Examination of Transannular Participation via SCF-MO Calculations and Far Ultraviolet Spectroscopy

Ronald D. Schultz

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EXAMINATION OF TRANSANNULAR PARTICIPATION VIA SCF-MO CALCULATIONS
AND FAR ULTRAVIOLET SPECTROSCOPY

BY

RONALD D. SCHULTZ

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
Chemistry, South Dakota
State University

1972
EXAMINATION OF TRANSANNULAR PARTICIPATION VIA SCF-NO CALCULATIONS AND FAR ULTRAVIOLET SPECTROSCOPY

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Advisor

Head, Chemistry Department

Date
EXAMINATION OF TRANSANNUlar PARTICIPATION VIA SCF-MO CALCULATIONS AND FAR ULTRAVIOLET SPECTROSCOPY

Abstract

RONALD D. SCHULTZ

Under the supervision of Professor James J. Worman

Dimethylketen dimer, tetramethylcyclobutane-1,3-biscyclohexylimine, and tetramethylcyclobutane-1,3-dithione have been studied by means of self-consistent field molecular-orbital calculations and far ultraviolet absorption spectroscopy.

The SCF-MO calculations showed transannular participation resulting in $\pi-\pi^*$ peak splitting in all three compounds with the order being diketone > diimine > dithione. The far ultraviolet absorption of the three compounds showed the lowest energy predicted absorptions in all cases but splitting in the $\pi-\pi^*$ could not be seen because the instrument was incapable of going below 185 nm.

In the $n-\pi^*$ region of these three compounds, splitting has been observed with the order being diketone > diimine > dithione. However, the splitting shown for the dithione in the ultraviolet is shown to be $0$ while predictions by the SCF-MO calculations, although less than both the diketone and the diimine, show a splitting of $0.24 eV$. 
ACKNOWLEDGEMENTS

The author wishes to express his gratitude to all who helped to make this thesis possible. A special thanks are extended to Hans H. Jaffe' for furnishing computer programs, Dave Ochsner for his help in computer programming, and to the Research and Data Processing Department and Dr. Paul Koepsell for access to computer facilities. And, of course, appreciation is extended to Dr. James J. Worman, whose intuitive insight and patient guidance along with a friendly manner forced me to complete this thesis.
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</tbody>
</table>
INTRODUCTION

Since the advent of the computer the chemist has taken great strides in bringing the mathematical aspects of chemical systems up to date. Before this time physical data on a tremendous number of different chemical systems had constantly been accumulating without theoretical backing. However, now with the tools available the chemist can at last begin the tedious and difficult task of explaining the data he has been receiving.

One particular area of mathematical interest in chemistry is that which deals with the energy of a particular chemical system. In order to study this area of chemistry, theoretical or semi-empirical energy calculations of these systems are necessary. Theoretical calculations are indeed very tedious and tend to discourage most chemists. However, working from Roothaan's formulas for LCAO-SCF calculations \(^1\) Pariser and Parr \(^2\) and Pople \(^3\) came up with a semiempirical SCF-MO method. \(^4\) This method allows predictions of the \(\pi\)-energy of molecules and the \(\pi-\pi^*\) singlet transition energies.

The P-P-P SCF method for determining \(\pi\)-electron orbital energies and \(\pi-\pi^*\) transition energies is quite analogous to the Huckel MO procedure except that it takes into account electron repulsions and
attractions that the Huckel MO theory neglects. Indeed, the theory usually starts with the Huckel equations to get the starting LCAO wave functions.

In Huckel MO theory the Schrodinger equation in matrix form is: \[ \text{HC} = \text{SCE} \] (1)

In this equation the C matrix is the coefficient matrix which diagonalizes the secular determinant. The H matrix is the Hamiltonian matrix which is the same as the Huckel determinant without the energy terms. The E matrix is the diagonalized energy matrix and finally the S matrix is the overlap matrix containing as elements each of the overlap integrals between pairs of atomic orbitals.

The secular determinant for Huckel MO theory\(^6\) for the four atom butadiene system, as an example is:

\[
\begin{vmatrix}
H_{11} - S_{11} \text{E} & H_{12} - S_{12} \text{E} & H_{13} - S_{13} \text{E} & H_{14} - S_{14} \text{E} \\
H_{12} - S_{12} \text{E} & H_{22} - S_{22} \text{E} & H_{23} - S_{23} \text{E} & H_{24} - S_{24} \text{E} \\
H_{13} - S_{13} \text{E} & H_{23} - S_{23} \text{E} & H_{33} - S_{33} \text{E} & H_{34} - S_{34} \text{E} \\
H_{14} - S_{14} \text{E} & H_{24} - S_{24} \text{E} & H_{34} - S_{34} \text{E} & H_{44} - S_{44} \text{E}
\end{vmatrix} = 0
\]

The \(H_{11}\) terms are called coulomb integrals and represent approximately the energy of an electron in a valence p orbital. The \(H_{1i}\) terms are usually replaced by the symbol \(\alpha\). The \(H_{ij}\) terms are called resonance or bond integrals commonly referred to as \(\beta\) and represent the energy of interaction between two adjacent atomic orbitals. \(H_{ij}\)
or β terms are usually set equal to 0 if the atoms or orbitals on the atoms are not directly adjacent since β is a function of bond distance.

The S integrals are called the overlap integrals, which in a sense are almost self-describing. They are integrals which are proportional to bond strength. In the Huckel MO approximation $S_{ii} = 1$ for the same atom and $S_{ij} = 0$ if the atoms are different. This is not entirely true but it does make the calculations much simpler.

Our "Huckel determinant in equation (2) may now be reduced to something which looks like this:

$$
\begin{pmatrix}
\alpha_{11}E - \beta_{12} & 0 & 0 \\
\beta_{21} & \alpha_{22}E - \beta_{23} & 0 \\
0 & \beta_{32} & \alpha_{33}E - \beta_{34} \\
0 & 0 & \beta_{43} - \alpha_{44}E
\end{pmatrix}
$$

The determinant can now be solved although the answers obtained depend on the approximations made.

In the P-P-P SCF theory the Schrodinger equation to be solved is:

$$
FC = S \sigma e
$$

where F is now the Hartree-Fock matrix which is analogous to the $H$ matrix but includes energy repulsion terms. The S and C terms are the same as in the "Huckel theory and the e matrix is the same as the Huckel E matrix."
Reiterating then, the difference between Hückel and SCF theory is that P-P-P SCF theory takes into account repulsion and overlap integrals for all electrons in the system even though the integral themselves are semiempirically evaluated.\textsuperscript{10,11}

In the P-P-P method equation (4) is solved and the eigenvalues found are \( e_1 \), the eigenvalues to the Fock operator. The eigenvectors are still the LCAO coefficients for the molecular orbitals. The new coefficients are then used to find a new charge distribution and to construct a new \( F \) matrix. The new \( F \) matrix is again diagonalized, another new charge distribution is calculated, and the process is repeated until the final charge distribution agrees with the initial one. This agreement in charge distribution is usually checked by comparing the eigenvectors at the end of an iteration with those from the previous iteration. The process is terminated when the eigenvalues agree to within a specified degree of accuracy.

Pariser and Parr, working from their basic SCF-MO calculations\textsuperscript{12} came up with excellent energy values for ethylene, butadiene, and benzene.\textsuperscript{13}

In P-P-P SCF theory the determinant solved is called the Fock determinant which, for the butadiene problem, looks like this:
The $F_{uu}$ terms are similar to the $\alpha$ terms in Hückel theory and the $F_{uv}$ terms resemble the $\beta_{uv}$ terms in Hückel theory. The procedure is further explained in the experimental section of this thesis.

The basic parameters necessary for the formulas in the P-P-P SCF theory are: the effective nuclear charge, $Z_u$, the $n$-electron density, $P_{uu}$, and the valence state ionization potential, $I_u$. The integrals used in the theory itself are: the one-electron, one-center integral, $\alpha_u$, the one-electron, two-center integral, $\beta_{uv}$, the two-electron, one-center repulsion integral, $(uu/uu)$, and the two-electron, two-center repulsion integral, $(uu/vv)$. The $\alpha_u$, $(uu/uu)$, and $(uu/vv)$ integrals are semiempirically evaluated while $\beta_{uv}$ is usually empirically evaluated from spectroscopic data.

Having achieved such good results with simple hydrocarbons, the P-P-P theory was soon expanded to take in heterogenous compounds. Brown and Heffernan tried the new theory on formaldehyde. In order to resolve the problem of choosing electronegativities used for various parameters, they used atomic spectroscopic data in assigning electronegativities.
It had been customary in SCF procedure up until this time to use fixed values for the effective nuclear charge, $Z_u$, of each atom $u$. Thus, in order to allow for variation in the electronegativity of atom $u$ with the $n$-electron density, $P_{uu}$, on that atom, $Z_u$ was regarded as a function of $P_{uu}$. The functional dependence followed directly from Slaters rules. For atoms in the first row of the periodic table the relationship is:

\begin{equation}
Z_u = N_u - 1.35 - 0.35(\sigma_u + P_{uu})
\end{equation}

where $N_u$ is the atomic number of $u$ and $\sigma_u$ is the number of $\sigma$-electrons contributed to the electronic structure by atom $u$.

