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Multiple $n\pi^*$ Transitions in Tetramethyl-1,3-cyclobutanedione. II. Through-Bond Effects

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Abstract: The four singlet $n\pi^*$ transitions observed in the diketone tetramethyl-1,3-cyclobutanedione (TMCBD) have been analyzed theoretically. The interaction of the carbonyls' nonbonding (n) and π antibonding orbitals are discussed qualitatively in terms of "through-space" vs. "through-bond" mechanisms. Through-bond interactions are shown to be the major cause of the large n orbital splitting, confirming the previously observed photoelectron spectroscopic results. The transannular (through-space) interaction of the π antibonding orbitals, a mechanism invoked by earlier workers to explain the TMCBD solution spectrum, is shown to be dominated by a "circumannular" interaction where the π^* orbitals interact with ring carbon-methyl carbon σ orbitals of the correct symmetry. Finally, it is shown that the simple extended Hückel theory gives more satisfactory results for the position, ordering, and spacing of the four $n\pi^*$ states than do the more sophisticated semiempirical CNDO methods, with or without configuration interaction.

I. Introduction

There have been many studies on the interaction of nonbonding electron pairs in diketones. In the preceding paper,[1] we have presented the results of our recent investigation on the low-temperature, single-crystal, polarized absorption spectrum of tetramethyl-1,3-cyclobutanedione (TMCBD). The presence of four clearly resolved electronic singlet $n\pi^*$ transitions was shown and the assignments of these transitions deduced from an analysis of vibrational structure, polarization data, and relative intensities.

In the present paper we have investigated theoretically the interaction between the two carbonyl groups in cyclobutanedione (CBD) and TMCBD. In 1970 Swenson and Hoffmann[2] predicted from extended Hückel theory (EHT) and CNDO/2 calculations that there should be a large "through-bond" interaction between the nonbonding orbitals of certain diketones. Since that time specific diketones have been sought to experimentally test this idea. Because of its relatively accurate prediction of the large n orbital splittings observed in photoelectron spectra of diketones,[3] among other molecules, the "through-bond" mechanism of interaction has been generally accepted. However, the application of this idea to the electronic absorption spectra of diketones has been hindered by experimental difficulties. Problems such as unknown crystal structure, unknown ground state conformation, impurity absorption, and overlapping spectral bands have hindered the precise location of the expected $n\pi^*$ transitions.

The molecule presently under study (TMCBD) does not appear to be beset by these difficulties. Its ground state conformation and crystal structure are well characterized.[4] Its photoelectron spectrum is known and understood.[3] Its infrared and Raman spectra[5] and gas-phase vacuum ultraviolet spectrum[6,7] have been investigated, and the location and assignments of its four $n\pi^*$ transitions are now known.[1]

In this paper, we have chosen to employ the EHT, CNDO/2, and CNDO/S semiempirical molecular orbital methods to investigate the carbonyls' nonbonding orbital interaction and π antibonding orbital interaction. Evidence is presented for the existence of "through-bond" interactions which influence both n and π^* orbital splittings. It is also pointed out that the extended Hückel theory is superior to the CNDO/2 and CNDO/S techniques, with or without configuration interaction, in predicting the energies and relative ordering of the singlet $n\pi^*$ states. Finally, some of the reasons for the EHT's better performance are discussed.

II. Computational Procedures

Calculations were performed using extended Hückel theory (EHT), CNDO/2, and CNDO/S semiempirical methods; both CNDO methods were run with and without configuration interaction (CI). Some of the approximations used in the latter two methods are discussed later. Programs were supplied by QCPE. In our calculations using EHT and CNDO/S techniques, we have investigated both CBD and TMCBD to determine the effect of the methyl groups. The geometry of CBD was taken to coincide with the planar part of TMCBD, as determined by an x-ray structure determination.[4] The C-C bonds are 1.56 Å, the C-O distances 1.20 Å, the C-H distances 1.10 Å, the C-C-C ring angles 90°, and the HCH angles 116°. The conformation of the methyl groups in TMCBD was deduced from the x-ray structure determination. The methyls across the ring and on the same side of the molecular plane are slightly skewed in opposite directions, so that the true molecular point group is D_2, and not D_{2h} as for CBD. For one EHT calculation the methyl groups were chosen eclipsed (across the ring) such

