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A CNDO Study of Biphenyl

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The ground-state electronic structure of biphenyl were studied by the use of the CNDO/2 method. It was found that the lengthening of the central C–C bond in biphenyl gave a reasonable minimum point for the potential energy curve. A modified version of the CNDO/2 method was used in order to calculate the electronic spectra of biphenyl for three possible (planar, angular, and vertical) conformations. The method gave a reasonable interpretation of the spectral features of biphenyl.

The most important aspect of the CNDO/2 method[1–3] has been considered to lie in its usefulness for the predictions of the equilibrium nuclear arrangements and the stable conformations of various kind of molecules in their ground states. In fact, the CNDO/2 method has been shown to lead to reasonably successful predictions of the equilibrium bond angles and lengths of small molecules.[2,3] It has been theoretically illustrated for the H_2 molecule[4] that the approximate location of its potential energy minimum is established on a balance between the total Coulombic repulsion between the two atoms and the resonance integral. As for the predictions of the equilibrium bond lengths of relatively large conjugated hydrocarbons, composed of 10—15 carbon atoms,[5] the CNDO/2 method leads to satisfactory results comparable to those obtained from the more sophisticated LCAO–MO–SCF theory on the basis of the π-electron approximation, in which the σ-bond compression energies are taken into account.[6]

Unfortunately, however, several authors have failed in using the CNDO/2 method to calculate the rotational barriers and to predict the stable conformers in some conjugated systems. This is the case with biphenyl. The angle of twist around the central C–C bond in biphenyl is about 42°[7,8] in the gaseous phase, while the molecule is planar in the crystal.[9] Recently, Tinland[10] has calculated the total energy of biphenyl as a function of the twisting angle, θ (Fig. 1), by means of the CNDO/2 method, assuming the fixed bond length of 1.50 Å[11] observed for the twisted bond. The potential energy decreases as the twisting angle, θ, increases and is minimized at 90°, in disagreement with the experimental results.

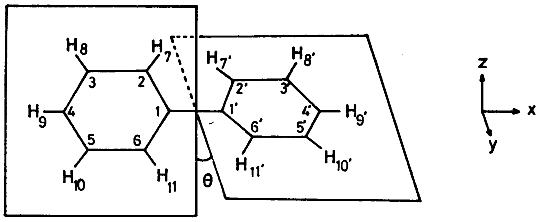

Fig. 1. Numbering of atoms and choice of axis in biphenyl.

More recently, Gropen and Seip[12] have given conclusive results for the CNDO/2 calculations aimed at making it possible to predict the stable conformation of the molecules. Their calculation for biphenyl has given the same result as Tinland's. Even for rather simple molecules such as glyoxal, the calculated total energy minimum was found for a torsional angle, θ, slightly above 90°, in disagreement with the experimental results.

In spite of the deficiencies of the CNDO/2 method pointed out, we venture to present this article out of our desire to elucidate the electronic spectra of biphenyl, which have long been of interest both to theoretical and experimental chemists, especially from a stereochemical point of view.

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[2] J. A. Pople and G. A. Segal, *ibid.*, **43**, s136 (1965).

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Method of Calculation

Although the calculation of the electronic transition energies of biphenyl is of much interest, it has been well established that the original CNDO/2 method predicts markedly high excitation energies, almost twice as high, of molecules.[13] Several authors[13-19] have proposed some modifications of the CNDO/2 method aimed at making it more useful for predicting and interpreting spectroscopic data. One of the present authors[5,20] has succeeded in interpreting the electronic spectra of some non-alternant conjugated hydrocarbons and heterocyclics by use of a modified version of the CNDO/2 method, using a new parametrization for the Del Bene-Jaffé's parameter, κ, for the π-bonds and the bonding parameter, $\beta_x{}^0$, which correlates with the two-center core matrix element, $\beta_{\mu\nu}$, by menas of the following equation:

