The Photoelectron Spectroscopy of Dicarbonyls and Biological Molecules.

David Russell Dougherty

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AND BIOLOGICAL MOLECULES.

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by

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May 1977
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Dean of the Graduate School

EXAMINING COMMITTEE:

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Date of Examination:

April 21, 1977
DEDICATION

To Jean, Samantha and my family.
ACKNOWLEDGEMENTS

I wish to express my gratitude to my major professor, Dr. Seán P. McGlynn, for his expert guidance and continuous encouragement throughout the course of this work.

I would also like to thank the other members of Dr. McGlynn's research group, past and present, with whom I have worked: Mrs. Anne Wahlborg, Dr. W. S. Felps, Dr. J. D. Scott, Dr. T. P. Carsey, Dr. H. -t. Wang, Dr. P. Hochmann, Dr. P. Brint, Dr. K. Wittel, Dr. B. Dzhagarov, Mr. S. Chattopadhyay, Mr. G. Findley, Mr. D. Bouler, Mr. T. Mathers, Mr. T. Baldwin, Mr. C. S. Hsue and Mr. R. Moore. Thanks are also expressed to the rest of the faculty, staff and graduate students at Louisiana State University for their collaboration.

Special thanks are due to my wife and family for their support and encouragement throughout this effort.

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ABSTRACT

Ultraviolet photoelectron spectroscopy (UPS) was performed on a series of dicarbonyls and a series of biological molecules.

The dicarbonyl investigations were undertaken to study the interactions of the carbonyl oxygen lone pair orbitals. In dicarbonyls there are two such orbitals, denoted $n_+$ and $n_-$, which are energetically split by "through bond" interaction with the $\sigma$ MO's intervening between the carbonyl groups. The magnitude of this splitting, $\Delta n$, as gauged by the difference of the UPS ionization energies for these MO's, decreases with increasing carbonyl separation, and $\Delta n$ is approximately constant in any series of dicarbonyls with the same carbonyl separation. The energetic order of the ionization events, $I(n_+) > I(n_-)$ or vice versa, is also dependent on the carbonyl separation. Additionally, it is noted that $I(n_+)$ and $I(n_-)$ have different band shapes and this observation is rationalized from the forms of LCAO eigenvectors from semi-empirical quantum chemical computation. Finally, it is noted that situating the two carbonyl groups coaxially, as in 1,4-benzo-quinone, inverts the $I(n_+)/I(n_-)$ order observed for non-coaxially situated dicarbonyls.

The UPS study of the biological molecules was undertaken to test the body of theoretical data available in the work of the Pullmans. The photoelectron spectra of a series of biochemicals were obtained and the MO assignments made. The measured ionization energies of the highest occupied $\pi$ MO were plotted vs. the Pullamns' Hückel coefficient, $k$, from the equation $I = \alpha + k\beta$. An absolute scale of electron
donor capability is also provided and is based on the ionization energy of the highest occupied molecular orbital.
CHAPTER ONE

INTRODUCTION
Ultraviolet Photoelectron Spectroscopy (UPS) is one of the more useful methods for investigating the electronic structure of molecules. This usefulness derives from two characteristics: First, the ease of the experimental measurement and second, the simple, straightforward theoretical interpretation of the experimental results via Koopmans' Theorem.

The quantities measured are ground state ionization energies. By Koopmans' Theorem, the measured ionization energies can be equated to Self Consistent Field-Molecular Orbital (SCF-MO) computational canonical eigenvalues. The assignment of a photoelectron spectrum is usually made, therefore, by direct comparison with some SCF-MO computational result. Furthermore, the measured one electron ionization event should result in a transition to a pure (i.e., no configuration interaction) cationic state.

However, the derivation of Koopmans' Theorem involves two approximations which limit its generality: (1), the orbital reorientation approximation in which it is assumed that the MO's are unchanged on going from the molecule to its cation and (2), the correlation energy approximation in which it is assumed that the correlation energy is the same in both the molecule and its cation. For valence shell orbitals the reorientation and correlation energy corrections tend to cancel. The fact that Koopmans' Theorem is better practically than theoretically is generally attributable to these fortuitous circumstances.

This work is concerned with the UPS of dicarbonyl compounds and
biological molecules. The purpose of this work is twofold: first, we wanted to say something general about the interactions of two carbonyl groups in the same molecule with each other. Considering the importance of dicarbonyls in chemistry and biochemistry, and especially in light of recent theories on the function of α-dicarbonyls in regulating cell division and in the electron transport mechanism of the cell, this study is both important and timely.

Second, we investigated, via UPS, the electronic structure of a selection of biologically active molecules. Considering the importance of biochemical electronic structures, surprisingly little work has been invested in the UPS of such molecules. Chapters two and three of this work are concerned with the dicarbonyls and with the biological molecules, respectively.
REFERENCES


2. T. Koopmans, Physica, 1, 104(1934).


CHAPTER TWO

PHOTOELECTRON SPECTROSCOPY OF DICARBONYLS
INTRODUCTION

The carbonyl group is one of the more important functional groups in both organic and biological chemistry. As a result, considerable work has been invested in the ultraviolet photoelectron spectroscopy (UPS) of carbonyl compounds in order to determine the manner in which carbonyl groups interact among themselves and with other functional groups. The existing experimental work consists largely of the assignment of the photoelectron spectrum via Koopmans' Theorem, a procedure which usually implies no more than a simple correlation of UPS energies with the results of some semi-empirical molecular orbital (MO) calculations.

A "simple dicarbonyl compound" is loosely defined as one which contains neither heteroatoms (other than two oxygens) nor carbon-carbon unsaturation. The two highest-occupied MO's of simple dicarbonyls consist predominantly of linear combinations of the two oxygen non-bonding 2p atomic orbitals, \( n_1 \) and \( n_2 \). For symmetrical dicarbonyls (i.e., those for which the carbonyl groups are interchanged by some symmetry operation of the molecule), two symmetry adapted, semi-localized functions are specified as

\[
\begin{align*}
    n_+ &= \frac{1}{\sqrt{2}} (n_1 + n_2) \\
    n_- &= \frac{1}{\sqrt{2}} (n_1 - n_2)
\end{align*}
\]

where the subscripts +/- refer to phasing. These functions, \( n_+/- \) are degenerate in a zeroth-order approximation.

For non-symmetrical dicarbonyls we can prescribe semi-localized MO's...
\[ n_+ = an_1 + bn_2 \]
\[ n_- = cn_1 - dn_2 \]

where, in the absence of overlap of \( n_1 \) and \( n_2 \), \( b = \sqrt{1-a^2} \), \( c = b \) and \( d = a \). These functions are non-degenerate even in zeroth-order.

Nonetheless, in order to discuss dicarbonyl interactions in the simplest possible way, we will assume degeneracy even for these latter functions. It turns out that such an assumption is not unreasonable.

The purpose of this work is to provide experimental criteria for the assignment of the non-bonding MO's of dicarboxyls. This is accomplished by collecting UPS data for a large number of dicarboxyls and noting regularities in the data. It is found that relevant assignment criteria can be derived directly from the following investigations.

(a) The nature of the interactions which lift the zero-order degeneracy of the \( n_+ \) and \( n_- \) MO's.

(b) The magnitude of this splitting as a function of the separation of the two carbonyl centers.

(c) The energetic order of the \( n_+ \) and \( n_- \) MO's which results from the splitting.

(d) The Franck-Condon band shapes of the \( n_+/n_- \) ionization bands.

It has been shown\(^1,2,4\) that the interactions of item (a) are satisfactorily categorized in terms of the heuristic concept of "through-bond" interaction\(^3\). Hence, since a qualitative mechanism for dicarbonyl interactions is already available for modeling purposes, we will confine ourselves largely to considerations of
items (b), (c) and (d).

The magnitude of interaction as a function of carbonyl separation is experimentally determinable. One merely obtains an average value of $|I(n^+) - I(n^-)| = A_n$ for fixed carbonyl separations and notes that this average is quite representative of the splitting $\Delta n$ found in all such compounds. Molecules for which $\Delta n \neq \Delta n$ do exist but such molecules are always exceptional in some particularly obvious way (e.g., perfluorination).

The energetic order of $n^+$ and $n^-$ is usually obtained by MO computations. One attempt at greater generality does exist: This study concluded that the MO order should be $n^+ > n^-$ (i.e., $I(n^-) > I(n^+)$) for any through-bond interaction over an odd number of intervening bonds. We agree with this conclusion, but only when the carbonyl groups are non-coaxial.

The removal of the $n^+/n^-$ degeneracy is accomplished, on a theoretical level, by through-bond mixing with other skeletal $\sigma$ orbitals. Since these $\sigma$ orbitals are more tightly bound than the $n$ orbitals, these interactions always destabilize the $n$ MO's. Therefore, the more thoroughly mixed $n$ orbital is always of higher energy (i.e., less tightly bound) than the less skeletally mixed $n$ orbital.

The ionization of an electron from a skeletally delocalized $n$ orbital should produce a considerable geometry change of the cation (compared to the ground state). Thus, the adiabatic and vertical transition for such an ionization event should be quite different and the resulting band shape might well be broad and Gaussian. The removal of an electron from a skeletally non-delocalized $n$ orbital
should produce little geometry change of the cationic state. Therefore, the adiabatic and vertical transitions might well be coincident. If only approximately coincident, the intensity of such a band will drop less sharply to higher energies, generating a band shape which we refer to as "blue degraded". For somewhat obvious reasons, we refer\textsuperscript{25} to the ionization event of gaussian band shape as \( I(n^0) \) and to the blue-degraded event as \( I(n^0) \).
I. EXPERIMENTAL

The HeI photoelectron spectra were obtained on a Perkin-Elmer PS-18 photoelectron spectrometer which was equipped with a heated sample probe for vaporizing solids. The resolution prior to each spectral run was 20-25meV. Calibration of spectra was accomplished using the $^2P$ lines of Xe and Ar. Sample temperatures during each spectral run were maintained constant to within $\pm 2^{\circ}$C.

All compounds were purified, prior to use, by vacuum sublimation.

Quantum chemical calculations were performed using QCPE 141-CNDO/2 and QCPE 174-CNDO/s-CI.
II. THE INTERACTION MODEL

The two semi-localized linear combinations \( n_+ \) and \( n_- \), are assumed to be degenerate in zero-order. The through-space interaction of the individual lone pair AO's on oxygen, \( n_1 \) and \( n_2 \), is neglected since it is very small\(^1\). Through-bond interaction, therefore, is the principal means for lifting the degeneracies. Interaction is supposed to occur between the \( n_+/n_- \) MO's and the set of skeletal orbitals, \( \{\chi_j\} \) which exists on the rest of the molecule. This view facilitates a simple representation:

(i) The interacting \( n_I \), where \( I = + \) or \( - \), and \( \chi_j \) orbitals must be of identical symmetry in the molecular point group.

(ii) The magnitude of the \( n_I/\chi_j \) interaction is inversely proportional to the zero-order energy separation of \( n_I \) and \( \chi_j \). This energy denominator criterion justifies the exclusion of interactions with the virtual orbital set which, because of its dominant \( \sigma^* \) nature, is of very high energy.

(iii) The magnitude of interaction is proportional to the \( n_I/\chi_j \) interaction matrix element and, hence, to overlap. Thus, the extent of interaction is very sensitive to the amplitude of \( \chi_j \) in the vicinity of the carbonyl groups.

A. \( \alpha \)-DICARBONYLS

\( \alpha \)-Dicarbonyls exhibit the largest interactions. The magnitude of the interaction is thought to be independent of the dihedral angle between the carbonyl units\(^1\). Figure 1 is a schematic of the interaction model. An unspecified \textit{cis}-\( \alpha \)-dicarbonyl is pictured,
Figure 1. Schematic diagram of through-bond orbital interactions in $\alpha$-dicarbonyls. cis-Carbonyl units are shown, but the results are general for any dihedral angle.
ENERGY (SCHEMATIC)
although the same results obtain for all dihedral angles, including the cis and trans conformations.

Criteria (i) - (iii) suggest the \( \sigma \) bond between the carbonyls and the bonds peripheral to the carbonyls are the only ones which will interact strongly with the \( n \) MO's. Furthermore, symmetry considerations indicate that only the \( n^+ \) MO will be affected. Hence, we use the labelling \( n^\sigma_+ \), where the superscript \( \sigma \) suggests that the \( I(n^\sigma) \) event should possess a gaussian band shape. The non-interacted orbital is denoted \( n^\sigma_- \) and should exhibit a blue-degraded \( I(n^\sigma_-) \) band shape. Therefore, the predicted MO order is \( n^\sigma_+ > n^\sigma_- \) and the expected band shape characteristics are gaussian and blue degraded, respectively.

The MO diagrams, as obtained by CNDO/s for the simplest \( \alpha \)-dicarbonyl, namely trans-glyoxal, are shown in Figure 2. The observed \( n \) orbital ionization bands are also shown in Figure 2. The LCAO coefficients of Figure 2 clearly demonstrate the dominance of \( \sigma \) mixing in the \( n^+ \) MO and its near absence in the \( n^- \) MO. Figure 2 exemplifies all points presented in our discussion of \( \alpha \)-dicarboxyls.

These comments on the UPS band shapes of glyoxal should apply to \( \alpha \)-dicarboxyls generally. Thus, biacetyl\(^9\), oxamide\(^{10}\) and pyruvamide\(^9\) have \( n^\sigma_+ \) and \( n^\sigma_- \) band shapes similar to those of glyoxal. In larger molecules, the mixing of \( n^+_+ \) and \( n^-_+ \) with the greater number of skeletal MO's which exists in such molecules produces a loss of structure in \( I(n^\sigma_-) \), and both \( I(n^\sigma_+) \) and \( I(n^\sigma-) \) exhibit structureless band contours.

