum of bicyclo[2.2.2] octenone in cyclohexane has been investigated and discussed in detail by

Labhart and Wagniere.⁸ The charge transfer band for this compound appears at 202 mµ with $\varepsilon_{max} = 3000$ and is identified as a $\pi \rightarrow \pi^*$ band similar to that of α,β -unsaturated ketones. The singlet $n \rightarrow \pi^*$ transition is found at 290 mµ, as for aliphatic ketones in nonpolar solvents. The intensity of this band, however, is considerably increased with $\varepsilon_{max} = 110$. The nonplanarity of the double bonds again allows for overlap between the nonbonding orbital, n, and the ethylene pi system, resulting in intensity borrowing by the $n \rightarrow \pi^*$ transition from the charge transfer $\pi \rightarrow \pi^*$ transition.

The energy of an $n \rightarrow \pi^*$ transition may also be slightly altered by the presence of a non-conjugated double bond. Labhart and Wagniere show that a small red shift should be obtained for this band when overlap between the two pi systems exists. A notable exception to this, however, is mentioned by Snyder and Franzus.⁹ The absorption maxima for the band of 7-ketonorbornene and 7-ketonorbornane are reported as 274 and 290 mµ, respectively. Molecular orbital calculations by Snyder and Franzus also predict the observed blue shift for 7-ketonorbornene.

The spectra of α -diketones may be viewed in a similar manner to those of α,β -unsaturated ketones with some notable differences. The pi-electron system may again be described by four pi molecular orbitals. The energies of these MO's, however, are different for α -diketones and α,β -unsaturated ketones as seen in Figure 1, and may qualitatively be discussed on the basis of interaction parameters suggested by Labhart and Wagniere.⁸ Ignoring only small interactions between the non-bonding orbitals, due to the large spatial separation, the energies of the nonbonding orbitals in the two systems may be taken to be the same. The bonding and antibonding MO's of an isolated ketone (π_K and π_K ^{*}) are about





n

 $\pi_{\mathbf{K}}$



FIGURE 1. Interactions of pi MO's in α,β -unsaturated ketones and α -diketones depicting a red shift of the $n \rightarrow \pi^*$ and a blue shift of the $\pi \rightarrow \pi^*$ transitions of the α diketone relative to those of the α,β -unsaturated ketone.

2.1 and 0.5 eV, respectively, lower than the corresponding MO's of an ethylene group $(\pi_{E} \text{ and } \pi_{E}^{*})$.⁸ Less interaction is expected between the two antibonding MO's of the unsaturated ketone, due to the difference in energy, than between the two identical antibonding MO's of the α -diketone. This places the lowest empty MO of the diketone (π_3) below the corresponding MO of the unsaturated ketone (π_3) . Similar interactions are expected between the bonding MO's of the systems. The large energy difference between $\pi_{\rm E}$ and $\pi_{\rm K}$, however, leaves π_2 below π_2 . The energy levels of Figure 1 thus suggest that the lowest-energy $\pi \rightarrow \pi^*$ transition should be observed at shorter wavelengths for α -diketones than for α,β -unsaturaged ketones while the $n \rightarrow \pi^*$ transition should be seen at longer wavelengths for α -diketones than for α , β -unsaturated ketones. As a result of the blue-shifted $\pi \rightarrow \pi^*$ transition, a second $n \rightarrow \pi^*$ band is also usually seen for α -diketones due to the transition $n \rightarrow \pi_4$ (Figure 1). This band occurs at shorter wavelengths than the $n \rightarrow \pi_3$ transition and appears as either a distinct peak or as a shoulder on the high intensity $\pi \rightarrow \pi^*$ or $n \rightarrow \sigma^*$ bands. Singlet-triplet $n \rightarrow \pi^*$ transitions $(n \rightarrow \pi_3^-)$ are sometimes also observable for α -diketones. These absorptions have been identified for camphorquinone¹⁰ and biacety1^{11,12} with unusually large molar absorption coefficients for such transitions, $\varepsilon_{max} = 0.12$ (550 mµ) and 0.07 (505 mµ) for camphorquinone and biacetyl, respectively.

The extent of interaction between pi MO's in α -diketones also depends upon the dihedral angle between the carbonyl groups. This interaction should be minimal for a dihedral angle of 90[°] and begin to increase as trans-planarity is approached, thereby increasing the energy splitting of the MO levels $\pi_1 - \pi_2$ and $\pi_3 - \pi_4$ (Figure 1). The

transition energy of $n \rightarrow \pi_3$ should thus decrease and that of $n \rightarrow \pi_4$ should increase as coplanarity is approached. Experimental evidence of these trends has been established by Leonard and Mader¹³ in their investigation of the visible-UV absorption spectra of a series of α -diketones with varying dihedral angles. Camphorquinone, a molecule expected to have a dihedral angle that is very close to zero, shows $n \rightarrow \pi^*$ bands at 460 and 280 mµ for $n \rightarrow \pi_3$ and $n \rightarrow \pi_4$, respectively.¹⁰ The absorption spectra of several homologs of camphorquinone in cyclohexane solvent have also been taken.¹⁴ For these compounds the carbonyl groups are also expected to be very nearly cis-coplanar. Absorption maxima for the long-wavelength absorption band are found in the range of 462-482 mµ with ε 30 , while the second weak absorption band has peak maxima in the region of 272-293 mµ. From these, as well as other spectral studies of diketones ^{15,16} it is evident that the long-wavelength $n \rightarrow \pi^*$ absorption for most unsubstituted α -diketones, which are not further conjugated with other π bonds, appears at approximately 480 mµ or less. A somewhat unusual exception to this has only recently been reported by de Groot^{17} for the spectrum of 3,4-Di-t-butylbutane-dione which has an absorption peak at 536 mµ with ϵ =64.

Conjugating a diketone with other double bonds in a molecule may lower the lowest antibonding MO, compared to that of an isolated diketone, and thus impart a red shift to the $n \rightarrow \pi^*$ absorption band. Thus, the orthoquinones show $n \rightarrow \pi^*$ bands at wavelengths greater than 480 mµ. For o-benzoquinone and 1,2-naphthoquinone they are found at 610 and 540 mµ, respectively.¹⁸

The spectral features of ketones and diketones, saturated as well as unsaturated, have been discussed in terms of the energy levels of the

pi molecular orbitals only. A valid study of these spectral features requires also an assessment of the extent to which the nonbonding orbitals in a diketone can interact, the effects of different molecular substituents on the energy of the nonbonding orbitals, and the participation of sigma bonds in the interaction between molecular fragments which are separated by saturated bonds. Calculations of the interactions between nonconjugated ethylene groups in molecules have recently been made by Hoffmann, Heilbronner and Gleiter.¹⁹ It was pointed out here that not only the direct overlap between the pi systems but also the interaction through the intervening sigma bonds is necessary for spectral interpretations. Calculations presented in Chapter III will show the importance of these effects on $n+\pi^*$ transition energies in α -diketones.

The nature of the visible solution absorption of the three diketones, tricyclo[4.4.2.0^{1,6}] dodeca-3,8-diene-11,12-dione and its dihydro and tetrahydro derivatives, were investigated here by theoretical methods. These compounds will be referred to by abbreviated names which conveniently indicate the number of carbon-carbon double bonds. Thus the diene will be called 2DB, the dihydro derivative 1DB, and the saturated, tetrahydro derivative will be called 0DB.



The visible and near-UV absorption spectra of these compounds in cyclohexane solvent have been reported by Bloomfield and Moser 20 and are

reproduced in Figure 2. The spectral parameters reported for the longwavelength absorption band of each compound are shown in Table 2. The

TABLE 2

SPECTRAL PARAMETERS FOR THE LONG-WAVELENGTH ABSORPTION

BAND OF 2DB, 1DB, AND ODB IN CYCLOHEXANE

Compound	λ _{max} (mμ)	e _{max}
2DB	537.5	71.7
1DB	532-535	32.0
	460–464	38.8
ODB	461	73

molar absorptivities and wavelengths of the peak maxima are in the neighborhood of ε_{max} and λ_{max} values of $n \rightarrow \pi^*$ transitions of α -diketones. It may be seen that 1DB exhibits two absorption maxima which coincide very closely with the single absorption maxima of 2DB and 0DB, and that the sum of the two molar absorptivities of 1DB at the peak maxima is practically equal to ε_{max} of either of the two other compounds. Virtually no change is obtained in the spectra for solutions in ethanol, mixtures of ethanol and cyclohexane, and in the presence of benzene, acetic acid, or triethyl-amine. No deviation from Beer's law can be detected for any of these solutions.²¹

It was suggested by Bloomfield and Moser that the long-wavelength $n \rightarrow \pi^*$ absorptions for these compounds may be explained when assuming a staggered conformation for the molecules, as shown below. On this basis,







only one unique conformation exists for 2DB and ODB, conformations 1 and 3, respectively, while 1DB may have the double bond down or up to yield the two distinct species, 2a and 2b. It was further suggested by Bloomfield and Moser that interaction between the double bond and dione system is most favorable when the double bond is up, as in 1 and 2a, and that such a conformation enhances resonance stabilization of the $n \rightarrow \pi^*$ excited state and yields red-shifted $n \rightarrow \pi^*$ absorption peaks. Based on this argument, 1DB should show two absorption maxima while 2DB and ODB should each have only one peak, in agreement with the observed spectra.

The existence of staggered conformations in solution, however, is speculative and becomes questionable in view of the crystal structure results obtained for 2DB. This molecule was found to have both cyclohexene rings folded toward the dione system in the solid state and may favor this conformation in solution also.

This investigation employed various quantum mechanical calculations to test the effects of non-conjugated double bonds on the longwavelength $n \rightarrow \pi^*$ transition energy in α -diketones and to seek the mechanism whereby these effects are transmitted. The most favorable ground state conformations for the molecules under consideration were also investigated in an attempt to explain the absorption spectra.

CHAPTER II

MOLECULAR ORBITAL METHODS

The development of the molecular orbital (MO) method by Mulliken²² and Hund²³ as a method of describing the electronic structure of diatomic molecules has been well documented. This procedure was first extended to organic molecules by Hückel²⁴ and has since then become a popular tool for the theoretical investigation of the properties of a large variety of chemical species. Several levels of sophistication have developed within the framework of the molecular orbital approach. These methods differ in the extent to which they attempt to describe the electronic structure of the molecule, the type of wave function representing the molecular states, and the manner in which parameters in the calculation are evaluated.

One major division can readily be made for MO calculations on organic molecules. For planar, unsaturated molecules with conjugated double bonds, the simplifying pi-electron approximation is usually invoked when interest lies only in the properties of the pi-electrons. Only those atomic orbitals which contribute directly to the pi-electron structure of the molecule are treated explicitly. The remainder of the molecule is viewed as merely supplying a constant potential field for the pielectrons. The Hückel Molecular Orbital (HMO) method and the pi approximation of the Self-Consistent Field (SCF) method are two such approximations

used in this work and will be discussed in more detail later in this chapter.

More complete MO calculations, applicable to saturated as well as unsaturated molecules, can be made by the so-called all-valence-shell MO methods. In these methods, the atomic orbitals of all valence shell electrons are explicitly included in the calculation and information about the sigma, pi, and nonbonding orbitals will therefore be obtained. The Extended Hückel Molecular Orbital (EHMO) method and the Self-Consistent Field method with Complete Neglect of Differential Overlap (CNDO/2) were used for calculations at this level of approximation.

One common feature is found in the different calculational methods mentioned. An approximate wave function (ψ) is chosen to represent the electronic structure of the molecule. This function may be in the form of an MO constructed from a linear combination of atomic orbitals (LCAO-MO) or a Slater determinant^{25,26} built from such MO's. The expectation energy for the system described by ψ is then calculated as

$$E = \frac{\int \psi * H \psi d\tau}{\int \psi * \psi d\tau}$$

where H is the Hamiltonian for the system. Since the energy calculated in this manner, by use of an approximate wave function, is always too large, according to the variation principle, E is minimized with respect to all adjustable parameters imbedded in the wave function chosen. A clear presentation of the well-known variation theorem is given in the book by Eyring Walter, and Kimball.²⁷ Solution of the simultaneous equations obtained from the minimization procedure yields discrete MO energies and the corresponding molecular orbitals.
Pi-Electron MO Methods

The pi-electron approximation of the molecular orbital method attempts to describe only the properties of the pi electrons in an unsaturated molecule. Such an approach may be deemed valid for planar, conjugated molecules where the different symmetries of sigma and pi orbitals prohibit sigma-pi interactions. For nonplanar or nonconjugated systems, the effects of sigma bonds on the pi electron structure can not be taken into account. Any interaction between separate molecular fragments can only be revealed as a consequence of direct, through-space interactions. Two types of calculations, restricted to the frame work of the pi-electron approximation, were used. The approach and equations utilized by these methods will now be discussed.

The Hückel Molecular Orbital (HMO) Method

The pi-electrons in an organic molecule are considered to be free to move over the conjugated portion of the molecule. To reflect this property, the wave function describing a pi electron is chosen as an MO in the form of LCAO's as shown in Eq. 1.

$$\phi_{i} = \sum_{j=1}^{n} C_{ij} \chi_{j}$$
(1)

 ϕ is considered a one-electron MO, χ_j is the 2p atomic orbital (AO) from atom j which contributes to the pi-electron structure, n is the number of AO's, and the coefficients C_{ij} are adjustable parameters. Minimizing the expectation energy (E) of ϕ

$$E = \frac{\int \phi_{i} *H\phi_{i} d\tau}{\int \phi_{i} *\phi_{i} d\tau}$$
(2)

with respect to the coefficients C_{ij} for j=l to n yields n simultaneous equations,

$$\sum_{j=1}^{n} C_{ij} \left(\int \chi_{i} * H \chi_{j} d\tau - \varepsilon \int \chi_{i} * \chi_{j} d\tau \right) = 0$$
(3)

for i=1 to n. The notation may be simplified by letting

$$H_{ij} = \int \chi_i * H \chi_j d\tau$$
 (4)

and

$$S_{ij} = \int \chi_i * \chi_j d\tau$$
 (5)

 H_{ij} is called a coulomb integral when i=j and represents the energy of an electron in AO χ_i . When i \neq j, H_{ij} is called a resonance integral. S_{ij} is the overlap integral between the two AO's χ_i and χ_j . With this notation, the secular equations (3) may be expressed as

$$\sum_{j=1}^{n} C_{ij}(H_{ij} - \varepsilon S_{ij}) = 0 \quad \text{for } i=1,n.$$
 (6)

Solutions to these equations can be obtained by diagonalizing the determinant

$$|H_{ij} - \varepsilon S_{ij}| = 0$$
 (7)

This yields n distinct values of ε , which may now be called ε_i , for i=1 to n, and the corresponding coefficients C_{ij} . Each of the n allowed energy levels, ε_i , is associated with a unique MO, ϕ_i . The pi-electrons are placed pairwise, with opposing spins, into the lowest available MO's to form the electronic ground state.

The form of the Hamiltonian (H) is not specified explicitly in this approximation but treated as an effective one-electron Hamiltonian. The integrals H_{ij} in equation 7 are thus empirical parameters and the MO energies are obtained in terms of these parameters. The HMO approximation, applied to pure hydrocarbons, sets all coulomb integrals equal to a common value, the standard coulomb integral, α . Resonance integrals between AO's centered on nuclei which are bonded to each other are all assigned a common value, the standard resonance integral, β , while H_{ij} 's between all other AO pairs are taken as zero. All overlap integrals are taken as zero when $i\neq j$ and set equal to one when i=j, thereby assuming an orthonormal set of basis functions.

A number of variations and additions have been introduced to the HMO method so far described. Among these are the inclusion of overlap integrals and the use of variable coulomb and resonance integrals.²⁸⁻³³ The latter variations allow the method to be applied to systems with heteroatoms and varying bond lengths. The HMO method was used here with some of these variations. All coulomb integrals of carbon atoms were taken as the standard coulomb integral, α , while those of oxygen atoms were expressed as

$$\alpha_{v} = \alpha + h\beta \tag{8}$$

A summary of values of h which have been used by various authors for different heteroatoms systems is given by Streitwieser.³³ The value h=1 seemed appropriate for carbonyl oxygens and was used here. All overlap integrals were included and evaluated by the method of Mulliken, Rieke, Orloff, and Orloff.³⁴ Resonance integrals were set proportional to overlap integrals, a procedure suggested by Mulliken, ^{30,31} and evaluated by

$$H_{ij} = \frac{S_{ij}}{S_0} \beta$$
(9)

With coulomb and resonance integrals expressed in this way, the solutions of the secular determinant still yields values of the energy levels in

terms of the two parameters, α and β .

Electronic transition energies are taken as the difference in orbital energies between the leaving and accepting MO's, thereby neglecting any other electron rearrangements upon transition, while the total pielectron energy of a molecule is given as the sum of the one-electron energies. Due to the empirical nature of this method, little can be said about the absolute MO energies although experimentally observed trends in the $\pi \rightarrow \pi^*$ transition energies for series of similar compounds can readily be correlated by the relative MO spacings.

The Self-Consistent Field Molecular Orbital (SCF MO) Method

The pi-electron approximation of the self-consistent field method develops a more rigorous treatment of the electronic structure of molecules than the HMO method. A more satisfactory formulation is obtained by defining the molecular Hamiltonian and also including the important electron repulsion terms. However, some empiricism is usually employed in this method.