Since the variation of $Z_u$ with $P_{uu}$ was included in the SCF MO procedure then, as well as the usual dependence of the SCF matrix elements on the charge distribution, the two-electron, one-center repulsion integral, $(uu/uu)$, the two-electron, two-center repulsion integral, $(uu/vv)$, and the neutral atom penetration integral, $(u/vv)$, became functions of $P_{uu}$ from their dependence on $Z_u$. These last integrals are called electron repulsion integrals because they result from the various repulsions of the electrons within the system.

This new procedure was referred to as the "self-consistent electronegativity method," SCE, because the iterative procedure led to self-consistent values of $Z_u$ as well as of $P_{uu}$.

Coulomb integrals, $\alpha_u$, were calculated from the formula:

\begin{align}
\alpha_c &= -I_c - (cc/oo) - \sum_{u/c} (u/cc) \\
\alpha_o &= -I_o - (cc/oo) - \sum_{u/o} (u/oo)
\end{align}
where \( I_c \) and \( I_o \) are the valence state \( 2p^{n} \)-electron ionization potentials of carbon and oxygen.

In the SCE procedure, since \( I_c \) and \( I_o \) were functions of \( Z_c \) and \( Z_o \), \( I_u \) was plotted against \( Z_u \) for the \((sp^3,v_4)\) valence state of the isoelectronic series, \( C, N^+, O^{2+}, F^{3+} \) giving a parabolic curve:

\[
(9) \quad I_u(sp^3,v_4 \rightarrow sp^3,v_3) = 3.490Z_u^2 = 9.767Z_u + 4.048eV
\]

and this was used for evaluating \( I_c \). The value of \( Z_u \) was the mean Slater value for \( C \) and \( C^+ \) to make allowance for the change in \( Z_u \) accompanying ionization.

Since the valence state was not definitely known for oxygen in formaldehyde two hybrid bonding orbitals were selected to cover the probable range in which the oxygen hybridization lay; i.e., \( sp \) and \( sp^2 \) hybrids. They corresponded to valence states \((s^{3/2}p^{9/2},v_2)\) and \((s^{5/2}p^{13/2},v_2)\), both of which were combinations of the more common \((s^2p^4,v_2)\) and \((sp^5,v_2)\). When the \( 2p^{n} \)-electron ionization potentials of the second pair of valence states for \( O, F^+, Ne^{2+}, \) and \( Na^{3+} \) were plotted against functions of \( Z_u \) the following parabolic relationships were obtained:

\[
(10) \quad I_u(s^2p^{4},v_2 \rightarrow s^2p^3,v_1) = 3.775Z_u^2 - 17.099Z_u + 13.790eV
\]

\[
(11) \quad I_u(sp^5,v_2 \rightarrow sp^4,v_1) = 3.505Z_u^2 - 14.537Z_u + 8.195eV
\]

from which were derived

\[
(12) \quad I_u(s^{3/2}p^{9/2},v_2 \rightarrow s^{3/2}p^{7/2},v_1) = 3.640Z_u^2 - 15.818Z_u + 10.993eV
\]
The monocentric integrals \((cc/cc)\) and \((oo/oo)\) were obtained from the formula derived by Paolini: \(^{16}\)

\[(uu/uu) = 3.294Z_u\]

The two-center coulomb repulsion integral \((cc/oo)\) was evaluated according to the method outlined by Pariser and Parr: \(^{17}\)

\[ar + br^2 = \frac{1}{2}((cc/cc) + (oo/oo)) - (cc/oo)\]

where \(r\) is the distance between \(c\) and \(o\) and \(a\) and \(b\) are numerical coefficients. The integrals on the right are functions of \(Z_u\) as well as \(P_{cc}\) and \(P_{oo}\) and thus \(a\) and \(b\) also show a dependence on the \(n\)-electron densities.

The penetration integrals, \((v/uu)\), were evaluated from tabulations of molecular integrals \(^{18}\) where the \(\sigma\)-bonds were taken to be purely covalent so that one electron was assigned to each of the \(\sigma\)-orbitals of the two atoms forming the \(\sigma\)-bond.

The resonance integral, \(B_{uv}\), was obtained from ultraviolet (UV) spectroscopic data for formaldehyde. The spectroscopic integral for the first \(n-n^*\) transition was evaluated in terms of \(\beta_{co}\) involving the following singlet configurations:

\[\phi_1 = (x_0)^2, \phi_2 = (x_c)^2, \phi_3 = (x_o) (x_c)\]

where \(X\) is a \(2p\pi\)-orbital on atom \(u\). The secular equation for the configuration interaction reduces to:

\[
\begin{vmatrix}
(2\alpha_o + (oo/oo) - E) & 0 & 2\beta_{co} \\
0 & (2\alpha_c + (cc/cc) - E) & 2\beta_{co} \\
2\beta_{co} & 2\beta_{co} & (\alpha_o + \alpha_c + (cc/oo) - E)
\end{vmatrix}
= 0
\]
A uniform π-electron density in formaldehyde was assumed; i.e., $P_{cc} = P_{00} = 1$ and from (17) $\beta_{co}$ was found equal to $-2.73\text{eV}$. This led to values given in the following tables:

### TABLE 1. Formaldehyde Molecular Integrals: sp-Hybridized O

<table>
<thead>
<tr>
<th>Integral</th>
<th>Value, eV</th>
<th>Integral</th>
<th>Value, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(cc/00)</td>
<td>8.545</td>
<td>(H/CC)</td>
<td>0.655</td>
</tr>
<tr>
<td>(cc/cc)</td>
<td>10.827</td>
<td>(H/00)</td>
<td>0.003</td>
</tr>
<tr>
<td>(00/00)</td>
<td>14.867</td>
<td>$\alpha_C$</td>
<td>-23.608</td>
</tr>
<tr>
<td>(c/00)</td>
<td>1.167</td>
<td>$\alpha_O$</td>
<td>-26.569</td>
</tr>
<tr>
<td>(c/cc)</td>
<td>1.692</td>
<td>$I_C$</td>
<td>12.061</td>
</tr>
<tr>
<td>$\beta_{co}$</td>
<td>-2.736</td>
<td>$I_O$</td>
<td>16.841</td>
</tr>
</tbody>
</table>

### TABLE 2. Formaldehyde Molecular Integrals: sp$^2$-Hybridized O

<table>
<thead>
<tr>
<th>Integral</th>
<th>Value, eV</th>
<th>Integral</th>
<th>Value, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(cc/00)</td>
<td>8.545</td>
<td>(H/CC)</td>
<td>0.649</td>
</tr>
<tr>
<td>(cc/cc)</td>
<td>10.767</td>
<td>(H/00)</td>
<td>0.008</td>
</tr>
<tr>
<td>(00/00)</td>
<td>14.931</td>
<td>$\alpha_C$</td>
<td>-24.394</td>
</tr>
<tr>
<td>(c/00)</td>
<td>1.184</td>
<td>$\alpha_O$</td>
<td>-26.848</td>
</tr>
<tr>
<td>(c/cc)</td>
<td>2.770</td>
<td>$I_C$</td>
<td>11.781</td>
</tr>
<tr>
<td>$\beta_{co}$</td>
<td>-2.690</td>
<td>$I_O$</td>
<td>17.103</td>
</tr>
</tbody>
</table>
This new SCE method allowed excellent agreement with spectroscopic data. The following table shows some of the results:

**TABLE 3. π-π* Spectral Transition in Formaldehyde**

<table>
<thead>
<tr>
<th></th>
<th>SCE eV</th>
<th>A</th>
<th>Fixed Z eV</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-V₁</td>
<td>7.94</td>
<td>1560</td>
<td>7.94</td>
<td>1560</td>
</tr>
<tr>
<td>N-V₂</td>
<td>11.64</td>
<td>1065</td>
<td>11.96</td>
<td>1035</td>
</tr>
<tr>
<td>N-T₁</td>
<td>3.66</td>
<td>3385</td>
<td>3.77</td>
<td>3290</td>
</tr>
</tbody>
</table>

These results are for sp²-hybridization on O. The first π-π* transition for formaldehyde has been observed at 1560Å or 7.95eV.¹⁹

Later SCF-MO calculations were also undertaken by C. Sandorfy²⁰ on C=N again achieving excellent agreement with UV spectroscopic data. The following table summarizes the results.

