Calculation of the State Energies of Benzaldehyde. I. Semi-Empirical Molecular Orbital Method

By Kōzō INUZUKA and Toshio YOKOTA

(Received March 9, 1964)

Experimental and theoretical studies of the electronic structures of organic molecules have been made by many authors. In particular, the benzene molecule, a representative aromatic compound, has been investigated thoroughly. Studies now extend to the electronic structures of the derivatives of benzene. Benzaldehyde is an example of these derivatives. The ultraviolet absorption measurement of benzaldehyde at longer wavelengths (n-π transition) has been carried out by Imanishi et. al.[1] The theoretical assignment of the absorption bands at shorter wavelengths (π-π transition) has been made by Tanaka.[2] Recently, the phosphorescence and the S–T absorption spectra of benzaldehyde were measured by Kanda.[3]

For benzaldehyde there are experimental data concerning the singlet and triplet states, which can be compared with the results of the theoretical calculation. In spite of these experimental studies, however, there are few theoretical considerations of its electronic structure.

The semi-empirical molecular orbital method proposed by Pariser and Parr[4] succeeded in the calculation of the π, π state energies and was extended to that of the n, π state energies by Anno et al.[5,6] In this article, the calculation of the state energies of benzaldehyde will be carried out by the use of the semi-empirical molecular orbital method.

Calculation Procedure

Conventional Hückel Type LCAO MO's.—In the calculation of electronic state energies of benzaldehyde, we adopted the molecular structure model shown in Fig. 1. In actual benzaldehyde, which belongs to the C_s-symmetry group, all electronic transitions are allowed. Therefore, if we take account of the C_s symmetry we must solve an 8th-order seqular equation. Calculations then become more complex and tedious. In the present calculations we assume a simplified model with the C_{2v} symmetry for the structure of the benzaldehyde molecule and use Hückel type MO's.

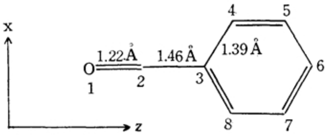


Fig. 1. The C_{2v} model* of benzaldehyde

* The bond distances were estimated from the calculated bond order and the experimental data for carbonyl compounds.

The Coulomb integral, α_1, of the oxygen atom and the resonance integral, β_{12}, between the carbon atom, 2, and the oxygen atom, 1, are expressed as:

$$\alpha_1 = \alpha + \delta_1 \cdot \beta$$

$$\beta_{12} = \rho_{12} \cdot \beta$$

where α is the Coulomb integral of the carbon atom and β is the resonance integral over the neighboring carbon atoms in benzene. The resonance integral, β_{23}, between the benzene ring and the carbonyl group is given by the usual approximation:

$$\beta_{23} = (S_{23}/S)\beta$$

where S_{23} is the overlap integral between the carbon atoms 2 and 3, and S the overlap integral of the neighboring carbon atoms in benzene. In the present calculations, the numerical values of the parameters δ_1 and ρ_{12} and the S_{23}/S ratio are chosen as follows:

$$\delta_1 = 1.5, \quad \rho_{12} = \sqrt{2}, \quad S_{23}/S = 0.894$$

The results of the calculations for Hückel MO's and their energies are listed in Table I, where χ_i is the $2p\pi$AO of the ith-atom.

In addition to the above MO's, the benzaldehyde molecule has a nonbonding orbital which can be represented approximately as follows:

$$\varphi_n = \chi_n$$

where χ_n is the $2p\pi$ AO of the oxygen atom. Its nodal plane is perpendicular to the molecular plane and contains the CO axis. Therefore, the symmetry of χ_n is b_1.

State Energies without Configuration Interaction.—In order to calculate the state energies of benzaldehyde by the methods proposed by Pariser and Parr[4] and by Anno et al[5,6] we need the values of the core integrals and the electronic repulsion integrals. The problem of obtaining these values

---

[1] S. Imanishi, K. Semba, M. Ito and T. Anno, This Bulletin, **25**, 150 (1952).

[2] J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 1114 (1958).

[3] Y. Kanda, Private Communication.

[4] R. Pariser and R. G. Parr, *J. Chem. Phys.*, 21, 466, 767 (1953).

[5] T. Anno, I. Matubara and A. Sadō, This Bulletin, **30**, 168 (1957).