The basic equations of the SCF approach were first developed by Hartree³⁵ for the study of atomic systems. The method was employed by Fock³⁶ for systems where the wave function is expressible in the form of a Slater determinant and shown by Roothaan³⁷ to be applicable to systems where the elements of the Slater determinant are LCAO's. The equations employed in the semiempirical SCF MO approximation for closed shell systems may be found in several textbooks on quantum mechanics^{38,39} as well as in the literature.⁴⁰⁻⁴⁴ A summary of the necessary equations will be given here. For a system with n AO's contributing to the pi electron structure, MO's are constructed as LCAO's, analogous to Eq. 1 of

the HMO method. A total wave function for a closed-shell configuration

$$\phi_{i} = \sum_{p=1}^{n} C_{ip} \chi_{p}$$
(10)

(2 electrons in each MO) is then expressed by a single Slater determinant,

$$\psi = \frac{1}{\sqrt{n!}} \left| \phi_1(1) \alpha(1) \phi_1(2) \beta(2) \phi_2(3) \alpha(3) \dots \phi_{n/2}(n) \beta(n) \right|.$$
(11)

Each element of the determinant is a product of an orbital function ϕ and a spin function α or β . The subscripts here identify the MO's and the numbers in parentheses label the electrons associated with the respective MO. The determinant antisymmetrizes the total wave function, as is required by the Pauli principle. The Hamiltonian for the electronic energy of the system may be expressed as

$$H = \sum_{u=1}^{n} [T(u) + H_{o}(u)] + \sum_{u>v} \frac{e^{2}}{r_{uv}}$$
(12)

The repulsion term between nuclei is left off here since this would only add a constant term to the energy. T(u) in Eq. 12 represents the kinetic energy of electron u, H_o(u) is the potential energy between electron u and the entire molecule after removing all pi-electrons, $\frac{e^2}{r_{uv}}$ is the electronelectron repulsion term. Using the wave function and Hamiltonian given above yields the expectation energy for the configuration as

$$E = 2\sum_{i} \varepsilon_{i} + \sum_{i,j} (2J_{ij} - K_{ij})$$
(13)

ł

where the summations range over the n/2 occupied MO's. The molecular integrals of Eq. 13 are defined as

$$\varepsilon_{i} = \text{Core energy for an electron in } \phi_{i}$$
$$= \int \phi_{i} \star (u) [T(u) + H_{o}(u)] \phi_{i}(u) d\tau_{u} \qquad (14)$$

J_{ij} = coulomb integral

$$= \iint \phi_{i}^{*}(u) \phi_{j}^{*}(v) \frac{e^{2}}{r_{uv}} \phi_{i}(u) \phi_{j}(v) d\tau_{u} d\tau_{v}$$
(15)

 K_{ii} = exchange integral

$$= \iint \phi_{i}^{*}(u) \phi_{j}^{*}(v) \frac{e^{2}}{r_{uv}} \phi_{i}(v) \phi_{j}(u) d\tau_{u} d\tau_{v} . \qquad (16)$$

Minimizing the total energy (E) leads to Roothaan's³⁷ equations which must be satisfied by the "best" MO's (ϕ_i)

$$\sum_{p} C_{ip} (F_{pq} - S_{pq} \varepsilon_{i}) = 0 \quad \text{for } q=1 \text{ to } n.$$
(17)

Solutions to these equations are obtained by solving the secular determinant

$$\left|F_{pq} - S_{pq} \varepsilon_{i}\right| = 0 , \qquad (18)$$

yielding n orbital energies (ϵ_i) and the corresponding MO coefficients (C_{ip}). The elements F_{pq} of the above determinant are defined as

$$\mathbf{F}_{\mathbf{pq}} = \int \chi_{\mathbf{p}} * \mathbf{F} \chi_{\mathbf{q}} d\tau \tag{19}$$

where F is the Hartree-Fock Hamiltonian operator. F may be divided into two parts, F=I + G, and thus

$$F_{pq} = I_{pq} + G_{pq}.$$
 (20)

 I_{pq} is the matrix element of the one-electron Hamiltonian (T + H_o) and G_{pq} is the matrix element due to the other pi-electrons. To evaluate I_{pq} , the core potential (H_o) may first be replaced by the contributions from the individual nuclei. With H_t^+ representing the contribution from mucleus t, Interaction elements with other pi-electrons (G_{pq}) are evaluated by

$$G_{pq} = \sum_{j=1}^{n/2} 2\int \chi_{p}^{*}(\mathbf{u})\phi_{j}^{*}(\mathbf{v}) \frac{e^{2}}{r_{uv}}\chi_{q}(\mathbf{u})\phi_{j}(\mathbf{v})d\tau$$
$$- \sum_{j=1}^{n/2} \int \chi_{p}^{*}(\mathbf{u})\phi_{j}^{*}(\mathbf{v}) \frac{e^{2}}{r_{uv}}\chi_{q}(\mathbf{v})\phi_{j}(\mathbf{u})d\tau \qquad (12)$$

where j sums over the n/2 occupied MO's. Replacing the MO's by their LCAO's, this yields

$$G_{pq} = \sum_{j=1}^{n/2} \sum_{r,s}^{n} C_{jr} C_{js} \left[2 \int \chi_{p} \star(u) \chi_{r} \star(v) \frac{e^{2}}{r_{uv}} \chi_{q}(u) \chi_{s}(v) d\tau \right]$$

- $\int \chi_{p} \star(u) \chi_{r} \star(v) \frac{e^{2}}{r_{uv}} \chi_{q}(v) \chi_{s}(u) d\tau].$ (30)

In the shortened notation defined above,

$$G_{pq} = \sum_{j=1}^{n/2} \sum_{r,s}^{n} C_{jr} C_{js} [2(pq;rs) - (ps;qr)]. \qquad (31)$$

The total expression for the matrix elements can now be written as

$$F_{pq} = W_{q}S_{pq} - \sum_{t\neq q}^{n} [(t:pq) + (pq;tt)] + \sum_{j=1}^{n/2} \sum_{r,s}^{n} C_{jr}C_{js}[2(pq;rs) - (ps;qr)].$$
(32)

To make this calculation feasible, the Pariser-Parr⁴¹ approximation of neglect of differential overlap is made. Integrals such as $\int \chi_p^*(u) \chi_q^*(v) \frac{e^2}{r_{uv}} \chi_r^{(u)} \chi_s^{(v)} d\tau$ are taken as zero unless both p=r and q=s. Thus only one-center (pp;pp) and two-center (pp;qq) repulsion integrals are retained. With these simplifications, diagonal elements of the F matrix are

$$H_{o} = \sum_{t=1}^{n} H_{t}^{+}$$
, and (21)

$$I_{pq} = \int \chi_{p}^{*} (T + H_{q}^{+} + \sum_{t \neq q}^{n} H_{t}^{+}) \chi_{q}^{} d\tau$$
(22)

$$I_{pq} = \int \chi_{p}^{*} (T + H_{q}^{+}) \chi_{q}^{d\tau} + \sum_{t \neq q}^{n} \chi_{p}^{*} H_{t}^{+} \chi_{q}^{d\tau}$$
(23)

$$I_{pq} = W_q S_{pq} + \sum_{t \neq q}^n \chi_p * H_t^+ \chi_q d\tau$$
(24)

where W_q is the ionization energy for removing a pi-electron from atom q. The remaining integrals may be evaluated by replacing H_t^+ by the Goeppert-Mayer and Sklar potential⁴⁵

$$H_{t}^{+}(u) = H_{t}^{+}(u) - \int \frac{e^{2}}{r_{uv}} \chi_{t}^{*}(v) \chi_{t}(v) d\tau_{v}.$$
 (25)

This implies that the potential by core t on electron u equals the potential due to a neutral atom (H_t^{\ddagger}) minus the repulsion of a hypothetical electron v. Now

$$\int \chi_{p}^{*}(u) H_{t}^{+}(u) \chi_{q}(u) d\tau = \int \chi_{p}^{*}(u) H_{t}^{\ddagger}(u) \chi_{q}(u) d\tau$$
$$- \int \chi_{p}^{*}(u) \chi_{q}(u) \frac{e^{2}}{r_{uv}} \chi_{t}^{*}(u) \chi_{t}(v) d\tau \qquad (26)$$

$$\int \chi_{p}^{*}(u) H_{t}^{+}(u) \chi_{q}(u) d\tau = -(t:pq) - (pq;tt)$$
(27)

using the shortened notation (t:pq) for the penetration integral and (pq;tt) for the three center atomic repulsion integral. The total expression for I now becomes

$$I_{pq} = W_{q}S_{pq} - \sum_{t \neq q}^{n} (t:pq) + (pq;tt) .$$
 (28)

Interaction elements with other pi-electrons (G_{pq}) are evaluated by

$$G_{pq} = \sum_{j=1}^{n/2} 2 \int \chi_{p}^{*}(u) \phi_{j}^{*}(v) \frac{e^{2}}{r_{uv}} \chi_{q}^{}(u) \phi_{j}^{}(v) d\tau - \sum_{j=1}^{n/2} \int \chi_{p}^{*}(u) \phi_{j}^{*}(v) \frac{e^{2}}{r_{uv}} \chi_{q}^{}(v) \phi_{j}^{}(u) d\tau$$
(29)

where j sums over the n/2 occupied MO's. Replacing the MO's by their LCAO's, this yields

$$G_{pq} = \sum_{j=1}^{n/2} \sum_{\mathbf{r},\mathbf{s}}^{n} C_{j\mathbf{r}} C_{j\mathbf{s}} \left[2 \int \chi_{p}^{*}(\mathbf{u}) \chi_{\mathbf{r}}^{*}(\mathbf{v}) \frac{e^{2}}{r_{uv}} \chi_{q}(\mathbf{u}) \chi_{s}(\mathbf{v}) d\tau - \int \chi_{p}^{*}(\mathbf{u}) \chi_{\mathbf{r}}^{*}(\mathbf{v}) \frac{e^{2}}{r_{uv}} \chi_{q}(\mathbf{v}) \chi_{s}(\mathbf{u}) d\tau \right].$$
(30)

In the shortened notation defined above,

$$G_{pq} = \sum_{j=1}^{n/2} \sum_{r,s}^{n} C_{jr} C_{js} [2(pq;rs) - (ps;qr)].$$
(31)

The total expression for the matrix elements can now be written as

$$F_{pq} = W_{q}S_{pq} - \sum_{t \neq q}^{n} [(t:pq) + (pq;tt)] + \sum_{j=1}^{n/2} \sum_{r,s}^{n} C_{jr}C_{js}[2(pq;rs) - (ps;qr)].$$
(32)

To make this calculation feasible, the Pariser-Parr⁴¹ approximation of neglect of differential overlap is made. Integrals such as $\int \chi_p^*(u) \chi_q^*(v) \frac{e^2}{r_{uv}} \chi_r^{(u)} \chi_s^{(v)} d\tau$ are taken as zero unless both p=r and q=s. Thus only one-center (pp;pp) and two-center (pp;qq) repulsion integrals are retained. With these simplifications, diagonal elements of the F matrix are

$$F_{qq} = W_{q} - \sum_{t \neq q}^{n} [(t:qq) + (qq;tt)] + \sum_{j=1}^{n/2} \sum_{r=1}^{n} C_{jr}^{2} (qq;rr) - \sum_{j=1}^{n/2} C_{jq} (qq;qq)$$
(33)

and off-diagonal elements are

$$F_{pq} = W_{q}S_{pq} - \sum_{t\neq q}^{n} (t:pq) - \sum_{j=1}^{n/2} C_{jp}C_{jq} (pp;qq) .$$
(34)

To execute an SCF MO calculation, starting MO's are usually obtained from an HMO calculation. Coefficients of these MO's are used in equations 33 and 34 to calculate the F matrix. Diagonalization of this matrix yields improved coefficients and orbital energies. The new coefficients are then reintroduced into Eqs. 33 and 34. The process is repeated until only negligible changes occur. Orbital energies, MO coefficients or elements of the bond order and charge density matrix, defined as

$$P_{pq} = 2 \sum_{j=1}^{n/2} C_{jp} C_{jq}$$
(35)

are commonly used as measures of convergence.

It must be noted that each diagonalization of the F matrix yields coefficients of n separate MO's, yet the energy minimization uses a Slater determinant which has only the n/2 MO's of lowest energy occupied. Strictly speaking then, only the energies and coefficients of these MO's are improved by the iterative procedure. The remaining n/2 MO's are termed virtual MO's. It was suggested by Roothaan³⁷ that these MO's may be used for the construction of excited electronic configurations. A more accurate, but also a much more tedious, way of constructing excited configurations utilizes linear combinations of Slater determinants.

Singlet-singlet and singlet-triplet configuration transition energies can be calculated from the orbital energies by equations 36 and 37 respectively. For a one-electron transition from an orbital ϕ_i to orbital ϕ_i ,

$$^{1,1}\Delta E = \varepsilon_{j} - \varepsilon_{i} - J_{ij} + 2K_{ij}$$
(36)

$$^{1,3}_{\Delta E} = \varepsilon_{j} - \varepsilon_{i} - J_{ij} .$$
(37)

The molecular integrals J_{ij} and K_{ij} have previously been defined by equations 18 and 19. The total pi-electron energy for the molecule can be found from Eq. 13 using the final orbital energies and coefficients. The molecular integrals involved here can be evaluated by replacing the MO's by their LCAO's and neglecting all but the one-center and twocenter atomic repulsion integrals.

The agreement between observed and calculated transition energies, as calculated by Eqs. 36 or 37, is generally improved by following an SCF MO calculation by a configuration interaction (CI). Such a calculation constructs molecular state functions from molecular configurations,

The functions $\Psi_{i,j,\ldots}^{k,1,\ldots}$ are termed configurational wave functions. They are single Slater determinants which represent excited electronic configurations obtained by moving one electron from ϕ_i to ϕ_k , another electron from ϕ_j to ϕ_1 , etc. The A's are mixing coefficients and Ψ_I is a state function. In theory the summation may extend over all possible excited configurations, although in practice only one-electron-excited configurations are generally considered, and of these only configurations which are within a few electron volts of the ground state are used in the summation. No mixing can occur between the closed-shell ground state (Ψ_0) and one-electron-excited configurations (Ψ_i^k) , i.e., all $\int \Psi_0 H \Psi_i^k d\tau = 0$ where H is the Hamiltonian given by Eq. 12. Applying the variation principle to equation 38 yields the CI interaction matrix whose eigenvalues are the excited state energies and the eigenvectors are the corresponding mixing coefficients. The CI matrix elements for singlet excited states are obtained from equations 39 and 40.⁴⁶

$$\int^{1} \psi_{i}^{k} H' \psi_{j}^{1} d\tau = \delta_{ij} \delta_{kl} (\varepsilon_{k} - \varepsilon_{i}) + 2 \langle ik|jl \rangle - \langle ij|kl \rangle$$
(39)

where δ 's are the Kroenecker deltas and the molecular integrals are given by

$$\langle ik|jl \rangle = \sum_{p q} C_{ip} C_{kp} C_{jq} C_{lq} (pp;qq).$$
 (40)

Electronic transition energies are then obtained from the differences between excited state energies and the ground state energy.

All-Valence-Shell MO Methods

The concepts developed in the pi-electron MO methods can be extended to make the MO approach suitable for saturated as well as unsaturated molecules. A theoretical description of the electronic structure and the bonding in such molecules can be obtained by expanding the MO basis set to include the valence-shell AO's of all atoms in the molecule. Thus the 1s AO of hydrogen and the 2s and three 2p AO's of any atoms from the second row of the periodic table would contribute as basis functions and be treated explicitly in these methods. The resulting MO's show not only the pi-electron structure but also the sigma orbitals and any nonbonding orbitals which may exist. The extended basis set allows mixing of sigma and pi orbitals in non-planar, unsaturated molecules where these interactions are not symmetry forbidden and is thereby also capable of showing the role of sigma bonds in the interactions between nonconjugated, unsaturated groups in such molecules. The variety of MO's obtained allows not only the calculation of $\pi \rightarrow \pi^*$ electronic transition energies but also those involving any combination of orbitals, particularly the $n \rightarrow \pi^*$ transition energies.

Extended Hückel Molecular Orbital Method (EHMO)

An extended molecular orbital method has recently been described by Hoffmann⁴⁷ and applied to a wide range of compounds. The method uses all valence orbitals as a basis set and is therefore applicable to aliphatic as well as aromatic compounds. The mechanics of this method are very similar to the simple HMO method previously described. MO's are expressed as linear combinations of all valence orbitals and the MO energy is minimized with respect to the atomic orbital coefficients to yield the secular determinant

$$|H_{ij} - \varepsilon S_{ij}| = 0$$
(7)

where H is an unspecified one-electron Hamiltonian. All overlap integrals are retained in this method and evaluated by the formulas of Mulliken,³⁴ et al., using Slater AO's as basis functions. Coulomb integrals, H_{ii} , for the various basis functions are taken as the valence state ionization potentials. Extensive tabulations of valence state ionization potentials

are given by Skinner and Pritchard. ^{48,49} Resonance integrals, H_{ij}, may be calculated by one of the three following methods:

$$H_{ij} = 0.5 \text{ K S}_{ij} (H_{ii} + H_{jj})$$
 (41)

$$H_{ij} = K' S_{ij}$$
(42)

$$H_{ij} = K' S_{ij} \left(H_{ii}H_{jj}\right)^{\frac{1}{2}}$$
(43)

where the K's are suitable proportionality constants. These, and similar equations, have been used by different authors to calculate resonance integrals in various methods of calculations. More details and references may be found in reference 47. Hoffmann⁴⁷ has primarily used equations 41 and 42 to obtain resonance integrals. Equation 42, with K' = -21eV, was found to be satisfactory for conformational analyses of boron hydrides⁵⁰ while equation 41 with K=1.75 seems more applicable to a wider range of heteroatoms and organic molecules.^{47,51}

Electronic transition energies and total ground state electronic energies are calculated as in the HMO method. The EHMO method seems quite useful for predicting molecular geometries and conformations although it tends to overemphasize steric factors.⁴⁷ Electronic transition energies are poorly predicted, with calculated values generally smaller than the observed transition energies.⁴⁷ Qualitative trends in transition energies, however, can still be reasonably well correlated for series of similar compounds.

The CNDO Methods

The broad applicability of the EHMO method has prompted the

development of all-valence-shell MO methods within the SCF framework. Several such formulations have been introduced and are currently in use.⁵²⁻⁵⁷ One of these, due to Pople, Santry, and Segal⁵² uses the approximation of complete neglect of differential overlap and is hence termed the CNDO method.

The formulation of the CNDO method parallels the SCF method previously described with the exception that the basis set has been expanded to include all valence-shell AO's. This is reflected in the elements of the Slater determinant (Eq. 11). The molecular Hamiltonian is again a many-electron Hamiltonian that includes electron repulsion terms as in Eq. 12,

$$H = \sum_{u=1}^{n} [T(u) + H_{o}(u)] + \sum_{u < v} \frac{e^{2}}{r_{uv}}$$

The ranges of u and v are now over the n valence-shell electrons and the core potential terms $H_0(u)$ represent the potential energy between electron u and the entire molecule after all valence-shell electrons have been removed. Elements of the Hartree-Fock matrix, from which orbital energies and MO coefficients are obtained, are expressed in a form more suitable to the case where one atom may donate more than one AO to the basis set.⁵³ For diagonal elements,

$$F_{pp} = -\frac{L_2}{2} (I_p + A_p) + [(P_{AA} - Z_A) - \frac{L_2}{2}(P_{pp} - 1)]\gamma_{AA} + \sum_{B \neq A}^{\sum} (P_{BB} - Z_B)\gamma_{AB}$$
(44)

and off-diagonal elements are

$$F_{pq} = \frac{1}{2} (\beta_A^{0} + \beta_B^{0}) S_{pq} - \frac{1}{2} P_{pq} \gamma_{AB} .$$
 (45)

In the notation above, subscripts A and B label atoms, subscript p labels an AO from atom A and q labels an AO from atom B. P_{pp} and P_{pq} are elements of the bond-order charge-density matrix defined as

$$P_{pq} = 2 \sum_{i=1}^{n/2} C_{ip} C_{iq}$$
(46)

while $\boldsymbol{P}_{\boldsymbol{A}\boldsymbol{A}}$ is the total charge on atom A, calculated by

$$P_{AA} = \sum_{p=1}^{n(A)} P_{pp}$$
(47)

where n(A) equals the number of AO's used from atom A. Z_A is the charge on core atom A and γ_{AB} is a repulsion integral that represents the average interaction energy between one electron in any valence orbital of atom A with another electron in any valence orbital of atom B. S_{pq} is the overlap integral and $\beta^{O'}$'s are empirical parameters which depend only on the type of atom from which the AO originates. Contributing terms of the diagonal matrix element F_{pp} may again be grouped into two parts, a term which shows the energy of an electron in atomic orbital p under the influence of its own atomic core only (this is the term W in Eq. 36) and terms which show the attractions and repulsions between this electron and the remaining atomic cores and valence electrons, respectively. To allow the theory to reflect an MO's tendency to either gain or lose an electron, W is related here to the ionization potential (I) and the electron affinity (A) of the atom.

$$-I_{p} = W_{p} + (Z_{A} - 1) \gamma_{AA},$$
 (48)

$$-A_{p} = W_{p} + Z_{A} \gamma_{AA} .$$
 (49)

The average value of W_{D} can now be used as

$$W_{p} = -\frac{l_{2}}{p} \left(I_{p} + A_{p} \right) - Z_{A} \gamma_{AA} + \frac{l_{2}}{2} \gamma_{AA}$$
(50)

The remaining terms in equation 47,

$$(P_{AA} - \frac{1}{2}P_{pp})\gamma_{AA} + \sum_{B \neq A} (P_{BB} - Z_B)\gamma_{AB}$$

include the interactions between atomic orbital p with the remaining atomic cores and all electron repulsions. The one- and two-center repulsion integrals (γ_{AA} and γ_{AB}) are calculated by Roothaan's formulas.⁵⁸ Calculating the elements of the Hartree-Fock matrix in the manner above reflects some modifications of the initial CNDO formulation by Pople⁵³ and is referred to as the CNDO/2 method in the literature. Iterations may be initiated by first carrying out a simple Hückel-type calculation with matrix elements

$$F_{pp} = -\frac{1}{2}(I_{p} + A_{p})$$
(51)

and

$$F_{pq} = \frac{1}{2} (\beta_{A}^{o} + \beta_{B}^{o}) S_{pq}.$$
 (52)

The approximate MO coefficients obtained here are used to calculate the complete matrix elements, Eqs. 47 and 48, and subsequent cycles utilize these equations until self-consistence has been attained. Calculations of ground-state energies and electronic transition energies, parallel the methods described for the pi-electron SCF MO calculations.