**TABLE 4. Numerical Values of Integrals for C=N**

\[ \begin{align*}
P_{CC} &= P_{NN} = 1, \quad Z_N = 3.90, \quad Z_C = 3.25 \\
\end{align*} \]

<table>
<thead>
<tr>
<th>Integral</th>
<th>Value, eV</th>
<th>Integral</th>
<th>Value, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CC/CC)</td>
<td>10.53</td>
<td>β_{CN}</td>
<td>-2.70</td>
</tr>
<tr>
<td>(NN/NN)</td>
<td>12.27</td>
<td>I_{C}</td>
<td>11.26</td>
</tr>
<tr>
<td>(CC/NN)</td>
<td>7.82</td>
<td>I_{N}</td>
<td>14.53</td>
</tr>
</tbody>
</table>

\[ E_{\pi} = -36.85\text{eV} \quad \text{and} \quad E_{\pi-\pi^*} = 7.05\text{eV (1900Å)} \]
Since the simple chromophoric data was realistic, the application to the more complicated systems

\[ \text{O=C} - \text{C=O}, \quad \text{N=O} - \text{C=N}, \quad \text{S=O} - \text{C=S}, \]

(1) (2) (3)

seemed reasonable.

The crystal structure of dimethylketen dimer, (1), was done by Friedlander and Robertson\textsuperscript{21}. They reported the symmetry to be $D_{2h}$, a planar ring with two perpendicular vertical planes. This symmetry was also applied to tetramethylcyclobutane-1,3-dithione, (2), because of the similarity of this compound to 1. Tetramethylcyclobutane-1,3-biscyclohexylimine, (2), was judged to have $C_{2v}$ symmetry which is only a slight variation of $D_{2h}$. This configuration keeps the ring planar but only has one vertical plane of symmetry.

Compound 1 was discovered by Chick and Wilsmore\textsuperscript{22} in 1908. Ed Schmidt\textsuperscript{23}, South Dakota State University, synthesized compound 2 in 1970. Compound 3 was prepared in 1967 by Elam and Davis\textsuperscript{24}.

In addition to simple electronic transitions there is the possibility of transannular participation. This was observed for $n-\pi^*$ transition in the UV for compounds 1 and 2 but not for 3. Work on 1 and 2 was reported by Ballard and Park\textsuperscript{25} in 1968. They reported seeing splitting in the $n-\pi^*$ band of compound 1. Two peaks were detected, one at 307 nm and the other at 350 nm. They
reported no such splitting in either the \( n-\pi^* \) or \( \pi-\pi^* \) band of \( \text{1} \). Schmidt et al\(^\text{26} \) reported observed splitting in the \( n-\pi^* \) transition of \( \text{2} \). No evidence has been documented for splitting in the \( \pi-\pi^* \) transition of either \( \text{1} \) or \( \text{2} \).
The purpose of this work was to study the possibility and magnitude of transannular π-interaction in dimethylketen dimer, (1), tetramethylcyclobutane-1,3-biscyclohexylimine, (2), and tetramethylcyclobutane-1,3-dithione, (3). The approach was to use semiempirical SCF-MO calculations to determine π-π* singlet transition energies and attempt to verify these by far ultraviolet spectroscopy.
RESULTS AND DISCUSSION

Ultraviolet Spectra

UV spectra were run to determine the high-energy \( \pi-\pi^* \) and \( \pi-\sigma^* \) transitions. Spectra were run on the diketone, 1, the diimine, 2, and the dithione, 3, with the results summarized in Table 5.

**Table 5**

UV Spectra

<table>
<thead>
<tr>
<th>System</th>
<th>Absorption, nm</th>
<th>( \epsilon_{\text{max}} )</th>
<th>Solvent</th>
<th>Calc Value(^1 ), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)CH(_3)</td>
<td>195 (n-(\sigma^*))</td>
<td>1,060</td>
<td>heptane</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>203 (n-(\sigma^*))</td>
<td>7,600</td>
<td>heptane</td>
<td>—</td>
</tr>
<tr>
<td>O=C C=O</td>
<td>227 (n-(\sigma^*))</td>
<td>112</td>
<td>heptane</td>
<td>161, 148, 117, 116(^2 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(145, 139, 134, 132)(^3 )</td>
</tr>
<tr>
<td>N=C C=N</td>
<td>197 ((\pi-\pi^*))</td>
<td>9,880</td>
<td>heptane</td>
<td>197, 172, 145, 143(^2 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(177, 170, 156, 154)(^3 )</td>
</tr>
<tr>
<td>N=C C=O</td>
<td>198 ((\pi-\pi^*))</td>
<td>8,800</td>
<td>heptane</td>
<td>—</td>
</tr>
<tr>
<td>S=C C=O</td>
<td>226 ((\pi-\pi^*))</td>
<td>185,000</td>
<td>heptane</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>198 (n-(\sigma^*))</td>
<td>325,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S=C C=S</td>
<td>228 ((\pi-\pi^*))</td>
<td>42,000</td>
<td>cyclohex.</td>
<td>262, 211, 187, 183(^2 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(235, 225, 196, 187)(^3 )</td>
</tr>
</tbody>
</table>

1 P\(^3\)-CI Program
2 Pariser-Parr values
3 Mataga values

The Mataga method referred to in Table 5 is discussed in detail later in this section under "discussion of computer work."

Some of the transitions appear to be \( \pi-\pi^* \) and allowed because of the high \( \epsilon_{\text{max}} \), 7,000-200,000. In conjunction with previous solvent
Studies, only acetone, \( \epsilon_{\text{max}} = 1060 \), dimethylketen dimer, \( \epsilon_{\text{max}} = 112 \), and cyclohexylamine, \( \epsilon_{\text{max}} = 7600 \), have small enough \( \epsilon_{\text{max}} \) to be considered \( n-\pi^* \) bands.

Higher energy peaks, below 185 nm, were not possible to see because of the limitations of the instrument. Vacuum UV would be necessary in order to see these high energy peaks. Higher energy transitions were predicted by the P\(^3\)-CI program to appear below 185 nm. These transitions appear in Table 10 in "discussion of computer work."

If there were transannular participation, one would expect to see two transitions for the \( \pi-\pi^* \) transition of the bisimine. Only one band was observed at 197 nm and no evidence from the spectrum indicated that this transition was split. The second \( \pi-\pi^* \) band would be expected at 167 nm, beyond the limit of our instrumentation. In any event, this \( \pi-\pi^* \) observed transition of the bisimine is lower in energy than that observed for simple imines (180 nm).\(^{27}\) This lowering in energy can be interpreted to represent transannular participation.

No splitting has been observed in the \( n-\pi^* \) band of the dithione. However, a very broad, moderately strong band is observed at about 500 nm for this molecule. It is possible that a second band, which could be attributed to transannular participation, is covered up under this large broad band. In the \( \pi-\pi^* \) region the dithione exhibits a peak at 227 nm. This peak would be broad enough to hide a secondary peak due to transannular participation if it were close enough to the main peak; i.e. approximately 10 nm.
Splitting of such small magnitude is quite possible for this system since it is likely that decreased overlap exists due to the decreased ability of the 3p orbital on sulfur to overlap significantly with the 2p orbital on carbon.

**Discussion of Hand Calculation**

The results obtained from the hand calculation for formaldehyde showed excellent agreement with the results obtained by Brown and Heffernan as well as the results given by QCPE-76. Table 6 summarizes the results.

**TABLE 6**

Comparison of Hand Calculation with Other Sources on the Ground State of Formaldehyde

\[ P_{oo} = 1.00, \ P_{cc} = 1.00, \ Z_0 = 4.55, \ Z_C = 3.25 \]

<table>
<thead>
<tr>
<th>Integral</th>
<th>Hand Calculation, eV</th>
<th>QCPE-76, eV</th>
<th>Brown &amp; Heffernan</th>
</tr>
</thead>
<tbody>
<tr>
<td>(cc/cc)</td>
<td>10.7</td>
<td>10.83</td>
<td>10.82</td>
</tr>
<tr>
<td>(oo/oo)</td>
<td>14.95</td>
<td>14.87</td>
<td>14.87</td>
</tr>
<tr>
<td>(cc/oo)</td>
<td>8.55</td>
<td>8.54</td>
<td>8.54</td>
</tr>
<tr>
<td>( \beta_{CO} )</td>
<td>-2.76</td>
<td>-2.74</td>
<td>-2.74</td>
</tr>
<tr>
<td>( \alpha_C )</td>
<td>-17.72</td>
<td>-</td>
<td>-23.61</td>
</tr>
<tr>
<td>( \alpha_O )</td>
<td>-24.26</td>
<td>-</td>
<td>-26.57</td>
</tr>
<tr>
<td>( F_{cc} )</td>
<td>-5.81</td>
<td>-4.51</td>
<td>-5.81</td>
</tr>
<tr>
<td>( F_{oo} )</td>
<td>-10.16</td>
<td>-6.97</td>
<td>-10.16</td>
</tr>
<tr>
<td>( F_{co} )</td>
<td>-7.03</td>
<td>-6.98</td>
<td>-7.03</td>
</tr>
</tbody>
</table>

Final energy = -36.50 - Hand
Final energy = -36.15 eV - QCPE-76
Final energy = -36.60 eV - Brown and Heffernan
It is interesting to compare the total ground state energies calculated by the three different methods. For example, the difference in total energy between Hand and QCPE-76 is 0.35 eV while the difference between Hand and Brown and Heffernan is 0.45 eV. It would appear therefore that QCPE-76 could be used to calculate accurate ground state energies.