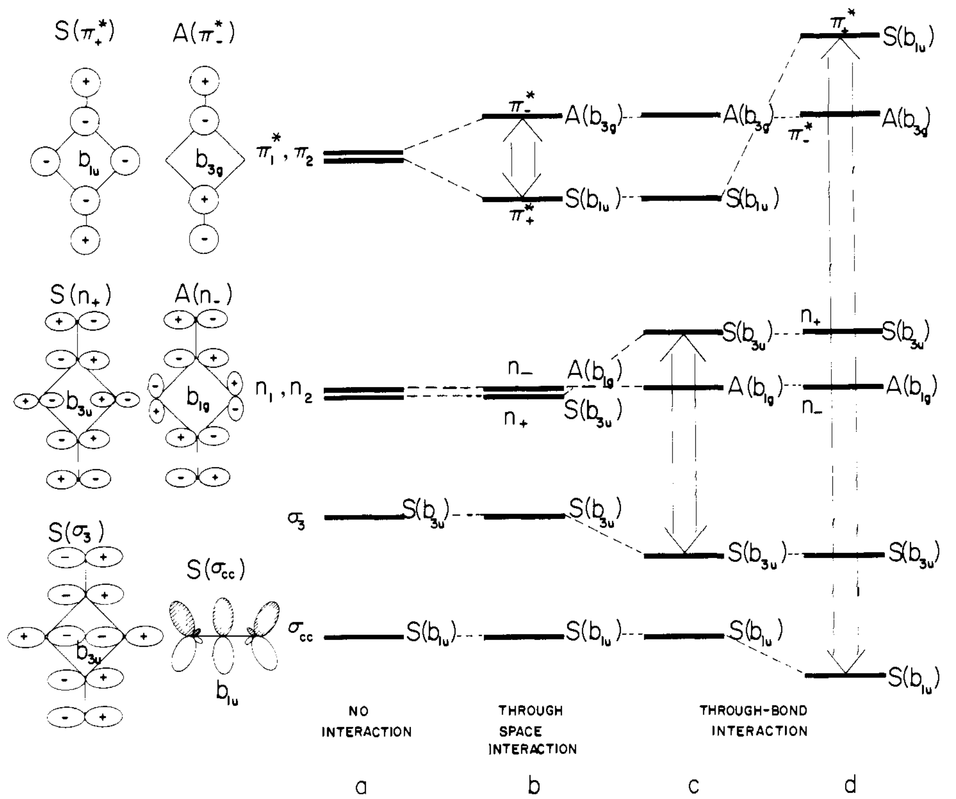

Figure 1. Molecular orbital energy level diagram with (a) no interaction between carbonyls, (b) through-space ("transannular") interaction, (c) in-plane through-bond interaction, and (d) out-of-plane through-bond hyperconjugative ("circumannular") interaction.

that the molecular point group was D_{2h}; no substantial change in the results was noted.

III. Spectral Results

There are four experimental results which are important to this study. First, the relative order observed[1] for the singlet $n\pi^*$ states is ^1A_u ($^1A_2$) < $^1B_{2g}$ (^1B_g) < $^1B_{2g}$ ($^1B_1$) < ^1A_u (^1A_u). In parentheses are designated the true state symmetries in the respective excited state distorted point groups. Secondly, the relative spacing[1] of the transitions is substantial: between $^1B_{2g}$ (^1B_g) and ^1A_u ($^1A_2$), 2989 cm^{-1} (0.371 eV); between $^1B_{2g}$ ($^1B_1$) and $^1B_{2g}$ (^1B_g), 1933 cm^{-1} (0.240 eV); and between ^1A_u (^1A_u) and $^1B_{2g}$ ($^1B_1$), 3024 cm^{-1} (0.375 eV). These energy differences are measured from the apparent band origins. Thirdly, the observed[3] splitting of the n orbitals in TMCBD is 0.7 eV. And finally, the first and third excited electronic states are distorted to a boat-like structure and the second and fourth to a chair-like structure.[1] In each of these distorted structures, the carbonyl carbon attains an out-of-plane pyramidal conformation.