The CNDO/2 method outlined has met considerable success in the calculation of molecular ground state properties. Calculations of electronic transition energies, however, were often considerably improved with the modifications introduced by Del Bene and Jaffé.⁵⁴ Onecenter coulomb repulsion integrals were evaluated semiempirically as the difference between the ionization potential and the electron affinity and two-center repulsion integrals were determined by the extrapolation technique developed by Pariser and Parr.⁴² The other change in parameterization involves the resonance integral portion of Eq. 45,

$$\beta_{pq} \equiv \frac{1}{2} (\beta_A^{o} + \beta_B^{o}) S_{pq}.$$
 (53)

For AO's p and q involved in sigma overlap, Eq. 53 is used as the leading term for F_{pq} . When p and q are involved in pi overlap,

$$\beta_{pq} = \frac{1}{2} k (\beta_A^{o} + \beta_B^{o}) S_{pq}$$
(54)

is used where k is an empirical parameter. Reasonably consistent spectroscopic data is obtained with these changes in parameterization when using k=0.585. The addition of configuration interaction to the CNDO/2 formulation has yeilded quite satisfactory results for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ (where applicable) transition energies for various organic compounds.^{54,55}

CHAPTER III

CALCULATIONS AND RESULTS

The four molecular orbital methods discussed in the previous chapter were used for a theoretical study of the three tricyclic diketones shown below. The major goals of these calculations were to test



the effects of the pi electrons in the cyclohexene rings on the lowenergy $n \rightarrow \pi^*$ transition of the diketones, determine the most favorable conformations for these molecules, and thereby attempt to correlate the calculated $n \rightarrow \pi^*$ transition energies with the solution spectra of Figure 2. The mechanism of interaction between the cyclohexene and diketone pi systems was also of interest. Were these interactions primarily due to spatial overlap of the pi systems or do the intervening sigma bonds exert a strong influence?

The calculations carried out treat the molecules above at three levels of complexity, as (1) interacting pi-electron systems, (2) interacting molecular aggregates, where the diketone segment and the unsaturated portions of the six-membered rings are replaced by glyoxal and ethylene molecules, respectively, but retain the bond distances and angles determined in the crystal structure of 2DB, and (3) whole molecules. The first two methods are capable of showing the through-space interactions in the systems while the last approach also includes the through-bond effects.

The atomic coordinates of 2DB in the crystal structure were symmetrized to C_{2v} symmetry and used as a guide for determining coordinates for the various systems considered. Since no crystal data is yet available on ODB and 1DB, the cyclobutadione segments of these molecules were maintained as in 2DB and the saturated six-membered rings were constructed with C-C bond length of 1.54 Å and tetrahedral bond angles.

Pi Electron Interactions

The pi-electron structures of the three diketones were described by means of the molecular fragments shown in Figure 3, using the coordinates of Table 3. This is basically the pi structure of a cis-glyoxal molecule and two ethylene molecules but with bond distances and angles equal to those found for 2DB in the solid state. For convenience of identifying MO's, the molecular fragments are also labeled by A, B, and C as shown in Figure 3. B represents the unsaturated portion of ODB, B and C (to be called BC) represents 1DB, and the three segments shown (ABC) constitute the pi-electron structure of 2DB. For the purpose of evaluating overlap integrals, the orientations of the 2p AO basis functions were chosen in the manner dictated by the molecular conformation found for 2DE in the solid state. A y-z projection of these orbitals is shown in Figure 4. The HMO and pi-electron SCF-MO methods were employed



FIGURE 3. Molecular fragments used for HMO and pi-electron SCF MO calculations.

TABLE 3

ATOMIC COORDINATES OF MOLECULES USED FOR HMO AND PI-ELECTRON

	SCF	MO	CALCUI	LATIONS
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Atom	x (Å)	y (Å)	z (Å)
0(1)	-1.625	0.0	2.368
C(2)	-0.775	0.0	1.533
C(3)	0.775	0.0	1.533
0(4)	1.625	0.0	2.368
C(5)	-0.658	2.504	-0.184
C(6)	0.658	2.504	-0.184
c(7)	-0.658	-2.504	-0.184
C(8)	0.658	-2.504	-0.184



FIGURE 4. Orientations of basis functions for HMO and pi-electron SCF MO calculations are illustrated in this y-z projection of the orbitals.

for these calculations. The systems B, C, BC, AC, and ABC were considered, thereby showing the MO's and MO energies of the individual as well as the interacting systems. The atom numbering scheme in Figure 3 identifies the basis functions in subsequent MO's.

HMO Calculations

The HMO method was used with heteroatom parameter h=1 (Eq. 8) and neglect of overlap. Since weakly-interacting systems were considered, the standard HMO formulation was slightly modified by using non-zero resonance integrals between any AO's where appreciable interaction is possible. These integrals were set proportional to overlap integrals and evaluated as $H_{ij} = \frac{s_{ij}}{s}\beta$ (Eq. 9), while $H_{ij} = \beta$ was used for the C-O resonance integrals.⁹³ The C(5)-C(6) bond of Figure 3 was used as the reference bond to define S_o . All overlap integrals were calculated by the method of Mulliken, et al.³⁴ for Slater atomic orbitals. Numerical values of the

overlap and resonance integrals calculated for all unique AO pairs are shown in Table 4. MO energies calculated for the systems are shown in

i	j	S _{ij}	H _{ij} (β)	
1	3	0.013	0.045	
1	4	0.0	0.0	
1	- 5	0.007	0.006	
1	6	0.0	0.0	
2	3	0.184	0.641	
2	5	0.036	0.126	
2	6	0.014	0.049	
5	6	0.287	1.000	
5	7	0.0	0.0	
5	8	0.0	0.0	

TABLE 4

OVERLAP AND RESONANCE INTEGRALS FOR WEAKLY-INTERACTING PI SYSTEMS

Figure 5, and nonredundant MO coefficients are shown in Tables 5 and 6 for the pi MO's of ODB and 1DB, respectively.

The interactions between the pi electrons in the cyclohexene ring (C) and the pi systems of the diketone (B) of 1DB can be seen from Figure 5. The bonding orbital of C, π_1^{C} at energy $\alpha+\beta$, interacts weakly with the lowest empty molecular orbital (LEMO) of system B, π_3^{B} at energy $\alpha - 0.240\beta$, and elevates it to the level shown for the composite system BC, π_4^{BC} at energy $\alpha - 0.253\beta$. The antibonding MO of C, at energy $\alpha-\beta$, interacts more strongly with the highest energy MO of B, π_4^{B} at energy $\alpha - 1.080\beta$. The stronger interaction is expected since π_2^{C} and π_4^{B} were initially almost degenerate. A weak interaction is also calculated between the bonding MO of C and the lowest energy MO of B. The interesting feature, however, appears in the results of the first interaction mentioned, the





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МО	π <mark>1</mark> Β	^π 2 ^Β	π_3^B	т <mark>4</mark> В
Energy	α +1.88 1β	α +1.438 β	α-0.240β	α-1.080β
C _{2v} Symmetry	^B 2	A ₂	^B 2	A ₂
C Symmetry*	A´	A11	A-	A**
Coefficient				
0(1) C(2)	0.5406 0.4557	0.6426 0.2950	0.4557 -0.5406	0.2950 -0.6426

PI MO'S AND ENERGIES FOR ODB BY THE HMO METHOD

 $*C_{s}$ plane perpendicular to the C-C bond.

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TABLE 6

PI MO'S AND ENERGIES FOR 1DB BY THE HMO METHOD

MO	BC	_π BC	BC	BC π.	π_ ^{BC}	BC π.	
	"1	"2	<i>"</i> 3	4	5		
Energy	α +1.897 β	α +1.439 β	α +0.998 β	α-0.253 β	α -0.962 β	α-1.118β	
C _S Symmetry	A	A**	Α-	A^	A	A	
Coefficients							
0(1)	0.5324	0.6424	0.1179	0.4502	0.1558	0.2511	
C(2)	0.4561	0.2953	0.0040	-0.5403	-0.3160	-0.5594	
C(5)	0.0926	0.0110	-0.6972	-0.0730	-0.6131	-0.3521	

fact that π_4^{BC} is at a higher energy than π_3^{B} . These are the LEMO's for systems BC and B, respectively, and are the accepting MO's for the lowenergy $n \rightarrow \pi^*$ transitions. Table 6 shows that π_4^{BC} is an MO that is primarily centered on the diketone with only small contributions from the ethylene pi system. Inspection of the coefficients shows that a node exists between the basis functions from the carbonyl carbons and those from the ethylene group. This antibonding interaction gives rise to the destabilization of the LEMO.

The HMO method employed here allows no assessment of the effects of the ethylene pi orbitals on the nonbonding orbitals of the diketone system. If one assumes that no significant interaction occurs between these orbitals, then the results presented here predict a higher $n \rightarrow \pi^*$ transition energy for 1DB than for ODB, contrary to what is anticipated from the solution spectra of these compounds. The energy difference of 0.013 β calculated between the two LEMO's is not a very large effect, however. Using an approximate value of 2.38eV for β ,⁵⁹ this amounts to an energy difference of 0.031eV or an absorption maximum shift of 4 mµ.

The assumption that the pi orbitals of system C have no appreciable effect on the nonbonding orbitals of B as a result of a throughspace interaction was tested qualitatively by an HMO-type calculation with parameters evaluated as for the pi interactions. Lone-pair orbitals of the oxygen atoms were represented by 2p orbitals placed perpendicular to the C-O bonds and in the plane of system C. An HMO calculation for this two-orbital case was followed by one which included the basis functions from system C. The energies of the lone-pair MO's were only altered by 0.001 β when including the pi MO's of system C, a small change compared to the 0.013 β change of the LEMO of the pi system of B. This diminished

interaction is due to the very small overlap between the chosen lone-pair orbitals an oxygen and the ethylene pi orbitals. S = 0.001 between a 2p orbital on C(5) and a 2p orbital on O(1), while a much stronger overlap exists for pi interactions, with S = 0.036 for 2p orbitals on C(2) and C(5).

The effects of the two ethylene groups (A and C) on the diketone system (B) are shown in Figure 6. The alteration of MO energies is similar to the changes seen in Figure 5. Of interest again is the change in the LEMO, $\pi_3^{\ B}$. This orbital is raised in energy from α -0.240 β to α -0.267 β ($\pi_5^{\ ABC}$), about twice the effects produced by just one ethylene system. The coefficients of this orbital (Table 7) show that the pi system of the diketone is coupled to both ethylene pi systems in an antibonding manner with nodal surfaces between the carbonyl carbon basis functions and both sets of ethylene basis functions. Thus, when considering the effects of pi electrons only, 2DB should have the highest $n \rightarrow \pi^*$ transition energy for the three compounds considered, contrary to the trends observed experimentally. A calculation of the total pi-electron energy, as a sum of occupied orbital energies, shows that stabilization is obtained when the isolated systems are allowed to interact (Table 8).

Through-space interactions between the pi systems based on molecular conformations with the six-membered rings in the boat form but folded away from the diketone system were found to be negligible. Overlap integrals dropped to insignificant values and the MO energies calculated were essentially those of noninteracting pi systems. No results are therefore shown for pi systems based on these conformations.

The pi-electron stabilization energies calculated here would predict that the most stable conformations of these compounds would have



FIGURE 6. Glyoxal-2 ethylene pi-MO interactions by the HMO method.

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The pi-electron stabilization energies calculated here would predict that the most stable conformations of these compounds would have

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PI	MO'S	AND	ENERGIES	FOR	2DB	BY	THE	HMO	METHOD
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МО	ABC ^T 1	ΑBC ^π 2	^π 3 ^{ABC}	ABC [#] 4	aBC ¹⁷ 5	АВС ^π 6	ABC ^π 7	ABC ^π 8
Energy	α +1.912 β	α+1.440 β	α+1.000β	α +0.996 β	α -0. 267β	α -0.937 β	α-1.000β	α-1.144β
C _{2v} Symmetry	^B 2	A ₂	A ₁	^B 2	^B 2	A ₂	^B 1	^A 2
Coefficients								
0(1) C(2) C(5) C(7)	0.5245 0.4564 0.0911 -0.0911	0.6422 0.2955 0.0110 -0.0110	0.0 0.0 0.5000 0.5000	0.1643 0.0052 0.4864 0.4864	0.4449 -0.5400 0.0723 -0.0723	0.1765 -0.3525 -0.4151 0.4151	0.0 0.0 0.5000 0.5000	0.2376 -0.5320 0.2786 -0.2786

TABLE 8

TOTAL GROUND-STATE ENERGIES FOR PI SYSTEMS STUDIED BY THE HMO METHOD

System	Energy	Stabilization energy
С	2α+2.000β	
В	4α +6.638 β	
BC	6α+8.668β	0.030β
ABC	8α+10.696β	0.058β

the unsaturated rings folded toward the diketone. This is in agreement with the conformation found for 2DB in the solid state.

Pi-Electron SCF MO Calculations

The calculations discussed above were next repeated by a series of pi-electron SCF MO calculations for identical systems. The closedshell SCF program by Bloor and Gilson^{46,60,61} was employed for this purpose. This program used the SCF formalism with neglect of differential overlap as shown in the previous chapter. Elements of the Hartree-Fock matrix were calculated by Eqs. 33 and 34 with one change, the neglect of penetration integrals (t:qq). One-center repulsion integrals were set proportional to the Slater effective nuclear charge Z_p as⁴⁶

$$(pp;pp) = 3.294 Z_p eV.$$
 (55)

Two-center repulsion integrals were calculated by the formula of Mataga and Nishimoto, 62

$$(pp,qq) = \frac{14.397}{a_{pq} + r_{pq}} eV,$$
 (56)

where r_{pq} is the distance in Angstroms between nuclei p and q , and a_{pq} is calculated by

$$a_{pq} = \frac{28.794}{(pp;pp) + (qq;qq)} \stackrel{o}{\Lambda}.$$
 (57)

Valence state ionization energies (W_q) for carbon and oxygen were taken as 11.16 and 17.70eV, respectively. The elements of the bond-order chargedensity matrix (P_{pq}) were used as criteria of self-consistence. When every element of P_{pq} changed by less than 0.001 between successive interactions, self-consistence was deemed achieved. The final molecular orbitals and MO energies obtained for the pi systems of ODB, 1DB and 2DB are shown in Tables 9-11, respectively. It is evident that the SCF MO energy levels obtained here parallel the energy pattern obtained by the HMO method. Of interest again are the energies of LEMO's for B,BC, and ABC. The pattern $\pi_3^{B}(-3.265eV) < \pi_4^{BC}(-3.199eV) < \pi_5^{ABC}(-3.132eV)$ follows the trend obtained by the IMO methods showing a destabilization of the LEMO of the diketone upon interaction with the ethylene systems. The destabilization of LEMO's calculated here is almost exactly twice as large as the values obtained by the HMO method with $\beta = 2.38eV$.

Interactions between Molecules

The next level of approximation again considered the effects of the pi electrons in the cyclohexene rings on the electronic structure of the diketone system by the direct, through-space mechanism. In these calculations, however, the all-valence-shell MO methods, EHMO and CNDO/2, described in the previous chapter were utilized. These methods can more satisfactorily show the changes in the nonbonding as well as the pi orbitals in the diketone upon interaction with the ethylene orbitals since

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 $\pi_{1}^{B} \qquad \pi_{2}^{B} \qquad \pi_{3}^{B} \qquad \pi_{4}^{B}$

-13.036

-3.265

-0.205

ΡI	MO '	S	AND	ENERGIES	FOR	ODR	BY	THE	SCF	MO	METHOD	

C _{2v} Symmetry	^B 2	^A 2	^B 2	^A 2
C Symmetry	Α-	A	A^	A
Coefficients				
0(1) C(2)	0.5205 0.4769	0.6261 0.3311	0.4777 -0.5219	0.3299 -0.6249

 ${\rm *C}_{_{\rm S}}$ plane perpendicular to the C-C bond.

-14.581

MO

Energy (eV)

TABLE 10

PI MO'S AND ENERGIES FOR 1DB BY THE SCF MO METHOD

МО	π ₁ ^{BC}	^{BC} π2	BC ^π 3	^π 4 ^{BC}	^π 5 ^{BC}	^{BC} π ₆
Energy (eV)	-14.580	-12.988	-11.029	-3.199	-0.824	-0.086
C Symmetry	A^	A^^	Α΄	A	A	A
Coefficients				··· · · · · · · · · · · · · · · · · ·		
0(1) C(2) C(5)	0.5140 0.4774 0.0811	0.6256 0.3313 0.0086	0.1017 0.0089 -0.6996	0.4740 -0.5215 -0.0622	0.1207 -0.2106 -0.6642	0.3077 -0.5882 0.2428

·								
МО	π ABC 1	πABC 2	^π ABC 3	πABC 4	ABC π5	πABC 6	πABC 7	π ABC 8
Energy (eV)	-14.580	-12.941	-11.018	-11.007	-3.132	-0.869	-0.716	0.014
C _{2v} Symmetry	^B 2	A ₂	A ₁	^B 2	^B 2	A ₂	Bl	A ₂
Coefficients								
0(1) C(2) C(5) C(7)	0.5075 0.4776 0.0808 -0.0806	0.6252 0.3318 0.0087 -0.0093	0.0573 0.0055 -0.6547 -0.2606	0.1312 0.0122 -0.2467 0.6494	0.4704 -0.5211 0.0613 -0.0618	0.1484 -0.2561 -0.4821 0.4240	0.0104 -0.0183 0.4742 0.5241	0.2959 -0.5693 0.2069 -0.2127

PI	MO'S	AND	ENERGIES	FOR	2DB	ΒY	THE	SCF	MO	METHOD
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TABLE 11

the nonbonding orbitals are now more completely described as part of the diketone electronic structure.

The molecules shown in Figure 7, with atomic coordinates given in Table 12, were used to construct the unsaturated segments of ODB, 1DB, and 2DB for these calculations. The coordinates of carbon and oxygen atoms as well as those of H(5), H(6), H(9), and H(10) are C_{2v} -symmetry averages of the coordinates obtained from the crystal structure of 2DB. The remaining hydrogen atoms in Figure 7 were introduced into the mole-cular fragments to maintain the hybridization of the carbon atoms in the original systems. These hydrogens were placed 1.040 Å from the carbon atom to which they are shown bonded and in the direction dictated by the appropriate C-C bond in the crystal structure of 2DB. The atom-numbering scheme in Figure 7 will label AO basis functions in the following calculations.

Extended Hückel Molecular Orbital (EHMO) Calculations

EHMO calculations, as described in Chapter 2, were carried out with Hoffmann's computer program.⁶³ Slater atomic orbitals were used as basis functions with Slater exponents of 1.300, 1.625, 2.275 for hydrogen (1s), carbon (2s and 2p), and oxygen (2s and 2p) orbitals, respectively. Coulomb integrals (H_{ii}) were taken from the valence state ionization potentials of Skinner and Pritchard^{48,49} and are shown in Table 13. Resonance integrals were calculated by Eq. 41 as $H_{ij} = 0.5$ KS_{ij}($H_{ii} + H_{ij}$) with K = 1.75.

Calculations were carried out for the species B and C, and for the composite systems AC, BC, and ABC. For clarity of representation, the following tables and interaction diagrams only show data for those



FIGURE 7. Molecules used for intermolecular interaction studies by the EHMO and CNDO/2 methods.

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ATOMIC COORDINATES OF MOLECULES USED FOR INTERMOLECULAR INTERACTION

STUDIES	BY	THE	EHMO	AND	CNDO/2	METHODS	
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Atom	x (Å)	y (Å)	z (Å)
0(1)	-1.626	0.0	2.368
C(2)	-0.775	0.0	1.533
C(3)	0.775	0.0	1.533
0(4)	1.626	0.0	2.368
C(5)	-0.658	2.504	-0.184
C(6)	0.658	2.504	-0.184
C(7)	-0.658	-2.504	-0.184
C(8)	0.658	-2.504	-0.184
H(1)	-0.782	0.0	0.493
H(2)	0.782	0.0	0.493
H(3)	-1.194	1.651	-0.442
H(4)	1.194	1.651	-0.442
H(5)	-1.201	3.352	0.073
H(6)	1.201	3.352	0.073
H(7)	-1.194	-1.651	-0.442
H(8)	1.194	-1.651	-0.442
H(9)	-1.201	-3.352	0.073
H(10)	1.201	-3.352	0.073

TABLE 13

COULOMB INTEGRALS FOR EHMO CALCULATIONS

Orbital	‼ _{ii} (eV)	
ll(1s)	-13.60	
C(2s)	-21.40	
C(2p)	-11.40	
0(2s)	-32.30	
0(2p)	-14.80	

orbitals which were identified as pi MO's. The highest occupied molecular orbital (HOMO) is also shown for those systems which contain the diketone. This MO was always identified as the symmetric combination of two lone-pair orbitals from the oxygen atoms, delocalized somewhat over neighboring atoms. It is this combination of lone-pair AO's, identified as MO n, which can give rise to the symmetry-allowed $n \rightarrow \pi^*$ transition for the systems studied. The MO coefficients are identified by the atom symbol and numbers assigned in Figure 7 and also the AO's for the case of carbon and oxygen atoms. Here s, x, y, and z stand for the 2s, $2p_x$, $2p_y$, and $2p_z$ AO's, respectively.