Discussion of Computer Work

The PPP SCF theory is a very tedious, time consuming method. In order to be able to carry out calculations on more than one system, other than by several months of hand calculations, a computer program is necessary. Several universities and institutions were contacted about computer programs in the area of SCF-MO calculations. The major programs used were:

1. QCPE-76 from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana. This program was used for ground state energy calculations. The data obtained appeared to be logical. However, it was not able to compute excited state energy values. This program contained no configuration interaction.

2. QCPE-71.2 from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana. This program contained configuration interaction and gave ground state and excited configuration energy values. However, the program was not designed to give energy values of electronic transitions.

3. CN30/2 from Dr. Hans H. Jaffe', University of Cincinnati, Cincinnati, Ohio. This program was a total electron program, including σ and nonbonded electrons as well as π-electrons and contained configuration interaction. The output data gave all possible transition within the molecule. Resultant data obtained from this program was good for π-σ* transitions and n-σ* but the transition energy for the n-π* band was
the lowest vibrational band instead of the vibrational band at maximum absorption which one sees in a UV spectrum. The program also has the limitation of needing a large amount of computer core space to handle systems over ten atoms and thirty electrons. However, it is my belief that this program has great potential for further work, since it is an all electron program.

4. P^3-CI from Dr. Hans H. Jaffe*, University of Cincinnati, Cincinnati, Ohio. This program also contained a configuration interaction subroutine. Output data obtained contained n-n transition energy in electron volts, eV, and nanometers, nm. This program was used for the majority of the calculations needed for the results found in this paper.

The two main programs used were: QCPE-76 from the University of Indiana, and the P^3-CI program obtained from Dr. Jaffe* at the University of Cincinnati.

QCPE-76 was a good program for the calculation of ground state energies. However, when it was used to attempt to predict transition energies the program proved ineffectual. The reason for this probably lies in the fact that the program had to calculate the ground state energy and the first excited singlet state separately and then the energy values had to be subtracted to get the transition energy. Whenever an attempt is made to calculate the absolute energy of an excited state, trouble arises. Usually the most stable geometric arrangement for molecules in their excited electronic states is different from that in their ground states. This can result in substantial deviations from the desired excited state energy value. Another argument against using excited state energy values in determining transition values is the fact that the first excited singlet transition energy comes, not from a single excited state, but from a mixture of possible singlet configurations. This mixing
of configurations yields a dramatically different picture of the "excited state." A configuration interaction program which allows for this mixing of configurations is needed to give accurate transition energies.

Table 7 summarizes the data obtained from QCPE-76.

**TABLE 7**

<table>
<thead>
<tr>
<th>System</th>
<th>(VV/VV), eV</th>
<th>(CC/VV), eV</th>
<th>$\beta_{\text{CN}}$, eV</th>
<th>$\text{EN}$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O $^1$</td>
<td>14.87</td>
<td>8.55</td>
<td>-2.74</td>
<td>-36.15</td>
</tr>
<tr>
<td>C=O $^2$</td>
<td>14.87</td>
<td>6.18</td>
<td>-2.74</td>
<td>-37.49</td>
</tr>
<tr>
<td>O=C C=O $^1$</td>
<td>14.87</td>
<td>8.55</td>
<td>-2.74</td>
<td>-81.35</td>
</tr>
<tr>
<td>C=N $^1$</td>
<td>12.27</td>
<td>7.82</td>
<td>-2.70</td>
<td>-33.98</td>
</tr>
<tr>
<td>C=N $^2$</td>
<td>12.27</td>
<td>5.44</td>
<td>-2.70</td>
<td>-33.75</td>
</tr>
<tr>
<td>N=C C=N $^1$</td>
<td>12.27</td>
<td>7.82</td>
<td>-2.70</td>
<td>-77.03</td>
</tr>
<tr>
<td>C=S $^1$</td>
<td>9.94</td>
<td>4.34</td>
<td>-3.62</td>
<td>-31.32</td>
</tr>
<tr>
<td>C=S $^2$</td>
<td>9.94</td>
<td>4.84</td>
<td>-3.00</td>
<td>-30.08</td>
</tr>
<tr>
<td>S=C C=S $^2$</td>
<td>9.94</td>
<td>4.84</td>
<td>-3.00</td>
<td>-71.91</td>
</tr>
</tbody>
</table>

1 Pople Method
2 Mataga Method
The Mataga method, referred to earlier in Table 5 and here in Table 7, is basically the same as the Pariser-Parr method. The only difference in the two methods is in the calculation of the two-electron, two-center integral, \((uu/vv)\). In the Mataga method the formula:

\[(uu/vv) = \left(1/(r_{uv} + a)\right) \text{au}\]

where

\[a = 2/\left((uu/uu) + (vv/vv)\right)\]

and \(r\) is the distance between the two atoms, is used. All terms are in atomic units, au, which can be converted into electron volts, eV, after the calculation is finished; i.e., \(1 \text{ au} = 27.2 \text{ eV}\).

Once the two-electron, two-center integral, \((uu/vv)\), is calculated it is used to calculate the off-diagonal elements, \(F_{uv}\), in the Fock determinant. Once this determinant is set up it is a simple procedure to solve for the \(\pi\)-energy of the system. Since \((uu/vv)\) is used directly in calculating \(F_{uv}\), which is one of the final steps in the SCF procedure, a change in \((uu/vv)\) will result in a corresponding change for the total \(\pi\)-energy.

The \(P^{3}\)-CI program was the program which gave the most consistent data. In order to test the ability of this program to successfully work on systems involving transannular participation norbornadiene was first tested with the program. Norbornadiene is known to have interaction in the ground state resulting in splitting of energy levels.\(^{30}\)
The phenomenon of transannular participation merits some discussion. In the case of dimethylketen dimer, (1), the C=O groups are nonconjugated in the classical sense but are suitably oriented so that there can be orbital overlap in the usual \( \pi \) fashion (parallel orbitals). This \( \pi \)-overlap of the carbon 2p orbitals in the 1 and 3 positions of the ring causes the formation of two delocalized \( \pi^* \) orbitals, a low energy, in-phase orbital, \( \pi^*_+ \), and a high energy, out-of-phase orbital, \( \pi^*_\times \). The delocalization of energy levels allows the possibility of seeing more than one \( \pi-\pi^* \) transition in the UV; i.e. \( \Delta E_1 \), \( \Delta E_2 \), \( \Delta E_3 \), and \( \Delta E_4 \). The most probable transitions which can be seen in the UV are \( \Delta E_1 \) and either \( \Delta E_2 \) or \( \Delta E_3 \). The transition \( \Delta E_4 \) is of too high energy to be seen in the UV normally.

Tables 8 and 9 show the program results for norborandiene.
TABLE 8
Norbornadiene-Gamma by Pariser-Parr Ground State Geometry

<table>
<thead>
<tr>
<th>Atom</th>
<th>X-Coordinate</th>
<th>Y-Coordinate</th>
<th>Z-Coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.18500</td>
<td>-0.66500</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>-1.18500</td>
<td>0.66500</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>1.18500</td>
<td>0.66500</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>1.18500</td>
<td>-0.66500</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Row</th>
<th>Col</th>
<th>Core Attract. Integrals</th>
<th>Coulomb Replsn. Integrals</th>
<th>Expansion Basis Eigenvectors</th>
<th>Eigenvalues</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-11.18000</td>
<td>11.129999</td>
<td>0.49999999</td>
<td>-12.36216</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-2.57943</td>
<td>7.619151</td>
<td>0.49999999</td>
<td>-11.64588</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.0</td>
<td>4.987909</td>
<td>0.49999999</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>-0.35814</td>
<td>5.548229</td>
<td>0.49999999</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>-2.57943</td>
<td>7.619151</td>
<td>0.49999999</td>
<td>-12.36216</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>-11.18000</td>
<td>11.129999</td>
<td>0.49999999</td>
<td>-12.36216</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>-0.35814</td>
<td>5.548229</td>
<td>-0.49999999</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>0.0</td>
<td>4.987909</td>
<td>-0.49999999</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>0.0</td>
<td>4.987909</td>
<td>0.49999999</td>
<td>0.41585</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>-0.35814</td>
<td>5.548229</td>
<td>-0.49999999</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>-11.18000</td>
<td>11.129999</td>
<td>-0.49999999</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>-2.57943</td>
<td>7.619151</td>
<td>0.49999999</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>-0.35814</td>
<td>5.548229</td>
<td>0.49999999</td>
<td>1.13212</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0.0</td>
<td>4.987909</td>
<td>-0.49999999</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>-2.57943</td>
<td>7.619151</td>
<td>0.49999999</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>-11.18000</td>
<td>11.129999</td>
<td>-0.49999999</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 9
Norbornadiene - Output for Singlet States

<table>
<thead>
<tr>
<th>CI State</th>
<th>Transition Energy (eV)</th>
<th>Frequency (cm⁻¹)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.0116</td>
<td>48438.27</td>
<td>206.53</td>
</tr>
<tr>
<td>2</td>
<td>7.4746</td>
<td>60288.83</td>
<td>166.11</td>
</tr>
<tr>
<td>3</td>
<td>7.5099</td>
<td>60573.82</td>
<td>165.33</td>
</tr>
<tr>
<td>4</td>
<td>7.8524</td>
<td>63335.71</td>
<td>158.12</td>
</tr>
</tbody>
</table>

Wilcox, Winston, and McMillan³² reported experimentally weak UV bands at 205 nm, 214 nm, 220 nm, and 230 nm as well as a marked increase in absorption below 198 nm. This is substantiated in the table with three calculated values below 200 nm and one value at 206 nm.