$$\beta^{\sigma}_{\mu\nu} = \frac{1}{2}(\beta^0_{\mathrm{A}}+\beta^0_{\mathrm{B}})\mathrm{S}_{\mu\nu} \tag{1}$$

$$\beta^{\pi}_{\mu\nu} = \frac{\kappa}{2}(\beta^0_{\mathrm{A}}+\beta^0_{\mathrm{B}})\mathrm{S}_{\mu\nu} \tag{2}$$

where μ and ν denote the AO's on the A and B atoms respectively. The values of κ, $\beta_{\mathrm{C}}{}^0$, and $\beta_{\mathrm{H}}{}^0$ are chosen to be 0.75, -15.0 eV, and -8.0 eV so as to give the most consistent spectroscopic agreements for methane, ethylene and benzene. In this work, the above equation (2) is used to determine the value of the resonance integral for all π-type interactions, wherever they occur. It is also used to evaluate the π-component of the interaction of the two "2p" atomic orbitals which are part of the sigma framework, and to evaluate the interaction of the two "2p" orbitals which are perpendicular to the molecular plane. Only under these conditions could the symmetry of the nonplanar molecule hold; accordingly, this method could be used to study nonplanar molecules. One-center and two-center electron repulsion integrals are evaluated with the Sichel-Whitehead formula[21,22] and the Mataga-Nishimoto formula[23] respectively, and the local core matrix elements, with the Sichel-Whitehead procedures.

Results and Discussion

Ground-state Properties. As was dsecribed above, the CNDO/2 method has predicted a conformation with $\theta=90°$ instead of $42°$.[7,8] It is apparent that this is mainly due to the overestimation of the core repulsions evaluated from the point-charge approximation between non-bonded atoms, especially between ortho-hydrogen atoms at the 7, 7′, 11, and 11′ positions; that is, if we assume the central bond length to be 1.50 Å, the change in the core-repulsion energy overcomes the change in the electronic energy in the neighbourhood of the expected equilibrium conformation of biphenyl. The minimum point of the potential energy curve no longer exists at $\theta=42°$, but at $\theta=90°$, where the core repulsions between non-bonded atoms have the smallest values. Of course, these repulsions will be reduced if the distance of the central bond is increased in the case of biphenyl, as was suggested by Tinland. A minimization of the total energy with respect to an angle variation is possible when we adopt a value of 1.54 Å for the central bond, in accordance with the results of Karle and Blockway.[24] This is shown in Fig. 2. It is interesting to note that the curve has a very shallow trough and that the energy difference between $\theta=0°$ and $\theta=42°$ is calculated to be 0.08 eV (about 1.8 kcal/mol). This is in good agreement with the experimentally-determined rotational potential barrier in biphenyl, 2 kcal/mol.[25]

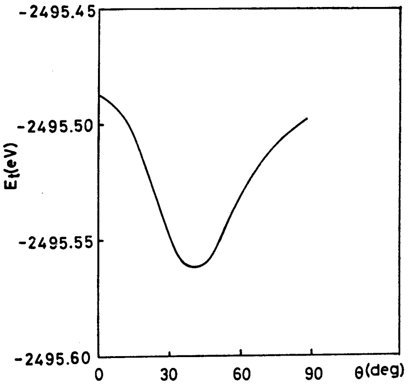

Fig. 2. Calculated potential energy curve for biphenyl with central C–C bond length 1.54 Å.

The calculated AO and atom populations calculated at this energy minimum point are summarized in Table 1. It should be stressed that the electron densities on the carbon atoms at the positions of 2, 6, 2′, and 6′ are larger than those on the other carbon atoms.

Excited-state Properties. The behavior of a so-called "conjugation band" has long been of interest to theoretical and experimental chemists. As early as 1936 Pickett[26] found a strong absorption band at

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$$g_{\mathrm{AA}} = \frac{1}{16}\sum_i\sum_j g_{ij}$$

where g_{ij}'s are evaluated from atomic valence state energies.