The LEMO for each of the three systems B, BC, and ABC $(\pi_3^{B}, \pi_4^{BC}, and \pi_5^{ABC}, respectively)$ is a pi MO centered on the diketone. The MO's π_4^{BC} and π_5^{ABC} also show significant contributions from those basis functions which build the pi MO's of the ethylene groups, C(5,y) and C(5,z) and their symmetry-related basis functions, with smaller contributions from those basis functions which build the sigma structure of the ethylenes. The interaction between the pi systems of the diketone and the ethylenes results in a destabilization of the LEMO's π_4^{BC} and π_5^{ABC} compared to the LEMO of the isolated diketone, π_3^{B} (Table 21). The interaction is again of an antibonding nature, as calculated by the HMO method, with nodes between the nearest-approaching basis functions from the separate systems.

The highest occupied orbital in each case, labeled n^B , n^{BC} , and n^{ABC} has its major contributions from the $2p_x$ and $2p_z$ AO's of the two oxygen atoms. The coefficients of these AO's are such that the resulting contributing orbital from each oxygen is nearly perpendicular to the carbonyl

TABLE	14
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PI MO'S AND ENERGIES FOR ETHYLENE BY THE EHMO METHOD

π ₁ ^C	π ₂ ^C
-13.276	-8.058
A	A
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
0.8339	0.6247
	π ₁ ^C -13.276 Α΄ 0.8339

 C_{s} plane is perpendicular to the C-C bond.

+The molecular plane is the xy plane.

TABLE 15

PI MO'S AND ENERGIES FOR ETHYLENE-ETHYLENE BY THE EHMO METHOD

МО	π 1 AC	π2 ^{AC}	ΑC ^π 3	4 π4
Energy (eV)	-13.277	-13.274	-8.058	-8.057
C _{2v} Symmetry	A ₁	^B 2	^B 1	A ₂
Coefficients				
C(5,y) C(5,z)	0.1275 -0.4220	0.1289 -0.4235	0.1709 -0.5645	0.1713 -0.5641

МО	π_1 ^B	^Β π2	n ^B	⁸ 3	π ₄ ^B
Energy (eV)	-15.659	-15.358	-12.657	-10.994	-7.521
C _s Symmetry*	A	A	A1	A	A
C _{2v} Symmetry	^B 2	A ₂	A ₁	^B 2	· A ₂
Coefficients					<u>y</u>
H(1) O(1,s) C(2,s) O(1,x) C(2,x) O(1,y) C(2,y)	0.0 0.0 0.0 0.0 0.0 0.7515 0.2847	0.0 0.0 0.0 0.0 0.0 0.6345 0.2162	-0.2242 -0.0038 0.1042 -0.4639 0.3653 0.0	0.0 0.0 0.0 0.0 0.0 0.4450 -0.6004	0.0 0.0 0.0 0.0 0.3584 -0.7793

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TABLE 16

PI and n MO'S AND ENERGIES FOR GLYOXAL BY THE EHMO METHOD

 C_{s} plane is perpendicular to the C-C bond.

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MO	BC ^π 1	^{BC} π2	BC ^π 3	nBC	BC π4	BC ^π 5	вс ^т б	
Energy (eV)	-15.652	-15.359	-13.273	-12.626	-10.914	-8.1698	-7.353	
C Symmetry	Α-	A	A-	A-	A^	A^^^	A**	
Coefficients						<u></u>		
H(1)	-0.0029	0.0110	0.0072	0.2265	-0.0082	0.0187	-0.0100	
H(3)	0.0273	-0.0162	-0.0009	-0.0223	0.0212	0.0059	0.0155	
H(5)	-0.0266	0.0230	0.0006	-0.0014	0.0001	-0.0009	-0.0053	
0(1,s)	0.0019	0.0054	0.0037	0.0046	-0.0010	0.0015	-0.0007	
C(2,s)	-0.0017	-0.0018	0.0153	-0.1010	-0.0015	0.0041	-0.0032	
C(5,s)	0.0077	0.0031	-0.0003	-0.0085	0.0106	0.0011	0.0056	
0(1, x)	0.0126	-0.0625	-0.0390	0.4579	-0.0063	0.0050	-0.0030	
C(2,x)	0.0112	-0.0067	0.0307	-0.3631	0.0057	-0.0069	0.0048	
C(5,x)	0.0124	-0.0038	0.0015	0.0320	-0.0012	-0.0040	-0.0158	
0(1,y)	-0.5686	-0.6297	0.0825	0.0164	0.4374	0.1528	0.3237	
C(2,y)	-0.2809	-0.2151	-0.0478	-0.0135	-0.6002	-0.3094	-0.7159	
C(5,y)	-0.0305	0.0209	0.1805	0.0449	-0.0477	0.2148	-0.1207	
0(1,z)	0.0296	-0.0144	-0.0120	0.2718	-0.0059	0.0059	-0.0040	
C(2,z)	0.0086	-0.0202	-0.0027	-0.2022	0.0099	-0.0169	0.0116	
C(5,z)	-0.0361	0.0010	-0.5901	-0.0266	0.0816	-0.7245	0.3228	

PI AND n MO'S AND ENERGIES FOR GLYOXAL-ETHYLENE BY THE EHMO METHOD

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TABLE	18
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PI AND n MO'S AND ENERGIES FOR GLYOXAL-2 ETHYLENE BY THE EHMO METHOD

МО	π1 ^{ABC}	πABC 72	авс тз	ABC ^π 4	nABC	ABC π5	ABC π6	ABC ^π 7	ABC TA
Energy (eV)	-15.646	-15.362	-13.309	-13.235	-12.592	-10.839	-8.269	-8.024	-7.232
C _{2v} Symmetry	^B 2	^A 2	^B 2	A ₁	A	^B 2	^A 2	^B 1	^A 2
Coefficients									
H(1) H(3) H(5) O(1,s) C(2,s) C(5,s) O(1,x) C(2,x) C(5,x) O(1,y) C(2,y) C(5,y) O(1,z)	0.0 0.0258 -0.0246 0.0 0.0 0.0072 0.0 0.0114 -0.5680 -0.2786 -0.0282 0.0	0.0 0.0220 -0.0296 0.0 0.0 -0.0039 0.0 0.00 0.0047 0.6299 0.2161 -0.0271 0.0	0.0 0.0024 -0.0004 0.0 0.0 0.0009 0.0 0.0001 0.1130 -0.0638 0.1236 0.0	0.0071 -0.0033 0.0013 0.0239 -0.0013 -0.0637 0.0496 0.0013 0.0 0.0 0.1312 -0.0213	0.2292 -0.0231 -0.0011 0.0056 -0.0972 -0.0090 0.4508 -0.3602 0.0318 0.0 0.0 0.0 0.0485 0.2714	$\begin{array}{c} 0.0 \\ -0.0203 \\ -0.0003 \\ 0.0 \\ 0.0 \\ -0.0101 \\ 0.0 \\ 0.0005 \\ -0.4311 \\ 0.6008 \\ 0.0452 \\ 0.0 \end{array}$	0.0 -0.0080 0.0025 0.0 -0.0025 0.0 0.0 0.0067 -0.1759 0.3518 -0.1413 0.0	0.0303 -0.0017 0.0020 0.0024 0.0075 -0.0017 0.0082 -0.0118 0.0031 0.0 0.0 0.1755 0.0102	0.0 0.0144 -0.0045 0.0 0.0 0.0049 0.0 -0.0144 0.3114 -0.6968 0.0998 0.0
C(2,z) C(5,z)	0.0 -0.0345	0.0 -0.0024	0.0 =0.4151	-0.0017 -0.4193	-0.2075 -0.0352	0.0 -0.0781	0.0 0.4955	-0.0290 -0.5628	0.0 0.2705



FIGURE 8. Glyoxal-ethylene through-space interactions by the EHMO method.



FIGURE 9. Glyoxal-2 ethylene through-space interactions by the EHMO method.

bond and coplanar with the diketone. Significant contributions to this MO are also obtained from the $2p_x$ and $2p_z$ AO's of the carbonyl carbons while smaller contributions arise from several other basis functions. This orbital is interpreted to be a molecular orbital arising from the interaction of two lone-pair 2p AO's of the oxygens through the C-C bond of the carbonyl carbons with additional delocalization over other parts of the molecule. Although it no longer has the appearance of an isolated nonbonding atomic orbital, it will be referred to as a nonbonding orbital. All-valence-shell as well as ab initio calculations of other molecular systems have also shown the liberal delocalization of lone-pair orbitals.^{64,65}

The interaction of this orbital with the ethylene MO's also results in a destabilization relative to the corresponding orbital in the isolated diketone. The effects in this case, however, are of smaller magnitude than those obtained for the LEMO's.

An electronic transition from the HOMO to the LEMO in each of the three cases corresponds to an $n \rightarrow \pi^*$ transition that is symmetry allowed and has a polarization perpendicular to the plane of the diketone. The $n \rightarrow \pi^*$ transition energies, summarized in Table 21, are all too low in magnitude compared to the observed solution spectra. As in the simpler HMO and the SCF MO calculations, the calculations by the EHMO method again predicts a blue-shifted $n \rightarrow \pi^*$ transition as the result of interacting the diketone with the ethylene group.

Since the effects of all valence-shell electrons can be utilized in these calculations, a glyoxal-ethane aggregate was also treated by the EHMO method to test the effects of a saturated group in close proximity to the diketone on the $n \rightarrow \pi^*$ transition energy. The atom-numbering

scheme and atomic coordinates used for this calculation are shown in Figure 10 and Table 19, respectively.



FIGURE 10. Glyoxal-ethane aggregate for all-valence-shell MO calculations.

TABLE	1	9
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ATOMIC COORDINATES FOR GLYOXAL-ETHANE CALCULATIONS

Atom	x(Å)	y (Å)	z (Å)
0(1)	-1.626	0.0	2.370
C(2)	-0.775	0.0	1.533
C(3)	0.775	0.0	1.533
0(4)	1.626	0.0	2.370
C(5)	-0.770	2.508	0.082
C(6)	0.770	2.508	0.082
H(1)	-0.782	0.0	0.493
H(2)	0.782	0.0	0.493
H(3)	-1.177	1.676	-0.390
H(4)	1.177	1.676	-0.390
H(5)	-1.100	2.522	1.068
Н(6)	1.100	2,522	1.068
H(7)	-1.100	3.362	-0.412
H(8)	1.100	3.362	-0.412

MO	π1	[#] 2	n	^π з	^π 4
Energy (eV)	-15.587	-15.375	-12.627	-10.903	-7.456
C symmetry	A^	A~~	Α-	Α-	A * *
Coefficients					
H(1)	0.0081	-0.0158	-0.2260	-0.0082	-0.0042
H(3)	-0.0348	-0.0087	0.0236	0.0277	0.0194
H(5)	-0.0680	0.0563	0.0030	0.0282	0.0204
H(7)	0.0992	-0.0573	-0.0045	-0.0297	-0.0299
0(1,s)	-0.0082	-0.0070	-0.0045	-0.0014	-0.0004
C(2,s)	0.0067	0.0020	0.1015	-0.0014	-0.0018
C(5,s)	-0.0124	-0.0065	0.0060	0.0173	0.0109
0(1,x)	-0.0107	0.0727	-0.4588	-0.0062	-0.0012
C(2,x)	-0.0300	0.0082	0.3642	0.0054	0.0020
C(5,x)	-0.0133	0.0060	-0.0239	-0.0022	-0.0330
·0(1,y)	0.5505	0.6179	-0.0117	0.4386	0.3561
C(2,y)	0.2561	0.2138	0.0095	-0.6046	-0.7802
C(5,y)	0.0877	-0.0300	-0.0383	-0.0248	-0.0164
0(1,z)	-0.0905	0.0163	-0.2720	-0.0051	-0.0018
C(2,z)	-0.0156	0.0244	0.2020	0.0095	0.0053
C(5,z)	-0.0824	0.0564	-0.0229	0.0263	0.0236

ΡI	AND n	MO'	S AND	ENERGIES	FOR	GLYOXAL-ETHANE	BY	THE	EHMO	METHOD

The ethane molecule was placed at that position which the outer segment of a cyclohexane ring of ODB would occupy when in the boat form and folded toward the diketone. This places the ethane molecule slightly closer to the diketone than ethylene in previous calculations due to the difference in bond distances and angles in cyclohexane and cyclohexene rings.

Inspection of Table 21 shows that for the orientations chosen, the effects of an ethylene or an ethane molecule on the nonbonding orbital of glyoxal are identical. For each case, this orbital is destabilized by 0.030 eV, from -12.657 eV to -12.627 eV. The effects on the LEMO, however, are slightly different. Ethylene destabilizes the LEMO of glyoxal by 0.080 eV while ethane destabilizes this MO by 0.091 eV. Although this is not a large energy difference, it does predict a smaller $n \rightarrow \pi^*$ transition energy for a glyoxal-ethylene than for glyoxal-ethane aggregate.

The total electronic ground-state energies of the aggregates, calculated as sums of one-electron orbital energies, show net destabilization for both glyoxal-ethylene and glyoxal-ethane aggregates when compared to the isolated noninteracting systems (Table 22). However, a smaller destabilization is calculated for glyoxal-ethylene than glyoxalethane.

CNDO/2 Calculations

The molecular species of Figures 7 and 10 were next used for a series of CNDO/2 calculations. Molecular aggregates were formed in the same manner as for the EHMO calculations with the atomic coordinates of Tables 12 and 19. The CNDO/2 formulation of Del Bene and Jaffé, 54,55 described in Chapter II, and a CNDO/2 computer program kindly provided by Dr. H. H. Jaffé⁶⁶ were employed for this purpose. These calculations are

$n \rightarrow \pi^*$ TRANSITION ENERGIES FOR MOLECULAR AGGREGATES STUDIED

System	LEMO(eV)	HOMO(eV)	∆E(eV)	λ (mµ)
Glyoxal	-10.994	-12.657	1.663	746
Glyoxal-Ethylene	-10.914	-12.627	1.713	723
Glyoxal-Ethane	-10.903	-12.627	1.724	718
Glyoxal-2 Ethylene	-10.839	-12.593	1.756	707

BY THE EHMO METHOD

TABLE 22

TOTAL GROUND-STATE ELECTRONIC ENERGIES FOR MOLECULAR AGGREGATES

STUDIED BY THE EHMO METHOD

System	Energy(eV)	Stabilization*(eV	
Glyoxal	-429.147		
Ethylene	-213.228		
Ethane	-248.656		
Ethylene-Ethylene	-426.536	-0.080	
Glyoxal-Ethylene	-642.096	+0.279	
Glyoxal-Ethane	-677.333	+0.470	
Glvoxal-2 Ethvlene	-855.026	+0.577	

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expected to provide the most sensitive tests of the effects of throughspace interactions on the $n \rightarrow \pi *$ transition energies of the diketones. As in the EHMO method, pi and lone-pair orbital energies are obtained explicitly by this all-valence-shell calculation but now electron repulsion terms are also included in the calculation of orbital energies and configuration transition energies. In addition, the method also allows $n \rightarrow \pi *$ transition energies to be calculated after configuration interaction (CI). In this work, all state-transition energies are based on CI calculations which utilize the forty lowest one-electronexcited configurations.

Basis functions for the CNDO/2 method are Slater atomic orbitals for which overlap integrals are calculable by the method of Mulliken, et al.³⁴ The Slater exponents, as well as other parameters used here are shown in Table 23. These parameters are the optimum values found by

TABLE 23

Parameter	H	С	0
Slater exponent Core integral of s orbital (eV) Core integral of p orbital (eV) One-center repulsion integral (eV) Resonance integral term, β [°] (eV)	1.200 -14.352 12.85 -12.00	1.625 -28.102 -11.144 11.11 -17.00	2.275 -50.780 -18.222 13.00 -45.00

PARAMETERS FOR CNDO/2 CALCULATIONS

Del Bene and Jaffé^{54,55} for predicting spectral data most consistently for a range of organic compounds. Resonance integrals were calculated by Eq. 54, as $\beta_{pq} = 0.5k(\beta_A^0 + \beta_B^0)S_{pq}$ with k=1.0 for sigma-overlap contributions to β_{pq} , while k=0.585 for pi-overlap contributions as suggested by Del Bene and Jaffé. Two-center repulsion integrals were evaluated by the extrapolation method of Pariser and Parr.⁴² Orbital energies were used as the criterion of self-consistence, interactions were terminated when every MO energy changed by less than 0.0001 hartree. The energies and coefficients of the pi MO's and the nonbonding MO in systems involving the diketone are shown in Tables 24-29. The HOMO for each system which contains the diketone is the nonbonding orbital of the dicarbonyl group. It is quite similar in form to the corresponding HOMO obtained by the EHMO method, a symmetric combination of two lonepair orbitals from the oxygens with lesser contributions from neighboringatom AO's. The LEMO for each system containing the diketone is an antibonding pi MO centered primarily on the diketone.

The interactions between the MO's of glyoxal and the ethylenes produce results (Figures 11 and 12) which are quite similar to those calculated by the EHMO method. The LEMO and HOMO of glyoxal are both destabilized upon aggregate formation. For aggregates of glyoxal and

TABLE 24

PI MO'S AND ENERGIES FOR ETHYLENE BY THE CNDO/2 METHOD

MO Energy (eV)	π_{1}^{C} -11.941	π ₂ ^C 1.281
C symmetry*	A	A
Coefficients C(5,y) C(5,z)	-0.1925 0.6802	-0.1924 0.6802

*C plane perpendicular to the C-C bond.

TABLE	25
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MO	π1 AC	π 2 AC	ΑC ^π 3	π_4^{AC}
Energy (eV)	-11.942	-11.936	1.282	1.283
C _{2v} Symmetry	Al	^B 2	Bl	^A 2
Coefficients				
C(5,y) C(5,z)	-0.1352 0.4801	-0.1370 0.4818	-0.1345 0.4760	-0.1376 0.4879

PI MO'S AND ENERGIES FOR ETHYLENE-ETHYLENE BY THE CNDO/2 METHOD

TABLE 26

PI AND n MO'S AND ENERGIES FOR GLYOXAL BY THE CNDO/2 METHOD

MO	π_1^B	π_2^{B}	n ^B	π_3^B	^B π4
Energy (eV)	-17.020	-15.052	-10.974	-0.170	2.077
C _s Symmetry*	A´	A	A´	A-	A
C _{2v} Symmetry	^B 2	A ₂	A ₁	^B 2	^A 2
Coefficients					
H(1)	0.0	0.0	-0.2263	0.0	0.0
0(1,s)	0.0	0.0	0.0086	0.0	0.0
С(2,в)	0.0	0.0	0.1170	0.0	0.0
0(1,x)	0.0	0.0	-0.4445	0.0	0.0
C(2,x)	0.0	0.0	0.3110	0.0	0.0
0(1,y)	0.5202	0.5933	0.0	0.4790	0.3847
C(2,y)	0.4790	0.3847	0.0	-0.5201	-0,5933
0(1,z)	0.0	0.0	-0.3442	0.0	0.0
C(2,z)	0.0	0.0	0.1490	0.0	0.0

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*C_s plane perpendicular to C-C bond.