The splitting in the energy levels is predicted by the program to be 0.7163 eV. This value compared favorably to the experimental photoelectron spectroscopy value of 0.85 eV³³ and the value of 0.43 eV predicted in an extended Hückel calculation performed by Raold Hoffmann, in 1969.³⁴

Once the capabilities of the program in the area of transannular participation were established the program was used on the diketone, ¹, the diimine, ², and the dithione, ³. Table 10 gives the results obtained from the program.
<table>
<thead>
<tr>
<th>System</th>
<th>Eigenvalues</th>
<th>CI Singlet Transition Energy (eV, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C=0^1$</td>
<td>-13.7005</td>
<td>9.2092 (134.82)</td>
</tr>
<tr>
<td></td>
<td>-1.2988</td>
<td></td>
</tr>
<tr>
<td>$C=0^2$</td>
<td>-14.0663</td>
<td>8.1918 (151.57)</td>
</tr>
<tr>
<td></td>
<td>0.1150</td>
<td></td>
</tr>
<tr>
<td>$O=C$, $C=0^1$</td>
<td>-14.0785</td>
<td>8.5571 (145.10)</td>
</tr>
<tr>
<td></td>
<td>-13.7039</td>
<td>8.9466 (138.78)</td>
</tr>
<tr>
<td></td>
<td>-2.0002</td>
<td>9.2915 (133.63)</td>
</tr>
<tr>
<td></td>
<td>-1.2774</td>
<td>9.4341 (131.61)</td>
</tr>
<tr>
<td>$O=C$, $C=0^2$</td>
<td>-15.6083</td>
<td>7.6866 (161.49)</td>
</tr>
<tr>
<td></td>
<td>-15.2475</td>
<td>8.2671 (148.39)</td>
</tr>
<tr>
<td></td>
<td>-0.9442</td>
<td>10.6370 (116.72)</td>
</tr>
<tr>
<td></td>
<td>-0.1714</td>
<td>10.7109 (115.92)</td>
</tr>
<tr>
<td>$C=N^1$</td>
<td>-13.1161</td>
<td>6.8844 (180.35)</td>
</tr>
<tr>
<td></td>
<td>-0.2918</td>
<td></td>
</tr>
<tr>
<td>$N=C$, $C=N^1$</td>
<td>-12.2474</td>
<td>7.0134 (177.03)</td>
</tr>
<tr>
<td></td>
<td>-11.8844</td>
<td>7.3090 (169.87)</td>
</tr>
<tr>
<td></td>
<td>-2.0203</td>
<td>7.9755 (155.68)</td>
</tr>
<tr>
<td></td>
<td>-1.3445</td>
<td>8.0847 (153.57)</td>
</tr>
</tbody>
</table>
TABLE 10 (cont.)

<table>
<thead>
<tr>
<th>System</th>
<th>Eigenvalues</th>
<th>CI Singlet Transition Energy (eV (nm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N=C C=N^2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-13.6406</td>
<td>6.2977 (197.15)</td>
</tr>
<tr>
<td></td>
<td>-13.1730</td>
<td>7.2209 (171.94)</td>
</tr>
<tr>
<td></td>
<td>-1.0814</td>
<td>8.5659 (144.95)</td>
</tr>
<tr>
<td></td>
<td>-0.3587</td>
<td>8.6781 (143.07)</td>
</tr>
<tr>
<td>C=S^1</td>
<td>-12.0415</td>
<td>5.3541 (231.90)</td>
</tr>
<tr>
<td></td>
<td>-1.4752</td>
<td></td>
</tr>
<tr>
<td>S=C C=S^1</td>
<td>-11.4097</td>
<td>5.2856 (234.90)</td>
</tr>
<tr>
<td></td>
<td>-10.9435</td>
<td>5.5262 (224.68)</td>
</tr>
<tr>
<td></td>
<td>-3.0611</td>
<td>6.3363 (195.95)</td>
</tr>
<tr>
<td></td>
<td>-2.3747</td>
<td>6.6403 (186.98)</td>
</tr>
<tr>
<td>S=C C=S^2</td>
<td>-12.6518</td>
<td>4.7410 (261.89)</td>
</tr>
<tr>
<td></td>
<td>-12.1805</td>
<td>5.8714 (211.47)</td>
</tr>
<tr>
<td></td>
<td>-2.2461</td>
<td>6.6299 (187.27)</td>
</tr>
<tr>
<td></td>
<td>-1.5087</td>
<td>6.7653 (183.52)</td>
</tr>
</tbody>
</table>

1 Mataga values
2 Pople values

These results compare favorably to the UV spectral values given in Table 5. In all cases only the lowest energy π-π* transition, calculated by the program, is observed experimentally.

In the case of Dimethylketen dimer, (1), no UV π-π* transition is observed. This is because the transition energy is higher than
the capabilities of the instrument used. However, the Pariser-Parr predicted value of 7.69 eV by the $P^3$-CI program is 0.50 eV lower than that predicted for formaldehyde (8.19 eV). This lowering in energy is consistent with what would be expected from transannular conjugation. Tetramethylcyclobutane-1, 3-biscyclohexylimine, (2), shows an absorption band at 197 nm in the UV. The Pariser-Parr values calculated by the program are 197 nm and 167 nm. Tetramethylcyclobutane-1, 3-dithione, (2), has a peak at 228 nm in the UV absorption spectrum. The Pariser-Parr program value is 262 nm. However, it should be mentioned here that the dithione has 2p-3p $\pi$-overlap. Little work has been done on systems of this type with the Pariser-Parr calculations. The Mataga value of 235 nm is more accurate in this case. No peaks were observed lower than 195 nm for any system even though they were calculated by the $P^3$-CI computer program because of the limitations of the UV instrument.

The $P^3$-CI program gave fairly reliable values for transition energies, but how about splitting of energy levels? Table 11 summarizes the results given by the program.

### TABLE 11

<table>
<thead>
<tr>
<th>System</th>
<th>$N-\pi^*$ (observed), eV</th>
<th>$\pi-\pi^*$ (calculated)$^a$, eV</th>
<th>$\pi-\pi^*$ (calculated)$^b$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O=C$</td>
<td>0.53</td>
<td>0.39</td>
<td>0.65</td>
</tr>
<tr>
<td>$N=C$</td>
<td>0.27</td>
<td>0.92</td>
<td>0.30</td>
</tr>
<tr>
<td>$S=C$</td>
<td>0</td>
<td>1.13</td>
<td>0.24</td>
</tr>
</tbody>
</table>

$^a$ Pariser-Parr method  
$^b$ Mataga Method
It was not possible to see splitting in the $\pi-\pi^*$ bands in the UV. However, $n-\pi^*$ splitting has been observed in compounds 1 and 2. No splitting was observed in the $n-\pi^*$ band of compound 2. The actual splitting between the $n-\pi^*$ bands of each compound when converted to eV appears to show the same trend as the predicted splitting for the $\pi-\pi^*$ on going from the diketone to the bisimine to the dithione. The absolute values of the splitting are not necessarily the same. (See Addendum).

It can be seen from Table 11 that compound 1 has an observed splitting of 0.53 eV while the value calculated by the Mataga method is 0.65 eV. In compound 2 the difference is even less. The observed splitting is 0.27 eV while the calculated value is 0.30 eV by the Mataga method. The observed splitting for compound 2 is 0 while the Mataga method predicted a splitting of 0.24 eV. This value, although not in agreement with the experimental, is lower than that predicted for either compound 1 or 2 and fits the same trend as the observed values. This trend is not observed in the Pariser-Parr predicted values and this is not understandable at this time.