The vertical ionization energies for the two \( n \) MO's of 34
Figure 2. Pictorial MO diagram of $n^+_\sigma$ and $n^0_\sigma$ for trans-glyoxal. The observed UPS ionization bands are also schematized. The geometric parameters used in the calculation are the following: All bond angles were 120°; the C-C bond length was 1.53Å; the C=O bond length was 1.22Å; and the C-H bond length was 1.00Å. LCAO MO coefficients are also shown.
TABLE 1

VERTICAL IONIZATION ENERGIES (eV)
FOR THE NON-BONDING MO's OF α-DICARBONYLS.

The difference Δn is defined as Δn ≡ |I(n+) - I(n_-)|

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<td>C2H5OCOCOCld</td>
<td>10.77</td>
<td>12.76</td>
<td>1.99</td>
</tr>
<tr>
<td>13</td>
<td>(CH3)HNCOCONH(CH3)e</td>
<td>9.33</td>
<td>11.20</td>
<td>1.87</td>
</tr>
<tr>
<td>14</td>
<td>(CH3)2NCOCON(CH3)2e,f</td>
<td>9.0</td>
<td>10.49</td>
<td>1.49</td>
</tr>
<tr>
<td>15</td>
<td>1,2-cyclobutanedioneg</td>
<td>9.58</td>
<td>11.70</td>
<td>2.12</td>
</tr>
<tr>
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<td>[4.4.2]propella-11,12-dioneh</td>
<td>8.65</td>
<td>10.4</td>
<td>1.75</td>
</tr>
<tr>
<td>17</td>
<td>[4.4.2]propell-3-ene-11,12-dioneh</td>
<td>8.60</td>
<td>10.5</td>
<td>1.9</td>
</tr>
<tr>
<td>18</td>
<td>[4.4.2]propella-3,8-diene-11,12-dioneh</td>
<td>8.70</td>
<td>10.7</td>
<td>2.0</td>
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<td>NUMBER INDEX</td>
<td>COMPOUND</td>
<td>$I(n_+)$</td>
<td>$I(n_-)$</td>
<td>$\Delta n$</td>
</tr>
<tr>
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<td>-----------------------------------------------</td>
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<td>----------</td>
<td>------------</td>
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<tr>
<td>19</td>
<td>3,3,7,7-tetramethyl-1,2-cycloheptanedione</td>
<td>8.70</td>
<td>10.60</td>
<td>1.90</td>
</tr>
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<td>3,3,7,7-tetramethyl-5-oxa-1,2-cycloheptanedione</td>
<td>8.90</td>
<td>10.90</td>
<td>2.0</td>
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<tr>
<td>21</td>
<td>3,3,7,7-tetramethyl-7-thia-1,2-cycloheptanedione</td>
<td>8.75</td>
<td>10.65</td>
<td>1.90</td>
</tr>
<tr>
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<td>3,3-dimethylindanedione</td>
<td>8.7</td>
<td>10.8</td>
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<tr>
<td>23</td>
<td>diphenylglyoxal</td>
<td>9.1</td>
<td>11.1</td>
<td>2.0</td>
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<tr>
<td>24</td>
<td>Camphorquinone$^i$ (3,7,7-trimethylbicyclo[2.2.1]hept-2,3-dione)</td>
<td>8.71</td>
<td>10.46</td>
<td>1.75</td>
</tr>
<tr>
<td>25</td>
<td>Bicyclo[2.2.1]hept-2,3-dione$^j$</td>
<td>9.00</td>
<td>10.85</td>
<td>1.85</td>
</tr>
<tr>
<td>26</td>
<td>7,7-cyclopropylbicyclo[2.2.1]hept-2,3-dione</td>
<td>8.75</td>
<td>10.7</td>
<td>1.95</td>
</tr>
<tr>
<td>27</td>
<td>Tetrafluoro-1,2-cyclobutanedione$^g$</td>
<td>10.45</td>
<td>13.04</td>
<td>2.59</td>
</tr>
<tr>
<td>28</td>
<td>Bicyclo[2.2.1]hept-5-ene-2,3-dione$^j$</td>
<td>8.73</td>
<td>11.17</td>
<td>2.44</td>
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<td>29</td>
<td>5-methylbicyclo[2.2.1]hept-5-ene-2,3-dione$^j$</td>
<td>8.50</td>
<td>10.90</td>
<td>2.40</td>
</tr>
<tr>
<td>30</td>
<td>7,7-dimethylbicyclo[2.2.1]hept-5-ene-2,3-dione$^j$</td>
<td>8.50</td>
<td>10.80</td>
<td>2.30</td>
</tr>
<tr>
<td>31</td>
<td>7,7-cyclopentylbicyclo[2.2.1]hept-5-ene-2,3-dione$^j$</td>
<td>8.45</td>
<td>10.75</td>
<td>2.30</td>
</tr>
<tr>
<td>32</td>
<td>7,7-cyclopropylbicyclo[2.2.1]hept-5-ene-2,3-dione$^j$</td>
<td>8.50</td>
<td>10.95</td>
<td>2.45</td>
</tr>
<tr>
<td>33</td>
<td>7-isopropenylbicyclo[2.2.1]hept-5-ene-2,3-dione$^j$</td>
<td>8.30</td>
<td>10.90</td>
<td>2.60</td>
</tr>
<tr>
<td>34</td>
<td>7-oxabicyclo[2.2.1]hept-5-ene-2,3-dione$^j$</td>
<td>8.95</td>
<td>11.55</td>
<td>2.60</td>
</tr>
</tbody>
</table>
FOOTNOTES TO TABLE 1


\(^f\)The position of I(\(n_+\)) is approximate since the two \(\pi\)-type, nitrogen lone-pair, ionization events occur within the same one ionization band as I(\(n_+\)).

\(^g\)E. Heilbronner, private communication.


α-dicarbonyls are listed in Table 1 along with the difference, Δn, between them. The α-dicarbonyls listed in Table 1 are of such diverse natures that any trends evident in the data should be quite general. The data show that, although I(n⁺) and I(n⁻) vary widely for different molecules, Δn is relatively constant. In fact, for the first 26 compounds listed, it is found that \( \Delta n = 1.9 \pm 0.15 \text{eV} \) (mean and standard deviation). This constancy is emphasized in Figure 3 where Δn for the α-dicarbonyls of Table 1 is plotted.

The last eight molecules listed in Table 1 are of particular interest since they exhibit substantially larger Δn values. The abnormally large splitting in tetrafluoro-1,2-cyclobutanedione is attributable to the presence of fluorines since the value of Δn for 1,2-cyclobutanedione is quite normal. Since perfluorination --- as evidenced by the perfluoro effect\(^{19} \) --- tends to produce unusual behavior, tetrafluoro-1,2-cyclobutanedione is clearly a special case. Another, and very definitive, special case occurs in the bicyclo-[2.2.1]-5-ene-2,3-dione compounds: The 5-ene moiety is forced stearically into such a location that it interacts strongly with n⁺ (Note that Δn has a normal value for bicyclo-[2.2.1]-2,3-dione in which the 5-ene moiety is absent). The photoelectron spectra and assignments for these latter molecules are presented in detail elsewhere\(^{20} \).

B. β-DICARBONYLS

The through-bond interactions in β-dicarbonyls are mediated by two intervening σ bonds. The n MO eigenvectors are schematized in Figure 4 for 1,3-propanedial, the smallest β-dicarbonyl. Calcu-
Figure 3. Diagrammatic presentation of $\Delta n$ for the $\alpha$-dicarboxyls listed in Table 1. The numbering index on the abscissa corresponds to the compound number in Table 1. The dashed line is the mean of $\Delta n$, $\Delta n$, from Table 5.
Figure 4. Diagrammatic presentation of the $n_-$ and $n_+^0$ MO's for 1,3-propanedial. LCAO MO coefficients are also shown. The geometry used in the CNDO/s calculation were as follows: Trigonal carbon angles were $120^\circ$ while the bond angles about the tetrahedral carbon were $109.5^\circ$. The C-C bond length was 1.54Å, C=O was 1.22Å, C-H was 1.00Å on carbons one and three, while C-H was 1.08Å on carbon two.
lations suggest that $n^- > n^+$ by 0.8eV. The same MO order and similar energetic splittings are obtained for all conformations, except those for which direct overlap between the two lone pairs is significant. In this latter case, the MO order is unchanged but $\Delta n$ increases. Since such conformations are energetically unfavorable, we consider them to be unreasonable. According to the CNDO/s algorithm, the conformation shown in Figure 4 should also be the equilibrium geometry.

The equality of the LCAO MO coefficients for $n^+$ and $n^-$ suggests that differential mixing with the skeletal $\sigma$ structure is not the primary reason for the energy difference between the non-bonding orbitals in the $\beta$-dicarbonyls. We note, however, that although $n^-$ and $n^+$ both have five nodes, the carbon-carbon $\sigma$ bonds in $n^-$ overlap much more effectively with the (zeroth order) $n^-$ orbital than do those of $n^+$ with $n^+$. Criterion (ii), overlap, thus appears to be of prime importance to consideration of the splitting of the $n$ MO's of $\beta$-dicarbonyls.

Table 2 lists the vertical ionization energies and the values of $n$ for $\beta$-dicarbonyls. The behavior of $\Delta n$ for these molecules is shown in Figure 5. Acyclic molecules appear first and are followed, in order, by 5-membered ring cyclic compounds, 6-membered ring cyclic compounds and 2,2,4,4-tetramethyl-1,3-cyclobutanedione (TMCBD). Several observations are appropriate:

--- $\Delta n$ is considerably smaller for $\beta$-dicarbonyls than for $\alpha$-dicarbonyls.

--- The $\Delta n$ values for formylurea$^{15}$ and acetylurea$^{15}$ are slightly larger than those for the simple acyclic dicarbonyls.
TABLE 2

VERTICAL IONIZATION ENERGIES (eV)

FOR THE NON-BONDING MO's OF β-DICARBONYLS.

The difference Δn is defined as Δn = |I_{n_+} - I_{n_-}|

<table>
<thead>
<tr>
<th>NUMBER INDEX</th>
<th>MOLECULE</th>
<th>I_{n_-}</th>
<th>I_{n_+}</th>
<th>Δn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,2-dimethyl-1,3-propanedial(^a)</td>
<td>9.8</td>
<td>10.5</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>2,4-pentanedione(^a)</td>
<td>~9.6</td>
<td>10.15</td>
<td>~0.55</td>
</tr>
<tr>
<td>3</td>
<td>3-methyl-2,4-pentanedione(^a)</td>
<td>9.43</td>
<td>10.05</td>
<td>0.62</td>
</tr>
<tr>
<td>4</td>
<td>3,3-dimethyl-2,4-pentanedione(^a)</td>
<td>9.30</td>
<td>9.86</td>
<td>0.56</td>
</tr>
<tr>
<td>5</td>
<td>formylurea(^b)</td>
<td>~10.6</td>
<td>11.35</td>
<td>~0.75</td>
</tr>
<tr>
<td>6</td>
<td>acetylmethane(^b)</td>
<td>~10.3</td>
<td>11.1</td>
<td>~0.8</td>
</tr>
<tr>
<td>7</td>
<td>1,3-cyclopentanediol(^c)</td>
<td>9.53</td>
<td>10.40</td>
<td>0.87</td>
</tr>
<tr>
<td>8</td>
<td>2-methyl-1,3-cyclopentanediol(^c)</td>
<td>9.40</td>
<td>10.18</td>
<td>0.78</td>
</tr>
<tr>
<td>9</td>
<td>2,2-dimethyl-1,3-cyclopentanediol(^c)</td>
<td>9.34</td>
<td>10.05</td>
<td>0.71</td>
</tr>
<tr>
<td>10</td>
<td>succinic anhydride(^d)</td>
<td>10.80</td>
<td>11.61</td>
<td>0.81</td>
</tr>
<tr>
<td>11</td>
<td>maleic anhydride(^d)</td>
<td>11.10</td>
<td>11.95</td>
<td>0.85</td>
</tr>
<tr>
<td>12</td>
<td>succinimide(^e)</td>
<td>~10.1</td>
<td>~10.8</td>
<td>~0.7</td>
</tr>
<tr>
<td>13</td>
<td>N-methylsuccinimide</td>
<td>~10.0</td>
<td>10.71</td>
<td>~0.71</td>
</tr>
<tr>
<td>14</td>
<td>1,3-cyclohexanediol(^c)</td>
<td>9.60</td>
<td>10.04</td>
<td>0.44</td>
</tr>
<tr>
<td>15</td>
<td>2-methyl-1,3-cyclohexanediol(^c)</td>
<td>9.48</td>
<td>9.81</td>
<td>0.33</td>
</tr>
<tr>
<td>16</td>
<td>2-isopropyl-1,3-cyclohexanediol(^c)</td>
<td>9.29</td>
<td>9.61</td>
<td>0.32</td>
</tr>
<tr>
<td>17</td>
<td>2-t-butyl-1,3-cyclohexanediol(^c)</td>
<td>9.15</td>
<td>9.62</td>
<td>0.47</td>
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<tr>
<td>NUMBER INDEX</td>
<td>MOLECULE</td>
<td>$I_{(n^-)}$</td>
<td>$I_{(n^+)}$</td>
<td>$\Delta n$</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------------------</td>
<td>-------------</td>
<td>-------------</td>
<td>------------</td>
</tr>
<tr>
<td>18</td>
<td>glutaric anhydride</td>
<td>10.58</td>
<td>11.17</td>
<td>0.59</td>
</tr>
<tr>
<td>19</td>
<td>glutarimide $^e$</td>
<td>10.05</td>
<td>$\sim 10.5$</td>
<td>$\sim 0.45$</td>
</tr>
<tr>
<td>20</td>
<td>dihydrouracil $^b$</td>
<td>$\sim 10.1$</td>
<td>11.0</td>
<td>$\sim 0.9$</td>
</tr>
<tr>
<td>21</td>
<td>uracil $^b$</td>
<td>10.13</td>
<td>11.0</td>
<td>0.87</td>
</tr>
<tr>
<td>22</td>
<td>thymine $^b$</td>
<td>10.05</td>
<td>10.88</td>
<td>0.83</td>
</tr>
<tr>
<td>23</td>
<td>1,3-dimethyluracil $^b$</td>
<td>9.70</td>
<td>10.55</td>
<td>0.85</td>
</tr>
<tr>
<td>24</td>
<td>2,2,4,4-tetramethyl-1,3-cyclobutanedione</td>
<td>9.53</td>
<td>8.80</td>
<td>0.73</td>
</tr>
</tbody>
</table>


$^e$Enolization to the lactim-form occurred to some extent with succinimide and glutarimide; the ionization values listed for these molecules, therefore, are approximate.
Figure 5. Diagrammatic presentation of the $\Delta n$ values for the $\beta$-di-carbonyls listed in Table 2. The numbering index on the abscissa corresponds to the compound number in Table 2. The dashed line is the mean of $\Delta n$, $\Delta \Pi$, from Table 5.
Δn(eV), β-DICARBONYLS
The value of $\Delta n$ for the 5-membered-ring cyclic molecules is $0.8 \pm 0.1$ eV and is quite constant. This constancy may reflect the rigid nature of these systems, or it may simply be an artifact attributable to the limited data set.