IV. Through-Bond vs. Through-Space Effects

The molecular orbital combinations of the two carbonyl oxygen n orbitals (n_1 and n_2) are:

$$n_+(b_{3u}) = (n_1 + n_2)/\sqrt{2}$$

$$n_-(b_{1g}) = (n_1 - n_2)/\sqrt{2}$$

with the indicated D_{2h} group symmetries. Similar combinations may be formed with the π^* orbitals ($\pi_1{}^*$ and $\pi_2{}^*$):

$$\pi_+{}^*(b_{1u}) = (\pi_1{}^* + \pi_2{}^*)/\sqrt{2}$$

$$\pi_-{}^*(b_{3g}) = (\pi_1{}^* - \pi_2{}^*)/\sqrt{2}$$

Transitions from the filled molecular n orbitals to the empty π^* MO's give rise to four electronic $n\pi^*$ states, two of ^1A_u symmetry and two of $^1B_{2g}$ symmetry. Transitions to all four states are symmetry forbidden in the planar D_{2h} group.

A further understanding of the molecular orbital origin of the $n\pi^*$ transitions can be obtained by consideration of "through-space" vs. "through-bond" effects (see Figure 1). With simple orbital overlap (i.e., "through-space" interaction) between the component orbitals (n_1 and n_2, $\pi_1{}^*$ and $\pi_2{}^*$), an orbital scheme as shown in Figure 1b is expected. This situation, previously discussed by others,[1-4] can account for only two $n\pi^*$ transitions. In Figure 1c, in-plane "through-bond" interaction is included; the $n_+(b_{3u})$ orbital is greatly destabilized as a result of mixing with a lower-lying $\sigma(b_{3u})$ orbital. One would now predict four separate and distinct $n\pi^*$ transitions because of the large splitting between the n_+ and $n_-{}^*$ orbitals and between the $\pi_+{}^*$ and $\pi_-{}^*$ orbitals. However, this scheme also predicts that the lowest excited state will be $^1B_{2g}$, and not ^1A_u as observed. Reversal of the $\pi_+{}^*$ and $\pi_-{}^*$ can be expected (see Figure 1d) if *out-of-plane interaction of the* $\pi_+{}^*(b_{1u})$ orbital with the appropriate linear combinations of the ring carbon–methyl carbon σ orbitals is introduced. There can be no such interaction with the $\pi_-{}^*(b_{3g})$ orbital since it contains a nodal plane through the ring carbons attached to the methyl groups (see Figure 1). Now with the orbital ordering shown in Figure 1d, the observed $n\pi^*$ excited state symmetries of ^1A_u, $^1B_{2g}$, $^1B_{2g}$, and ^1A_u can be understood. The fact that this type of hyperconjugative π–σ around-the-ring ("circumannular") interaction is necessary to explain the observed state ordering indicates its dominance over the simple across-the-ring ("transannular") interaction.

V. Semiempirical Calculations

Although the above qualitative arguments account well for the observations, it is also of interest to determine whether current semiempirical theories are capable of predicting these results. Using the extended Hückel theory (EHT) and the CNDO methods (CNDO/S and CNDO/2 with and without