Why does the Mataga method give such good values for splitting as well as the best value for the transition energy for the dithione, 2? Perhaps it is best explained by saying that the Mataga method was originally designed to give satisfactory agreement with experimental values. The method has a completely empirical approach.
in evaluating the two-electron, two-center integral, \((uu/\gamma v)\). Just by taking such an approach allows good correlation between observed and calculated values. Why then is the Pariser-Parr method used at all? The answer is that it appears to work well for small molecules. Both methods have their merits but it appears that the Mataga method works better for larger molecules and appears to be the most versatile method overall.

One more thing must be mentioned concerning the results obtained from the \(P^2\)-CI program. It may be noticed from Table 10 that the Mataga results for the \(\pi-\pi^*\) transition energies is somewhat lower than that predicted by the Pariser-Parr method and also lower than the observed values. The program could have been adjusted to give good transition values for the Mataga method instead of the Pariser-Parr method. All that would have had to be done was to adjust the value for the resonance integral, \(S_{uv}\), for the two compounds. This integral is an input parameter and is an entirely empirical value for this program. It would thus be completely justified to change this value until the desired result was obtained for the monoketone, formaldehyde, and the monoimine, methyleneimine. Once this was done it is very likely that the correct values would have been obtained for the transition values for the diketone, \(1\), and the diimine, \(2\). Since the resonance integrals would not have to be changed drastically, it is not expected that the transition energy splitting predicted for the two compounds would differ much from that already obtained.
The $P^3$-CI program would not accommodate the use of the sulfur atom when the program was first received. However, the program was adapted by putting in the following integrals:

$$VSIP(S) = 12.70 \text{ eV}$$
$$\text{(SS/SS)} = 9.94 \text{ eV}$$

It was also necessary to add the following formulas for the 2p-3p Slater $\pi$-overlap integrals:

$$S(2\pi, 3p) = (120)^{-1}(30)^{-\frac{3}{2}}\int \left( A_4 - 6A_2 + A_0 \right) \text{ for } t = 0$$
$$S(2p, 3p) = (120)^{-1}(30)^{-\frac{3}{2}}\int ( + t)^{5/2}(1 - t)^{7/2}(A_5(B_0 - B_2) + A_4(B_3 - B_0) + A_3(B_4 - B_0) + A_2(B_1 - B_3) + A_1(B_2 - B_4) + A_0(B_5 - B_3) \text{ for } t \neq 0$$

where

$$A_k(p) = e^{-p} \sum_{u=1}^{k+1} \frac{(k!)^u}{(p^u(k - u + 1)!)}$$

$$B_k(pt) = e^{-pt} \sum_{u=1}^{k+1} \frac{(k!)^u}{(pt^u(k - u + 1)!)} - e^{-pt} \sum_{u=1}^{k+1} \frac{(-1)^{u-k}k!}{(pt^u(k - u + 1)!)}$$

and where

$$u = Z/n$$
$$p = \frac{1}{2}(u_a + u_b)R/aH$$
$$t = (u_a - u_b)/(u_a + u_b)$$

$$(a_H = 0.529 \text{ au/A})$$

For the above formulas, $Z$ is the effective nuclear charge, $n$ is the main quantum number, and $R$ is the radius between the two atoms $a$ and $b$ in angstroms.

Once the above formulas were added to the program the ensuing transition energies for the thione and dithione systems were calculated.
One other program was tested in conjunction with the present work. That was the CNDO/2 program written by Dr. Hans H. Jaffe at the University of Cincinnati. This program was an all electron program which included \( \sigma \) and nonbonding electrons as well as \( \pi \) electrons. When this program was tested on formaldehyde, it gave excellent results for the \( \pi-\pi^* \) transition. This transition was calculated by the program to be 149 nm which compares to the experimental value of 156 nm.\(^{37}\) However, the predicted \( n-\pi^* \) transition was calculated to be 393 nm while the actual experimental value is 304 nm.\(^{37}\) Likewise, the \( n-\sigma^* \) transition is calculated to be 133 nm while the experimental value is 174 nm.\(^{37}\) There appears to be some discrepancy with regard to the energy of the nonbonding electrons; i.e., the orbital energy. Moreover, the discrepancy doesn't appear to be consistent, being 89 nm high in the \( n-\pi^* \) prediction and 41 nm low with regard to the \( n-\sigma^* \) prediction. The error is most likely an internal one within the program itself.

Since the results from formaldehyde proved to be in error with regard to the \( n-\pi^* \) transition, the program was abandoned in favor of the less complicated \( P^3 \)-Cl program for the \( \pi-\pi^* \) calculations. However, much useful data has been obtained from the CNDO/2 program on many pyridines, and anilines with regard to \( n-\pi^* \) and \( n-\sigma^* \) transitions.\(^{38}\) Yet it must be remembered that these are all systems with a high degree of resonance and formaldehyde is only a single chromophore. It is believed that in the future the
CNDO/2 program and similar total electron programs will become the most prevalent programs used, provided they can predict spectral transitions.
CONCLUSIONS

Dimethylketen dimer, tetramethylcyclobutane-1,3-bis-cyclohexylimino, and tetramethylcyclobutane-1,3-dithione have been studied by means of self-consistent field molecular orbital calculations and far ultraviolet absorption spectroscopy.

Results from the P^3-CI SCF program indicate there is splitting in the \( \pi \) energy levels of the three compounds resulting from trans-annular overlap with the calculated splitting for the \( \pi-\pi^* \) region being: 0.50 eV, 0.30 eV, 0.24 eV for the diketone, the bisimine, and the dithione, respectively. No \( \pi-\pi^* \) splitting was observed in the UV as the instrument was unable to go below 185 nm where most of the transitions lie. One new high energy \( \pi-\pi^* \) transition was observed for the bisimine at 197 nm, and a new transition for the diketone was observed at 208 nm, which is possibly a \( n-\sigma^* \) transition. However, splitting was observed in the UV in the \( n-\pi^* \) region with the actual splitting being: 0.65 eV, 0.27 eV, and 0 eV for the diketone, the bisimine, and the dithione. Also when one compares the \( n-\pi^* \) values of 280 nm, 245 nm, and 490 nm^27 for the carbonyl, the azomethine and the thiocarbonyl groups respectively versus the values of 350 nm, 270 nm, and 510 nm for the diketone, the bisimine, and the dithione respectively, a lowering of energy is noticed in all three cases on going from the simple chromophore to the di-compound. This lowering in energy can be interpreted to represent transannular participation.
The results gained by the P³-CI program are consistent with the UV results for the order of magnitude of splitting for the three compounds. Although the actual values for splitting predicted by the computer are not entirely accurate, they are close enough to the observed values to give reason to believe that the splitting in peaks is indeed due to transannular overlap.
**EXPERIMENTAL**

**Ultraviolet Spectra**

UV spectra were taken on a Beckman DK-2A spectrophotometer using a hydrogen lamp. All spectra were between 180 nm and 260 nm. Samples were prepared as solutions in either hexane or heptane and spectra were run using a 1 cm quartz cell. All spectra were run with a 20 psi nitrogen flush through the cell compartment.

Dimethylketen dimer was dissolved in purified heptane at a concentration of $4.5 \times 10^{-3} \text{M}$. The far ultraviolet absorption spectrum was taken from 230-180 nm and showed absorption at $\lambda_{\text{heptane}}^{\max} = 227 \text{ nm}$ ($\epsilon_{\text{max}} = 112$). See Figure 1 in the Appendix.

Tetramethylcyclobutane-1,3-biscyclohexylamine was dissolved in purified heptane at a concentration of $8.1 \times 10^{-5} \text{M}$. Absorption in the far ultraviolet (230-180 nm) was seen at $\lambda_{\text{heptane}}^{\max} = 195 \text{ nm}$ ($\epsilon_{\text{max}} = 9,880$). See Figure 2 in the Appendix.

Tetramethylcyclobutane-1,3-dithione was dissolved in purified cyclohexane at a concentration of $1.2 \times 10^{-5} \text{M}$. The absorption spectrum in the far ultraviolet was taken from 260-180 nm and an absorption peak was seen at $\lambda_{\text{cyclohexane}}^{\max} = 228 \text{ nm}$ ($\epsilon_{\text{max}} = 42,000$). See Figure 3 in the Appendix.

**The Purification of Solvents**

Three liters of heptane were stirred with one liter of concentrated sulfuric acid for seventy-two hours after which the sulfuric acid was separated and one liter of fresh acid added. The mixture
was again stirred for seventy-two hours. The upper layer, heptane, was removed and washed with two liters of water three times. The water was separated and the heptane was dried over CaSO₄, Drierite, over night. The heptane was then filtered, passed through silica gel, and then through an alumina column (100 cm. x 3 cm.). Finally the heptane was stored in a bottle with Drierite for twenty-four hours before use.