Values of $\Delta n$ for the symmetrical 6-membered-ring cyclic molecules (numbers 14 through 19 of Table 2) are generally less than for other compounds of Table 2. The large values of $\Delta n$ for the uracils is probably due both to their rigid, planar structures (dihydouracil excepted) and the non-symmetrical environments of the individual carbonyl units.

The I(n) events of 1,3-cyclopentanedione and 1,3-cyclohexanedicarboxylic acid are shown in Figure 6. The gaussian and blue-degraded band shapes are very evident for 1,3-cyclopentanedicarboxylic acid, but are less clear for 1,3-cyclohexanedicarboxylic acid. The I(n) band in the latter molecule is partially obscured by overlap with I(n°), but there is little doubt that the I(n°) event is the sharper. The I(n) band shapes of all non-coaxial $\beta$-dicarboxylic acids exhibit this pattern: The gaussian band occurs at lower ionization energies than the blue-degraded band.

We now rationalize the observed I(n) band shapes of non-coaxial $\beta$-dicarboxylic acids. We proceed straightforwardly from the diagrammatic MO's of Figure 4. It is empirically clear that the $n_\sigma$ MO must be significantly more skeletally involved than $n_\pi$. This conclusion also follows from Figure 4: The directed carbon-carbon bonds of $n_\sigma$ contribute significantly to bonding between the carbonyls and, therefore, ejection of an electron from $n_\sigma$ should produce a geometry change in the $\sigma$ structure between the carbonyls and generate a gaussian UPS
Figure 6. The HeI photoelectron spectra of the non-bonding MO's of 1,3-cyclopentanedione and 1,3-cyclohexanedione.
band. In \( n^0_+ \), the bonds between the carbonyls are not directed; in fact, the atomic orbital on carbon two (C2) is so directed that it is effectively non-bonding (i.e., there is little overlap with the AO's on C1 and C3). Ejection of an electron from \( n^0_+ \), therefore, should produce a negligible effect on the skeletal geometry and cause I(\( n^0_+ \)) to be blue-degraded.

C. 2,2,4,4-TETRAMETHYL-1,3-CYCLOBUTANEDIONE (TMCBD)

TMCBD is unique among \( \beta \)-carbonyls in that the MO order\(^1 \) is \( n^0_+ > n^\sigma_- \). The UPS of TMCBD is shown in Figure 7. The inversion, relative to other \( \beta \)-dicarbonyls, of blue-degraded and gaussian shapes is quite striking. Since TMCBD is the only \( \beta \)-dicarbonyl with coaxial carbonyl groups and the only one in which the UPS band shapes are inverted, it is clear that coaxial \( \beta \)-dicarbonyls must be treated separately.

The \( n \) MO's of TMCBD are schematized in Figure 8. The \( n^+_+ / n^-_- \) functions are differentially mixed with skeletal \( \sigma \) orbitals, \( n^+_+ \) having more \( \sigma \) character than \( n^-_- \). Thus \( n^0_+ \) is expected to lie above \( n^\sigma_- \). Due to the larger \( O=C-C \) angle in TMCBD (135\(^\circ \)) than in other \( \beta \)-dicarbonyls (\( \sim 120\(^\circ \)), the overlap of \( n^+_+ \) and \( n^-_- \) with the intervening \( \sigma \) bonds is expected to be less in TMCBD. The reason for the inversion of the \( n \) MO order lies in the energy denominator, criterion (ii). The large AO coefficients of opposite sign on carbons 2 and 4 of \( n^0_+ \) are directly opposed and this destabilizing interaction increases the energy of the \( \sigma \) MO which mixes with \( n^+_+ \) well above that of the directed-bond \( \sigma \) orbital that mixes with \( n^-_- \) in \( n^\sigma_- \).
Figure 7. The HeI photoelectron spectrum of the non-bonding MO's of 2,2,4,4-tetramethyl-1,3-cyclobutanedione (TMGCB).
Figure 8. Diagrammatic representation of $n_+^0$ and $n_-^0$ from CNDO/s computations for 2,2,4,4-tetramethyl-1,3-cyclobutanedione. LCAO coefficients are also listed. Geometrical parameters are taken from the crystallographic data of reference 26a, with the exception of the C-CH$_3$ bond lengths which are taken from the electron diffraction data of reference 26b.
A previous rationalization\textsuperscript{5} of the n MO inversion in TMCBD made use of the fact that only n\textsuperscript{+} can mix with cyclobutane Walsh σ orbitals. This rationale, however, is inadequate. Although the symmetry of n\textsuperscript{+} is compatible with Walsh orbital mixing, the AO amplitudes are completely different. This difference is not superficial since the bonding characteristics of the Walsh orbital and the σ orbital which mixes into n\textsuperscript{0} are totally different.

The observation that I(n\textsuperscript{0}) is blue-degraded even though n\textsuperscript{+} is more heavily mixed with the skeletal σ MO's can be attributed to the bonding characteristics of the mixing σ orbitals. Thus, in Figure 8, just as in Figure 4, the gaussian band shape corresponds to the MO with directed-bond σ orbitals, I(n\textsuperscript{σ}). The skeletal σ orbitals in n\textsuperscript{0} are not of directed-bond nature, therefore, are much less bonding. This suggests that the gaussian and blue-degraded band shapes are more dependent on MO form than degree of mixing.

D. \(\gamma\)-DICARBONYLS

The investigation of \(\gamma\)-dicarbonyls is limited for two reasons. First, UPS data exist only for eight such molecules. These data are listed in Table 3 and the Δn values are plotted in Figure 9. Second, the carbonyl groups in all eight of these molecules are coaxial. As for \(\beta\)-dicarbonyls, coaxial carbonyl groups are found to invert the n MO order obtained for non-coaxial \(\gamma\)-dicarbonyls.

The computationally predicted n MO order in non-coaxial \(\gamma\)-dicarbonyls is n\textsuperscript{+} > n\textsuperscript{−} according to CNDO/s calculations for 1,4-butanedial in various conformations. The calculated values of Δn were \(\sim 0.2 \text{eV}\) for butanedial and UPS band shape considerations predict n\textsuperscript{0}.
<table>
<thead>
<tr>
<th>NUMBER INDEX</th>
<th>MOLECULE</th>
<th>$I(n_-)$</th>
<th>$I(n_+)$</th>
<th>$\Delta n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,4-cyclohexanedione</td>
<td>9.65</td>
<td>9.85</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>1,4-benzoquinone&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.99</td>
<td>10.29</td>
<td>0.30</td>
</tr>
<tr>
<td>3</td>
<td>2-methyl-1,4-benzoquinone&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>9.78</td>
<td>10.17</td>
<td>0.39</td>
</tr>
<tr>
<td>4</td>
<td>2,5-dimethyl-1,4-benzoquinone&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.60</td>
<td>10.05</td>
<td>0.45</td>
</tr>
<tr>
<td>5</td>
<td>tetramethyl-1,4-benzoquinone&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.25</td>
<td>9.75</td>
<td>0.50</td>
</tr>
<tr>
<td>6</td>
<td>tetrachloro-1,4-benzoquinone&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.90</td>
<td>10.10</td>
<td>0.2</td>
</tr>
<tr>
<td>7</td>
<td>2,3-dichloro-5,6-dicyano-1,4-benzoquinone</td>
<td>10.58</td>
<td>10.76</td>
<td>0.18</td>
</tr>
<tr>
<td>8</td>
<td>tetrafluoro-1,4-benzoquinone&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11.21</td>
<td>10.96</td>
<td>0.25</td>
</tr>
</tbody>
</table>


Figure 9. Diagrammatic presentation of $\Delta n$ for the $\gamma$-dicarbonyls listed in Table 3, and for the $\delta$-dicarbonyls listed in Table 4. The numbering indices on the respective abscissas correspond to the compound numbers in Table 3 and 4. The dashed line is the mean of $\Delta n$, $\Delta \overline{n}$, from Table 5.
and \( n^0 \). This latter based on directed-bonds in the \( \sigma \) MO mixing with 
\( n_+ \), and negligible bonding between carbons 2 and 3 (i.e., the central 
bond) in the \( \sigma \) MO mixing with \( n_- \). Unfortunately, no UPS data being 
available, computational results provide the only data for non-coaxial 
\( \gamma \)-dicarbonyls.

The six membered ring is the smallest cyclic configuration that 
can accomodate \( \gamma \)-dicarbonyl units as an integral part of the ring. 
The 1,4-benzoquinones are the most important examples of this type 
of molecule ---hence, the dearth of UPS literature on \( \gamma \)-dicarbonyls\(^1\) 
other than the 1,4-benzoquinones\(^1,2,17,19,21,23\). The assignment of 
the photoelectron spectrum of 1,4-benzoquinone meets with difficulty\(^17\) 
either because Koopmans' Theorem\(^18\) is inapplicable or because the 
MO calculations are of poor quality. Our attempts to formulate a 
coherent model of dicarbonyl interactions indicated the presence of 
inconsistencies in the previous UPS assignments\(^1,2,19,23\) and forced 
us to make reassignments for 1,4-benzoquinone\(^17\). This reassignment 
is presented in the Appendix. The Appendix is also the source of data 
for molecules 2 through 8 in Table 3. The photoelectron spectra of 
these molecules are also provided in the Appendix.

The low-energy UPS of 1,4-cyclohexanedione is shown in Figure 10. 
This molecule is supposed to exist in three conformations (symmetries): 
boat (\( C_{2v} \)), chair (\( C_{2h} \)) and skew (\( D_2 \)). While the skew configuration, 
in which the carbonyl groups are coaxial, is apparently preferred\(^1\), 
the spectrum of Figure 10 probably consists of an average over all 
three conformations, the skew configuration being dominant.

It has been shown\(^24\) that any two lone-pair orbitals separated
Figure 10. The HeI photoelectron spectrum of the non-bonding MO's of 1,4-cyclohexanedione.
by an odd number of bonds will exhibit the MO order \( n_+ > n_- \). This result derives directly from the unique location of the central \( \sigma \)-bond and the coupling which it mediates. This coupling destabilizes \( n_+ \) in a fashion identical to that discussed for the \( \alpha \)-dicarbonyls. In 1,4-benzoquinone, however, this \( \sigma \) orbital extends around the 6-membered ring in a very strongly bonding manner, as shown in Figure 1 of Appendix B. Thus, the energy denominator consideration of criterion (ii) dictates that very little \( n_+ /\sigma \) mixing will occur. Conversely, the ring \( \sigma \) bond that mixes with \( n_- \) has a node through the center of the ring and perpendicular to the line of the carbonyls. This ring \( \sigma \) orbital, therefore, is of much higher energy than the one which interacts with \( n_+ \). By the energy denominator criterion, then, \( n_- \) should be destabilized to a greater extent than \( n_+ \). The resulting MO order in 1,4-benzoquinone, consequently, is expected to be \( n_- > n_+ \). The coaxial arrangement of the carbonyl groups in the benzoquinones produces an inversion of the \( n_+ > n_- \) MO order expected for non-coaxial \( \gamma \)-dicarboxyls.

An exception to this MO order occurs in tetrafluoro-1,4-benzoquinone, where \( n_+ > n_- \). It is of interest to note that substitution of electron donating methyl groups onto the benzoquinone ring increases \( \Delta n \), while substitution of electron withdrawing groups decreases \( \Delta n \) and that, in the perfluoro derivative, the MO order is actually inverted.

E. \( \delta \)-DICARBONYLS

CNDO/s calculations on 1,5-pentanedial yield \( n_-^\sigma > n_+^\sigma \), just as in non-coaxial \( \beta \)-dicarboxyls. Computed \( \Delta n \) values for several molecular
conformations are effectively constant at \( \pm 0.4 \text{eV} \).

The UPS data for three \( \delta \)-dicarbonyls are listed in Table 4 and the \( \Delta n \) values are plotted in Figure 9. Since only three compounds are listed in Table 4, the results can hardly be considered general. However, in view of the nature of the molecules being investigated, it does not seem likely that this list will be appreciably lengthened in the near future.