[6] T. Anno, I. Matubara and A. Sadō, *J. Chem. Phys.*, **26**, 967 (1957).

is reduced to the calculation of Coulomb repulsion integrals over atomic orbitals, Coulomb integrals, α_p, and resonance integrals, β_{pq}. The values of Coulomb repulsion integrals are evaluated by the use of the equation derived by Roothaan and by Anno et al.[5] in the case of $r>2.80$ Å and $r\leqq 2.80$ Å respectively. The value of the resonance integral β_{CC} over carbon and oxygen atoms is calculated by

TABLE I. HÜCKEL MO'S AND THEIR ENERGIES OF BENZALDEHYDE

MO*	Sym	χ_1	χ_2	χ_3	$(\chi_4\pm\chi_8)$	$(\chi_5\pm\chi_7)$	χ_6	Energy, e_i
φ_1	b$_2$	0.73575	0.52737	0.31893	0.16511	0.09610	0.07647	−2.51368
φ_2	b$_2$	0.36631	0.11745	−0.32283	−0.36782	−0.39567	−0.40510	−1.95344
φ_3	b$_2$	0.28326	−0.09035	−0.55409	−0.25020	0.29165	0.55611	−1.04889
φ_4	a$_2$				0.50000	0.50000		−1.00000
φ_5	b$_2$	0.40548	−0.58446	−0.28942	0.33917	0.10679	−0.39667	0.53844
φ_6	a$_2$				0.50000	−0.50000		1.00000
φ_7	b$_2$	0.25937	−0.52573	0.39329	−0.03371	−0.34722	0.50819	1.36650
φ_8	b$_2$	0.11211	−0.28625	0.49861	−0.39834	0.34231	−0.32431	2.11106

* The ith-MO φ_i is $\sum_p C_{pi}\,\chi_p$, where C_{pi}'s are listed under the corresponding χ_p. The signs + and − refer to MO's of symmetry b$_2$ and a$_2$ respectively.

TABLE II. TRANSITION ENERGIES OF THE n-π AND π-π TRANSITIONS OF BENZALDEHYDE WITHOUT CONFIGURATION INTERACTION (E in eV.)

	Orbital Jump	Calculated	Observed		Jump	Calculated	Observed
^{3}A$_2$:	n-5	3.955	3.22[a]	^{1}A$_2$:	n-5	4.235	3.34[a, b]
	n-7	7.374			n-7	7.488	
	n-8	10.289			n-8	10.311	
^{3}B$_2$:	n-6	7.905		^{1}B$_2$:	n-6	7.905	
^{3}A$_1$:	4−6	4.192		^{1}A$_1$:	4−6	6.261	6.36[c, d]
	3−5	4.688			3−5	6.229	5.32[e]
	3−7	6.342			3−7	7.599	
	1−5	6.376			1−5	8.022	
	2−5	7.674			2−5	8.569	
	3−8	8.035			3−8	8.913	
^{3}B$_1$:	4−5	5.172		^{1}B$_1$:	4−5	6.054	4.50[e]
	4−7	6.783			4−7	7.514	
	3−6	6.861			3−6	8.047	
	2−6	7.754			2−6	8.624	
	4−8	7.988			4−8	8.817	
	1−6	9.929			1−6	10.049	

a) Ref. 3, b) Ref. 1, c) Ref. 9, d) Ref. 10, e) Ref. 2,

TABLE III. WAVE FUNCTIONS* FOR THE GROUND AND LOWER EXCITED STATES OF BENZALDEHYDE

$^1\mathrm{A}_1$: $\psi_1 = 0.9900V_0 - 0.0758V_3^5 + 0.0039V_4^6 - 0.1008V_3^7 + 0.0079V_1^5 + 0.0285V_2^5 - 0.0545V_3^8$
$\psi_2 = 0.0136V_0 + 0.7102V_3^5 - 0.5794V_4^6 - 0.3870V_3^7 + 0.0042V_1^5 - 0.0455V_2^5 - 0.0888V_3^8$
$\psi_3 = 0.0432V_0 + 0.5777V_3^5 + 0.7449V_4^6 - 0.0058V_3^7 - 0.2196V_1^5 - 0.2250V_2^5 - 0.1030V_3^8$
$^3\mathrm{A}_1$: $\psi_1 = -0.5140T_3^5 + 0.7607T_4^6 - 0.3711T_3^7 - 0.0297T_1^5 - 0.1132T_2^5 - 0.0756T_3^8$
$\psi_2 = 0.8533T_3^5 + 0.4640T_4^6 - 0.2252T_3^7 - 0.0483T_1^5 + 0.0290T_2^5 - 0.0517T_3^8$
$^1\mathrm{B}_1$: $\psi_1 = 0.8314V_4^5 - 0.4298V_4^7 + 0.3380V_3^6 + 0.0452V_2^6 - 0.0835V_4^8 + 0.0285V_1^6$
$^3\mathrm{B}_1$: $\psi_1 = 0.8653T_4^5 - 0.4725T_4^7 - 0.0767T_3^6 + 0.0582T_2^6 - 0.1343T_4^8 - 0.0257T_1^6$
$^1\mathrm{A}_2$: $\psi_1 = 0.9025V_n^5 + 0.4103V_n^7 + 0.1307V_n^8$
$^3\mathrm{A}_2$: $\psi_1 = 0.8962\mathrm{T}_n^5 + 0.4216T_n^7 + 0.1382T_n^8$