**Computer Work**

The IBM 360-40 computer was used for all calculations.

The format used in the P³-CI program is shown here as it appears in the actual program readout:

<table>
<thead>
<tr>
<th>ATOM CODE</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbon (Tr,Tr,Tr,PI)</td>
</tr>
<tr>
<td>2</td>
<td>Nitrogen (Tr₂,Tr,Tr,PI)</td>
</tr>
<tr>
<td>3</td>
<td>Nitrogen (Tr,Tr,Tr,PI₂)</td>
</tr>
<tr>
<td>4</td>
<td>Oxygen (Tr₂,Tr₂,Tr,PI)</td>
</tr>
<tr>
<td>5</td>
<td>Oxygen (Tr₂,Tr,Tr,PI₂)</td>
</tr>
<tr>
<td>6</td>
<td>Boron (Tr,Tr,PI)</td>
</tr>
<tr>
<td>7</td>
<td>Fluorine (S₂,P₂,P₂,P)</td>
</tr>
<tr>
<td>8</td>
<td>Chlorine (S₂,P₂,P₂,P)</td>
</tr>
<tr>
<td>9</td>
<td>Sulfur (Tr₂,Tr₂,Tr,PI)</td>
</tr>
</tbody>
</table>

**TR- TRIGONAL HYBRID, PI- PI ORBITAL (2P₂).**

**VSIP- THE VALENCE STATE IONIZATION POTENTIALS**

<table>
<thead>
<tr>
<th>VSIP(1)</th>
<th>VSIP(2)</th>
<th>VSIP(3)</th>
<th>VSIP(4)</th>
<th>VSIP(5)</th>
<th>VSIP(6)</th>
<th>VSIP(7)</th>
<th>VSIP(8)</th>
<th>VSIP(9)</th>
</tr>
</thead>
</table>
ZAMA- ONE-CENTER, TWO-ELECTRON REPULSION INTEGRALS, GAMMA (I-A).

ZAMA(1) = 11.13
ZAMA(2) = 12.34
ZAMA(3) = 16.76
ZAMA(4) = 15.23
ZAMA(5) = 18.82
ZAMA(6) = 6.91
ZAMA(7) = 17.36
ZAMA(8) = 11.30
ZAMA(9) = 9.94

ZCHG- THE ATOMIC CHARGE
ZCHG(1) = 1.0
ZCHG(2) = 1.0
ZCHG(3) = 2.0
ZCHG(4) = 1.0
ZCHG(5) = 2.0
ZCHG(6) = 1.0
ZCHG(7) = 1.0
ZCHG(8) = 1.0
ZCHG(9) = 1.0

ETA- PARAMETER USED IN MODIFIED MATAGA METHOD.
ETA(1) = 0.45908
ETA(2) = 0.53499
ETA(3) = 0.54723
ETA(4) = 0.73289
ETA(5) = 0.9844

THE FOLLOWING INPUT CARDS ARE REQUIRED:

FIRST CARD- TITLE CARD ANY COMMENT, ALL 80 COLUMNS.
SECOND CARD- SYMMETRY CARD (ALL FORMATS I2).
ISUB= 00 NO SYMMETRY
01 D2H SYMMETRY
02 C2V SYMMETRY
IRXY - THE NUMBER OF CENTERS RELATED BY THE XY-PLANE.
IF IRXY = 0 WRITE 01 AND SKIP 4 COLS.
ICEN1(I) AND ICEN1(I+1)- THE ATOM NUMBERS OF RELATED PAIRS.
IRYZ- THE NUMBER OF CENTERS RELATED BY THE YZ-PLANE
IF IRYZ = 0 WRITE -1 AND SKIP 4 COLS.
ICEN2(I) AND ICEN2(I+1)- THE ATOM NUMBERS OF RELATED PAIRS.
THIRD CARD- INPUT PARAMETERS.
ECONV- CONVERGENCE CRITERIA (F6.5).
N- NUMBER OF CENTERS (FORMAT I2).
NOCC- NUMBER OF OCCUPIED ORBITALS (FORMAT I2).
NBETA- NUMBER ON BONDS (FORMAT I2).
*NGAMMA- TYPE OF GAMMAS TO BE CALCULATED
NGAMMA = 1- MATAGA METHOD
NGAMMA = 2- PARISER-PARR METHOD
NGAMMA = 3- EVERIDGE-HINZE METHOD

FOURTH CARD- ATOM KIND, SEE ATOM CODE IN MAIN ROUTINE
(FORMAT II).

FIFTH CARD- NBOND- BONDED ATOMS BY ATOM NUMBER IN PAIRS
(FORMAT I2).

SIXTH PLUS N-1 CARDS- X,Y,Z COORDINATES (FORMAT F10.6).

LAST CARD- RESONANCE INTEGRAL VALUE IN E.V., BY ATOM KIND
(FORMAT F6.2).

Sample Input:

FORMALDEHYDE GAMMAS BY PARISER-PARR
00
0.000102010102
14
0102
  0.0  0.0  0.0
  0.0  0.0  1.21
-9.4 -14.2 0.0 -17.0
/*
/+ 

DIMETHYLKETEN DIMER GAMMAS BY MATAGA
00
0.000104020301
4114
010202030304
  0.0  0.0 -2.32
  0.0  0.0 -1.10
  0.0  0.0  1.10
  0.0  0.0  2.32
-9.4 -14.2 0.0 -17.0
/*
/+ 

* Gammas in this program are the two-electron, two-center repulsion
integrals, (uu/vv).
The following input cards were placed before the data cards to initiate the program:

```
// JOB PPCIC000
* PPCIC00

// ASSGN SYS002,X'00C'
// ASSGN SYS003,X'00E'
// EXEC PPCIC00
```

One line of the sample data on the preceding page refers to one card of computer data. The explanation of the input data which immediately precedes the sample data explains what data goes in which column on the computer data cards.
Sample Calculation—Formaldehyde

The basic molecular orbitals for formaldehyde are the same as those for ethylene:

\[ Y_1 = 0.707X_1 + 0.707X_2 \]
\[ Y_2 = 0.707X_1 - 0.707X_2 \]

Using these wave functions the following charge distributions are obtained:

\[ q_o = \sum Y_{occ} \]
\[ q_c = \sum Y_{occ} \]

along with the mobile bond order:

\[ P_{co} = \sum Y_{occ}^{2} = 2(0.707) = 1 \]

According to Slater's rules:

\[ Z_u = N_u - 1.35 - 0.35(\sigma_u + P_{uu}) \]

where:

- \( Z_u \) = electronegativity of atom \( u \).
- \( N_u \) = atomic number of atom \( u \).
- \( \sigma_u \) = number of \( \sigma \)-electrons contributed to the molecule by \( u \).
- \( P_{uu} \) = \( \pi \)-electron density.

and using this formula for C and O the following results are obtained:

\[ Z_C = 6 - 1.35 - 0.35(3 + 1) = 3.25 \]
\[ Z_O = 8 - 1.35 - 0.35(5 + 1) = 4.55 \]
The two-electron, one-center integrals are calculated from the formula by Paoloni: 38

\[
(cc/cc) = 3.29(Z_c) = 3.29(3.25) eV \approx 10.7 eV
\]

\[
(cc/oo) = 3.29(Z_o) = 3.29(4.55) eV = 14.95 eV
\]

The two electron, two-center integral is calculated from a formula derived by Pariser and Parr: 39

\[
(uu/vv) = \frac{1}{2}((uu/uu) + (vv/vv)) = ar_{uv} - br_{uv}^2 \quad (r < r_0)
\]

where \( r_0 = 2.65 \) Å. The constants \( a \) and \( b \) are found by using the formula:

\[
(uu/vv) = (7.195/r)((1 + (1/(2r))^2(R_u - R_v)^2)^{-\frac{1}{2}}
\]

\[
+ (1 + (1/(2r))^2(R_u + R_v)^2)^{-\frac{1}{2}} \text{eV}
\]

in which

\[
R_u = (4.597/Z_u) \times 10^{-8} \text{ cm}
\]

and where the constants \( a \) and \( b \) are found by fitting values calculated by equation (20) for \( r = 2.8 \) Å and \( r = 3.7 \) Å. Using this equation the value of \( (cc/oo) \) using \( r = 2.8 \) Å is:

\[
(cc/oo) = (7.195/2.8)((1 + (1/(2)(2.8))^2(1.4 - 1.0)^2)^{-\frac{1}{2}}
\]

\[
+ (1 + (1/(2)(2.8))^2(1.4 + 1.0)^2)^{-\frac{1}{2}} \text{eV}
\]

\[
(cc/oo) = 4.94 \text{ eV}
\]

and using \( r = 3.7 \) Å the value is:

\[
(cc/oo) = 3.80 \text{ eV}
\]