Table I. Energies of Singlet nπ^* States in CBD and TMCBD

Obsd energies,[d] eV		Calculated Energies, eV					
			CNDO/S[e]			CNDO/2	
	State	EHT[e]	*a*	*b*	*c*	*a*	*b*
^1A_u 3.363	$^1A_u(n_+\pi_-^*)$	2.738 (2.328)	10.811 (10.230)	5.277 (4.962)	3.538 (3.381)	16.297	7.723
$^1B_{2g}$ 3.733	$^1B_{2g}(n_+\pi_+^*)$	3.450 (2.583)	10.800 (10.352)	5.376 (5.180)	3.545 (3.399)	14.713	6.799
$^1B_{2g}$ 3.973	$^1B_{2g}(n_-\pi_-^*)$	3.760 (2.967)	11.529 (10.797)	5.795 (5.371)	7.233 (6.725)	18.602	9.469
^1A_u 4.348	$^1A_u(n_-\pi_+^*)$	4.472 (3.222)	11.519 (10.920)	5.915 (5.597)	7.257 (6.746)	17.018	8.726

[a] $\Delta\epsilon_{ij}$ contribution to the singlet state energy. [b] Singlet state energy, including $-J_{ij} + 2K_{ij}$ contribution. [c] Singlet state energies after configuration interaction for CBD: $\psi_1(^1A_u) = 0.7312\ (n_+\pi_-^*) - 0.6568\ (n_-\pi_+^*) - 0.1673\ (\sigma\pi_+^*)$, $\psi_2(^1A_u) = 0.6811\ (n_+\pi_-^*) + 0.6975\ (n_-\pi_+^*) + 0.2168\ (\sigma\pi_+^*)$, $\psi_1(B_{2g}) = -0.7120\ (n_+\pi_+^*) + 0.6782\ (n_-\pi_-^*) + 0.1623\ (\sigma\pi_-^*)$, $\psi_2(B_{2g}) = 0.7004\ (n_+\pi_+^*) + 0.6794\ (n_-\pi_-^*) + 0.2117\ (\sigma\pi_-^*)$, where the σ orbital is the same one in all four cases above. [d] Origin bands for single crystal tetramethyl-1,3-cyclobutanedione (TMCBD). [e] Values in parentheses are for TMCBD, run in molecular point group D_2, giving A and B_2 states for the nπ^* transitions.