* V_0 represents the ground configurational wave function. $V_i{}^j$ and $T_i{}^j$ represent singlet and triplet excited configurational wave functions respectively, in which an electron has been raised from ψ_i to ψ_j. The subscript n represents nonbonding orbital.

TABLE IV. COMPARISON OF EXPERIMENT AND HÜCKEL MO CALCULATION WITH INTERACTION OF SINGLY-EXCITED CONFIGURATIONS

State	Calculated		Experimental	
	E, eV.	f	E, eV.	f
$^1A_1$	0	0	0	0
$^1B_1$	5.333	0.091	4.50[a]	0.026[a]
$^1A_1$	5.567	0.057	5.32[a]	0.29[a]
$^1A_1$	6.658	0.832	6.36[b,c]	0.45[b,c]
$^3A_1$	3.930			
$^3B_1$	4.318			
$^3A_1$	4.472			
$^1A_2$	3.614	0	3.34[d,e]	0.55×10^{-3} [d]
$^3A_2$	3.124		3.22[d]	1.8×10^{-7} [d]

a) Ref. 2, b) Ref. 9, c) Ref. 10, d) Ref. 3, e) Ref. 1

the use of Kon's formula,[8] while the value of β_{CC} over carbon atoms is obtained by Pariser and Parr's formula.[4] The Coulomb penetration integrals, which are needed to evaluate the Coulomb integrals, α_p, are estimated approximately by taking account of the integrals over only the nearest neighboring atoms. The π electronic states belong to the irreducible representations, A_1 and B_1, of the symmetry group C_{2V}. Electronic transitions from the ground state, A_1, to the excited A_1 and B_1 states will have a transitions moment directed along the z axis and the x axis respectively. In the n-π excitation, there are two symmetry types, A_2 and B_2, since the symmetry of the n orbital is b_1. Type A_2 is forbidden, but type B_2 is allowed. The transition moment is perpendicular to the molecular plane; that is, it is parallel to the y axis. This conclusion comes from the assumption of C_{2V} symmetry. In actual benzaldehyde, which has a C_S symmetry, the n-π transition of the A_2 type will also be allowed. In Table II we show all the energies of the n-π and π-π transitions within the range of about 10 eV. These energies are in poor agreement with the experimental values.

State Energies with Configuration Interaction.—Configuration mixing with respect to the π-π transition leads to an 11th-order seqular equation for the $^1A_1$ singlet state, a 10th-order equation for the $^3A_1$ triplet state, and two 6th-order equations for the $^1B_1$ and $^3B_1$ states respectively. As configurations of remarkably higher energies have a negligible effect on lower-lying states, we need consider only the configurations listed in Table II. In the present calculations of the π-π transition, we solve a 7th-order seqular equation for the $^1A_1$ state and a 6th-order equation for the $^3A_1$ state. In the case of n-π transition, configuration mixing leads to two 3rd-order seqular equations, for $^1A_2$ and $^3A_2$ respectivly. The solution of these seqular equations leads to a set of state energies and wave functions. These results are listed in Tables III and IV. The ground state energy is lowered by 0.168 eV.

From a comparison with Tables II and IV, it may be seen that the effect of the configuration interaction for the states separated by a small energy is large and that it is important for complex molecules.