MO Energy (eV)	^π 1 -16.852	π2 -14.857	π ₃ -12.273	n ^{BC} -10.821	^π 4 -0.037	ΒC ^π 5 0.772	ΒC ^π 6 2.204
C symmetry	A	A**	A´	A´	Α-	A**	A
Coefficients							
H(1)	0.0123	-0.0015	0.0060	-0.2296	0.0064	0.0130	-0.0045
H(3)	-0.1660	-0.1585	-0.0082	0.0231	-0.0151	0.0081	0.0045
H(5)	-0.0935	0.1398	0.0014	-0.0066	0.0106	0.0082	-0.0110
0(1,s)	0.0049	0.0015	0.0052	0.0078	0.0003	0.0007	0.0001
C(2,s)	0.0094	0.0024	0.0314	0.1112	0.0014	0.0079	-0.0052
C(5,s)	0.0005	-0.0127	-0.0111	0.0180	-0.0193	-0.0135	0.0186
0(1,x)	-0.0321	-0.0760	-0.0598	-0.4382	0.0047	0.0017	-0.0008
C(2,x)	-0.0084	-0.0160	0.0375	0.3077	-0.0041	-0.0031	-0.0018
C(5,x)	0.2993	0.0099	0.0190	-0.0249	0.0066	0.0048	-0.0095
0(1,y)	0.4423	0.5388	0.1091	-0.0216	-0.4733	0.0836	0.3747
C(2,y)	0.4026	0.3409	0.0333	0.0034	0.5220	-0.1054	-0.5840
C(5,y)	0.0256	0.1803	0.1960	-0.0495	0.0262	0.1891	-0.0472
0(1,z)	-0.0220	-0.0723	-0.0374	-0.3416	0.0048	0.0022	-0.0026
C(2,z)	-0.0248	-0.0221	-0.0105	0.1540	-0.0062	-0.0125	0.0035
C(5,z)	0.1155	0.0649	-0.6637	0.0576	-0.0438	-0.6674	0.1251
5(3,2)	0.1177	0.0043	-0.0037	0.0070	-0.0430	-0.007	4

PI AND n MO'S AND ENERGIES FOR GLYOXAL-ETHYLENE BY THE CNDO/2 METHOD

TABLE	28
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PI AND n MO'S AND ENERGIES FOR GLYOXAL-2-ETHYLENE BY THE CNDO/2 METHOD

MO Energy (eV)	ABC ^π 1 -16,751	π^{ABC}_{2}	π_{3}^{ABC}	$^{\text{ABC}}_{\pi_4}$	n ^{ABC}	ABC ^T 5 0.089	ABC ¹⁷ 6 0,733	ABC ^π 7 0,844	ABC ^π 8 2,319
C _{2v} Symmetry	^B 2	A ₂	^B 2	A1	A1	^B 2	A2	^B 1	A ₂
Coefficients									
H(1)	0.0	0.0	0.0002	0.0096	-0.2331	0.0	0.0	0.0195	0.0
H(3)	0.1252	-0.1269	0.0053	-0.0064	0.0233	0.0148	-0.0066	0.0047	-0.0043
H(5)	0.0602	0.1095	-0.0004	0.0016	-0.0070	-0.0104	-0.0043	0.0076	0.0106
0(1,s)	0.0	0.0	0.0001	0.0076	0.0070	0.0	0.0	0.0010	0.0
C(2,s)	0.0	0.0	0.0007	0.0444	0.1053	0.0	0.0	0.0124	0.0
C(5,s)	0.0044	-0.0123	0.0073	-0.0085	0.0185	0.0188	0.0070	-0.0127	-0.0179
0(1,x)	0.0	0.0	-0.0013	-0.0843	-0.4321	0.0	0.0	0.0028	0.0
C(2,x)	0.0	0.0	0.0008	0.0527	0.3044	0.0	0.0	-0.0040	0.0
C(5,x)	-0.2088	0.0095	-0.0135	0.0134	-0.0246	-0.0063	-0.0020	0.0051	0.0091
0(1,y)	-0.4387	0.5351	-0.1544	0.0024	0.0	0.4681	-0.1082	0.0	-0.3676
C(2,y)	-0.3973	0.3326	-0.0475	0.0008	0.0	-0.5239	0.1343	0.0	0.5783
C(5,y)	-0.0220	0.1427	-0.1348	0.1424	-0.0500	-0.0251	-0.1300	0.1387	0.0433
0(1,z)	0.0	0.0	-0.0008	-0.0522	-0.3390	0.0	0.0	0.0040	0.0
C(2,z)	0.0	0.0	-0.0002	-0.0157	0.1594	0.0	0.0	-0.0186	0.0
C(5,z)	-0.1068	0.0533	0.4593	-0.4791	0.0581	0.0427	0.4668	-0.4799	-0.1133

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PI AND n MO'S AND ENERGIES FOR GLYOXAL-ETHANE BY THE CNDO/2 METHOD

MO	π1	^π 2	n	^π 3	^π 4
Energy (eV)	-16.547	-14.530	-10.828	-0.042	2.151
C _S Symmetry	A^	A**	A´	A^	A**
Coefficients					
H(1)	0.0183	-0.0018	-0.2260	0.0068	-0.0039
H(3)	0.0235	-0.0530	0.0241	-0.0204	0.0108
H(5)	0.0116	-0.1730	0.0022	-0.0172	0.0085
H(7)	0.1784	0.2030	-0.0120	0.0398	-0.0289
0(1,s)	0.0125	0.0012	0.0081	0.0006	0.0005
C(2,s)	0.0120	0.0009	0.1124	0.0014	-0.0041
C(5,s)	-0.0764	-0.0215	0.0138	-0.0320	0.0240
0(1,x)	-0.0249	-0.0755	-0.4418	0.0047	-0.0007
C(2,x)	0.0165	-0.0196	0.3097	-0.0039	-0.0018
C(5,x)	-0.3437	0.0141	-0.0145	0.0075	-0.0143
0(1,y)	0.4280	0.4980	-0.0141	-0.4721	0.3817
C(2,y)	0.3699	0.3016	0.0040	0.5229	-0.5936
C(5,y)	0.1239	0.1726	-0.0342	0.0096	-0.0053
0(1,z)	0.0142	-0.0871	-0.3443	0.0043	-0.0024
C(2,z)	-0.0214	-0.0151	0.1541	-0.0059	0.0021
C(5,z)	-0.0771	-0.2068	-0.0157	-0.0128	0.0087

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FIGURE 11. Glyoxal-ethylene through-space interactions by the CNDO/2 method.



FIGURE 12. Glyoxal-2 ethylene through-space interactions by the CNDO/2 method.

ethylenes, the destabilization of both orbitals is almost exclusively due to the bonding pi MO's of the ethylenes. A CNDO/2 calculation was also made for a glyoxal-ethane aggregate for comparison. A destabilization was also calculated here for both the HOMO and the LEMO of the diketone. This is attributable to the nearest lying sigma orbital of ethane with A' symmetry, an orbital at -16.126 eV that is strongly C-C bonding with considerable C-H bonding, involving hydrogens 3,4,5, and 6. The ethylene and ethane molecules are nearly equally effective in this throughspace interaction, destabilizing the LEMO by 0.13 eV and the HOMO by 0.15 eV (Table 30). This fact in itself seems to clearly indicate that a consideration of the through-space interaction between the pi systems alone can not be used to explain the absorption spectra of the tricyclic compounds considered.

With the inclusion of electron repulsion, transition energies are properly calculated by Eq. 36 as configuration transition energies and improved by configuration interaction to yield state transition energies. Values of the $n \rightarrow \pi^*$ transition energies for the molecular aggregates considered are shown in Table 30. For all cases, a larger $n \rightarrow \pi^*$ transition energy is calculated for the molecular aggregates than for glyoxal alone. Glyoxal-ethylene and glyoxal-ethane show nearly identical values, particularly after configuration interaction, with predicted absorption maxima at 484 and 485 mµ, respectively. The presence of two ethylene molecules shows a larger blue-shift. The peak maximum for glyoxal-2 ethylene is calculated at 457 mµ, compared to 494 mµ for glyoxal alone. It may be noted that the observed $n \rightarrow \pi^*$ transition energies are much closer to the CI energies which were calculated here than to the transition energies calculated by the EHMO method.

$n {\rightarrow} \pi {\ast}$ TRANSITION ENERGIES FOR MOLECULAR AGGREGATES

			$n \rightarrow \pi *$ Transition					
	LEMO	HOMO	Configuration		State			
System	(eV)	(eV)	∆E(eV)	λ (m μ)	$\Delta E(eV)$	λ (mμ)		
Glyoxal	-0.170	-10.974	3.132	396	2.508	494		
Glyoxal-Ethylene	-0.037	-10.821	3.202	387	2.562	484		
Glyoxal-Ethane	-0.042	-10.828	3.165	39 2	2.545	485		
Glyoxa1-2 Ethylene	0.089	-10.673	3.263	380	2.712	457		

STUDIED BY THE CNDO/2 METHOD

TABLE 31

TOTAL GROUND-STATE ELECTRONIC ENERGIES FOR MOLECULAR AGGREGATES

STUDIED BY THE CNDO/2 METHOD

System	Energy	Stabilization* (eV)
Glvoxal	-759.825	
Ethylene	-246.244	
Ethane	-270.133	
Ethylene-Ethylene	-482.567	+9.921
Glvoxal-Ethylene	-962.341	+43.728
Glyoxal-Ethane	-962.208	+67.750
Glyoxal-2 Ethylene	-1154.937	+97.376

*Compared to noninteracting systems. Positive values indicate destabilization.

The total electronic ground-state energy for all molecular aggregates formed shows a large destabilization compared to the isolated noninteracting systems. These effects are much larger than those calculated by the EHMO method, as expected, since electron repulsion terms are included in the CNDO/2 formulation. The glyoxal-ethane system again shows a larger destabilization than glyoxal-ethylene. But the small energy difference infers that the through-space interaction of the saturated or unsaturated species in the six-membered rings with the glyoxal moiety is not very large and can not be used to explain the variation of the n+ π * transition in the series.

Intramolecular Interactions

The above studies of through-space interactions between molecules has clearly failed to show a red-shifted $n \rightarrow \pi *$ transition for the diketone when allowed to interact with one or two ethylene molecules. Indeed, a blue-shifted transition was calculated for the interacting systems. Calculations presented here are based on whole molecules which include the segments previously considered. Electronic interactions can proceed not only through spatial overlap but also through the intervening bonds of the molecule which are now included. The likely importance of this inclusion can be seen by examining the overlaps of the pi systems with the sigma bonds now present in the model. The total effect is reflected in the resulting MO energies.

The fourteen species shown in Figure 13 were used for these calculations. These represent the nonredundant geometric configurations of five different molecules with the six-membered rings always in the boat form. The atomic coordinates of the fourteen species used in these

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FIGURE 13. Configuration of the five molecules considered in the investigation of intramolecular interactions.

calculations are shown in Appendix A. Coordinates of V are the C21 symmetrized values of the coordinates obtained from the crystal structure of this molecule. For VI and VII, the cyclohexene rings were folded away from the diketone system in such a way that all bond lengths and angles remained unchanged from the corresponding values in V. The saturated six-membered rings in VIII-XIV were constructed by keeping the geometry at the bridge-head carbons very close to that of V and making all other C-C-C, C-C-H, and H-C-H angles tetrahedral. Bond lengths for C-C and C-H were taken at 1.540 and 1.040 Å, respectively. Coordinates of the six-membered rings in I-IV are identical to those of the tricyclic analogs. Two hydrogen atoms were introduced into these species to maintain the hybridization of the bridge-head carbons the same as in the tricyclic species. They were placed at 1.040 Å from the carbon atom to which they are bonded in the direction of the carbon atoms they replace in the tricyclic analogs. The four-membered ring and the two oxygen atoms are kept coplanar for all species, using the bond lengths and angles from the crystal structure of V.

A common atom-numbering scheme for the identification of atomic coordinates and AO basis functions is used here for all species, although only XII-XIV possess all the atoms shown in Figure 14. For VIII-XI, H(15) and H(16) are deleted, while for V-VII, H(13) and H(14) are also deleted. Removal of these hydrogens and the formation of double bonds alters the coordinates of nearby atoms, as seen in Appendix A. The two introduced hydrogens in I-IV are labeled H(17) and H(18), while the remaining atoms have the labels of the corresponding atoms in the tricyclic analogs. The EHMO and CNDO/2 methods were used here with all parameters unchanged



FIGURE 14. Atom-numbering scheme for the intramolecular interaction studies.

from those used in the previous calculations described (Tables 13 and 23).

EHMO Calculations

The energies of all pi MO's and the HOMO (n) for the fourteen species of Figure 13 are shown in Table 32. The corresponding values for glyoxal, previously discussed, are also included here for reference. The labels chosen for the pi MO's reflect the bonding and antibonding characteristics of these orbitals as well as the major contributing basis functions. Thus, π_1 (CO) and π_2 (CO) are the lowest and second-lowest bonding pi MO's which have their major contributions from basis functions of the dicarbonyl segment of the molecules and $\pi_1^*(CO)$ and $\pi_2^*(CO)$ are the antibonding orbitals centered on this part of the molecule. For the unsaturated diketones, the pi MO's which are centered on the C-C double bonds are labeled $\pi_1(CC)$ and $\pi_2(CC)$ for bonding MO's and $\pi_1^*(CC)$ and $\pi_2^*(CC)$ for the antibonding orbitals. The orbital labeled n contains the symmetric combination of the oxygen lone-pair orbitals and was found to be the HOMO for each of the molecules studied. The LEMO for each molecule was found to be the orbital labeled $\pi_1^*(CO)$, the lowest-energy antibonding pi MO centered on the diketone part of the molecule. The coefficients of the HOMO and LEMO of all molecules are tabulated in Appendix B.

The effects of the six-membered rings on the energies of the HOMO and LEMO can be seen in Figure 15 and Table 32. One six-membered ring elevates both the HOMO and the LEMO by approximately 0.4 eV while two rings raise the energy of these MO's by average values of 0.6 and 0.5 eV, respectively, compared to the corresponding MO's of glyoxal. These effects are 5-10 times as large as the corresponding energy level changes calculated for the through-space interactions (Table 21). Definite

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MO C Summo		π ₁ (CO)	π ₂ (CO)	π ₁ (CC)	π ₂ (CC)	n	π ₁ *(CO)	π ₁ *(CC)	^π 2 ^{*(CC)}	^π 2 ^{*(CO)}
s S	etru	R	A A	A A	R	Α Δ	R	R	Δ	Δ
2v 3ymm		¹ 2	^A 2	^A 1	² 2	^ <u>1</u>	<u> </u>	1	<u>^2</u>	<u>~2</u>
Molecule	Point Group				Energy	(eV)				
Glyoxal	C ₂₁₇	-15.659	-15.358			-12.657	-10.994			-7.521
I	ເຼັ	-15.481	-15.331	-12.751		-12.141	-10.589	-7.624		-7.202
II	ເຼັ	-15.688	-15.331	-12.666		-12.199	-10.556	-7.652		-7.146
III	ິ	-15.567	-15.307			-12.234	-10.580			-7.202
IV	ເຼັ	-15.610	-15.367			-12.217	-10.583			-7.211
v	C _{2v}	-15.911	-15.467	-12.884	-12.517	-12.001	-10.531	-7.724	-7.512	-7.158
VI	C _s	-15.790	-15.272	-12.827	-12.504	-12.019	-10.502	-7.725	-7.538	-7.104
VII	C _{2v}	-15.728	-15.402	-12.867	-12.414	-12.051	-10.476	-7.732	-7.547	-7.052
VIII	C	-15.638	-15.217	-12.711		-12.048	-10.522	-7.616		-7.158
IX	ເຼັ	-15.740	-15.422	-12.697		-12.028	-10.527	-7.614		-7.167
X	ເຼັ	-15.605	-15.286	-12.597		-12.087	-10.492	-7.637		-7.108
XI	ເຼັ	-15.687	-15.388	-12.572		-12.065	-10.498	-7.625		-7.115
XII	C2v	-15.536	-15.208			-12.122	-10.513			-7.156
XIII	C	-15.585	-15.283			-12.104	-10.518			-7.165
XIV	с ₂	-15.634	-15.383			-12.085	-10.523			-7.175

ENERGIES OF PI AND n MO'S OF GLYOXAL AND I-XIV BY THE EHMO METHOD



FIGURE 15. LEMO and HOMO energies of I-XIV by the EHMO method.

trends can also be seen in the MO energies which depend both on the nature of the six-membered rings and their conformations. A cyclohexene ring which is folded toward the diketone destabilizes the HOMO more and the LEMO less than when such a ring is folded away from the diketone. The destabilizing effects produced by a saturated six-membered ring are exactly opposite in nature and of somewhat smaller magnitudes. This pattern holds for the tricyclic as well as the bicyclic molecules studied.

To understand this pattern of MO energies, several important features must be considered. The HOMO and LEMO of each system is much closer in energy to lower, occupied MO's than to higher, unoccupied MO's with the proper symmetry for mixing. The orbitals n through $\pi_2^*(CO)$ in Table 32 are all consecutive levels with the next, higher level about 7 eV removed. The MO's $\pi_1^*(CC)$, $\pi_2^*(CC)$, and $\pi_2^*(CO)$ are of different symmetries than n and π_1 *(CO) and are therefore not mixed with these orbitals. The nearest higher-energy MO's to n and π_1 *(CO) are thus 10-12 eV removed. The occupied orbitals, however, are much closer in energy to n and $\pi_1^*(CO)$. Not only are $\pi_1(CC)$ and $\pi_2(CC)$ (for molecules where they exist) less than one electron-volt below n, but the three electron-volt gaps between n and π_1 (CO) contain 4-5 sigma orbitals, for bicyclic species, and 7-8 sigma orbitals, for the tricyclic species, which have the proper symmetries for mixing with n or $\pi_1^*(CO)$. Due to the presence of these nearby energy levels, any interaction between an isolated orbital $\pi_1^*(CO)$ or an isolated n orbital with MO's in the rings results in the destabilization of $\pi_1^*(CO)$ or n, since when two isolated systems are allowed to interact, the level of higher energy is destabilized and the level of lower energy is stabilized. The result of such interactions is evident in Figure 15 where

the energies of n and $\pi_1^*(CO)$ for I-XIV are always higher than the energies of the corresponding MO's in glyoxal.

The trends in the energy levels shown in Figure 15 can be explained by noting the orientations of the orbitals which can best mix with n and $\pi_1^*(CO)$. Species I-IV suffice for this purpose (Figure 16). The ethylene pi system mixes best with the HOMO when folded toward the diketone group, as in I, and best with the LEMO when folded away from the diketone, as in II, thereby causing maximum destabilization of these MO's. Participation by the intervening sigma orbitals is required for both cases. For III and IV, where only sigma orbitals are available for mixing with n and $\pi_1^*(CO)$, the opposite trend is expected. A sigma orbital in the sixmembered rings destabilizes $\pi_1^*(CO)$ more when folded toward the diketone (III) and has a larger effect on n when folded away (IV). The actual compositions of the calculated HOMO's and LEMO's can be deduced from the MO coefficients in Appendix B. The MO's in the tricyclic systems are similar except that basis functions from both six-membered rings contribute.

The fact that a change in the conformation of a cyclohexene ring induces a larger change in the energies of n and $\pi_1^*(CO)$ than when the conformation of a cyclohexane ring is altered can be attributed to two factors. First, the $\pi(CC)$ orbitals are higher in energy than most of the sigma orbitals with the same symmetry and can induce more significant changes in the energies of n and $\pi_1^*(CO)$. For I, II, X, and XI, $\pi_1(CC)$ is the closest MO to n with A' symmetry, while for VIII and IX one sigma MO lies less than 0.1 eV above $\pi_1(CC)$. For V-VII, $\pi_2(CC)$ is always closest to n with one sigma orbital between $\pi_1(CC)$ and $\pi_2(CC)$. Second, the $\pi(CC)$





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FIGURE 16. Hybridized AO's making major contributions to the HOMO's(I,IV) and LEMO's(II,III) for the conformations favorable for maximum interaction between the diketone and the six-membered ring.

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orbitals do not have sigma analogs of comparable energy in the saturated rings. Thus I, II, and V-XI have more nearby MO's which can mix with n and $\pi_1^*(CO)$ and a conformational change in the six-membered rings can, therefore, alter the energies of the latter MO's more drastically in these species.