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Table 1. AO(q_{ao}) and atom (q_{at}) populations in biphenyl

Atom	AO	q_{ao}	q_{at}
C_1	2s	0.994	3.979
	$2p_x$	0.985	
	$2p_y$	1.000	
	$2p_z$	1.000	
C_2	2s	1.014	4.005
	$2p_x$	1.003	
	$2p_y$	0.985	
	$2p_z$	1.003	
C_3	2s	1.013	3.986
	$2p_x$	1.007	
	$2p_y$	0.982	
	$2p_z$	0.984	
C_4	2s	1.011	3.995
	$2p_x$	0.958	
	$2p_y$	1.011	
	$2p_z$	1.011	
H_7	1s	1·007	1.007
H_8	1s	1.008	1.008
H_9	1s	1.008	1.008

about 250 nm characteristic of a series of biphenyl derivatives, and suggested a correlation between the location of this strong band and the conformation of biphenyl. It has also been shown[27] that the intensity of this band weakens as the conjugation of the two benzene rings decreases.

From the theoretical point of view, several authors[28–33] have tried to elucidate the spectral shift of the conjugation band with the conformational change of the biphenyl skeleton on the basis of the π-electron LCAO–MO method. Murrell and Longuet-Higgins[28] have calculated the lower singlet excitation energies by the use of the "molecules in molecules" method, while Gondo[31] and Grinter[32] have compared the transition energies calculated using a modified version of the PPP method[34,35] over a wide range of twisting angles, θ.

According to the above discussions, it seems to be appropriate to compare the results calculated over the wide range of θ values from $\theta=0°$ to $\theta=90°$ in order to clarify the spectral change in biphenyl. We have calculated the transition energies of biphenyl at each point corresponding to the planar ($\theta=0°$; D_{2h}), angular ($\theta=42°$; D_2), and vertical ($\theta=90°$; D_{2d}) conformations. In the CI calculations, 55 singly-excited configurations are taken into account for each conformation. Throughout the calculations, the central C–C bond length has been assumed to be 1.50 Å[11] and the C–C bond lengths of the two benzene rings to be equal and 1.40 Å.

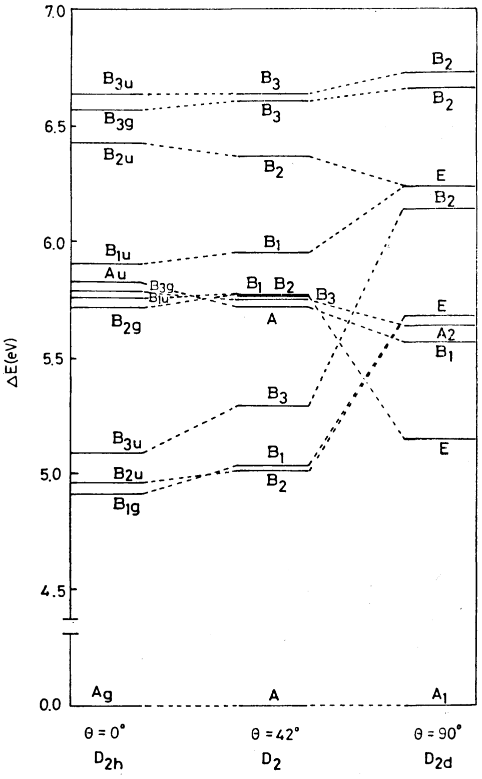

Fig. 3. The energies and symmetries of the lower excited states of three possible conformations of biphenyl.

Figure 3 shows a schematic diagram of the lower singlet states of biphenyl predicted for the three possible conformations. It is apparent from Fig. 3 that the conjugation band is to be assigned to the $A_g \rightarrow B_{3u}$ electronic transition in the D_{2h} conformation, to the $A \rightarrow B_3$ transition in the D_2 conformation, and to the $A_1 \rightarrow B_2$ transition in the D_{2d} conformation, respectively. Table 2 summarizes the calculated energies and symmetries of the lower singlet states of biphenyl, together with the oscillator strengths due to the transitions from the totally-symmetric ground state to the excited states.