The UPS of compound 2 of Table 4 is shown in Figure 11. The ionization bands are so poorly resolved that the actual band shapes cannot be elicited. Nonetheless, the band at higher ionization energy does appear to be sharper, in accord with its expected \( n^0_+ \) nature.
<table>
<thead>
<tr>
<th>NUMBER INDEX</th>
<th>MOLECULE</th>
<th>I(n-)</th>
<th>I(n+)</th>
<th>Δn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,3-diacetylazulene&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>~9.1</td>
<td>~9.1</td>
<td>~0</td>
</tr>
<tr>
<td>2</td>
<td>cis-bicyclo[3.3.0] octane-3,7-dione&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.45</td>
<td>9.78</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>4,6,8-trimethyl-1,3-diacetylazulene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.4</td>
<td>8.75</td>
<td>0.35</td>
</tr>
</tbody>
</table>


<sup>b</sup>The I<sub>(n+)</sub> and I<sub>(n-)</sub> events and an I(π) event of 1,3-diacetylazulene all occur in one unresolved ionization band. The maximum of this band is ~9.1 eV and the half-width is ~0.1 eV.
Figure 11. The HeI photoelectron spectrum of the non-bonding MO's of cis-bicyclo[3,3,0]octane-3,7-dione.
COUNT RATE

IONIZATION ENERGY (eV)

$\text{n}_-^\sigma$  $\text{n}_+^0$
III. CONCLUSIONS

The conclusions of this work follow directly from Tables 1 through 4.

The through-bond nature of dicarbonyl interactions is confirmed. Through-space interactions are also observed: These are most clearly exemplified by entries 28 through 34 in Table 1. In these cases, special interactions appear to be enforced by rather specific molecular geometries. Entry 27 of Table 1, a perfluoro compound, is also exceptional, presumably because of the peculiarities of the perfluoro effect.

The magnitude of the through-bond dicarbonyl interaction as a function of the spatial separation of the carbonyl groups is summarized in Table 5. The interaction, as measured by $\Delta \tilde{\eta}$, decreases rapidly with increasing carbonyl separation. The concept of an average interaction energy, gauged by $\Delta \tilde{\eta}$, possesses considerable validity.

The energetic order of the non-bonding MO's of dicarboxyls can be synopsized by dividing them into two classes: Those in which the carbonyl groups are coaxial, and those in which they are not. Figure 12 provides a schematic of the results obtained. The only case in which this order does not hold is tetrafluoro-1,4-benzoquinone (which, as a perfluoro compound, is expected to be somewhat unusual).

Finally, the UPS observed band shape differences are noted and rationalized. This is accomplished by noting that the form of the n MO's between the carbonyls controls the band shape tendencies. The gaussian band always derives from the n MO with directed $\sigma$ bonds,
TABLE 5

MEAN VALUES OF $\Delta n$ AND STANDARD DEVIATION (RMS) FOR $\alpha$, $\beta$ AND $\gamma$-DICARBONYLS. ALL VALUES ARE IN eV.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta n$</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-dicarbonyls(^a)</td>
<td>1.9</td>
<td>0.15</td>
</tr>
<tr>
<td>$\beta$-dicarbonyls(^b)</td>
<td>0.65</td>
<td>0.17</td>
</tr>
<tr>
<td>$\gamma$-dicarbonyls(^c)</td>
<td>0.3</td>
<td>0.13</td>
</tr>
<tr>
<td>$\delta$-dicarbonyls</td>
<td>(0.23)</td>
<td>---</td>
</tr>
</tbody>
</table>

\(^a\)Only the first 26 entries in Table 1 were used to calculate $\Delta n$ since the $\Delta n$ values for the last 8 entries are modified by anomalous interactions which pertain only to the last eight molecules listed (See text).

\(^b\)All entries in Table 2, TMCBD included, were used. It should be noted that the MO order in TMCBD is reversed compared to that of all other listed $\beta$-dicarbonyls.

\(^c\)All entries in Table 3 including tetrafluoro-1,4-benzoquinone, were used. It should be noted that the MO order in this last molecule is reversed from that of the other $\gamma$-dicarbonyls listed.
while the blue-degraded band always arises from the n MO in which the skeletal σ orbital between the carbonyls are effectively non-bonding. The summary of Figure 12 shows that the gaussian shaped UPS band is always expected at lower ionization energy in non-coaxial dicarbonyls, and that the blue-degraded band appears at lower ionization energy in coaxial dicarbonyls.
Figure 12. Schematic summary of results for the non-bonding MO's of dicarbonyls. The various dicarbonyls are specified by carbonyl group separations (α, β, etc.) and divided into two classes (coaxial and non-coaxial). The value of $\Delta \bar{n}$ plotted for the coaxial β-dicarbonyls is $\Delta n$ for TMCBD, the only available example of such a molecule.
DICARBONYL COMPOUNDS

\[ \Delta n (\text{eV}) \]

\[ n_+^\sigma \]

\[ n_+^\sigma \quad n_+^\sigma \quad n_+^\sigma \quad n_+^\sigma \]

\[ n_+^\sigma \quad n_+^\sigma \quad n_+^\sigma \]

\[ n_+^\sigma \quad n_+^\sigma \quad n_+^\sigma \]

\[ \alpha \quad \beta \quad \gamma \quad \delta \]

\[ \beta \quad \gamma \]

\[ \leftarrow \text{NON-COAXIAL} \rightarrow \]
REFERENCES


CHAPTER THREE

PHOTOELECTRON SPECTROSCOPY OF BIOLOGICAL MOLECULES
INTRODUCTION

It is surprising, in view of the importance of their electronic structures, that so little work has been invested in the ultraviolet photoelectron spectroscopy (UPS) of moderately large biological molecules\(^1\text{--}^{13}\). In particular, there exists a great number of correlative studies between electronic structure (usually deduced by quantum chemical computational means) and biological "function". Such studies are nicely exemplified in the comprehensive work of the Pullmans\(^\text{14}\).

UPS data, via the intermediacy of Koopmans' Theorem\(^\text{15}\), provide the most direct test of quantum chemical computations\(^\text{16}\). Therefore, the problems addressed in this work are twofold:

(i) To obtain UPS data for a diverse selection of biological molecules.

(ii) To compare the UPS data so obtained with the most extensive collection of quantum chemical calculations available --- namely, the Hückel calculations of the Pullmans\(^\text{14}\).
I. EXPERIMENTAL

Photoelectron spectra were obtained on a Perkin-Elmer PS-18 photoelectron spectrometer. This instrument is equipped with a heated sample probe which is capable of sustaining temperatures as high as $350^\circ$C to within $\pm 2^\circ$C. The resolution normally attainable is 20 to $25^{17}$ millielectron volts (meV). However, for temperatures greater than $\sim 140^\circ$C the resolution decreases and, at $300^\circ$C, it is no better than 75 to 100meV.

Sample heating is mandatory for most biochemicals since they tend to have negligible vapor pressure at room temperature. Many of these chemicals also tend to decompose when heated and, if not careful, one could record a totally spurious spectrum. The general procedure consists of a slow temperature increase ($\sim 1^\circ$/minute) until the sample pressure ($\sim 10^{-3}$ mm Hg) is adequate for recording a spectrum. The sample is then checked for signs of decomposition (e.g., change of color, charring, or time dependence of the spectrum). Spectra can not be obtained for those compounds that decompose before an adequate vapor pressure has been reached.

The experimental experience associated with the photoelectron spectroscopy of biochemicals, as documented in this work, suggests that most small to medium sized molecules should be tractable. Larger molecules will be intractable because of decomposition at the higher temperatures necessary to generate an adequate vapor pressure. Examples of such intractability are provided by vitamin $K_1$ and protophorphyrin IX dimethyl ester.
II. PHOTOELECTRON SPECTRA

The photoelectron spectra of various biochemicals will now be presented, and assigned via Koopmans' Theorem, which equates ionization energies to the negative of eigenvalues calculated from self consistent field-molecular orbital (SCF-MO) computations. Since all of the molecules discussed here can be categorized in the $C_s$ (or near $C_s$) point group, their MO's can be labelled $a''$ and $a'$. We use the symbol $\pi$ for the $a''$ representation and the symbol $\pi$ for the $a'$ representation. The $\pi$ designation connotes a non-bonding, "lone pair" orbital, which is the only type of $\sigma$-MO that can occur in the low energy UPS region of these molecules.

All biochemicals investigated here are presented pictorially in Figure 1, which should also be consulted for abbreviations. The observed ionization energies and the MO assignments are collected in Table 1.

A. 2,4-DINITROPHENOL AND 2,4-DINITROANISOLE

The UPS of 2,4-dinitrophenol (DNP) and 2,4-dinitroanisole (DNAn) are shown in Figure 2 and their ionization energies are listed in Table 1. Except for a loss of vibronic structure in $I(2)$ and a general shift to lower ionization energies in DNAn, the two spectra are essentially identical. The correlation diagram of Figure 3 indicates that the $I(1)$ and $I(2)$ events of DNP and DNAn correlate directly with similar events in phenol.

The ionization events associated with the nitro groups reside in the intense bands centered at $\sim$11.7eV in DNP, and $\sim$11.4eV in
Figure 1. Pictorial representations of the biological molecules investigated in this work. The names of the compounds along with the abbreviations used in the figure are: 2,4-dinitrophenol (DNP), nicotinic acid (NA), nicotinamide (N), barbituric acid (BA), hypoxanthine (HX), xanthine (X), uric acid (UA), cytosine (C), guanine (G), adenine (A), uracil (U), thymine (T), β-carotene (βC), menadione (K₃—for vitamin K₃), purine (Pu) and pyrimidine (Py).
**TABLE 1**

IONIZATION ENERGIES, MOLECULAR ORBITAL (MO) ASSIGNMENTS AND CATION VIBRATIONAL FREQUENCIES, WHERE OBSERVED, FOR THE MOLECULES LISTED

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>I(1)</th>
<th>I(2)</th>
<th>I(3)</th>
<th>I(4)</th>
<th>I(5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-Dinitrophenol</td>
<td>9.85</td>
<td>10.70</td>
<td>11.4±1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.57(i)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\bar{\nu}_{\text{vib}}, \text{cm}^{-1}$</td>
<td>1260(±50)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MO type</td>
<td>π</td>
<td>π</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Nitro group ionizations</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4-Dinitroanisole</td>
<td>9.55</td>
<td>10.40</td>
<td>11.1±1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.30(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MO type</td>
<td>π</td>
<td>π</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Nitro group ionizations</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>-</td>
<td>10.0±1</td>
<td>-</td>
<td>10.77</td>
<td>10.93</td>
</tr>
<tr>
<td></td>
<td>9.38(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\bar{\nu}_{\text{vib}}, \text{cm}^{-1}$</td>
<td>1600(±50)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>MO type</td>
<td>[n&amp;n]</td>
<td>[π&amp;n]</td>
<td>π</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nicotinic acid, methyl ester</td>
<td>-</td>
<td>9.85±1</td>
<td>-</td>
<td>10.65</td>
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<td></td>
<td>9.25(1)</td>
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<tr>
<td>MO type</td>
<td>[n&amp;n]</td>
<td>[π&amp;n]</td>
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<td></td>
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<tr>
<td>Nicotinamide</td>
<td>-</td>
<td>9.85</td>
<td>-</td>
<td>10.35</td>
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<td></td>
<td>9.18(1)</td>
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<td>MO type</td>
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<td>[n&amp;n]</td>
<td>π</td>
<td></td>
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<tr>
<td>N,N-diethylnicotinamide</td>
<td>-</td>
<td>9.0</td>
<td>9.4±2</td>
<td>9.98</td>
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</tr>
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<td></td>
<td>8.65(1)</td>
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<tr>
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<td>[n&amp;n]</td>
<td>π</td>
<td>n</td>
<td>π</td>
<td></td>
</tr>
<tr>
<td>COMPOUND</td>
<td>I(1)</td>
<td>I(2)</td>
<td>I(3)</td>
<td>I(4)</td>
<td>I(5)</td>
</tr>
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<td>-------</td>
<td>-------</td>
<td>-------</td>
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<td>-------</td>
</tr>
<tr>
<td>Hypoxanthine</td>
<td>8.87</td>
<td>-</td>
<td>10.3±2</td>
<td>11.15</td>
<td>11.4±1</td>
</tr>
<tr>
<td>V_vib, cm⁻¹</td>
<td>1360(±50)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>MO type</td>
<td>π</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xanthine</td>
<td>8.85</td>
<td>10.1</td>
<td>10.4</td>
<td>10.9</td>
<td>11.5</td>
</tr>
<tr>
<td>MO type</td>
<td>π</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Uric acid</td>
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<td>10.5</td>
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<td>11.2</td>
<td>11.8</td>
</tr>
<tr>
<td>MO type</td>
<td>π</td>
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<td></td>
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<tr>
<td>Caffeine</td>
<td>8.25</td>
<td>9.6</td>
<td>9.95</td>
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<tr>
<td>MO type</td>
<td>π</td>
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<td></td>
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<tr>
<td>Cytosine</td>
<td>8.82</td>
<td>9.45</td>
<td>9.90</td>
<td></td>
<td>11.8±2</td>
</tr>
<tr>
<td>MO type</td>
<td>π</td>
<td>n</td>
<td>π</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Guanine</td>
<td>8.30</td>
<td>9.90</td>
<td>10.45</td>
<td>11.15</td>
<td></td>
</tr>
<tr>
<td>MO type</td>
<td>π</td>
<td>n</td>
<td>n</td>
<td>π</td>
<td></td>
</tr>
<tr>
<td>Barbituric acid</td>
<td>10.40</td>
<td>11.05</td>
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<td>11.45±2</td>
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</tr>
<tr>
<td>MO type</td>
<td>n</td>
<td>π</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[one π]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[two n's]</td>
</tr>
<tr>
<td>8-Carotene</td>
<td>7.65</td>
<td>8.25</td>
<td>8.65</td>
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<td></td>
</tr>
<tr>
<td>MO type</td>
<td>π</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Menadione</td>
<td>9.51</td>
<td></td>
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<tr>
<td>(spectrum not presented)</td>
<td></td>
<td></td>
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</table>
Figure 2. The He I photoelectron spectra of 2,4-dinitrophenol and 2,4-dinitroanisole.
Figure 3. Correlation diagram of the UPS data for phenol\textsuperscript{18}, 2,4-dinitrophenol and 2,4-dinitroanisole.
VERTICAL IONIZATION ENERGY (eV)
DNAn. This conclusion is based on the observation of the two nitro group ionizations — one \( n \) and one \( \pi \) — in nitrobenzene\(^{19}\) at 11.15eV and 11.30eV. The intense ionization bands centered at \( \sim 11.7 \) eV and 11.4 eV in DNP and DNAn, respectively, are compatible with a model having the following characteristics:

---A total of four ionization events occur in each of these bands. Each nitro group contributes an \( I(n) \) and an \( I(\pi) \) event and, since there are two such groups, it is expected that doubling will occur to yield \( I(n^+) \), \( I(n^-) \), \( I(\pi^+) \) and \( I(\pi^-) \) events. The \( \pm \) symbols denote linear combinations of the individual nitro group MO's.