The overall effects of changing the molecular conformations on the $n \rightarrow \pi^*$ transition energies and the total electronic ground-state energies can be seen from Table 33. Although the calculated transition energies are always too small, several interesting trends can be seen. A larger difference in transition energies and total ground-state energies is calculated between two species where a cyclohexene ring has changed conformation than when a saturated ring has been altered. Only one exception to this trend is seen, XIV is nearly one electron volt less stable than XII. XIV requires H(13) and H(16) as well as H(14) and H(15) to be about 1.5 Å apart, a separation less than two hydrogen van der Waals' radii. For the bicyclic species, I is 0.059 eV more stable than II and has an $n \rightarrow \pi^*$ transition energy that is nearly 0.1 eV smaller than that of II. The opposite effects are seen for the saturated analogs of I and II. IV is 0.048 eV more stable than III and also has the smaller transition energy, but only a 0.02 eV difference. The same trends in transition energies follow in the tricyclic species, a cyclohexene ring folded toward the diketone induces a red shift while a cyclohexane ring folded toward the diketone induces a blue shift to the $n \rightarrow \pi^*$ transition. The total ground-state energies of the tricyclic species are always calculated to be most stable when both rings are folded toward the diketone and least stable when both rings are folded away.

 $n{\rightarrow}\pi{*}$ Transition energies and total electronic ground-state energies

FOR GLYOXAL AND I-XIV BY THE EHMO METHOD

Molecule	n→π* Tr ΔE(eV)	ansition λ(mμ)	Total Ground- State Energy (eV)	∆(eV)*	N**
Glyoxal	1.663	746	-429.147		
I	1.552	799	-958.142		
II	1.643	755	-958.083	0.059	0.100
III	1.654	750	-993.550	0.048	0.154
IV	1.634	759	-993.598		
v	1.470	844	-1310.080		
VI	1.517	818	-1309.972	0.108	0.030
VII	1.575	788	-1309.843	0.237	0.000
VIII	1.526	813	-1345.459		
IX	1.501	826	-1345.453	0.006	0.792
Х	1.595	778	-1345.373	0.086	0.035
XI	1.567	792	-1345.342	0.117	0.009
XII	1.609	771	-1380.865		
XIII	1.586	782	-1380.838	0.027	0.699
XIV	1.562	794	-1379.933	0.932	0.000

*Ground-state energy above that of the most stable conformation.

**Number of molecules in the stated conformation per molecule of the most stable conformation as predicted by a Boltzmann distribution at 25°C. An interpretation of the solution spectra of the three tricyclic diketones is possible on the basis of these calculations. This was not possible with the molecular aggregate studies discussed earlier. The saturated molecule (ODB) may be expected to exist primarily as XII and XIII. The calculated $n \rightarrow \pi *$ transition energies of these conformations



differ by only 0.024 eV, and a single, broad absorption peak may be expected from a mixture of XII and XIII. The diene (2DB) is predicted to exist primarily as V with successively smaller contributions from the conformations VI and VII. Such an interpretation is consistent with



the solution absorption spectrum of this compound which shows a broad,
unsymmetric absorption peak with a diminishing absorbance toward the highenergy side. This could correspond to the smaller concentrations of VI and VII for which higher transition energies are calculated, compared to V.

The total ground-state energies calculated for the four conformations of 1DB (VIII-XI) differ by less than 0.12 eV and significant concen-



trations of all species may thus be expected in solution. Species X, which is only 0.086 eV less stable than the most stable conformation (VIII), has the largest transition energy of the four species. The value of 1.595 eV is practically the average value of the transition energies of the saturated species XII and XIII. An absorption due to X should thus be seen at the same wavelength as the peak of ODB. One of the two peak maxima of 1DB does indeed appear at this wavelength. The calculated transition energies of VIII and IX are not too far removed from that of V. Absorption due to these conformations can give rise to the long-wavelength absorption peak of 1DB which is closed to the peak maximum of the 2DB absorption band. The relative intensities of the two absorption peaks of 1DB are not well explained, however. On the basis of these calculations, the predominant species of 1DB should be VIII and IX and both of these conformations were assigned as contributors to the long-wavelength peak in the spectrum. Yet the intensity of the

short-wavelength peak is slightly larger. A plot of $\varepsilon(M^{-1}cm^{-1})$ vs. $\tilde{v}(cm^{-1})$ of the 1DB spectrum was resolved into two separate peaks and the peak areas were measured with a planimeter. The integrated intensity of the short-wavelength band was determined to be about 2.5 times as large as that of the second band.

CNDO/2 Calculations

The computer-time requirements of this method did not make it feasible to allow CNDO/2 calculations on the tricyclic species (V-XIV) for Figure 13. Thus only the bicyclic species (I-IV) were treated here both for comparison with the EHMO results and the CNDO/2 intermolecular interaction studies. The CNDO/2 parameters used here are the same as those employed earlier (Table 23). The atom-numbering scheme, atomic coordinates (Appendix A), and MO labels are identical with those used for I-IV with the EHMO calculations.

The orbital energies of the pi MO's and the orbital n are shown in Table 34. The corresponding values for cis-glyoxal are also included here for reference. Some close similarities were found between these and the EHMO results. Again the orbital n is the HOMO while $\pi_1^*(CO)$ is the LEMO for each case (coefficients for these MO's are in Appendix B). The energy differences between the LEMO's and HOMO's follow the same pattern as the EHMO results, the energy gap increases in the order I, II, IV, III, glyoxal. The effects of the intervening sigma bonds on the interaction between the ethylene pi system and the orbitals $\pi_1^*(CO)$ and n can be assessed by comparing the LEMO and HOMO energies of I with the glyoxal-ethylene aggregate previously described (Table 30). The energy

TABLE	34
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ENERGIES	OF	PI	AND	n	MO'	S ·	OF	GLYOXAL	AND	I-IV	BY BY	THE	CNDO.	/2	METHOD
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MO	π ₁ (co)	π ₂ (CO)	π ₁ (CC)	n	^π 1*(CO)	π ₁ *(CC)	^π 2 ^{*(CO)}	$E[\pi_1^*(CO)] - E[n]$
C _s Symmetry	A´	A**	A´	A	A	A ~ ^	A	
Molecule				Energy	(eV)			
Glyoxal	-17.020	-15.052		-10.974	0.170		2.077	10.804
I	-15.489	-14.475	-11.264	-10.204	0.304	0.998	2.421	10.508
II	-15.344	-13.736	-11.211	-10.262	0.260	1.004	2.371	10.522
III	-15.234	-14.501		-10.264	0.308		2.413	10.572
IV	-15.491	-14.795		-10.242	0.297		2.416	10.539

of $\pi_1^*(CO)$ in I is 0.341 eV higher than that of the aggregate while n is 0.617 eV higher in I than in the aggregate. The inclusion of sigma bonds has thus decreased the energy gap by 0.276 eV. A similar comparison of MO energies calculated by the EHMO method (Tables 17 and 32) shows that $\pi_1^*(CO)$ of I is 0.325 eV higher than that of the aggregate while n is 0.485 eV higher in I than in the aggregate. Inclusion of the intervening sigma bonds in this method has reduced the LEMO-HOMO energy gap by 0.160 eV.

Electronic transition energies, of course, are not taken as simple orbital-energy differences in this approximation but are evaluated by Equation 36 and improved by a configuration interaction. The calculated $n \rightarrow \pi^*$ transition energies as well as the total ground-state energies for glyoxal and I-IV are shown in Table 35. The results here are quite dif-

TABLE 35

$n \rightarrow \pi^*$ TRANSITION ENERGIES AND TOTAL ELECTRONIC GROUND-STATE ENERGIES FOR GLYOXAL AND I-IV BY THE CNDO/2 METHOD

	Configu Transi	ration tion	Sta Transi	te tion	Total Ground- State Energy	
Molecule	∆E (eV)	λ (mµ)	∆E(eV)	λ (m μ)	(eV)	∆(eV)*
Glyoxal	3.123	396	2.508	494	-759.825	
I	3.341	371	2.753	450	-1179.301	6.497
II	3.228	384	2.753	450	-1185.798	
III	3.182	390	2.605	476	-1174.762	15.469
IV	3.159	392	2.640	470	-1190.231	

*Ground-State energy above that of the more stable conformation.

ferent from the EHMO results. After CI, the $n \rightarrow \pi^*$ transition energies are not very dependent upon the conformations of the six-membered rings. For I and II, this value is 2.753 eV while for III and IV, values of 2.605 and 2.640 eV, respectively, are calculated. Lower transition energies are obtained for the saturated species than for I and II, in conflict with the EHMO results where I had the lowest transition energy followed by IV, II, and III in order of increasing transition energies.

The total ground-state energies show a strong dependence on the conformations of the six-membered rings. In each case, the conformation with the six-membered ring folded away from the diketone system is the more stable conformation. EHMO calculations also show IV to be more stable than III, but for the unsaturated species, I was calculated as more stable than II. The conformational energy differences are also considerably smaller by the EHMO method than by the CNDO/2 method.

CHAPTER IV

CONCLUSIONS

The effects of including all intervening sigma bonds on the interactions between weakly-coupled systems have been tested for a series of compounds by four molecular orbital methods. A molecular aggregate of a <u>cis</u>-glyoxal and an ethylene molecule, used for the through-space interaction studies, showed by the four MO methods that the pi system of ethylene destabilizes the LEMO of glyoxal, an antibonding pi MO. The all-valence-shell calculations also showed that ethylene also destabilizes the HOMO of glyoxal. The combined effects were such that all MO methods predicted a larger $n \rightarrow \pi^*$ transition energy for the aggregate than for the isolated glyoxal molecule. An aggregate formed from one glyoxal and two ethylene molecules showed even a larger $n \rightarrow \pi^*$ transition energy.

All-valence-shell calculations on bicyclic and tricyclic diketones, whose unsaturated segments the molecular aggregate studies approximated, showed the participation of intervening sigma bonds in the pi-electron interactions. EHMO calculations showed that the pi system in a six-membered ring actually destabilized the LEMO in the diketone system more when the separation between the centers increased to distances where the orbital overlap becomes negligible but the

orientations became favorable for both pi systems to mix with the intervening sigma orbitals. Thus, for the molecules studied, the interaction between the pi systems was primarily transmitted through the sigma bonds. The interaction between the nonbonding orbital of the diketone and the ethylene pi MO is even more strongly dependent upon the molecular conformations, with maximum effects again calculated for those geometries where both orbitals could mix most effectively with the intervening sigma bonds.

The trends in $n \rightarrow \pi^*$ transition energies established by the molecular aggregate studies can be completely reversed by the EHMO wholemolecule calculations. Replacing a cyclohexane ring by a cyclohexene ring can result in a lower $n \rightarrow \pi^*$ transition energy, although the result is dependent on the molecular conformation (Table 33). It was also seen that only the whole-molecule EHMO calculations yielded $n \rightarrow \pi^*$ transition energies which are in qualitative agreement with the solution absorption spectra of the tricyclic diketones.

The discrepancies between the EHMO and CNDO/2 results for the calculations on species I-IV were not completely unexpected. Hoyland,⁶⁷ in a recent review article of semiempirical MO methods cites several examples where conformational analyses by these two methods have yielded diverse results. He concludes that the EHMO method seems to be more satisfactory than the CNDO/2 method for predicting molecular conformations, although it still leaves much to be desired, and that the entire area of predicting molecular conformations by semiempirical methods has not yet reached a very satisfactory level.

Conclusions about favored conformations of the tricyclic molecules, based on calculations, may be drawn from the results of the EHMO

calculations which treated the whole molecules explicitly. For all molecules, the conformations with both six-membered rings folded toward the four-membered ring (V, VIII, and XII) yielded the lowest ground-state energy, and conformations with both six-membered rings folded away from the four-membered ring (VII, XI, and XIV) had the highest ground-state energy. The two staggered conformations of 1DB showed a lower groundstate energy for IX, the species with the carbon-carbon double bond closest to the four-membered ring. It must be emphasized that the coordinates used to construct the various conformations were not the result of a minimum-energy search, but were based on the crystal structure of the The cyclobutadione segments of all molecules were kept planar diene. and the six-membered rings were kept in the boat form. Conformational changes in the six-membered rings were always made such that no changes in bond distances or bond angles occured, thus no additional bond strain was introduced.

Available experimental data, in addition to the solution absorption spectra, may be used to test the validity of the calculations. Powder reflection spectra in the visible region were recorded for the three tricyclic diketones. The two unsaturated species showed quite similar spectra, each had a broad, single peak with λ_{max} at about 520-530 mµ. The saturated diketone showed a single peak with λ_{max} at about 450 mµ. The conformation of the diene is certainly expected to be the same in powder form as in single crystals used for the x-ray study, conformation V. The close similarity between the powder reflection spectra of 2DB and 1DB indicates that the conformation of the dihydro derivative in the solid state is probably VIII or IX (or both), since the calculated n+π* transition



energies for these conformations are close to the calculated value for conformation V of the diene. EHMO calculations also showed that VIII and IX are the two most stable conformations of 1DB. Little can be said about the conformation of the saturated diketone in the solid state from these spectra since the calculated $n \rightarrow \pi^*$ transition energies of the three conformations employed differ by less than 0.05 eV.

More extensive spectral studies have been made of these compounds by J. J. Freeman⁶⁸ using different media and variable temperatures. Visible spectra were taken of the saturated diketone in organic solvent from room temperature to -191° C. The single absorption band of this compound showed only a smooth, continuous intensity increase with temperature lowering, due to solvent contraction, and a shift in the peak maximum from 463 mµ at room temperature to 471 mµ at -191° C. No significant fine structure was obtained for this band even at the lowest temperature. The small shift in the peak maximum may be attributed to enhanced solvent effects at the lower temperature or to a conformational change. EHMO calculations would predict a blue-shifted band with lower temperature since the largest $n + \pi *$ transition energy was calculated for the most stable conformation. Since less than a 0.03 eV energy difference was calculated for the $n + \pi *$ transition energies and total ground-

state energies of XII and XIII, no definite conclusions can be drawn about the favored conformation.

The visible absorption spectrum of the diene was taken by Freeman in organic solvent and as a polycrystalline thin film over the temperature range mentioned above. The two spectra are quite similar in appearance, thus indicating that the same conformation predominates in solution as in the solid state. A temperature decrease again showed an intensity increase and a small red shift. More significantly, the unsymmetric solution absorption band of this compound splits into six clearly resolved vibronic bands at lower temperatures with peaks ranging from 550 to 485 mµ. The vibronic splittings range from 212 to 863 cm⁻¹ and are in the range of IR-active deformation modes associated with alkenes. The broad nature of this absorption band thus seems to be due to one conformation and vibronic structure instead of a mixture of conformations. Based on the structure found for the diene by x-ray diffraction and the similarity between solution and solid state spectra, V appears to be the predominant species in solution. This is also supported by the EHMO



V

calculations which show V to be 0.11 and 0.24 eV more stable than VI and and VII, respectively.

Spectra were taken of the dihydro derivative in organic solvent, as a polycrystalline thin film, and as a molten film. The spectrum of

the polycrystalline material is similar to the solid state spectrum of the diene. It showed only one band with peak maximum at 540-550 mµ and leads to the same conclusions about preferred conformations in the solid state as those based on powder reflection spectra previously mentioned. The spectrum of 1DB in the molten state is similar to its solution spectrum. It shows two absorption bands with peak maxima at 470 and 540 mµ. A variable temperature study of the solution spectrum also showed that the intensity of the high-energy band increases while the intensity of the low-energy band decreases as the temperature is lowered from 110 to -190° C. This is in conflict with the EHMO calculations which predict that the two most stable conformations of 1DB (VIII and IX) have $n \rightarrow \pi^*$ transitions which contribute to the low-energy band in the spectrum and that this band should increase in intensity at lower temperatures.

Variable-temperature studies of the infrared carbonyl absorptions of the three compounds were also made by Freeman. Spectra were taken of the polycrystalline material in KBr pellets and also of solutions using methylcyclohexane-isopropanol solvent in a 7:3 volume ratio from room temperature to about -196° C at 20° C intervals. With one exception, he observed no significant differences in the carbonyl bands with changes in temperature or in the matrix. The exception was observed for the dihydro derivative in the organic matrix. A broad, structureless peak at 5.60μ at room temperature splits into a doublet (5.58 and 5.65μ) at about -90° C. At lower temperatures the 5.65μ band weakens while the 5.58μ band becomes more intense. This again indicates that at least two conformations exist in solution at room temperature.

Electron spin resonance spectra of compounds similar to the tricyclic diketones discussed here have been reported, notably the spectra

of tricyclo[4.4.2.0^{1,6}]dodeca-3,8-diene-11,12-semidione and the di- and tetrahydro derivatives.⁶⁹ Only the spectrum of the diene has been interpreted with the conclusion that the staggered conformation, analagous to VI, is of lowest energy, with a half-life of at least 10^{-5} seconds and a rate of interconversion with other conformations less than 10^{5} per second at room temperature. The difference between the most stable conformation deduced for this compound and for 2DB must be attributable to the different pi systems in a semidione as compared to a diketone.

The EHMO method has thus yielded results which are consistent with other data. It has predicted the most stable conformation of 2DB as that found in the solid state. For this conformation, it has also shown a lower $n \rightarrow \pi^*$ transition energy than for any expected conformation of the saturated diketone, in agreement with the solution absorption spectra.

BIBLIOGRAPHY

.

1.	J.	N. Murrell, <u>The Theory of the Electronic Spectra of Organic</u> <u>Molecules</u> , John Wiley and Sons, Inc., New York, 1963, pp 158-174.
2.	Α.	Burawoy, J. Chem. Soc., 1177 (1939).
3.	М.	Kasha, Discuss. Faraday Soc., <u>9</u> , 14 (1950).
4.	R.	S. Mulliken, J. Chem. Phys., <u>3</u> , 564 (1935).
5.	н.	L. McMurry, J. Chem. Phys., <u>9</u> , 231 (1941).
6.	s.	F. Mason, Quarterly Reviews, <u>15</u> , 287 (1961).
7.	G.	Herzberg and H. Teller, Z. Phys. Chem., <u>B21</u> , 410 (1933).
8.	н.	Labhart and G. Wagniere, Helv. Chim. Acta, <u>42</u> , 2219 (1959).
9.	E.	I. Snyder and B. Franzus, J. Am. Chem. Soc., <u>86</u> , 1166 (1964).
10.	R.	A. Ford and F. Parry, Spectrochim. Acta, <u>12</u> , 78 (1958).
11.	J.	W. Sidman and D. S. McClure, J. Am. Chem. Soc., <u>77</u> , 646 (1955).
12.	L.	S. Forster, J. Chem. Phys., <u>26</u> , 1761 (1957).
13.	N.	J. Leonard and P. M. Mader, J. Am. Chem. Soc., <u>72</u> , 5388 (1950).
14.	К.	Alder, H. K. Schæfer, H. Esser, H. Krieger, and R. Reubke, Ann., <u>593</u> , 23 (1955).
15.	Н.	Birnbaum, R. C. Cookson and N. Levin, J. Chem. Soc., 1244 (1961).
16.	Т.	R. Evans and P. A. Leermakers, J. Am. Chem. Soc., <u>89</u> , 4380 (1967).
17.	Α.	de Groot, D. Oudman and H. Wynberg, Tetrahedron Letters, No. 20, 1529 (1969).
18.	s.	Nagakura and A. Kuboyana, J. Am. Chem. Soc., <u>76</u> , 1003 (1954).
19.	R.	Hoffmann, E. Heilbronner and R. Gleiter, J. Am. Chem. Soc., <u>92</u> , 706 (1970).