In the D_{2h} conformation, the lowest $\pi \rightarrow \pi^*$ electronic transition energy is predicted to be 4.91 eV, corresponding to a symmetry-foribidden $A_g \rightarrow B_{1g}$ transition. The excitation energy corresponding to the next $\pi \rightarrow \pi^*$ electronic transition, $A_g \rightarrow B_{2u}$, is calculated to be 4.96 eV, with its moment directed along the short axis. As for the order of these two states, the results are in disagreement with those obtained by Grinter[32], who concluded that the B_{2u} state was lower than the B_{1g} state, while it is in agreement with the results of Suzuki.[30] An $A_g \rightarrow B_{3u}$ transition which gives rise to the conjugation band is predicted at 5.04 eV, and its oscillator strength is calculated to be 0.80. Although several transitions associated with σ–MO's are predicted to exist in the range of 5.5—5.6 eV, they are predicted to be forbidden by symmetry or very weak in intensity. It should be noted that the higher $\pi \rightarrow \pi^*$ transition energies, corresponding to the $A_g \rightarrow B_{2u}$ and $A_g \rightarrow B_{3u}$ electronic transitions, are

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TABLE 2. CALCULATED SINGLET TRANSITION ENERGIES ΔE(eV) AND OSCILLATOR STRENGTHS f(C.G.S)

$\theta=0°$		$\theta=42°$		$\theta=90°$	
Type	$\Delta E(f)$	Type	$\Delta E(f)$	Type	$\Delta E(f)$
$A_g \rightarrow B_{1g}$	4.91 (forb.)	$A \rightarrow B_2$	5.01 (0.02)	$A_1 \rightarrow E$	5.15 (0.04)
$A_g \rightarrow B_{2u}$	4.96 (0.01)	$A \rightarrow B_1$	5.03 (0.00)	$A_1 \rightarrow B_1$	5.57 (forb.)
$A_g \rightarrow B_{3u}$	5.04 (0.80)	$A \rightarrow B_3$	5.29 (0.68)	$A_1 \rightarrow A_2$	5.64 (forb.)
$A_g \rightarrow B_{2g}$	5.71 (forb.)	$A \rightarrow A$	5.72 (forb.)	$A_1 \rightarrow E$	5.67 (0.00)
$A_g \rightarrow B_{1u}$	5.75 (0.00)	$A \rightarrow B_3$	5.75 (0.01)	$A_1 \rightarrow B_2$	6.14 (0.41)
$A_g \rightarrow B_{3g}$	5.78 (forb.)	$A \rightarrow B_1$	5.76 (0.00)	$A_1 \rightarrow E$	6.22 (0.02)
$A_g \rightarrow A_u$	5.82 (forb.)	$A \rightarrow B_2$	5.76 (0.00)	$A_1 \rightarrow B_2$	6.65 (0.00)
$A_g \rightarrow B_{1u}$	5.90 (0.00)	$A \rightarrow B_1$	5.95 (0.00)	$A_1 \rightarrow B_2$	6.72 (1.52)
$A_g \rightarrow B_{2u}$	6.42 (0.67)	$A \rightarrow B_2$	6.36 (0.24)		
$A_g \rightarrow B_{3g}$	6.56 (forb.)	$A \rightarrow B_3$	6.60 (0.02)		
$A_g \rightarrow B_{3u}$	6.63 (0.90)	$A \rightarrow B_3$	6.63 (0.83)		

predicted to be 6.42 eV and 6.36 eV, with their moments directed along the short and long axes of biphenyl respectively.

The correlation between two point groups, D_{2h} and D_2, is easily found. The B_{1g} and B_{2u} states turn out to be B_1 and B_2 states respectively in an angular conformation. It should be noted that the B_2 state is lower than the B_1 state. It can clearly be seen from Fig. 3 that the conformational change in biphenyl is well reflected in the change both in the energy and in the intensity of the electronic transition, which has the same character as the $A_g \rightarrow B_{3u}$ transition in planar biphenyl. The excitation energy corresponding to this electronic transition is calculated to be 5.29 eV, with its moment directed along the long axis. Its oscillator strength is predicted to be 0.68, which is smaller than that of the corresponding transition in D_{2h} biphenyl because of the decrease in the conjugation of π-electrons in the two benzene rings. It is interesting to note that the higher $A \rightarrow B_3$ transition energy is unaffected by the conformational change in biphenyl.