Discussion

Benzaldehyde has four absorption bands in the region from 400 to 190 mμ. An absorption band on the longer wavelength side of this region was measured by Imanishi et al.[1] They assigned this band to an n-π transition and observed that the 0–0 band of the n-π transition is at 26,929 cm^{-1}. The energy, 3.614 eV. in Table IV, which is the $^1A_1$–$^1A_2$ transition energy, may correspond to the above n-π transition. In the present calculations, this transition is forbidden because of the assumption of the C_{2v} symmetry, but it is allowed in the actual molecule, with a symmetry C_s. The observed oscillator strength of this transition is 0.55×10^{-3}.[3]

Three absorption bands are observed in the region from 300 to 190 mμ. These are assigned to π-π transitions. The band at 285 mμ (4.50 eV.) is the weakest of them; it may correspond to the energy 5.333 ev. in Table IV, although the calculated value is larger than the observed value. Therefore, this band at 285 mμ is assigned to the $^1A_1$–$^1B_1$ transition. The next stronger band is at 233 mμ (5.32 eV.)[2]; this may be correlated with the energy 5.567 eV. in Table IV and is assigned to the $^1A_1$–$^1A_1$ transition. The strongest band is at 195 mμ (6.36 eV.);[9,10] it may be assigned to the $^1A_1$–$^1A_1$ transition (6.658 eV.). In the above assignments, the theoretically-calculated values of the oscillator strengths of these π,π bands are in poor agreement with the results of the experiments.

According to the experiment of Kanda,[3] the

---

[7] C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 116 (1951).

[8] H. Kon, This Bulletin, **28**, 275 (1955).

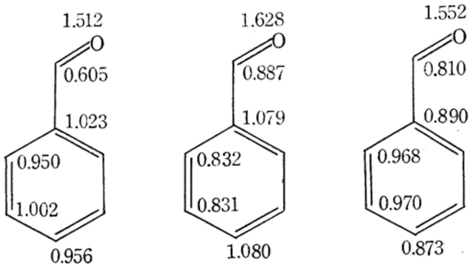
[9] W. C. Price and A. D. Walsh, *Proc. Roy. Soc.*, **A191**, 22 (1947).

[10] H. B. Klevens and J. R. Platt, Technical Report, Laboratory of Molecular Structure and Spectra," (1953-1954).

S–T absoption spectrum appears at 25,195 cm^{-1} (3.22 eV.), and its oscillator strength is 1.8$\times$10^{-1}. In Table IV this may be related to the energy 3.124 eV. of the n, π triplet state. Therefore, the above band may be assigned to $^1A_1$–$^3A_2$ transition.

The exsistence of π, π triplet states has not yet been confirmed experimentally, but in the present calculations three lower-lying π, π triplet states are obtained. The energies of these triplet states are about 4 ev; they are also listed in Table IV. These values seem reasonable judging from an average S–T separation for the π-π transition.[11]

The charge densities for the ground and two excited states are shown in Fig. 2. In the ground state, the charge density of the meta position is higher than those of the ortho- and para-positions. This is consistent with the tendency toward a meta orientation of the carbonyl group for electrophylic reagents. Similarly, from Fig. 2 it may be seen that the $^1B_1$ state has a tendency toward a para orientation and that the 1st $^1A_1$ excited state has a tendency toward meta and ortho orientations. Tanaka[2] pointed out that the transition from the ground state to the 1st $^1A_1$ excited state is attended with the migration of electrons from the benzene ring to the carbonyl group, and he assigned it to the charge transfer band. A similar phenomenon is seen in Fig. 2. The charge density on the carbonyl group becomes larger in the 1st $^1A_1$ excited state than in the ground state. This is in agreement with Tanaka's assignment. The calculation of charge density is very sensitive to the wave function used. Therefore, it is better to calculate it by the use of SCF MO's under a C_s symmetry than by the use of Hückel MO's assuming a C_{2v} symmetry. The results of such improved calculations[12] will be reported in the near future.



(I) (II) (III)

Fig. 2. π Electron densities of benzaldehyde
(I) in the ground state;
(II) in the 1st excited $^1B_1$ state;
(III) in the 1st excited $^1A_1$ state.

Summary

The electronic structure and the nature of the electronic transitions in the benzaldehyde molecule have been elucidated by the use of a semi-empirical MO method assuming a C_{2v} symmetry. The results of the calculations conform to the observed values for the singlet and triplet states in spite of the use of a crude approximation. In benzaldehyde, it has been found that the *n*, π triplet state is the lowest. The charge transfer band may be explained by means of our calculations.

The authors wish to express their thanks to Mr. Masuo Suzuki and Dr. Toshinori Munakata for their kind assistance in carrying out the digital computations. They also wish to express their gratitude to Professor Yoshiya Kanda of Kyushu University, who had the kindness to send them his experimental data. The present study was partially financed by the Scientific Research Fund of the Ministry of Education.

Department of Applied Science
Tokyo Electrical Engineering College
Kanda, Chiyoda-ku, Tokyo

---

[11] C. Reid, *J. Chem. Phys.*, **21**, 1906 (1953).

[12] K. Inuzuka and T. Yokota, to be published.