- J. J. Bloomfield and R. E. Moser, J. Am. Chem. Soc., <u>90</u>, 5625 (1968).
- J. J. Bloomfield, Central Research Department, Monsanto Company, St. Louis, Missouri 63166, Personal Communication.
- 22. R. S. Mulliken, Phys. Rev., <u>26</u>, 561 (1925).
- 23. F. Hund, Z. Physik, 36, 657 (1926).
- 24. E. Hückel, Z. Physik, 70, 204 (1931).
- 25. J. C. Slater, Phys. Rev., <u>34</u>, 1293 (1929).
- 26. J. C. Slater, Phys. Rev., 38, 1109 (1931).
- H. Eyring, J. Walter and G. E. Kimball, <u>Quantum Chemistry</u>, John Wiley and Sons, New York, 1944, p. 99.
- 28. J. E. Lennard-Jones, Proc. Roy. Soc., <u>A158</u>, 280 (1937).
- 29. R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc., <u>63</u>, 41 (1941).
- 30. R. S. Mulliken, J. Chim. Phys., <u>46</u>, 497 (1949).
- 31. R. S. Mulliken, J. Phys. Chem., 56, 295 (1952).
- 32. G. W. Wheland, J. Am. Chem. Soc., 64, 900 (1942).
- 33. A. Streitwieser, <u>Molecular Orbital Theory for Organic Chemistry</u>, J. Wiley and Sons, Inc., New York, 1961, pp. 97-125.
- 34. R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys., <u>17</u>, 1248 (1949).
- 35. D. R. Hartree, Proc. Cambridge Phil. Soc., 24, 89 (1927).
- 36. V. Fock, Z. Physik, 61, 126 (1930).
- 37. C. C. J. Roothaan, Rev. Mod. Phys., 23, 69 (1951).
- C. Sandorfy, <u>Electronic Spectra and Quantum Chemistry</u>, Prentice-Hall, Inc., New Jersey, 1964.
- M. Orchin and H. H. Jaffé, <u>Symmetry</u>, Orbitals, and Spectra, Wiley-Interscience, New York, 1971.
- 40. R. Pariser, J. Chem. Phys., 24, 250 (1956).
- 41. R. Pariser and R. G. Parr, J. Chem. Phys., <u>24</u>, 466 (1953).

- 178
- 42. R. Pariser and R. G. Parr, J. Chem. Phys., 24, 767 (1953).
- 43. J. S. Pople, Proc. Phys. Soc. (London), A68, 81 (1955).
- 44. R. G. Parr and R. S. Mulliken, J. Chem. Phys., <u>18</u>, 1338 (1950).
- 45. M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys., 6, 645 (1938).
- J. E. Bloor, P. N. Daykin, and P. Boltwood, Can. J. Chem., <u>42</u>, 121 (1964).
- 47. R. Hoffmann, J. Chem. Phys., <u>39</u>, 1397 (1963).
- 48. H. A. Skinner and H. O. Pritchard, Trans. Faraday Soc., <u>49</u>, 1254 (1953).
- 49. H. O. Pritchard and H. A. Skinner, Chem. Rev., <u>55</u>, 745 (1955).
- 50. R. Hoffmann and W. N. Lipscomb, J. Chem. Phys., 36, 2179 (1962).
- 51. W. Adam, A. Grimison, R. Hoffmann, and C. Z. de Ortiz, J. Am. Chem. Soc., 90, 1509 (1968).
- 52. J. A. Pople, D. P. Santry and G. A. Segal, J. Chem. Phys., <u>43</u>, S129 (1965).
- 53. J. A. Pople and G. A. Segal, J. Chem. Phys., 44, 3289 (1966).
- 54. J. Del Bene and H. H. Jaffé, J. Chem. Phys., <u>48</u>, 1807 (1968).
- 55. J. Del Bene and H. H. Jaffé, J. Chem. Phys., 48, 4050 (1968).
- 56. M. J. S. Dewar and G. Klopman, J. Am. Chem. Soc., 89, 3089 (1967).
- 57. J. A. Pople, D. L. Beveridge and P. A. Dobosh, J. Chem. Phys., <u>47</u>, 2026 (1967).
- 58. C. C. J. Roothaan, J. Chem. Phys., 19, 1445 (1951).
- M. W. Hanna, <u>Quantum Mechanics in Chemistry</u>, W. A. Benjamin, Inc., New York, 1966, p. 193.
- 60. J. E. Bloor and N. Brearley, Can. J. Chem., <u>43</u>, 176 (1965).
- 61. QCPE program 71.2, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.
- 62. N. Mataga and K. Nishimoto, Z. Physik. Chem., 13, 140 (1957).
- QCPE program 64, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.

- 64. J. M. Foster and S. F. Boys, Rev. Mod. Phys., <u>32</u>, 303 (1960).
- 65. J. R. Swenson and R. Hoffmann, Helv. Chim. Acta, <u>53</u>, 233 (1970).
- 66. H. H. Jaffé, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio.
- 67. J. R. Hoyland, <u>Molecular Orbital Studies in Chemical Pharmacology</u>, Edited by L. B. Kier, Springer-Verlag, New York, 1970, pp. 31-81.
- J. J. Freeman, Central Research Department, Monsanto Company, St. Louis Missouri 63166, Private Communication.

.

 J. M. Fritsch and J. J. Bloomfield, Spectroscopy Letters, <u>1</u>, 277 (1968).

APPENDIX A

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ATOMIC COORDINATES

The following tables list the atomic coordinates used for molecules I-XIV for the all-valence-shell calculations. The atom numbers are with reference to Figure 14. Distances are expressed in angstroms.

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Atom	x	Y	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.431	1.276	-0.556
C(3)	-0.658	2.504	-0.184
C(4)	0.658	2.504	-0.184
C(5)	1.431	1.276	-0.556
C(6)	0.786	0.000	0.000
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-2.395	1.358	-0.177
H(2)	-1.473	1.206	-1.593
н(3)	-1.201	3.352	0.073
H(4)	1.201	3.352	0.073
H(5)	2.395	1.358	-0.177
H(6)	1.473	1.206	-1.593
H(17)	-1.223	-0.865	-0.377
H(18)	1.223	-0.865	-0.377

ATOMIC COORDINATES FOR MOLECULE I

Atom	х	Y	_ Z
C(1)	-0.786	0.000	0.000
C(2)	-1.431	1.276	-0.556
C(3)	-0.658	1.838	-1.710
C(4)	0.658	1.838	-1.710
C(5)	1.431	1.276	-0.556
C(6)	0.786	0.000	0.000
.C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-1.473	1.988	0.200
H(2)	-2.395	1.053	-0.874
H(3)	-1.201	2.227	-2.506
H(4)	1.201	2.227	-2.506
H(5)	1.473	1.988	0.200
H(6)	2.395	1.053	-0.874
H(17)	-1.223	-0.865	-0.377
11 (18)	1.223	-0.865	-0.377

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ATOMIC COORDINATES FOR MOLECULE II

TABLE 38	
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Atom	Х	Y	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.373	1.276	-0.617
C(3)	-0.770	2.508	0.082
C(4)	0.770	2.508	0.082
C(5)	1.373	1.276	-0.617
C(6)	0.786	0.000	0.000
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-2.405	1.277	-0.493
H(2)	-1.145	1.307	-1.631
H(3)	-1.100	2.522	1.068
H(4)	1.100	2.522	1.068
H(5)	2.405	1.277	-0.493
H(6)	1.145	1.307	-1.631
H(13)	-1.100	3.362	-0.412
H(14)	1.100	3.362	-0.412
H(17)	-1.223	-0.865	-0.377
H(18)	1.223	-0.865	-0.377

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ATOMIC COORDINATES FOR MOLECULE III

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Atom	Х	Y	Z	
C(1)	-0.786	0.000	0.000	
C(2)	-1.373	1.276	-0.617	
C(3)	-0.770	1.493	-2.018	
C(4)	0.770	1.493	-2.018	
C(5)	1.373	1.276	-0.617	
C(6)	0.786	0.000	0.000	
C(11)	-0.775	0.000	1.533	
C(12)	0.775	0.000	1.533	
0(13)	-1.626	0.000	2.368	
0(14)	1.626	0.000	2.368	
H(1)	-1.145	2.090	-0.012	
H(2)	-2.405	1.179	-0.696	
H(3)	-1.100	2.410	-2.380	
H(4)	1.100	2.410	-2.380	
Н(5)	1.145	2.090	-0.012	
H(6)	2.405	1.179	-0.696	
H(13)	-1.100	0.728	-2.641	
H(14)	1.100	0.728	-2.641	
H(17)	-1.223	-0.865	-0.377	
11(18)	1.223	-0.865	-0.377	

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ATOMIC	COORDINATES	FOR	MOLECULE	IV
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Atom	Х	Y	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.431	1.276	-0.556
C(3)	-0.658	2.504	-0.184
C(4)	0.658	2.504	-0.184
C(5)	1.431	1.276	-0.556
C(6)	0.786	0.000	0.000
C(7)	1.431	-1.276	-0.556
C(8)	0.658	-2.504	-0.184
C(9)	-0.658	-2.504	-0.184
C(10)	-1.431	-1.276	-0.556
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-2.395	1.357	-0.177
H(2)	-1.473	1.206	-1.593
H(3)	-1.201	3.352	0.073
11(4)	1.201	3.352	0.073
H(5)	2.395	1.357	-0.177
H(6)	1.473	1.206	-1.593
11(7)	2.395	-1.357	-0.177
11(8)	1.473	-1.206	-1.593
H(9)	1.201	-3.352	0.073
H(10)	-1.201	-3.352	0.073
H(11)	-2.395	-1.357	-0.177
H(12)	-1.473	-1.206	-1.593

.

ATOMIC COORDINATES FOR MOLECULE V

	· · · · · · · · · · · · · · · · · · ·		
Atom	Х	Y	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.431	1.276	-0.556
C(3)	-0.658	2.504	-0.184
C(4)	0.658	2.504	-0.184
C(5)	1.431	1.276	-0.556
C(6)	0.786	0.000	0.000
C(7)	1.431	-1.276	-0.556
C(8)	0.658	-1.838	-1.710
C(9)	-0.658	-1.838	-1.710
C(10)	-1.431	-1.276	-0.556
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-2.395	1.358	-0.177
H(2)	-1.473	1.206	-1.593
H(3)	-1.201	3.352	0. 0 73
H(4)	1.201	3.352	0.073
H(5)	2.395	1.358	-0.177
H(6)	1.473	1.206	-1.593
H(7)	1.473	-1.988	0.200
H(8)	2.395	-1.053	-0.874
11(9)	1.201	-2.227	-2.506
11(10)	-1.201	-2.227	-2.506
11(11)	-1.473	-1.988	0.200
H(12)	-2.395	-1.053	-0.874

ATOMIC COORDINATES FOR MOLECULE VI

	·····		
Atom	X	Y	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.431	1.276	-0.556
C(3)	-0.658	1.838	-1.710
C(4)	0.658	1.838	-1.710
C(5)	1.431	1.276	-0.556
C(6)	0.786	0.000	0.000
C(7)	1.431	-1.276	-0.556
C(8)	0.658	-1.838	-1.710
C(9)	-0.658	-1.838	-1.710
C(10)	-1.431	-1.276	-0.556
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-1.473	1.988	0.200
H(2)	-2.395	1.053	-0.874
H(3)	-1.201	2.227	-2.506
H(4)	1.201	2.227	-2.506
H(5)	1.473	1.988	0.200
11(6)	2.395	1.053	-0.874
H(7)	1.473	-1.988	0.200
H(8)	2.395	-1.053	-0.874
H(9)	1.201	-2.227	-2.506
H(10)	-1.201	-2.227	-2.506
H(11)	-1.473	-1.988	0.200
H(12)	-2.395	-1.053	-0.874

ATOMIC COORDINATES FOR MOLECULE VII

TABLE 4	43
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Atom	X	Ŷ	Z	
	0.704			
C(1)	-0.786	0.000	0.000	
C(2)	-1.3/3	1.276	-0.617	
C(3)	-0.770	2.508	0.082	
C(4)	0.770	2.508	0.082	
C(5)	1.373	1.276	-0.617	
C(6)	0.786	0.000	0.000	
C(7)	1.431	-1.276	-0.556	
C(8)	0.658	-2.504	-0.184	
C(9)	-0.658	-2.504	-0.184	
C(10)	-1.431	-1.276	-0.556	
C(11)	-0.775	0.000	1.533	
C(12)	0.775	0.000	1.533	
0(13)	-1.626	0.000	2.368	
0(14)	1.626	0.000	2.368	
H(1)	-2.405	1.277	-0.493	
H(2)	-1.145	1.307	-1.631	
H(3)	-1.100	2.522	1.068	
H(4)	1.100	2.522	1.068	
H(5)	2.405	1.277	-0.493	
H(6)	1.145	1.307	-1.631	
H(7)	2.395	-1.358	-0.177	
н(8)	1.473	-1.206	-1.593	
H(9)	1.201	-3.352	0.073	
H(10)	-1.201	-3.352	0.073	
H(11)	-2.395	-1.358	-0.177	
H(12)	-1.473	-1.206	-1.593	
H(13)	-1.100	3.362	-0.412	
H(14)	1.100	3.362	-0.412	

ATOMIC COORDINATES FOR	MOLECULE	VIII
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Atom	X	Y	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.373	1.276	-0.617
C(3)	-0.770	1.493	-2.018
C(4)	0.770	1.493	-2.018
C(5)	1.373	1.276	-0.617
C(6)	0.786	0.000	0.000
C(7)	1.431	-1.276	-0.556
C(8)	0.658	-2.504	-0.184
C(9)	-0.658	-2.504	-0.184
C(10)	-1.431	-1.276	-0.556
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.262	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-1.145	2.090	-0.012
H(2)	-2.405	1.179	-0.696
H(3)	-1.100	2.410	-2.380
H(4)	1.100	2.410	-2.380
H(5)	1.145	2.090	-0.012
H(6)	2.405	1.179	-0.696
H(7)	2.395	-1.358	-0.177
H(8)	1.473	-1.206	-1.593
11(9)	1.201	-3.352	0.073
H(10)	-1.201	-3.352	0.073
H (11)	-2.395	-1.358	-0.177
H(12)	-1.473	-1.206	-1.593
H (13)	-1.100	0.728	-2.641
H (14)	1.100	0.728	-2.641

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ATOMIC COORDINATES FOR MOLECULE IX

TABLE 44

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Atom	X	. Ү	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.373	1.276	-0.617
C(3)	-0.770	2.508	0.082
C(4)	0.770	2.508	0.082
C(5)	1.373	1.276	-0.617
C(6)	0.786	0.000	0.000
C(7)	1.431	-1.276	-0.556
C(8)	0.658	-1.838	-1.710
C(9)	-0.658	-1.838	-1.710
C(10)	-1.431	-1.276	-0.556
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-2.405	1.277	-0.493
H(2)	-1.145	1.307	-1.631
H(3)	-1.100	2.522	1.068
H(4)	1.100	2.522	1.068
н(5)	2.405	1.277	-0.493
H(6)	1.145	1.307	-1.631
11(7)	1.473	-1.988	0.200
11(8)	2 .39 5	-1.053	-0.874
11(9)	1.201	-2.227	-2.506
11(10)	-1.201	-2,227	-2.506
H(11)	-1.473	-1.988	0.200
H(12)	-2.395	-1.053	-0.874
11(13)	-1.100	3.362	-0.412
H(14)	1.100	3.362	-0.412

ATOMIC COORDINATES FOR MOLECULE X

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Atom	X	Y	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.373	1.276	-0.617
C(3)	-0.770	1.493	-2.018
C(4)	0.770	1.493	-2.018
C(5)	1.373	1.276	-0.617
C(6)	0.786	0.000	0.000
C(7)	1.431	-1.276	-0.556
C(8)	0.658	-1.838	-1.710
C(9)	-0.658	-1.838	-1.710
C(10)	-1.431	-1.276	-0.556
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-1.145	2.090	-0.012
H(2)	-2.405	1.179	-0.696
H(3)	-1.100	2.410	-2.380
H(4)	1.100	2.410	-2.380
H(5)	1.145	2.090	-0.012
H(6)	2.405	1.179	-0.696
H(7)	1.473	-1.988	0.200
H(8)	2.395	-1.053	-0.874
H(9)	1.201	-2.227	-2.506
H(10)	-1.201	-2.227	-2.506
H(11)	-1.473	-1.988	0.200
H(12)	- 2.395	-1.053	-0.874
H(13)	-1.100	0.728	-2.641
H(14)	1.100	0.728	-2.641

ATOMIC COORDINATES FOR MOLECULE XI

Atom	х	Y	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.373	1.276	-0.617
C(3)	-0.770	2.508	0.082
C(4)	0.770	2.508	0.082
C(5)	1.373	1.276	-0.617
C(6)	0.786	0.000	0.000
C(7)	1.373	-1.276	-0.617
C(8)	0.770	-2.508	0.082
C(9)	-0.770	-2.508	0.082
C(10)	-1.373	-1.276	-0.617
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-2.405	1.277	-0.493
H(2)	-1.145	1.307	-1.631
H(3)	-1.100	2.522	1.068
H(4)	1.100	2.522	1.068
H(5)	2.405	1.277	-0.493
H(6)	1.145	1.307	-1.631
H(7)	2.405	-1.277	-0.493
H(8)	1.145	-1.307	-1.631
H(9)	1.100	-2.522	1.068
H(10)	-1.100	-2.522	1.068
H(11)	-2.405	-1.277	-0.493
H(12)	-1.145	-1.307	-1.631
н(13)	-1.100	3.362	-0.412
H(14)	1.100	3.362	-0.412
н(15)	-1.100	-3.362	-0.412
H(16)	1.100	-3.362	-0.412

ATOMIC COORDINATES FOR MOLECULE XII

Atom	х	Y	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.373	1.276	-0.617
C(3)	-0.770	2.508	0.082
C(4)	0.770	2.508	0.082
C(5)	1.373	1.276	-0.617
C(6)	0.786	0.000	0.000
C(7)	1.373	-1.276	-0.617
C(8)	0.770	-1.493	-2.018
C(9)	-0.770	-1.493	-2.018
C(10)	-1.373	-1.276	-0.617
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-2.405	1.277	-0.493
H(2)	-1.145	1.307	-1.631
11(3)	-1.100	2.522	1.068
H(4)	1.100	2.522	1.068
н(5)	2.405	1.277	-0.493
H(6)	1.145	1.307	-1.631
н(7)	1.145	-2.090	-0.012
H(8)	2.405	-1.179	-0.696
H(9)	1.100	-2.410	-2.380
H(10)	-1.100	-2.410	-2.380
H(11)	-1.145	-2.090	-0.012
H(12)	-2.405	-1.179	-0.696
H(13)	-1.100	3.362	-0.412
11(14)	1.100	3.362	-0.412
H(15)	1.100	-0.728	-2.641
H(16)	-1.100	-0.728	-2.641

ATOMIC COORDINATES FOR MOLECULE XIII

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Atom	х	У	Z
C(1)	-0.786	0.000	0.000
C(2)	-1.373	1.276	-0.617
C(3)	-0.770	1.493	-2.018
C(4)	0.770	1.493	-2.018
C(5)	1.373	1.276	-0.617
C(6)	0.786	0.000	0.000
C(7)	1.373	-1.276	-0.617
C(8)	0.770	-1.493	-2.018
C(9)	-0.770	-1.493	-2.018
C(10)	-1.373	-1.276	-0.617
C(11)	-0.775	0.000	1.533
C(12)	0.775	0.000	1.533
0(13)	-1.626	0.000	2.368
0(14)	1.626	0.000	2.368
H(1)	-1.145	2.090	-0.012
H(2)	-2.405	1.179	-0.696
H(3)	-1.100	2.410	-2.380
H(4)	1.100	2.410	-2.380
H(5)	1.145	2.090	-0.012
H(6)	2.405	1.179	-0.696
H(7)	1.145	-2.090	-0.012
11(8)	2.405	-1.179	-0.696
H(9)	1.100	-2.410	-2.380
H(10)	-1.100	-2.410	-2.380
H(11)	-1.145	-2.090	-0.012
H(12)	-2.405	-1.179	-0.696
!!(13)	-1.100	0.728	-2.641
H(14)	1.100	0.728	-2.641
11(15)	1.100	-0.728	-2.641
H(16)	-1.100	-0.728	-2.641

ATOMIC COORDINATES FOR MOLECULE XIV

APPENDIX B

MO COEFFICIENTS FROM EHMO AND CNDO/2 CALCULATIONS

The following Tables list the coefficients of the highest occupied molecular orbital, identified as n, and the lowest empty molecular orbital, identified as $\pi_1^*(CO)$. Coefficients are given for I-XIV from the EHMO calculations and for I-IV from the CNDO/2 calculations. The atom numbers are with reference to Figure 14.