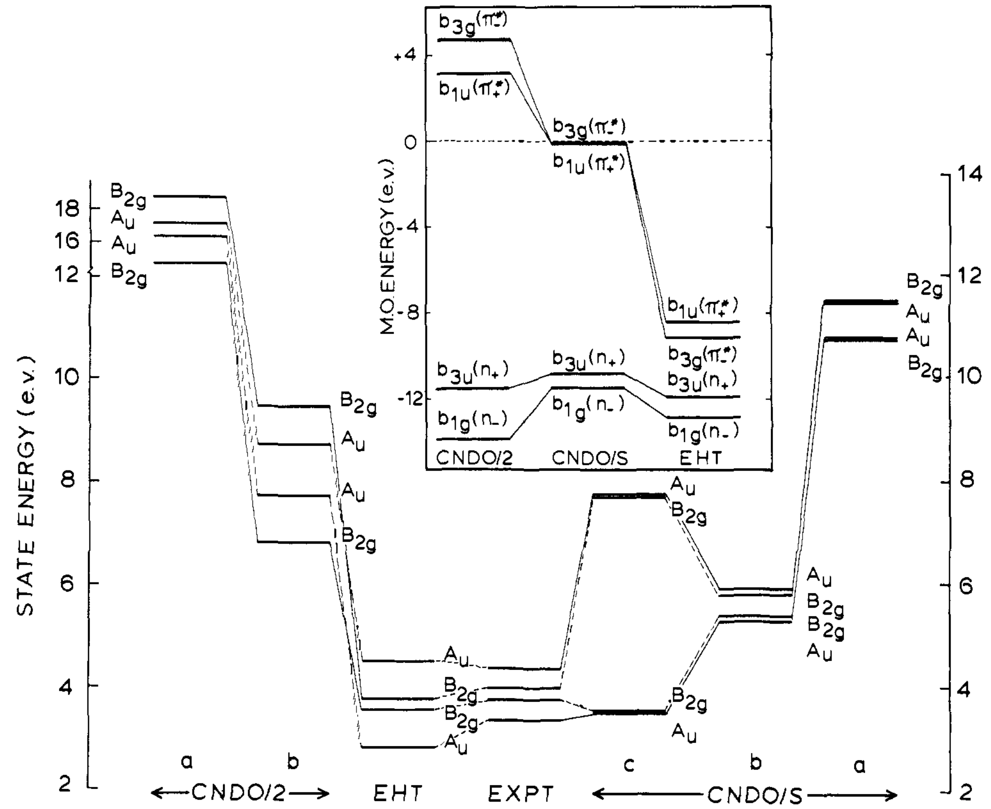

Figure 2. Diagram of energies of the singlet nπ^* states of 1,3-cyclobutanedione. In the CNDO/2 approximation, at the left, column a includes only the $\Delta\epsilon_{ij}$ contribution, whereas column b includes the $\Delta\epsilon_{ij}$, J_{ij}, and K_{ij} contributions. In the CNDO/S approximation, at the right, column a includes only the $\Delta\epsilon_{ij}$ contribution, column b the $\Delta\epsilon_{ij}$ and J_{ij} and K_{ij} contributions, and column c includes configuration interaction. The inset shows the molecular orbital energies of the n and π^* orbitals in each approximation.

CI), we have calculated the positions of the nπ^* excited states in CBD and TMCBD. The results are given in Table I and Figure 2. It can be seen that the EHT results give a more reliable prediction of the position, ordering, and relative spacing of the four nπ^* transitions than do either of the CNDO methods. The CNDO/2 calculation predicts an incorrect ordering of states, both before and after CI, whereas the CNDO/S calculation predicts the experimentally observed ordering, although the spacings are grossly misproportioned and the positions misplaced after CI.

To understand the reason for the success of the EHT calculation compared with the two CNDO schemes and the reasons for the incorrect state ordering predicted by CNDO/2, we have investigated the various contributions to the singlet nπ^* excited state energies in each computational method.

We first briefly review the important approximations in the CNDO methods. The energy involved in a singlet-singlet transition from an occupied molecular orbital (i) to a virtual orbital (j) is given by:[8]

$$E_S{}^{ij} - E_G = \Delta\epsilon_{ij} - J_{ij} + 2K_{ij} \tag{1}$$

Thus the contributions to the energy of the excited singlet are $\Delta\epsilon_{ij}$, the difference in orbital energies ($\epsilon_j - \epsilon_i$), and the molecular coulomb (J_{ij}) and exchange (K_{ij}) integrals. Within the CNDO approximation[9] the latter two electron integrals are given by:

$$J_{ij} = \Sigma_{\mu,\nu} C^2{}_{\mu i} C^2{}_{\nu j} \gamma_{AB} \tag{2}$$

$$K_{ij} = \Sigma_{\mu,\nu} C^*{}_{\mu i} C^*{}_{\mu j} C_{\nu i} C_{\nu j} \gamma_{AB}$$

where the $C_{\mu i}$ represent the ith molecular orbital coefficient for the μth atomic orbital. The γ_{AB} is calculated in the CNDO/2 method[9] using atomic s functions as follows:

$$\gamma_{AB} = \int\int s_A{}^2(1)(1/r_{12}) s_B{}^2(2)\, d\tau_1\, d\tau_2 \tag{3}$$

and evaluated semiempirically in the CNDO/S method using

Table II. Values of γ_{AA} Used by CNDO Methods[13] and Resulting Values of J_{ij} and K_{ij} (Eq 4)[a]

	γ_{AA}(C)	γ_{AA}(H)	γ_{AA}(O)	J_{ij}[b]	K_{ij}[b]
CNDO/S	12.85	10.93	15.13	5.447	0.011
CNDO/2	20.40	16.06	22.48	8.086	0.086