In a vertical conformation, the lowest excitation energy corresponding to an electronic transition from the ground state, A_1, to a degenerate excited state, E, is predicted to be 5.15 eV, with a small value of oscillator strength, 0.04. This lowest degenerate excited state can be correlated to the nearly degenerate B_1 and B_2 states located near 5.8 eV in D_2 conformation, while in the study of Grinter the lowest E state come from the lowest B_1 and B_2 states. A long-axis polarized transition, $A_1 \rightarrow B_2$, in the D_{2d} conformation has come from the $A \rightarrow B_3$ electronic transition in the D_2 conformation. The effect of the twist is most evidently reflected in the blue-shift of this transition and in the oscillator strength. The higher B_2 state is little affected, as in the case of reduction from D_{2h} to D_2.

From the experimental point of view, many authors[26,27,36-42] have been interested in the electronic spectra of biphenyl and its derivatives. Unfortunately, however, we have no spectral data on biphenyl itself with a vertical conformation.

We are forced to compare the calculations for $\theta=0°$ and $\theta=42°$ with solid[43-47] and solution or vapor-phase[48,49] spectra of the unsubstituted biphenyl respectively.

With regard to the energy of the transition which gives rise to the conjugation band, it is unfortunate that the measurement of this band has not been made for crystalline biphenyl. Dale,[48] however, has measured the spectrum of solid biphenyl by the pressed KCl-disk technique and found an intense, structureless band with a maximum at 2530 Å (=4.94 eV). Suzuki[30] has suggested, after a correction for the normal red-shift observed when samples are measured in KCl-disks, that planar biphenyl which is free from intermolecular interactions should show the characteristic conjugation band at 2495 Å (=4.97 eV). This is in excellent agreement with the results of this calculation for $\theta=0°$, *i. e.*, 5.04 eV. Coffman and McClure[43,44] have reported bands at 33340 cm^{-1} (=4.13 eV, B_{1g}) and 33714 cm^{-1} (=4.18 eV, B_{2u}). The order of these states is in agreement with this calculation, while the predictions of their energy are too high.

The spectrum of biphenyl has also been measured in the vapor phase[50]; absorption maxima were found at 5.2 eV and 5.18 eV for the temperatures of 170° and 520°C respectively. In non-polar solvents, the

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Table 3. Singlet transition energies ΔE(eV) and oscillator strengths f(C.G.S.) calcuted at the point corresponding to the energy minimum in Fig. 2

Type	$\Delta E(f)$	Type	$\Delta E(f)$
$A \rightarrow B_2$	5.00(0.03)	$A \rightarrow B_2$	5.92(0.00)
$A \rightarrow B_1$	5.01(0.01)	$A \rightarrow B_1$	6.05(0.00)
$A \rightarrow B_3$	5.41(0.67)	$A \rightarrow B_3$	6.30(0.01)
$A \rightarrow A$	5.77(forb.)	$A \rightarrow B_2$	6.44(0.35)
$A \rightarrow B_3$	5.79(0.00)	$A \rightarrow B_3$	6.62(0.75)
$A \rightarrow B_1$	5.92(0.00)		

conjugation band is found at 2480 Å (=5.00 eV)36), with an oscillator strength of 0.411.50) These values are to be compared with the value of 5.29 eV determined here for $\theta=42°$. The agreement between theory and experiment seems to be fairly good.

Finally, we have listed the transition energies calculated with $\theta=42°$ and the central C–C bond length of 1.54 Å in Table 3. It is apparent from the table that the bond lengthening has little, if any, effect on the electronic spectra.

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