Molecule		Ι		I
MO	ц	π ₁ *(CO)	u	π ₁ *(CO)
Energy (eV)	-12.141	-10.589	-12.199	-10.556
C _s Symmetry	A^	A´	A^	A´
Coefficients				
H(1)	-0.0276	0.0123	-0.0162	0.0119
H(2)	0.1352	-0.0305	0.0328	-0.0082
н(3)	-0.0153	0.0265	-0.0230	0.0288
H(17)	-0.0695	-0.1086	-0.0765	-0.1061
C(1,s)	0.0376	0.0037	0.0467	0.0067
C(2,s)	-0.0183	0.0358	-0.0157	0.0396
C(3,s)	-0.0020	-0.0036	0.0211	-0.0170
C(11,s)	-0.0746	0.0017	-0.0787	0.0003
0(13,s)	0.0108	-0.0012	0.0112	-0.0013
C(1,x)	0.0827	-0.0128	0.0773	-0.001
$c(2, \mathbf{x})$	-0.0400	0.0628	-0.0398	0.0571
C(3, x)	0.0329	-0.0089	-0.0060	-0.0049
C(11,x)	-0.3277	0.0117	-0.3454	0.0179
0(13,x)	0.3592	-0.0099	0.3872	-0.0147
C(T,Y)	9050.0-	2650.0 101 0-	-0.03/4 0.0761	19/0.0-
C(3.v)	-0.0474	0,0000	-0.1351	0.0463
c(11,y)	-0.0320	-0.6058	-0.0456	-0.6053
0(13,y)	0.0330	0.4140	0.0472	0.4109
C(1,z)	0.2528	-0.0156	0.2675	-0.0260
C(2,z)	-0.1114	0.0602	-0.0610	0.0780
C(3,z)	0.2164	0.0076	-0.0035	-0.0116
C(11, z)	-0.2167	0.0106	-0.2292	0.0189
0(13,z)	0.2224	0.0055	0.2414	-0.0113

MO COEFFICIENTS OF n AND $\pi_1^*(\text{CO})$ ORBITALS FOR I AND II BY THE EHMO METHOD

MO COEFFICIENTS OF n AND π_1^* (CO) ORBITALS FOR III AND IV

BY THE EHMO METHOD

Molecule	11	-	I	.v
MO	n	π ₁ *(CO)	n	π ₁ *(CO)
Energy (eV)	-12.234	-10.580	-12.217	-10.583
C _s Symmetry	A	A-	A´	A
Coefficients	. <u></u>			
H(1)	0.0196	0.0018	-0.0409	0.0105
H(2)	0.0779	-0.0202	0.0305	-0.0051
Н(3)	0.0082	0.0176	-0.0337	0.0280
H(13)	-0.0238	0.0066	0.0038	0.0013
H(17)	-0.0819	-0.1075	-0.0804	-0.1055
C(1,s)	0.0580	0.0010	0.0536	0.0038
C(2,s)	-0.0212	0.0368	-0.0144	0.0374
C(3,s)	-0.0047	0.0059	0.0247	-0.0147
C(11,s)	-0.0842	0.0021	-0.0799	0.0017
0(13,s)	0.0118	-0.0015	0.0116	-0.0013
C(1,x)	0.0876	-0.0171	0.0734	-0.0168
C(2,x)	-0.0442	0.0603	-0.0333	0.0577
C(3,x)	0.0460	-0.0198	0.0018	-0.0159
C(11,x)	-0.3539	0.0069	-0.3505	0.0131
0(13 , x)	0.4012	-0.0067	0.3958	-0.0112
C(1,y)	-0.0156	0.0646	-0.0195	0.0711
C(2,y)	0.0513	-0.0983	0.0626	-0.0998
C(3,y)	0.0276	0.0042	-0.0280	0.0110
C(11,y)	-0.0196	-0.6069	-0.0335	-0.6047
0(13,y)	0.0201	0.4136	0.0350	0.4129
C(1,z)	0.2581	-0.0097	0.2649	-0.0164
C(2,z)	-0.0802	0.0665	-0.0813	0.0780
C(3,z)	0.0342	0.0289	0.0785	-0.0375
C(11,z)	-0.2292	0.0055	-0.2330	0.0120
C(13,z)	0.2440	-0.0015	0.2468	-0.0065

MO COEFFICIENTS OF n AND π_1^* (CO) ORBITALS FOR V-VII

BY THE EHMO METHOD

Molecule	,	v	7	Ί	V	II
MO	n	π ₁ *(CO)	n	π ₁ *(CO)	n	π ₁ *(CO)
Energy (eV)	-12.001	-10.531	-12.019	-10.502	-12.051	-10.476
C _S Symmetry			A	A1		
C _{2v} Symmetry	Al	^B 2			A ₁	^B 2
Coefficients						
H(1)	0.0081	0.0140	-0.0186	0.0119	0.0337	-0.0048
H(2)	-0.1113	-0.0267	0.1243	-0.0236	-0.0410	0.0029
H(3)	0.0208	0.0247	-0.0198	0.0240	0.0265	-0.0259
H(10)			-0.0269	-0.0267		
H(11)			-0.0356	-0.0076		
H(12)			0.0467	0.0032		
C(1,s)	-0.0278	0.0	0.0295	-0.0031	-0.0327	0.0
C(2,s)	0.0237	0.0350	-0.0242	0.0343	0.0208	-0.0373
C(3,s)	0.0044	-0.0050	-0.0035	-0.0052	-0.0216	0.0158
C(9,s)			0.0186	0.0167		
C(10,s)	0.0700	• •	-0.0198	-0.0380		
C(11,s)	0.0722	0.0	-0.0705	0.0013	0.0699	0.0
0(13,s)	-0.0129	0.0	0.0130	0.0001	-0.0131	0.0
U(1, x)	-0.1259	0.0	0.01089	-0.0033	-0.0912	0.0
C(2, x)	0.0370	-0.0052	-0.0328	0.0568	0.0455	-0.0519
C(3, x)	-0.0432	-0.0055	0.0307	-0.0048	0.0037	0.0040
$C(10 \ y)$			-0.0000	-0.0530		
C(10, x)	0.3247	0 0	-0.0494	-0.0000	0 3382	0 0
0(13 x)	-0 3438	0.0	0 3510	0.0007	-0.3655	.0.0
C(1, v)	0.0	0.0839	-0.0179	0.0900	0.0	-0.0964
C(2, y)	-0.0633	-0.0973	0.0690	-0.0948	-0.0777	0.0921
C(3, y)	0.0168	0.0040	-0.0276	0.0045	0,1028	-0.0439
C(9,y)			0.0800	0.0452	002020	
C(10,y)			-0.0687	-0.0944	•	
C(11,y)	0.0	-0.6049	0.0105	-0.6048	0.0	0.6050
0 (13, y)	0.0	0.4086	-0.0102	0.4064	0.0	-0.4046
C(1,z)	-0.2573	0.0	0.2675	0.0108	-0.2823	0.0
C(2,z)	0.0951	0.0572	-0.1071	0.0546	0.0711	-0.0717
C(3,z)	-0.1460	0.0086	0.1691	0.0101	-0.0118	0.0100
C(9,z)			0.0118	0.0116		
C(10,z)		• •	-0.0651	-0.0743		
C(11,z)	0.2197	0.0	-0.2275	-0.0089	0.2389	0.0
U(13,Z)	-0.2090	0.0	0.2185	0.0061	-0.2334	0.0

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MO COEFFICIENTS OF n AND π_1^* (CO) ORBITALS FOR VIII AND IX

Molecule	V	II	I	IX		
МО	n	π ₁ *(CO)	n	π ₁ *(CO)		
Energy (eV)	-12.041	-0.522	-12.028	-10.527		
C Symmetry	A-	Α-	Α-	A-		
Coefficients						
H(1)	0.0285	-0.0044	-0.0514	0.0050		
H(2)	0.0646	0.0179	0.0433	-0.0008		
H(3)	0.0000	-0.0163	-0.0313	0.0263		
H(10)	-0.0224	0.0244	-0.0209	-0.0239		
H(11)	-0.0105	0.0154	-0.0164	-0.0148		
H(12)	0.1233	-0.0274	0.1255	0.0260		
H(13)	-0.0200	-0.0059	-0.0057	0.0004		
C(1,s)	0.0360	0.0025	0.0324	0.0002		
C(2,s)	-0.0238	-0.0351	-0.0179	0.0360		
C(3,s)	-0.0072	-0.0048	0.0209	-0.0142		
C(9,s)	-0.0018	-0.0046	-0.0024	0.0050		
C(10,s)	-0.0253	0.0345	-0.0247	-0.0340		
C(11,s)	-0.0748	-0.0006	-0.0709	0.0002		
0(13,s)	0.0131	0.0003	0.0130	-0.000		
C(1,x)	0.1296	0.0049	0.1143	-0.0048		
C(2,x)	-0.0552	-0.0558	-0.0474	0.0534		
C(3,x)	0.0491	0.0169	0.0219	-0.0130		
C(9,x)	0.0419	-0.0053	0.0391	0.0045		
C(10,x)	-0.0589	0.0569	-0.0550	-0.0559		
C(11,x)	-0.3276	0.0044	-0.3263	0.0017		
0(13,x)	0.3524	-0.0028	0.3495	-0.0016		
C(1,y)	0.0367	-0.0787	0.0306	0.0850		
C(2,y)	0.0532	0.0939	0.0626	-0.0956		
C(3,y)	0.0363	-0.0082	-0.0138	0.0122		
C(9,y)	0.0355	-0.0028	0.0335	0.0040		
C(10,y)	-0.0755	0.0955	-0.0/33	-0.0943		
C(11,y)	0.0133	0.0000	-0.0004	-0.604		
O(13,y)	-0.0130 0.2520	-0.4003	0.0500	0.408		
C(2, z)		-0.0034	0.2399	0.0011		
C(2, 2)	-0.0747 0.0328	-0.0030	-0.0700	0.0739		
C(0, 2)	0.0320	0.0008	0.0/24	-0.0339		
C(3,2)	-0 1078	0.0090	_0 1008	-0.0100		
C(11, 2)	-0.2189	0.0040	-0.1090	0.0000		
0(13,2)	0.2215	-0.0049	0.2152	_0_0011		

BY THE EHMO METHOD
MO COEFFICIENTS OF n AND $\pi_1^*(CO)$ ORBITALS FOR X AND XI

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Molecule		Х	Х	I
MO	n	^π 1*(CO)	n	$\pi_{1}^{*(CO)}$
Energy (eV)	-12.087	-10.492	-12.065	-10.498
C _s Symmetry	A	A .	A	A
Coefficients				
H(1)	0.0253	-0.0032	0.0520	0.0024
H(2)	0.0742	0.0152	-0.0379	-0.0012
H(3)	0.0021	-0,0159	0.0330	0.0259
H(10)	-0.0289	0,0265	0.0270	-0.0260
H(11)	-0.0177	0.0095	0.0235	-0.0072
H(12)	0.0438	-0,0029	-0.0395	0.0021
H(13)	-0.0217	-0.0054	0.0026	0.0001
C(1,s)	0.0413	0,0054	-0.0369	-0.0028
C(2,s)	-0.0255	-0.0343	0.0188	0.0353
C(3,s)	-0.0075	-0,0044	-0.0236	-0.0136
C(9,s)	0.0203	-0.0169	-0.0216	0.0167
C(10,s)	-0,0226	0,0375	0.0218	-0.0370
C(11,s)	-0.0760	-0.0020	0.0709	0.0016
0(13,s)	0.0134	0.0002	-0.0132	0.0000
C(1,x)	0.1185	0,0083	-0.0971	-0.0082
C(2,x)	-0.0543	-0.0548	0.0431	0.0523
C(3,x)	0.0497	0.0159	-0.0109	-0.0136
C(9,x)	0.0045	-0.0037	0.0018	0.0029
C(10,x)	-0.0548	0.0519	0.0486	-0.0509
C(11,x)	-0.3396	0.0109	0.3375	-0,0049
C(13,x)	0.3709	-0,0080	-0.3669	0.0037
C(1,y)	0.0236	-0.0854	-0.0175	0.0919
C(2,y)	0.0584	0.0914	-0.0683	-0.0932
C(3,y)	0.0360	-0,0096	0.0196	0.0122
С(9,у)	0.1184	-0.0443	-0.1171	0.0456
C(10,y)	-0.0899	0.0923	0.0861	-0.0915
C(11,y)	0.0263	0.6057	-0.0127	-0.6042
0 (13,y)	-0.0264	-0.4058	0.0127	0.4059
C(l,z)	0.2659	-0,0158	-0.2750	0.0096
C(2,z)	-0.0830	-0,0608	0.0862	0.0714
C(3,z)	0.0336	-0,0320	-0.0820	-0.0304
C(9,z)	-0.0016	-0,0127	-0.0040	0.0116
C(10,z)	-0.0653	0.0745	0.0688	-0.0730
C(11,z)	-0.2304	0.0137	0.2367	-0.0073
0(13,z)	0.2268	-0.0098	-0,2322	0.0051

BY THE EHMO METHOD

MO COEFFICIENTS OF n AND $\pi_1^*(CO)$ ORBITALS FOR XII-XIV

	BY	THE	EHMO	METHOD
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Molecule	х	II	XI	II	Х	IV
MO	n	π ₁ *(CO)	n	π ₁ *(CO)	n	π ₁ *(CO)
Energy (eV)	-12.122	- 10.513	-12.104	- 10.518	-12.085	-10.523
C Symmetry			A	A		
C ^S Symmetry	A,	B			A,	B ₂
20		<u>۲</u>			ـــــــــــــــــــــــــــــــــــــ	
Coefficients						
H(1)	-0.0356	0.0058	-0.0282	0.0056	0.0451	0.0045
H(2)	-0.0689	-0.0188	-0.0734	-0.0177	-0.0384	0.0002
H(3)	-0.0032	0.0166	-0.0035	0.0162	0.0346	0.0265
H(10)			0.0360	-0.0260		
H(11)			0.0439	-0.0065		
H(12)			-0.0460	0.0000		
H(13)	0.0271	0.0053	0.0251	0.0052	0.0008	-0.0002
H(16)			0.0023	-0.0006		
C(1,£)	-0.0512	0.0	-0.0473	-0.0027	-0.0427	0.0
C(2,s)	0.0273	0.0346	0.0268	0.0341	0.0201	0.0350
C(3,s)	0.0044	0.0056	0.0055	0.0048	-0.0241	-0.0143
C(9,s)			-0.0228	0.0144		
C(10,s)			0.0208	-0.0355		
C(11,s)	0.0830	0.0	0.0781	0.0004	0.0727	0.0
0(13,s)	-0.0142	0.0	-0.0139	-0.0002	-0.0135	0.0
C(1,x)	-0.1477	0.0	-0.1259	0.0	-0.1024	0.0
C(2,x)	0.0620	0.0551	0.0570	0.0541	0.0452	0.0517
C(3,x)	-0.0544	-0.0168	-0.0506	-0.0161	-0.0107	-0.0134
C(9,x)			-0.0193	0.0131		
C(10,x)			0.0513	-0.0528		
C(11,x)	0.3442	0.0	0.3425	-0.0060	0.3402	0.0
C(13,x)	-0.3800	0.0	-0.3766	0.0043	-0.3725	0.0
C(1,y)	0.0	0.0735	-0.0049	0.0801	0.0	0.0867
C(2,y)	-0.0691	-0.0919	-0.0667	-0.0909	-0.0757	-0.0925
C(3,y)	-0.0288	0.0071	-0.0300	0.0085	0.0237	0.0120
C(9,y)			-0.0207	0.0117		
C(10,y)			0.0783	-0.0936		
C(11,y)	0.0	-0.6071	-0.0142	-0.6052	0.0	-0.6035
0(13,y)	0.0	0.4081	0.0143	0.4077	0.0	0.4075
C(1,y)	-0.2513	0.0	-0.2604	0.0064	-0.2698	0.0
C(2,z)	0.0836	0.0625	0.0851	0.0615	0.0865	0.0725
U(3, 2)	-0.0336	0.0310	-0.0327	0.0316	-0.0785	-0.0338
U(9,z)			-0.0749	0.0353		
U(10, z)	0.0007	0.0	0.0839	-0.0737		
U(11, Z)	0.2236	0.0	0.2303	-0.0065	0.2370	0.0
0(13,2)	-0.2211	0.0	-0.2273	0.0048	-0.2335	0.0

MO COEFFICIENTS OF n AND $\pi_1^{*}(CO)$ ORBITALS FOR I AND II

Molecule		I		II
MO	n	^π 1*(CO)	n	π ₁ *(CO)
Energy (eV)	-10.204	Ō.304	-10.262	Ō.260
C _s Symmetry	A^	Α´	A-	Α΄
Coefficients				
H(1)	-0.0328	-0.0045	-0.0137	0.0057
H(2)	0.0882	0.0311	0.0100	-0.0157
H(3)	-0.0015	-0.0025	-0.0217	0.0117
H(17)	-0.0411	0.0632	-0.0435	-0.0639
C(1,s)	0.0626	0.0009	0.0664	0.0006
C(2,s)	-0.0148	-0.0478	-0.0147	0.0540
C(3,s)	-0,0038	-0.0002	0.0238	-0.0196
C(11,s)	-0.0901	-0.0008	-0.0902	0.0006
0(13,s)	-0.0038	0.0004	-0.0038	-0.0004
C(1,x)	0.0083	0.0015	0.0057	0.0002
C(2,x)	-0.0128	-0.0298	-0.0157	0.0245
C(3,x)	0,0092	-0.0043	-0.0055	0.0116
C(11,x)	-0.3035	-0.0028	-0.2067	0.0054
0(13,x)	0.4071	0.0035	0.4172	-0.0059
C(1,y)	-0.0219	-0.0322	-0.0198	0.0337
C(2,y)	0.0352	0.0360	0.0512	-0.0313
C(3,y)	-0.0373	0.0046	-0.1184	0.0110
C(11,y)	-0.0027	0.5267	-0.0056	-0.5261
0(13 , y)	0.0081	-0.4590	0.0223	0.4590
C(1,z)	0.2284	0.0050	0.2335	-0.0086
C(2,z)	-0.0923	-0.0190	-0.0470	0.0358
C(3,z)	0.1482	-0.0314	-0.0146	-0.0164
C(11,z)	-0.1714	-0.0030	-0.1751	0.0057
0(13,z)	0.3222	0.0025	0.3324	-0.0049

BY THE CNDO/2 METHOD

MO COEFFICIENTS OF n AND $\pi_1^*(CO)$ ORBITALS FOR III AND IV

Molecule		JII		IV
MO	n	$\pi_{1}^{*(CO)}$	n	π ₁ *(CO)
Energy (eV)	-10.264	0.308	-10.242	0.297
C Symmetry	A'	A -	A -	A'
Coefficients				
H(1)	-0.0078	0.0023	-0.0270	0.0000
H(2)	0.0573	0.0286	0.0069	0.0084
H(3)	0.0102	-0.0139	-0.0297	-0.0085
H(13)	-0.0053	0.0263	0.0016	-0.0039
H(17)	-0.0511	0.0629	-0.0504	0.0632
C(1,s)	0.0809	0.0035	0.0771	0.0015
C(2,s)	-0.0171	-0.0501	-0.0137	-0.0534
C(3,s)	-0.0092	-0.0176	0.0282	0.0195
C(11,s)	-0.0947	-0.0012	-0.0926	-0.0012
0(13 , s)	-0.0046	0.0004	-0.0042	0.0002
C(1,x)	0.0057	0.0013	0.0047	0.0016
C(2,x)	-0.0119	-0.0300	-0.0132	-0.0286
C(3,x)	0.0101	0.0040	0.0003	-0.0071
C(11,x)	-0.3107	-0.0009	-0.3101	-0.0032
0(13,x)	0.4254	0.0021	0.4231	0.0039
C(1,y)	-0.0001	-0.0300	-0.0050	-0.0318
C(2,y)	0.0266	0.0354	0.0344	0.0331
C(3,y)	0.0132	-0.0100	-0.0233	-0.0046
C(11,y)	-0.0020	0.5269	-0.0033	0.5256
0(13,y)	0,0069	-0.4578	0.0154	-0.4599
C(1,x)	0.2267	0.0030	0.2304	0.0044
C(2,z)	-0.0636	-0.0268	-0.0624	-0.0326
C(3,z)	0.0199	-0.0199	0.0466	0.0268
C(11,z)	-0.1722	-0.0005	-0.1751	-0.0027
0(13,z)	0.3372	0.0007	0.3363	0.0029

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BY THE CNDO/2 METHOD