---The various \( (\pm) \)-linear combinations will exhibit a small energy splitting. Thus all four nitro group ionization events will occur in a narrow energy band, just as do the nitro group ionization events in nitrobenzene\(^{19}\).

Finally, if the energy pattern of the three \( I(\pi) \) events in phenol holds also for DNP and DNAn, the UPS bands at 12.8 eV (DNP) and 12.25 eV (DNAn) correlate with the third \( I(\pi) \) event in phenol. This assignment is also supported by the Pullman calculations\(^ {14}\) for DNP.

B. NICOTINIC ACID AND NICOTINIC ACID METHYL ESTER

The UPS of nicotinic acid (NA) and nicotinic acid methyl ester (NAME) are shown in Figure 4. Their ionization energies are listed in Table 1. There are five low-energy ionizations expected for these molecules: Three \( I(\pi) \) and two lone pair \( I(n) \) events. Two of the \( \pi \) MO's are located on the pyridine ring while the third is on the acid group. The nitrogen lone pair provides one of the \( n \)
Figure 4. The He I photoelectron spectra of nicotinic acid and nicotinic acid methyl ester.
MO's while the acid group carbonyl lone pair furnishes the other. The low-energy ionization region in both NA and NAME consists of three bands with relative cross sections 2:2:1 (as one proceeds toward higher ionization energy). Thus, \( I(1) \) and \( I(2) \) lie within the first band in both compounds; \( I(3) \) and \( I(4) \) lie within the second; and \( I(5) \) comprises the totality of the third band.

The spectra are analyzed in terms of the correlation diagram of Figure 5. The assignments follow directly from Figure 5. The n MO centered on the nitrogen and the highest-occupied \( \pi \) MO of the pyridine ring remain nearly degenerate in both NA and NAME, just as in pyridine\(^{20}\) itself. The large destabilization of \( I(5) \) which occurs upon methyl esterification (i.e., NA to NAME) shows that \( I(5) \) arises from the \( \pi \) MO of the acid group or, equivalently, that this MO is mainly localized on the oxygen atom which is subjected to methylation. The second \( \pi \) MO of the pyridine ring as well as the n MO of the acid carbonyl group are, therefore, responsible for the second UPS band in both compounds.

C. NICOTINAMIDE AND N,N-DIETHYLNICOTINAMIDE

The UPS of nicotinamide (N) and N,N-diethylnicotinamide (DEN) are shown in Figure 6. Their ionization energies are listed in Table 1. Five low-energy ionizations are expected for these molecules: Three \( I(\pi) \) and two \( I(n) \) events. Two of the \( \pi \) MO's are located on the pyridine ring, while the third is largely situated on the amidic nitrogen. One of the n-MO's is a \( \sigma \) lone pair of the pyridinic nitrogen, while the second possesses large amplitude on the oxygen atom of the carbonyl acid group.
Figure 5. Correlation diagram of the UPS data for pyridine$^{20}$, nicotinic acid, nicotinic acid methyl ester, methyl formate$^{21}$ and formic acid$^{21}$. 
Figure 6. The He I photoelectron spectra of nicotinamide and N,N-diethylnicotinamide.
The assignment of these spectra is based on a correspondence to the correlation diagram of Figure 7. As in the cases of NA and NAME, the highest-energy occupied MO's of N and DEN are expected to be the nearly degenerate, low-energy n and \( \pi \) MO's of pyridinic nature. I(5) is assigned to the second \( \pi \) MO of pyridine on the basis of its null destabilization upon diethylating N to DEN and by reference to the Pullman Hückel calculations\(^{22}\). The n and \( \pi \) MO's of the amide group, therefore, are bracketed to low energy by the n and \( \pi \) MO's of the pyridinic moiety, and to high energy by the second \( \pi \) MO of the pyridine moiety.

The lack of resolution of the single, broad, low-energy UPS band of N precludes accurate location of the vertical ionization transitions, except for I(5). This lack of resolution is denoted by the hatching in the correlation diagram of Figure 7. The three ill-defined maxima evident in the UPS band are marked in the hatched area.

Diethylation of N to yield DEN segregates two bands at higher energy, leaving three events still unresolved in a lower-energy band. This low-energy unresolved band cannot contain the I(n) event of the carbonyl group: This conclusion follows directly from a comparison of the data presented in Figure 7 for N, DEN and N,N-dimethylformamide. Indeed, I(4) of DEN must arise from the n MO of the carbonyl group. Therefore the I(n) and I(\( \pi \)) events associated with the n and \( \pi \) MO's of the pyridine ring and the I(\( \pi \)) event associated with the \( \pi \) MO of the amide group must all occur in the unresolved low-energy band. The amidic I(\( \pi \)) event is presumably
Figure 7. Correlation diagram of the UPS data for pyridine\textsuperscript{20},
nicotinamide, N,N-diethylnicotinamide, N,N-dimethyl-
formamide\textsuperscript{21} and formamide\textsuperscript{21}. 
of slightly higher ionization energy than the pyridinic $I(\pi)$ event.

It is noteworthy that diethylation of $N$ to yield DEN produces a large destabilization of the low-energy $n$ and $\pi$ MO's of pyridine, while having little or no effect on the second $I(\pi)$ event of the pyridine moiety. The form of the Hückel eigenvectors for $N$ suggests that this effect is attributable to a lack of mixing of the second pyridinic $\pi$ MO with the amidic $\pi$ MO, whereas the highest-energy occupied pyridinic $\pi$ MO and the amidic $\pi$ MO are heavily mixed. In any event, the pyridinic $\pi$ orbital splitting is $\approx 50\%$ greater in DEN than in pyridine itself or in any other pyridine derivatives studied in this work (including NA, NAME and $N$).

The results of CNDO/2 and CNDO/s semiempirical MO calculations on NA and $N$ are shown in Figure 8. Since no crystal or electron diffraction geometries were available for these compounds, standard bond lengths and angles were used for the geometrical parameters.

D. BARBITURIC ACID

The UPS of barbituric acid (BA) is shown in Figure 9. Its ionization energies are listed in Table 1.

This molecule should exist only in the keto form$^{14}$ since the resonance energy gained by enolization is inadequate to compensate the inherent stability of the carbonyl groups. Thus, the set of low-energy MO's should consist of five: Three $n$ MO's, one for each carbonyl, and two $\pi$ MO's, one for each nitrogen lone pair orbital of $\pi$ type.$^{23}$ Molecular orbital computations of CNDO/s type on BA$^{24}$ produce the following set of eigenvalues and eigen-
Figure 8. Correlation diagram of CNDO/s and CNDO/2 MO computational results and UPS experimental results for nicotinic acid and nicotinamide.
Figure 9. The He I photoelectron spectrum of barbituric acid. The sharp spikes are due to the Xe and Ar reference gases.
The agreement between these computational results and the experimentally measured ionization energies, as detailed in Table 1, is excellent. Therefore, Koopmans' theorem$^{15}$, which equates ionization energy to the negative of the SCF MO eigenvalue, is adequate to the assignment of the UPS of BA if the CNDO/s results listed above are taken to be a good mimic of SCF MO results.

E. HYPOXANTHINE, XANTHINE, URIC ACID AND CAFFEINE

The experimental investigation of the compounds hypoxanthine (HX), xanthine (X), uric acid (UA) and caffeine, was especially difficult. The high temperature ($\sim 300^\circ C$) required to produce adequate vapor pressures was difficult to contend with and caused rather poor resolution (75 to 100meV). The spectrum of caffeine was the easiest to obtain. Caffeine is only 25% as likely to form hydrogen bonds as are HX, X and UA.

The poor quality of the spectra for HX, X and UA precludes discussion of any but the most obvious spectral features. Fortunately, the feature of most interest, namely the lowest-energy
ionization event, is well separated from the higher-energy ionization events in all four cases.

The UPS of X and caffeine are shown in Figure 10 and those of HX, X and UA are presented in Figure 11. Their ionization energies are listed in Table 1. Those ionization energies connected by dashed lines in Table 1 for X and UA are unreliable (i.e., they are educated guesses made from spectra of poor quality): They do not represent well-defined ionization events, but merely spectral features which may or may not correspond to vertical transitions.

Calculations\textsuperscript{14} on the relative stabilities of the keto and enol forms of these molecules indicate that the keto form is slightly favored. The similarity of the UPS of X and caffeine suggests that both forms do not exist simultaneously in the gas phase: If they did, the spectrum of X would be expected to be more complex than that of caffeine and the lowest-energy ionization band of X, being a composit of at least two ionization events, should be broader than that of caffeine. That is to say, the shape of the lowest-energy ionization band would be very different for X than for caffeine. Since this is not so, it can be assumed that all these molecules exist predominantly in the keto form in the gas phase.

Hückel calculations\textsuperscript{14} predict the existence of one rather isolated, low-energy \pi MO in all these molecules. This prediction agrees with the UPS data. Hence, \textit{I(1)} is assigned as \textit{I(\pi)} in HX, X, UA and caffeine (see Table 1). The higher-energy orbital structure, however, is considerably more complex.

For purposes of discussion of HX, X and UA, the region \textasciitilde10-12eV
Figure 10. The He I photoelectron spectra of xanthine (bottom) and caffeine (top). The sharp spikes in the spectrum of caffeine are due to Xe and Ar reference gases.
Figure 11. The He I photoelectron spectra of hypoxanthine (bottom), xanthine, and uric acid (top). The sharp spikes in the spectra of uric acid and hypoxanthine are due to Xe and Ar reference gases.
is designated the "medium energy range" (MER). All π MO's referred to in the following discussion are taken from the Pullman Hückel calculations\textsuperscript{14}.

---In HX, a total of four ionization events are expected to occur in the MER: One I(π) and three I(n) events. The carbonyl lone pair furnishes one n MO while the other two are lone pair n MO's of the nitrogen centers.

---In X, five ionization events are expected to occur in the MER. These arise from two carbonyl n, one nitrogen n, and two π MO's.

---In UA the MER is also expected to contain five ionization events. Three of these arise from carbonyl n MO's and two from π MO's.

Comparison of relative band areas of I(1) with that of the MER in each spectrum indicates that the expectations listed above are reasonable. However, the actual determination of the electronic nature of the MER ionization events in these molecules will require better UPS spectra, better MO calculations and probably the UPS of a selection of related compounds.

Analysis of the UPS of caffeine is also helpful. The medium energy region in caffeine extends from approximately 9 to 12eV. No calculation for caffeine is available in reference 14; however, it is expected that the same five MO ionizations listed for X will also be present in caffeine. In addition, a sixth I(π) ionization may be present because of destabilization of a higher-energy π MO caused by hyperconjugation with the three methyl groups. This
possibility appears likely because the band at 12.2eV in X probably moves into the MER in caffeine.

No correlation diagram is presented for these molecules since only I(1) can be assigned with any assurance.

F. CYTOSINE AND GUANINE

Cytosine (C) and guanine (G), along with thymine (T) and adenine (A), form the set of DNA bases. Substitution of uracil (U) for T forms the set of RNA bases. It is evident that a knowledge of the ground state electronic structure of the compounds U, T, C, A and G is of great importance. Since the UPS of U, T, and A are already available, those of C and G complete the UPS data set for the DNA/RNA bases.

The UPS of C is shown in Figure 12 and that of G is presented in Figure 13. Their ionization energies are listed in Table 1. The spectra of C and G are discussed with reference to the diagrammatic presentation of the vertical ionization energies in Figure 14. The CNDO/2 results for these molecules are shown in Figure 15 and are used to assign the photoelectron spectra of C and G.

The vertical transitions of the three lowest-energy ionization events in C are easily recognizable even though I(2) and I(3) do overlap. Since I(1) is well resolved, relative band area considerations eliminate the possibility of a fourth ionization event under the band containing I(2) and I(3). The broad band at 11.8eV is puzzling in that band area considerations do not discriminate between the presence of one or two ionization events in this band.
Figure 12. The He I photoelectron spectrum of cytosine. The sharp spikes are due to Xe and Ar reference gases.
Figure 13. The He I photoelectron spectrum of guanine. The sharp spikes are due to Xe and Ar reference gases.
Figure 14. Plot of the vertical ionization energies and MO assignments of the four or five highest occupied MO's for uracil (U)\textsuperscript{11}, thymine (T)\textsuperscript{11}, cytosine (C), adenine (A)\textsuperscript{13} and guanine (G).
Figure 15. Plot of the MO eigenvalues from the CNDO/2 computations of S. Abdulner\textsuperscript{25} for uracil (U), thymine (T), cytosine (C), adenine (A) and guanine (G).
Although the matter is still in doubt, comparison with the 13.0eV band suggests the presence of two ionization events. Comparison of the measured ionization energies with the CNDO/2 eigenvalues of Figure 15 is of little help since the energy level pattern does not mimic the UPS data of Figure 14 very well. Nevertheless, the cytosine assignments are taken from the CNDO/2 results because of the absence of any better discriminants.

The lowest-energy ionization band in G is well separated from those of higher-energy. The ionization band which lies in the region 9-12eV is presumed to contain three events because of the observation of three well-defined maxima. Comparison of the plotted UPS data, Figure 14, with that of the calculated results of Figure 15 shows good agreement. The UPS assignments for G are based on CNDO/2 results because of the absence of any better discriminants.