Solving these two equations simultaneously using equation (19) the values for \( a \) and \( b \) are:

\[
a = 4.05
\]

\[
b = -0.445
\]
Putting these values into equation (19) and using the correct C=O bond distance of 1.2Å the value for the two electron, two-center integral is:

\[
\frac{\text{cc}}{\text{oo}} = \frac{1}{2}(10.7 + 14.95) - 4.05(1.2) - (-0.445)(1.2)^2
\]

\[
\frac{\text{cc}}{\text{oo}} = 8.55\text{eV}
\]

From Flurry:\n
\[
\alpha_c = W_c - N_0(\text{cc/oo})
\]

where:

\[
\alpha_c = \text{one-electron, one-center integral}
\]

\[
W_c = \text{valence state ionization potential}
\]

\[
N_0 = \text{the number of electrons that center o donates to the system}
\]

Using this equation:

\[
\alpha_c = -11.16\text{eV} - 1(8.55)\text{eV}
\]

\[
\alpha_c = -19.70\text{eV}
\]

This value is used to calculate the Fock integral, \(F_{cc}\):

\[
F_{cc} = \alpha_c + \frac{1}{2} q_c(\text{cc/cc}) + \sum_{\sigma^2} q_c(\text{cc/cc})
\]

\[
F_{cc} = -19.70\text{eV} + \frac{1}{2}(1)(10.7)\text{eV} + 1(8.55)\text{eV}
\]

which gives as a result:

\[
F_{cc} = -5.81\text{eV}
\]

Similarly, using the same procedure for O:

\[
F_{oo} = -10.16\text{eV}
\]

The resonance integral, \(\beta_{cc}\), is usually determined from UV spectroscopic data but can be estimated from a formula in Flurry:\n
\[
\beta_{cc} = -2524\exp(-5.047((Z_c + Z_o)/Z_c - 2)^2 - 5r_{cc})
\]
where \( Z_c \) and \( Z_o \) are the effective electronegativity index of carbon and oxygen respectively. Using this equation:

\[
\beta_{co} = -2.76eV
\]

This value is surprisingly close to the value of \(-2.73eV\) found by Brown and Heffernan\(^3\) who got their value from UV spectroscopic data.

Using this value for the resonance integral the off-diagonal Fock integral is found to be:

\[
F_{co} = \beta_{co} - \frac{1}{2} P_{co}(cc/oo)
\]

\[
F_{co} = -2.76eV - \frac{1}{2}(1)(8.55)eV
\]

\[
F_{co} = -7.03eV
\]

Finally the Fock determinant is set up:

\[
\begin{vmatrix}
F_{cc} & F_{co} & \\
F_{co} & F_{oo} & \\
-5.81 - e & -7.03 & \\
-7.03 & -10.16 - e & \\
\end{vmatrix} = 0
\]

which solves:

\[
e^2 + 15e + 10 = 0
\]

giving

\[
e = -14.3eV, -0.7eV
\]

which are the eigenvalues or molecular orbital energy values for formaldehyde.
APPENDIX

This section contains the ultraviolet spectra of dimethylketen dimer, tetramethylcyclobutane-1,3-biscyclohexylimine, tetramethylcyclobutane-1,3-dithione. In the Results and Discussion Section these spectra are referred to in order to stress certain high energy transitions.
Figure 1. Dimethylketen dimer dissolved in heptane at a concentration of $4.5 \times 10^{-3}$ M.
Figure 2. Tetramethylyclobutane-1,3-biscyclohexylimine dissolved in heptane at a concentration of $8.1 \times 10^{-5}$ M.
Figure 3. Tetramethylcyclobutane-1,3-dithione dissolved in cyclohexane at a concentration of $1.2 \times 10^{-5}$ M.
ADDENDUM

Throughout this thesis there has been a comparison of the "trend" of the energy level splitting of the $\pi-\pi^*$ versus the $n-\pi^*$ of the three systems: dimethylketen dimer, tetramethylcyclobutane-1,3-bicyclohexyl imine, and tetramethylcyclobutane-1,3-dithione. Why are the absolute values of the $\pi$-energy level splitting not the same in the $n-\pi^*$ system as they are in the $\pi-\pi^*$ system of the respective compounds? The reason is relatively simple in context. The overall orbital symmetry of the two systems is not the same. The symmetry product of the nonbonded electron transition is quite different from the $\pi$-electron transition.

The diketone and the dithione systems have $D_{2h}$ symmetry. Using this symmetry and following the proper symmetry operations for the lowest energy orbital according to the following diagram:

![Diagram](image)

$\Sigma_u^+$ is obtained as the proper symmetry species (irreducible representation) for $\Upsilon$, or $\pi$- if following the diagram on page 21 of this thesis. Likewise, one obtains the symmetry species $B_{2g}$ for $\pi_+$, $\Sigma_u^+$ for $\pi_+^*$, and $B_{2g}$ for $\pi_-$. $^4$

In order to determine if a particular transition is "allowed" the symmetry product of the transition must be of a symmetry species which coincides with one of the three components of the dipole moment of the molecule. For $D_{2h}$ symmetry the three components of the dipole
moment coincide with the symmetry species $B_{1u}$, $B_{2u}$, and $B_{3u}$. Applying this rule to $E_1$ on page 21 of this thesis:

$$\Pi_4 \Pi_4^* = B_{3u} = \Delta E_1$$

which is an allowed transition since it coincides with the component $K_2$ of the dipole moment. Applying this rule to the rest of the transitions we find $\Delta E_2 = A_g$ (forbidden), $\Delta E_3 = A_g$ (forbidden), and $\Delta E_4 = B_{3u}$ (allowed).

In order to compare this with the $n-\Pi^*$ transitions one must first determine the symmetry species of the nonbonding orbital. Using the following diagram:

![Diagram](image)

and performing the correct symmetry operations, $B_{2u}$ is obtained as the correct symmetry species for the $n$ orbital. Now if we label $n-\Pi_4^*$ as $\Delta E_{n1}$ and $n-\pi^*$ as $\Delta E_{n2}$ the following is obtained for the symmetry product for the transitions:

$$\Delta E_{n1} = B_{2u}B_{1u} = B_{3g} \text{ (forbidden)}$$

$$\Delta E_{n2} = B_{2u}B_{2g} = A_u \text{ (forbidden)}$$

The fact that both transitions are forbidden concerns us not. However, the symmetry species for the symmetry products are of great interest. Herein lies the key to the dilemma in regard to the absolute value of
the splitting in energy levels. In order to get the actual value of
the splitting between the \( \pi \)-orbitals we must subtract the value for
\( \Delta E_1 \), in eV, from the value for \( \Delta E_2 \). Also we can subtract the value
for \( \Delta E_{n1} \), in eV, from \( \Delta E_{n2} \). However, on close inspection we notice
that using the \( \pi - \pi^* \) transitions we are subtracting the energy for
the symmetry species \( B_{3u} \) from the energy for the symmetry species \( A_g \),
while if we use the \( n - \pi^* \) transition we are subtracting the energy
for \( B_{3g} \) from \( A_u \). Clearly these symmetry species are different for
the different transitions; ie. \( \pi - \pi^* \) vs. \( n - \pi^* \). Since the energy would
be different for each symmetry species, no matter how small the difference
may be, it is not possible to compare absolute values in the two systems.

Perhaps it should be mentioned here that photoelectron spec-
troscopic studies have revealed that there is actually two separate
\( n \)-energy levels.\(^{45} \) They result from interaction between the \( n \)-electrons
on the separate oxygen atoms with the C-C \( \sigma \)-orbitals of the cyclobutane
ring. They found that an additional \( n \)-orbital of symmetry species
\( B_{3g}^* \). The two \( n - \pi^* \) transitions resulting from this \( n \)-orbital are
\( B_{2u} \) (forbidden) and \( B_{1g} \) (allowed). However, these are still different
than the symmetry species \( B_{3u} \) and \( A_g \), which coincide with the \( \pi - \pi^* \)
transitions \( \Delta E_1 \) and \( \Delta E_2 \). Thus the results still hold.

For the \( C_{2v} \) symmetry, which the bisimine exhibits, similar results
are obtained. For the \( \pi - \pi^* \) transitions \( \Delta E_1 \) yields the \( B_1 \) symmetry
species (allowed) and \( \Delta E_2 \) yields the symmetry species \( A_1 \) (allowed).
The \( n - \pi^* \) transitions show \( \Delta E_{m1} \) has the symmetry species \( B_2 \) (allowed)
and \( \Delta E_{n2} \) has the symmetry species \( A_2 \) (forbidden).
REFERENCES

5. Ibid., p. 130.
8. Ibid.
10. Ibid., pp. 201-235.
13. Ibid.
17. Pariser and Parr, p. 767.
23. Ed Schmidt, South Dakota State University, unpublished work.
31. Ballard and Park, p. 43.
35. Flurry, p. 213.
40. Flurry, p. 214.
41. Ibid., p. 205.
42. Ibid., p. 218.