[a] All values in eV. [b] Values given are for the ${}^1B_{2g}(n_+\pi_+^*)$ state of CBD. For the three $n\pi^*$ states K_{ij} is zero within the CNDO approximation for this molecule, whereas the values of J_{ij} are (CNDO/S values in parentheses): 8.574 (5.533); 8.292 (5.304); 9.133 (5.735) for ${}^1n_+\pi_-^*$, ${}^1n_-\pi_+^*$, and ${}^1n_-\pi_-^*$, respectively.

the Mataga expression:[11]

$$\gamma_{AB} = [R_{AB} + 2/(\gamma_{AA} + \gamma_{BB})]^{-1} \qquad (4)$$

where R_{AB} is the AB internuclear distance and γ_{AA}, γ_{BB} are set equal to the difference between the ionization potential and electron affinity for the valence p electrons of atoms A and B, respectively.[10] The values for γ_{AA} obtained using the above formulations and the resultant J_{ij} and K_{ij}'s are listed in Table II.

In Figure 2 we have sketched the various contributions to the excited state singlet $n\pi^*$ energies in CBD. Both CNDO schemes can be seen to give the same (and wrong) ordering of states at the $\Delta\epsilon_{ij}$ level; only the CNDO/S method predicts the correct ordering after addition of the two-electron coulomb and exchange contributions. Inclusion of the latter contribution in the CNDO/2 scheme does not cause the levels to interchange, only to become lower in energy. As pointed out above, the only difference between the CNDO/S and the CNDO/2 methods in the J_{ij} and K_{ij} terms is in the choice of the γ matrix. Table II shows that the values of γ_{AA} for the CNDO/S scheme are all consistently lower than for CNDO/2, resulting in a drop from about 8 eV for J_{ij} in CNDO/2 to approximately 5 eV in CNDO/S. (The K_{ij} terms are small relative to J_{ij} so the latter dominates.) The correct ordering predicted by the CNDO/S therefore stems from the better choice of γ. The γ's are also responsible in part for the lower $\Delta\epsilon_{ij}$ energies in CNDO/S compared with CNDO/2, although there are other differences in the two methods which must also be considered. We are presently studying these differences in an effort to improve the CNDO/S parameterization with respect to dicarbonyl compounds.

In comparison with the experimental energies it is apparent that the CNDO treatments do not describe the observed $n\pi^*$ singlets well. In fact, after inclusion of configuration interaction in both CNDO schemes (only the CNDO/S result is given in Figure 2), the agreement with experiment is decidedly worse. Experimental observations indicate that the geometries of the different $n\pi^*$ excited states with the same orbital symmetries are not the same, so that including CI as in the present CNDO/S calculation, which assumes similar (i.e., planar) geometries may overestimate the mixing between states of the same orbital symmetry.

That the simpler one-electron EHT method should yield so much better results in the present molecule than the CNDO methods, with or without CI, is perhaps surprising at first glance. The EHT method employs a model hamiltonian[12] composed of a sum of one-electron effective hamiltonians which implicitly take into account the nuclear-nuclear repulsion and the electron-electron repulsion energies well enough that the molecular energies are well described by the sum of one-electron energies. Slater[13] has pointed out that electron-electron repulsion and nuclear-nuclear repulsions in the Hartree-Fock hamiltonian roughly cancel and that their sum is not very dependent on geometry changes. Thus, by neglecting both of these repulsions, the EHT method introduces less error in the calculation than does the CNDO approximation where some electron-electron repulsion terms are retained, but are apparently not optimally parameterized.

Although the EHT results appear to do reasonably well in describing the interactions between the carbonyl orbitals, Wadt and Goddard[14] have recently pointed out that there are problems inherent in the molecular orbital approach to lone pair interactions. By requiring a delocalized description of the orbitals the MO wave functions are forced into having a comparable amount of covalent and ionic (i.e., localized vs. intramolecular charge-transfer type) character. The overemphasis on the ionic contribution is thus responsible for the calculated energies being generally too large. These authors present an alternate approach using valence bond theory and show that this method can account for the large n orbital splitting in pyrazine even though the n orbitals remain 90% localized on the nitrogens. Application of this approach to the present molecular system would be of great interest.

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