Finally, an over-all comparison of Figures 14 and 15 indicates, at best, only a fair agreement between the two data sets. All the CNDO/2 eigenvalues are too large (in an absolute sense) by at least one eV. The MO order predicted by the CNDO/2 algorithm is correct for U and T, but incorrect for A. And, the observed pattern of ionization energy levels is not satisfactorily reproduced by computation. There is some concern, therefore, that the MO ordering predicted for C and G may be incorrect — particularly for I(3) and I(4) of G. Further experimental data is required in order to verify these assignments.

G. β-CAROTENE

The UPS of β-carotene (βC) is presented in Figure 16. Its
Figure 16. The He I photoelectron spectrum of \(\beta\)-carotene. The sharp spikes are due to the Xe and Ar reference gases.
IONIZATION ENERGY (eV)

COUNT RATE

β-CAROTENE
Ionization energies are listed in Table 1. Since $\beta$C is not a rigid molecule, it can assume many conformations. The effect of this conformational multiplicity on the photoelectron spectrum probably consists of a general "smearing" of the ionization bands about some average value. The adiabatic ionization energy thus becomes nebulous since it refers to the unknown conformation of lowest energy.

The spectrum may be subdivided into lower- and higher-energy regions with a boundary at $\sim$9eV. The low-energy region, which is the region of most interest, contains three distinct maxima. Since no single ionization event stands in isolation in the UPS spectrum of $\beta$C, relative band area considerations may not be used. Hence, the actual number of events in the low-energy region can only be guessed, but three is certainly the lower limit. Hückel calculations are of no help in this regard since the eigenvalue spectrum cannot be partitioned into any obvious lower- and higher-energy sets.

The low-energy tail --- $\sim$6.5eV to the more or less definite shoulder at 7.2eV --- can be attributed to conformational "smearing". If this supposition be correct, it suggests that the effects of conformational smearing are not major in that the separate transitions by and large maintain their integrity.
III. DISCUSSION

We will now investigate the correlation of the UPS data obtained for these biochemicals with the Pullman K index (which is obtained from simple Hückel calculations). The theoretical value of the ionization energy is expressed as

\[ I = a + k\beta \]

where \( I \) is the ionization energy, \( a \) is the coulomb integral, \( \beta \) is the resonance integral and \( k \) is the coefficient of \( \beta \)(the Pullman index). Since, in a given series of related molecules \( a \) and \( \beta \) are constants, it is the value of \( k \) which determines the MO ordering in the individual molecules. Furthermore, since the lowest ionization energy is a direct measure of electron-donor ability, the \( k \) index of the highest occupied MO provides a relative ordering parameter for electron-donor capability (i.e., Lewis base strength) for different molecules.

The vertical ionization energies (UPS) and Hückel coefficients, \( k \), are tabulated in Table 2 and plotted in Figure 17. The best least squares regression line is also shown and, for comparison purposes, we also include a reference line for some aromatic hydrocarbons. The least squares line for the biochemicals was calculated using the vertical ionization energy of the highest-occupied \( \pi \) MO.

The lowest ionization energies of BA and pyrimidine involve removal of an \( n \) electron. These energies are denoted in Figure 17 by open circles. For \( \beta \)C we also plot two points: \( I(\pi)_{\text{vertical}} \)
TABLE 2

DATA PLOTTED IN FIGURE 17 FOR THE COMPARISON OF THE HÜCKEL k PARAMETER (a) AND THE MEASURED IONIZATION ENERGIES FROM PHOTOELECTRON SPECTROSCOPY

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>HOMO k coefficient (a) from Hückel expression $E = \alpha + k\beta$</th>
<th>HOMO Vertical Ionization energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purine (Pu)</td>
<td>0.69</td>
<td>9.52 (b)</td>
</tr>
<tr>
<td>Pyrimidine (Py)</td>
<td>1.06</td>
<td>9.7 (n) (c)</td>
</tr>
<tr>
<td>Adenine (A)</td>
<td>0.49</td>
<td>8.48 (d)</td>
</tr>
<tr>
<td>Guanine (G)</td>
<td>0.31</td>
<td>8.30</td>
</tr>
<tr>
<td>Cytosine (C)</td>
<td>0.60</td>
<td>8.82</td>
</tr>
<tr>
<td>Thymine (T)</td>
<td>0.51</td>
<td>9.20 (e)</td>
</tr>
<tr>
<td>Uracil (U)</td>
<td>0.60</td>
<td>9.60 (e)</td>
</tr>
<tr>
<td>Hypoxanthine (HX)</td>
<td>0.40</td>
<td>8.87</td>
</tr>
<tr>
<td>Xanthine (X)</td>
<td>0.40</td>
<td>8.85</td>
</tr>
<tr>
<td>Uric Acid (UA)</td>
<td>0.17</td>
<td>8.55</td>
</tr>
<tr>
<td>β-Carotene (βC)</td>
<td>0.08</td>
<td>7.65</td>
</tr>
<tr>
<td>Barbituric Acid (BA)</td>
<td>1.03</td>
<td>10.40 (n)</td>
</tr>
<tr>
<td>Menadione (K₃)</td>
<td>0.92</td>
<td>9.51</td>
</tr>
<tr>
<td>2,4-Dinitrophenol (DNP)</td>
<td>0.84</td>
<td>9.85</td>
</tr>
<tr>
<td>Nicotinic Acid (NA)</td>
<td>1.01 (f)</td>
<td>10.0</td>
</tr>
<tr>
<td>Nicotinamide (N)</td>
<td>1.00 (f)</td>
<td>9.85</td>
</tr>
</tbody>
</table>
FOOTNOTES TO TABLE 2


\(^f\) Calculated using the Hückel parameters listed in reference (a).

\(^g\) HOMO is an oxygen lone pair, \(n\), orbital, not a \(\pi\) MO.
Figure 17. Plot of vertical $\pi$ ionization energies vs. Hückel $k$ coefficients\textsuperscript{14} for the biochemicals listed in Table 2.

The solid line obeying the equation $I = 7.6 + 2.7k$ is the best least squares linear regression for the points indicated by solid circles and the open square for $\beta$C. Similar data for some aromatic hydrocarbons\textsuperscript{28} is also plotted. The solid square for $\beta$C was not used in obtaining the best least square linear regression (dashed line) for the unsaturated hydrocarbons.
VERTICAL $I(\pi)$, eV

$V = 7.6 + 2.7 k$

$V = 6.0 + 3.2 k$

Hückel coefficients, $k$
denoted by an open square while $I(\pi)_{\text{adiabatic}}$ is denoted by a solid square. The vertical and adiabatic transitions for the reference hydrocarbons are usually coincident, but, as is clearly evident in Figure 17, this is certainly not true of $\beta$-carotene.

Several observations concerning Figure 17 are pertinent:

---Firstly, despite the existence of some scatter of points, the biomolecule regression line provides a remarkable vindication of the Pullman attitudes.

---Secondly, the biomolecule regression line lies significantly higher than that of the aromatic hydrocarbons. This, of course, is expected: The values of $|\alpha|$ for nitrogen and oxygen are expected to be larger than that of carbon. Similar regression lines are also available for other series of unsaturated hydrocarbons. Eland, for example, found

$$I = 6.37 + 2.70k$$

for a hydrocarbon set consisting of naphthalene, azulene, biphenylene, indene and biphenyl; and Schmidt recently found

$$I = 5.652 + 3.214k$$

for a very extensive set consisting of 61 hydrocarbons. The Eland and Schmidt lines encompass the hydrocarbon line of Figure 17 and all three of these lines lie considerably lower than the biomolecule line.

---Thirdly, although the HOMO and therefore $I(1)$ is of $\pi$ type in most cases, the HOMO of BA (and possibly NA and nicotinamide) is of $n$ type. In these cases, frontier MO considerations
based on the supposition that $I(1) = I(\pi)$ is wrong (may be wrong).

The importance of the UPS data itself does not reside in any vindication of the Pullman attitudes which it might provide. The UPS data replace computed values and also provide an absolute scaling of electron-donor capability (of which $I(1)$ is a direct measure). In addition, these data provide the means for a more meaningful parametrization of semi-empirical models which, in turn, can be used to compute ionization energies for biomolecules for which UPS data is either unavailable or unobtainable.

A better parametrization of Hückel type calculations would be exceedingly useful. The large size of most biological molecules suggests that the Hückel approach may be the most efficient way to generate qualitative trends for such molecules. The use of such an empirically parametrized model for $\pi$ MO's, plus considerations such as those of Chapter 1 for the carbonyl lone pair orbitals, may be a useful approach to the study of larger biochemicals.

Electron donor and acceptor characteristics are at the very heart of biochemical processes $^{14,30,31}$. Knowledge of the absolute magnitudes of such quantities is very important. Measured electron affinities are still rare and, for biochemicals, almost non-existant $^{32}$. The ionization energy of the HOMO is a direct measure of the electron donor ability of a molecule. Figure 18 pictorially summarizes the absolute and relative (to each other) electron donor characteristics for most biochemicals so far investigated by the UPS method. This figure is the experimental counterpart of a theoretical diagram first presented by Pullman and it graphically demonstrates the power of the UPS technique.
Figure 18. Scale of electron-donor characteristics from UPS data. Ionization energy (eV) is plotted down the center of the chart. Abbreviations are: BC for β-carotene, Caff. for caffeine, G for guanine, A for adenine, UA for uric acid, C for cytosine, X for xanthine, HX for hypoxanthine, T for thymine, K₃ for menadione (vitamin K₃), BiAc for biacetyl, Val. for l-valine, U for uracil, Leu. for l-leucine, Ile. for l-isoleucine, P for pyruvamide, Ala. for l-alanine, N for nicotinamide, DNP for 2,4-dinitrophenol, DHU for dihydrouracil, NA for nicotinic acid, Urea for urea, BA for barbituric acid, PA for pyruvic acid, Glyoxal for glyoxal and PBA for parabanic acid.
IV. SUMMARY

This work is concerned with generating UPS data for biological molecules and assigning the resulting ionization energies. The ionization potential data were then used to gauge the "goodness" of the Pullman\textsuperscript{14} quantum chemical approach to relative acid/base characters of large biological molecules. Additionally, an absolute scale of electron-donor capability is provided for those biochemicals studied by the UPS method.
REFERENCES


17. The term "resolution", as used here, means the full width at half height (i.e., "half width") of the Xe or Ar $^2P_{3/2}$ ionization band. Most investigators refer this term to the Ar band since it is slightly narrower than the Xe band. Better resolution is implied by smaller half widths.
22. The Huckel calculations on nicotinic acid and nicotinamide were done using the parametrization listed in reference 14.
23. The MO computer programs were obtained from the Quantum Chemical Program Exchange and are listed as QCPE-141; CNDO/2 and QCPE-174; CNDO/s-CI.
25. S. Abdulnur, University of New Orleans, private communication. The geometrical parameters used are the following: For A and U -- K. Tornita, L. Katz and A. Rich, *J. Mol. Biol.*, 30, 545 (1967); For T, the U geometry was used and a methyl group was added in the 5-position using standard bond lengths and angles;
26. The constancy of $\alpha$ and $\beta$ is, of course, merely approximate. One of the objectives of this work was to test the validity of this assumed constancy. For the $k$ index to have any validity, the constancy of $\alpha$ and $\beta$ must be assured.

27. A Lewis base is defined as an electron pair donor; a Lewis acid is defined as an electron pair acceptor.


SELECTED BIBLIOGRAPHY


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PHOTOELECTRON SPECTROSCOPY OF CARBONYLs. 1,4-BENZOQUINONES*†

by

D. Dougherty and S. P. McGlynn

The Coates Chemical Laboratories
The Louisiana State University
Baton Rouge, Louisiana 70803

ABSTRACT

HeI photoelectron spectra have been obtained for 1,4-benzoquinone (PBQ) and some selected derivatives. A correlative study, which is based on the vibronic characteristics of the various ionization events and on the differential sensitivities of these events to chemical substitution (usually methylation, fluorination or chlorination) on the benzenoid ring, leads to an MO assignment for the low-energy ionization regime. The assignment for PBQ, in order of decreasing MO energy, is $n^- > n^+_z > \pi > n^-_x$; that for tetrafluoro-1,4-benzoquinone (TFFBQ) is $n^+_z > n^- > \pi > n^-_x$. The perfluoro effect on PBQ induces shifts of the $n$ orbitals which are approximately $10\text{eV}$. The perfluoro shifts of the $\pi$ orbitals are somewhat smaller than those of the $n$ orbitals. CND0/2 computations provide uniformly poor agreement with the experimental data and retain no assignment utility unless used in a perturbative sense.

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†Other papers in this series include:
INTRODUCTION

The topmost, filled molecular orbitals (MO's) of 1,4-benzoquinone (p-benzoquinone or PBQ) consist of two "lone pair" n MO's and two "delocalized" π MO's. These four MO's as calculated using the CNDO/2 algorithm, are shown in Figure 1. The ± subscripting on n refers to the phasing of the 2p\text{y} AO's on the two oxygen atoms. The subscript on π\text{π} (Read: "pi circle plus") denotes the phasing of the carbon-carbon double bonds and implies that the MO has significant π amplitude on the oxygen centers. The meaning of the π\text{π} notation is self-evident.

The HeI photoelectron spectra (UPS) of PBQ and several of its derivatives have been reported. Turner and coworkers have assigned the two n ionization events to the first UPS band in the 10.0-10.5 eV region (See Figure 2). Unfortunately, they cited no reasons for this assignment. Brundle and coworkers, during the course of their investigation of the "perfluoro effect", made a tentative assignment of the UPS of both PBQ and tetrafluoro-1,4-benzoquinone (TFPBQ). These latter assignments for PBQ, cited, per Koopmans' theorem, in an MO energy basis, are: n\text{π}^+ > π\text{π}(\pi\text{π}) > π\text{π}(\pi\text{π}) > n\text{π}^-. The corresponding assignments for TFPBQ imply that the perfluoro effect shifts the n MO's to higher binding energy by ~5 eV -- an amount which is clearly too large.

Cowan and coworkers performed extended Hückel calculations on PBQ and assigned the MO's in the 10-11.5 eV UPS region as n\text{π} > π\text{π}(\pi\text{π}) > n\text{π}^+ > π\text{π}(\pi\text{π}). On this basis, the experimental splitting Δn = n\text{π} - n\text{π}^+ is 0.9 eV for PBQ.

Kobayashi reported the UPS for PBQ, toluquinone (TQ) and 2,5-dimethyl-1,4-benzoquinone (25DMFBQ). On the basis of CNDO/2 calculations and certain empirical judgements, Kobayashi concluded that the MO order for PBQ was that obtained.
by Cowan et al. The net result of these last two works is that semi-empirical calculations of both the extended Hückel and CNDO/2 type produce an identical MO order for PBQ.

The purpose of the present work is to make an empirical assignment of the UPS of PBQ. Towards this end, we have studied the photoelectron spectra of PBQ and certain of its derivatives. The vibronic structure of PES bands and substitution effects, particularly those produced by ring methylation, are used to correlate the PES bands of different molecules. MO calculations are used sparingly and only in a perturbative sense: The electron densities on the various atom centers of PBQ, for example, may suggest that certain differential effects will be produced by substitutions of different types.

**EXPERIMENTAL**

The He I photoelectron spectra of PBQ, TFPBQ, 25DMPBQ, tetramethyl-1,4-benzoquinone (TMBQ), tetrachloro-1,4-benzoquinone (TCfPBQ), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DCJCNPBQ), 1,2,4,5-tetrachlorobenzene (TCBz) and hexachlorobenzene (HCJBz) were obtained on a Perkin-Elmer PS-18 photoelectron spectrometer. Resolution was 25meV or better at the start of each spectral run. Xe and Ar were used as internal standards for calibration. The samples were obtained from commercial sources and were purified by vacuum sublimation. The temperature during each spectral run was maintained constant to within ±2°C for those compounds that required heating to obtain enough vapor pressure to record a spectrum.

Semi-empirical quantum chemical calculations were performed using the CNDO/2 routine. Geometrical parameters were taken from electron diffraction data for PBQ and benzene and from crystallographic data for 25DMPBQ, TMBQ,
TGjTBQ, TCjBz and HGjBz. The geometrical parameters used for TFPBQ, 2,5-
difluoro-1,4-benzoquinone and DCjDMCPBQ are also listed in reference 7.

RESULTS AND DISCUSSION

A. 1,4-BENZOQUINONE (PBQ), 2,5-DIMETHYL-1,4-BENZOQUINONE (25DMPBQ) AND TETRA-
METHYL-1,4-BENZOQUINONE (TMPBQ)

The UPS of the low-energy region of PBQ, 25DMPBQ and TMPBQ are shown in
Figure 2. The ionization energies, vibrational frequencies and assignments
are listed in Table 1.

The equal cross-sections (i.e., relative band areas) of the two low-energy ioniza­tion bands in PBQ suggest that each band contains two ionization events, that is one
half of the total of four ionization events expected in this region. The origins of
events I(1) and I(3) are quite intense and sharp and, as expected, the accompanying
vibronic transitions are of much lower intensity. The second transition within
each band is more diffuse: I(2) is somewhat structured and possesses a de­
finitive vertical transition at 10.29eV, while I(4) is unstructured and partially
hidden under I(3).

Inspection of Figure 1 suggests that methylation of PBQ will destabilize
the \( \pi \) orbitals, particularly \( \pi \), more than the \( \sigma \) orbitals, since the methyl­
ation occurs directly onto the carbon-carbon double bonds. The two bands
comprising the low-energy region of PBQ converge as one proceeds toward TMPBQ.
The decrease PBQ \( \rightarrow \) DMPBQ is \( \Delta \nu_{\pi} = 0.2eV \) and DMPBQ \( \rightarrow \) TMPBQ is \( \Delta \nu_{\pi} = 0.2eV \),
where \( \Delta \nu_{\pi} \) is the total spectral half-width of any spectrum of Figure 2. This
observation suggests that the two \( \pi \) orbital ionization events are contained
in the second UPS band (i.e., that I(3) and I(4) of PBQ are I(\( \pi \)) events).

The vibrational structure attributed to I(3) in PBQ is retained in I(4)
TABLE 1

VERTICAL IONIZATION ENERGIES (eV)\(^a\) OF 1,4-BENZOQUINONE, 2,5-DIMETHYL-1,4-BENZOQUINONE, TETRAMETHYL-1,4-BENZOQUINONE AND TETRAFLUORO-1,4-BENZOQUINONE

<table>
<thead>
<tr>
<th>Compound</th>
<th>I(1)</th>
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<td>(n_+)</td>
<td>(\pi_\sigma)</td>
<td>(\pi_-)</td>
</tr>
<tr>
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<td>(b_{3g})</td>
<td>(b_{2u})</td>
<td>(b_{3u})</td>
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<td>(\pi_-) &amp; (n_+)</td>
<td>(\pi_\sigma)</td>
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<td>(\gamma(C_{2v}))</td>
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<td>(b_u)</td>
<td>(a_u)</td>
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<td>(n_-)</td>
<td>(\pi_-)</td>
<td>(\pi_\sigma)</td>
</tr>
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<td>(\gamma(D_{2h}))</td>
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\(^a\)All ionization events listed are ±0.05eV unless otherwise indicated. The \(\gamma\) (point group) symbols refer to MO symmetries; the MO assignments are empirical and are largely based on the orbital pictures of Figure 1.

\(^b\)The question mark denotes our uncertainty as to whether the peak at 11.4eV is either vibrational or the vertical component of the \(\pi_-\) ionization event.
of both 25DMPBQ and TMPBQ, and provides an unambiguous correlation of these ionization events. If we retain our initial assumption (i.e., that both the π ionizations are contained in the second UPS band of PBQ), the inversion of orbital ordering which is suggested by the spectral data of Figure 2 must originate in the π⁻ orbital of Figure 1: Methylation must cause a larger destabilization of π⁻ than π⁺ because of the larger MO coefficients of the former on the centers of substitution.

The Δn/Δn⁺ orbital energy splitting, Δn, can be estimated from that observed in the saturated analog of PBQ (i.e., 1,4-cyclohexanediol) for which Δn = 0.15eV. In any event, the Δn value in PBQ should not be larger than the 0.6 to 0.7eV splitting found in 2,2,4,4-tetramethyl-1,3-cyclobutanedione (TMCBD). Indeed, the value Δn = 0.3eV for I(2) - I(1) in PBQ seems to be quite reasonable.

The band shapes in PBQ, if I(1) and I(2) are assigned as the π orbital ionization events, match those for TMCBD. In PBQ and TMCBD, the I(1) events exhibit a coincidence of adiabatic and vertical transitions, and similar vibrational structures. The I(2) events of PBQ and TMCBD are more nearly Gaussian, the vertical and adiabatic transitions being relatively well separated.

The methylation of PBQ to yield 25DMPBQ causes I(2) and I(3) of 25DMPBQ to meld into an unresolved feature. Since I(1) and I(4) of 25DMPBQ are uniquely correlatable, on the basis of vibronic structure, with I(1) and I(3), respectively, of PBQ, it follows that I(2) and I(3) of 25DMPBQ are related to I(2) and I(4) of PBQ. The two π MO's of 25DMPBQ are destabilized relative to PBQ, π⁻ being more affected than π⁺, with the result that Δn increases to ~0.5eV. This observation accords with conclusions drawn from Figure 1: π⁺ has less
electron density on the carbon skeleton and, hence, it should be influenced less by methylation than $n_-$.

All four ionization events are resolved in the UPS of TMPBQ. Since methylation has increased $\delta n$ to $\approx 0.5$ eV in 25DMPBQ, and since methylation should also destabilize $\pi_-$ more than either $n_+$ or $n_-$, the ionization events I(2) and I(3) of TMPBQ are best assigned as $\pi_-$ and $n_+$, respectively. Thus, on proceeding from PBQ to TMPBQ, the $\pi_-$ orbital has gone from the most-tightly bound MO to the second most-loosely bound MO of the set.

Further evidence in support of these assignments is provided by the additive effects of methylation. The additive effect of methylation on the $n$ orbital ionization energies of monocarbonyls is well documented. That such additivity should also be evidenced by such a symmetrical molecule as PBQ is not unreasonable. The $\Delta I(n)$ values for PBQ, TQ, 25DMPBQ and TMPBQ are shown in Figure 3. The data of Kobayashi for toluquinone were used in constructing Figure 3 (Note, however, that we have changed Kobayashi's assignments to accord with our own predilections). The $\Delta I(n)$ values remain reasonably constant: $\Delta I(\pi_-)$ decreases whereas $\Delta I(n_+)$ increases slightly with progressive methylation.

The variations of $I(\pi_-)$ and $I(n_+)$ are also included in Figure 3. Although certainly not additive, the behavior of $\Delta I(\pi_-)$ is readily rationalized: Methylation decreases the LCAO coefficients on carbon atoms by providing another center, the $\text{-CH}_3$ group, on which the charge can "spread out", and by reducing the symmetry and, hence, allowing $\pi_-$ density to appear on the carbonyl units. The resulting decrease in electron density on the remaining unmethylated carbon centers parallels, in a qualitative way, the observed decrease in $\Delta I(\pi_-)$. The behavior of $\Delta I(n_+)$ is puzzling: That monomethylation should produce a small effect, whereas substitution of a second methyl group should produce a much
larger effect is not inherent in the $\pi_{\sigma}$ MO diagram of Figure 1. If, however, we neglect the TQ data and fixate on the series PBQ → 25DMPBQ → TMPBQ, it is found that $\Delta I(\pi_{\sigma})$ is roughly additive.

Trommsdorff$^{10}$ has also commented on the magnitude of the $n$ orbital splitting in PBQ. Trommsdorff analyzed the VIS/UV absorption spectra of PBQ and derivatives. He concluded that a value $\Delta n \approx 0.2$eV for PBQ was reasonable, and he suggested that the previous assignment, for which $\Delta n \approx 0.9$eV, should be reconsidered.

Our conclusions concerning PBQ, 25DMPBQ and TMPBQ are presented in the correlation diagram of Figure 4. The results of the CNDO/2 MO calculations are shown in Figure 5. It is interesting that, whereas the calculated MO energies are particularly poor, the relative changes in orbital energies caused by substitution are more faithfully represented. In particular, the $\pi$ MO is shown to be the most strongly affected by methylation.

B. TETRAFLUORO-1,4-BENZOQUINONE (TFPBQ)

The UPS of TFPBQ is shown in Figure 6. It is quite different from the UPS of Figure 2. This difference is probably responsible for the dearth of comment on this molecule. The sole assignment available is that of Brundle et al.$^{3}$, which relies on a perfluoro shift of $\Delta I(n) \approx 5$eV -- by far the largest such shift ever suggested.

With the availability of reasonable, empirical assignments for PBQ and certain of its methyl derivatives, a starting point exists for the analysis of the UPS of TFPBQ. Our analysis of this spectrum is vested in three observations: 1) Vibronic similarity of the I(4) band of TFPBQ with the $\pi_{\sigma}$ bands of PBQ, 25DMPBQ and TMPBQ. 2) Orbital energy shift patterns suggested
by CNDO/2 computations and based on the empirical assignment of PBQ. 3) Band shape comparisons with TCgPBQ and DC&DGPNPBQ.

The UPS of the low-energy regions of TFPBQ, TCgPBQ and DC&DGPNPBQ are presented in Figure 6. The ionization energies and vibrational frequencies are listed in Table 1 for TFPBQ and in Table 2 for TCgPBQ and DC&DGPNPBQ. The most noticeable feature of the UPS of TFPBQ is the vibrational progression of \( \sim 1700 \text{cm}^{-1} \) beginning at 11.53eV. We identify this feature with the \( \pi \) band of PBQ. This done, considerations of the relative cross-sections (i.e., band areas) suggest that four ionization events are contained in the low-energy region of TFPBQ. The structures at 10.76 and 10.96eV constitute one single electronic ionization event and are of interest because of the band shape, which is unusual and without precedent in either PBQ or the methylated PBQ's. An origin with a band shape reminiscent of \( n_0 \) of PBQ appears at 11.21eV, and is so assigned. The remaining (or fourth) ionization event may be associated with the structure at 11.42eV: While this structure may well be a vibrionic feature built on the 11.21eV origin, it is important to note that relative band-area considerations do indicate the presence of two ionization events in the 11.2-11.4eV range.

Some CNDO/2 results for PBQ, 25DMPBQ, TMPBQ, 2,5-difluoro-1,4-benzoquinone and TFPBQ are presented in Figure 5. Since we know that the relative MO order produced by the CNDO/2 algorithm is incorrect for the first four MO's, as are the \( \Delta n \) and \( \Delta \pi \) splittings within each molecule, we will limit our use of Figure 5 to consideration of trends in the MO energies caused by substitution. For PBQ and its methyl derivatives, both the computational and experimental results indicate that all four orbitals are destabilized by methylation -- the \( n_0 \) orbital being most sensitive. Fluorination is expected to stabilize all four orbitals. This expectation is borne out by computation (See Figure 5) for \( n_0, \pi_0 \) and \( n_\pi \).
<table>
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<sup>a</sup> Vertical ionization energies (eV) of tetrachloro-1,4-benzoquinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 1,2,4,5-tetrachlorobenzene and hexachlorobenzene.
TABLE 2 (continued)

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All ionization energies listed are ±0.05eV unless otherwise indicated. The $\gamma$(point group) symbols are MO symmetry labels; the MO assignments are empirical and are based on MO pictures of Figure 1. The heavy mixing of the Cl "lone-pair" orbitals with the PBQ orbitals renders the designations $\pi_3$, $\pi^*_3$, $\pi_2$, and $\pi^*_2$ only approximately descriptive of the orbital composition in the chlorinated derivatives.

The symmetry axes devolve from $D_{2h} \rightarrow C_{2v}$ as $x \rightarrow x$, $y \rightarrow z$ and $z \rightarrow y$.

The 10.76eV peak contains a shoulder at 10.73eV. It seems apparent that one of these two entities is a vibrational member built on the 10.58eV origin; thus, the vibrational listing as either 1200cm$^{-1}$ or 1450cm$^{-1}$.

This value is one vibrational quantum of energy, 1130cm$^{-1}$, higher than the value 9.06eV reported by Streets and Caesar.12

This value is (1210-320)cm$^{-1}$ higher in energy than the 9.20eV value reported by Streets and Caesar.12.
but not for $\pi_-$. If we suppose that the computed pattern of shifts is valid, a comparison of the observed spectra of TFPBQ (See Figures 4 and 6) and PBQ (See Figure 2) indicates that both the $\pi_-$ and $\pi_0$ events, and the $n_-$ and $n_+$ events, have undergone energy inversions.

A comment on the use of the MO calculations is in order. Since the empirical correlations are fairly straightforward for PBQ, 25DMPBQ and TMPBQ, and, to some extent, even for TFPBQ, we have chosen to invest primacy in them. The CNDO/2 results possess little utility but, where they do, they support the empirical assignments. We maintain that the residual utility of the CNDO/2 results consists only of the relative energy shifts between different molecules and not of the MO order or spacings within any one molecule. The one obvious exception to this perturbative use of CNDO/2 results is provided by the $\pi_-$ orbital in the series PBQ $\rightarrow$ 25DFPBQ $\rightarrow$ TFPBQ: The $\pi_-$ orbital does not destabilize upon fluorination; it simply stabilizes to a lesser extent than does $\pi_0$ (See Figure 4).

The band shape of the lowest-energy ionization event in TFPBQ has no precedent in any UPS spectrum discussed so far in this work. Consequently, we have investigated the UPS of TCtPBQ and DCtDCNPBQ. The assignments for the two latter molecules will be presented in Section C. Here, we content ourselves with the observation that the $n_-$ and $n_+$ orbital ionization events correspond, respectively, to I(1) and I(2) in both TCtPBQ and DCtDCNPBQ. Very little can be learned from the band shape in TCtPBQ. The spectrum of DCtDCNPBQ, however, provides clear vibronic structure for the $n_+$ event: Two
peaks occur at ~10.76 and 10.9eV, the high intensity of the 10.76eV peak being due not only to the \( \text{n}^- \) event but also to a vibrational member associated with the \( \text{n}^- \) origin at 10.58eV. (Note that even though 10.76eV is the band maximum, a quite definite structure also occurs at 10.73eV. Which of these two bands is most properly associable with the 10.58 origin is not determinable.)

C. TETRACHLORO-1,4-BENZOQUINONE (TC\textsubscript{4}PBQ) AND 2,3-DICHLORO-5,6-DICYANO-1,4-BENZOQUINONE (DC\textsubscript{5}DCNPBQ).

The full HeI UPS of TC\textsubscript{4}PBQ and DC\textsubscript{5}DCNPBQ are shown in Figure 7. Cross-section considerations, based on the assumption that the band at 11.8eV in TC\textsubscript{4}PBQ represents a single orbital ionization event, indicate that two MO ionization events occur in the band at ~10eV, and that four such events occur in the band between 10.5 and 11eV. For DC\textsubscript{5}DCNPBQ, two MO ionization events are expected to lie within the structured band between 10.3 and 10.8eV, three in the band from 10.9-12.0eV and one under the band at 12.4eV. Obviously, the low-energy set of orbitals for these molecules consists of more than the two \( \text{n} \) and two \( \pi \) MO's pertinent for PBQ and TFPBQ.

Another problem is provided by the heavy mixing of the chlorine lone pairs -- both \( \text{n} \) and \( \pi \) type -- with the low-energy MO basis set of PBQ. We will continue to use the \( \text{n} \) and \( \pi \) orbital labels pertinent to PBQ and, as necessary, we will augment this set with chlorine \( \text{n} \) and \( \pi \) lone pair MO's. However, this is merely a convenience tactic which, we hope, does not cause confusion. The mixing of the low-energy MO set of PBQ with CH\textsubscript{3}, F and C \( \equiv \text{N} \) orbitals is more or less negligible. Thus, the \( \text{n}^- \), \( \text{n}^+ \), \( \pi^\text{\textbeta} \) and \( \pi^- \) nomenclature for PBQ, methylated PBQ's and TFPBQ is totally meaningful. In particular, the lack of mixing of the C \( \equiv \text{N} \) orbitals of DC\textsubscript{5}DCNPBQ with the low-energy PBQ set...
makes this molecule akin to a 2,3-dichlorinated PBQ, at least insofar as the lower-energy ionization events are concerned. Indeed, the highly electronegative nature of the C = N group should merely shift the low-energy MO ionization events of 2,3-DCfPBQ to higher energy.

No clear empirical correlations of the UPS spectra of DCfDCNPBQ or TCfPBQ with that of PBQ is feasible. Consequently, in order to better comprehend chlorination effects, we have investigated the series benzene → 1,2,4,5-tetrachlorobenzene (TCfBz) → hexachlorobenzene (HCfBz). The topmost MO of benzene (D_{5h}) and HCfBz (approximately D_{5h}) are formally degenerate. The UPS of benzene is known. The HeI UPS of TCfBz and HCfBz are shown in Figure 8. The lowest-energy ionization(s) in these molecules (9-11eV) is(are) known to be π and to correspond to the e_{1g} MO of benzene, now heavily mixed with chlorine π type lone-pair orbitals.

The correspondence of interest in these molecules is the effect of chlorination on the low-energy π orbitals. The assumption is made that the effect of chlorination on the low-energy π MO's of benzene -- whether stabilization, destabilization or a null effect -- will be mimicked by similar effects of chlorination on PBQ. The empirical correlations of interest for the benzene series and the PBQ series are presented in Figure 9. The ionization data for TCfBz and HCfBz are listed in Table 2.

The correlations of Figure 9 are quite clear. The lowest-energy ionization event of benzene and HCfBz are essentially identical. Additionally, two events, undoubtedly two Cl lone-pair ionization events, occur at ~11eV in HCfBz. Consequently, the correspondences between PBQ and TCfPBQ become almost self-evident. The further correlation with the DCfDCNPBQ data merely confirms the assignments. The very electronegative C = N groups, while contributing no
low-energy ionization events of their own, delete one of the two "extra" ionizations expected for TC\textsuperscript{2}PBQ. The chlorine origin of the extra ionization events is thus demonstrated.

CND\textsuperscript{2}O/2 MO calculations were also performed on this same set of molecules. No correlation of the calculated and experimental data was obvious. The disparity of the two data sets was quite extreme. Hence, we can offer no computational support for the empirical correlations of TC\textsuperscript{2}PBQ and DC\textsuperscript{2}DCNPBQ.

**CONCLUSIONS AND REMARKS**

The primary conclusions of this work are contained in the UPS data and assignments presented in Table 1 and 2. That these assignments are empirical is their greatest strength. It appears that parametrization of the CND\textsuperscript{2}O/2 program is totally inadequate for PBQ and all of its derivatives.

From the absorption spectroscopic work of Trommsdorff\textsuperscript{10}, we know the following: i), that the $^1\Gamma_{n^-n^+}$ transition occurs at 20,060cm\textsuperscript{-1} and the $^1\Gamma_{n_+n^+}$ transition occurs at 20,315cm\textsuperscript{-1}; and ii), that the exchange term, as measured by the singlet-triplet splitting, is very small, ~200cm\textsuperscript{-1}, for both transitions. The energy splitting of the $n^-/n_+$ orbitals as determined here is 0.30eV, while that for $^1\Gamma_{n_+\pi^*}-^1\Gamma_{n^-\pi^*}$ is 0.03eV. To a first approximation, the 0.27eV difference between the orbital energy split and the optical transition split must be caused by differences of the coulomb integrals, $J_{n_+\pi^*}$ and $J_{n^-\pi^*}$. To be in accord with the experimental data, $J_{n_+\pi^*}$ must be the larger of the two. Indeed, using the CND\textsuperscript{2}O/2 generated LCAO-MO coefficients and a one-center approximation, we found $J_{n_+\pi^*}$ to be larger than $J_{n^-\pi^*}$. Thus, even a calculation at this crude level suggests that the energetic splitting of the $^1\Gamma_{n^-\pi^*}/^1\Gamma_{n_+\pi^*}$ transitions
should be less than that of the $n^-_i/n^+_i$ orbitals, in accord with experimental observations.

This work, therefore, together with that of Trommsdorff, provides a very complete experimental determination of the electronic structure of PBQ. PBQ is a relatively small, very symmetrical molecule which is of considerable biological importance. Ab initio computational efforts, therefore, would appear to be mandatory. Two such efforts, in fact, are available in the literature. Unfortunately, the crystallographic molecular structure used in these computations differs considerably from the more recent electron diffraction structure. Despite this, the agreement of both sets of computed results with the absorption spectroscopic data is very good; however, the ground state MO predictions, namely $\pi^+_0 > n^-_i > \pi^-_i > n^+_i$, are not in accord with photoelectron spectroscopy.

Finally, we re-emphasize that the UPS assignments presented here do not accord with either semi-empirical or ab initio computational results. The discord with semi-empirical results is unfortunate and is undoubtedly correctable by re-parametrization. The discord with the ab initio results may be a function of the non-optimized, minimal basis-set nature of these calculations and the questionable geometry alluded to previously. The calculations by Cederbaum, et al., on formaldehyde suggest, however, that the breakdown of Koopmans' Theorem may be more to blame. Nevertheless, it was this lack of computational support which provided the impetus for a rather complete empirical assignment. The calculated results of the vertical ionization energies for PBQ as per the method of Cederbaum, et al., would be welcome.
REFERENCES

1. The semi-empirical molecular orbital program used was QCPE 141, CND0/2.


8. Part of a dissertation presented to The Louisiana State University, Baton Rouge, Louisiana, by J. L. Meeks.


FIGURE CAPTIONS

Figure 1. Pictorial representations of the four highest-energy occupied MO's of 1,4-benzoquinone (PBQ) as generated by QCPE 141, CNDO/2. The diameter of the circular lobe is proportional to the size of the atomic orbital coefficient.

Figure 2. The expanded-scale HeI photoelectron spectra of 1,4-benzoquinone, 2,5-dimethyl-1,4-benzoquinone and tetramethyl-1,4-benzoquinone. Vibrational spacings indicated on the spectra are listed in Table 1 along with the vertical ionization energies.

Figure 3. Schematic of the ionization-energy differences between corresponding orbitals for 1,4-benzoquinone, toluquinone, 2,5-dimethyl-1,4-benzoquinone and tetramethyl-1,4-benzoquinone. (Note that Kobayashi's assignment for toluquinone has been altered to accord with the interpretation presented here).

Figure 4. UPS correlation diagram for tetramethyl-1,4-benzoquinone, 2,5-dimethyl-1,4-benzoquinone, 1,4-benzoquinone and tetrafluoro-1,4-benzoquinone.

Figure 5. CNDO/2 correlation diagram for tetramethyl-1,4-benzoquinone, 2,5-dimethyl-1,4-benzoquinone, 1,4-benzoquinone, 2,5-difluoro-1,4-benzoquinone and tetrafluoro-1,4-benzoquinone.

Figure 6. The expanded scale HeI photoelectron spectra of tetrafluoro-1,4-benzoquinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and tetrachloro-1,4-benzoquinone. Vibrational spacings indicated on the spectra are listed in Tables 1 and 2 along with the vertical ionization energies.

Figure 7. The HeI photoelectron spectra of tetrachloro-1,4-benzoquinone and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Figure 8. The HeI photoelectron spectra of 1,2,4,5-tetrachlorobenzene and hexachlorobenzene.

Figure 9. Correlation diagram based on UPS data for benzene, tetrachlorobenzene, hexachlorobenzene, tetrachloro-1,4-benzoquinone, 1,4-benzoquinone and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.
MO EIGENVALUES (CNDO/2)(eV)

-15.0  -14.0  -13.0  -12.0

\[ \text{Diagram of MO eigenvalues with various molecular orbitals and structures.} \]
VITA

David Russell Dougherty was born on September 13, 1945, in Enid, Oklahoma, to Russell A. and Arlene B. Dougherty, Jr. He was graduated from Enid High School in May, 1963.

In September of 1963 he entered Phillips University, Enid, Oklahoma, and was graduated with honors in January, 1968 with a B.A. degree. He married the former Sharon Kay Moore in August, 1964, in Enid, Oklahoma. They are the parents of a daughter, Samantha Lea Dougherty, born October 18, 1968, at Williams Air Force Base, Chandler, Arizona. He entered the United States Air Force in April, 1968, and graduated from Undergraduate Pilot Training, Williams Air Force Base, in July, 1969. He was then stationed at Dyess Air Force Base, Abilene, Texas, flying C-130E transport aircraft. While in Abilene he and Sharon were divorced in July, 1970. In August, 1972, he was sent to Southeast Asia where he flew AC-130A gunships out of Ubon Royal Thai Airbase, Thailand. Upon his return to the United States in July, 1973, he separated from the Air Force and received an honorable discharge from active duty. He entered the Louisiana State University at Baton Rouge in August, 1973, and is presently a candidate for the degree of Doctor of Philosophy in Physical Chemistry.

He married the former Jean Logan on November 15, 1976, in Baton Rouge, Louisiana.