The Calculation of the State Energies of Benzaldehyde. II. The SCF Molecular Orbital Method

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In the previous paper,[1] we calculated the state energies of benzaldehyde by the Pariser-Parr method[2] and assigned electronic transitions by adopting a model with C_{2v} symmetry for the sake of simplicity. In the actual molecule of benzaldehyde, however, the carbon atom of the carbonyl group is combined with the carbon atom of the benzene ring, where the bond angle of C–C=O is 120°, as is shown in Fig. 1.

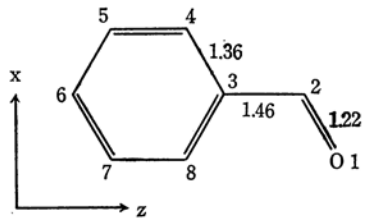

Fig. 1. A model* of benzaldehyde with C_s symmetry.

* Ref. 1

In this paper, therefore, the state energies of benzaldehyde with C_s symmetry are calculated by using the SCF-MO method.[3,4] The bond distances used are the same as those in the previous model.[1]

Calculation Procedure

The SCF-MO, φ_i, and its energy, ε_i, are obtained by the following formulas:

$$\varphi_i = \sum_\mu c_{i\mu}\chi_\mu$$

$$\sum_\nu F_{\mu\nu}c_{i\nu} = \varepsilon_i c_{i\mu}$$

$$F_{\mu\mu} = \alpha_\mu + \frac{1}{2}p_{\mu\mu}(\mu\mu/\mu\mu) + \sum_{\nu\neq\mu}(p_{\nu\nu}-1)(\mu\mu/\nu\nu)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2}p_{\mu\nu}(\mu\mu/\nu\nu)$$

$$p_{\mu\nu} = 2\sum_i c_{i\mu}c_{i\nu}$$

where χ_μ is 2pπAO of the μth-atom, α_μ is the ionization potential of the atom, μ, in the atomic valence state and $\beta_{\mu\nu}$ is the resonance integral over the nearest neighbor atoms, μ and ν.

The value of the resonance integral, β_{CO}, over carbon and oxygen atoms is calculated by using Kon's formula,[6] while the value of β_{CC} over carbon and carbon atoms is obtained from Pariser and Parr's formula.[2] $(\mu\mu/\nu\nu)$ is the Coulomb repulsion integral; that is,

$$(\mu\mu/\nu\nu) = \int\chi^*_\mu(1)\chi_\mu(1)(e^2/r_{12})\chi^*_\nu(2)\chi_\nu(2)\mathrm{d}v$$

It is evaluated from the equations derived by Roothaan[7] and by Anno et al.[5] for $r>2.80$ Å and $r\leqq 2.80$ Å respectively. The calculations were done using a digital computer. The iteration process in the calculation of SCF-MO's and MO energies started with Hückel MO's and continued until the energies converged.

The excitation energies corresponding to the i–k transition are expressed for singlet and triplet states respectively as follows:

$$^1E_{i\text{-}k} = \varepsilon_k - \varepsilon_i - [ii/kk] + 2[ik/ki]$$

$$^3E_{i\text{-}k} = \varepsilon_k - \varepsilon_i - [ii/kk]$$

where

$$[ii/kk] = \int\varphi_i(1)^*\varphi^*_k(2)(e^2/r_{12})\varphi_i(1)\varphi_k(2)\mathrm{d}v.$$

Neglecting the differential overlap, the integrals, $[ii/kk]$ and $[ik/ki]$, may be expressed in terms of the Coulomb repulsion integrals over such atomic orbitals as $(\mu\mu/\nu\nu)$.

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

$$\varphi_n = \chi_n$$

where χ_n is the $2p\bar{\pi}$ AO of the oxygen atom. Its nodal plane is perpendicular to the molecular plane and contains the CO axis.

The transition moment between the ground state, ψ_0, and an excited state, ψ_i, is defined by:

1) K. Inuzuka and T. Yokota, This Bulletin, 37, 1224 (1964).
2) R. Pariser and R. G. Parr, *J. Chem. Phys.*, 21, 466, 767 (1953).
3) J. A. Pople, *Trans. Faraday Soc.*, 49, 1375 (1953).
4) N. Mataga and K. Nishimoto, *Z. physik. Chem. N. F.*, 13, 140 (1957).
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6) H. Kon, ibid., 28, 275 (1955).
7) C. C. J. Roothaan, *J. Chem. Phys.*, 19, 116 (1951).

Table I. SCF-MO's and MO energies of benzaldehyde

ε_i (eV.)

$-15.64805\ \varphi_1 =$
$0.35064\ \chi_1 + 0.31879\ \chi_2 + 0.45265\ \chi_3 + 0.38416\ \chi_4 + 0.32816\ \chi_5 + 0.30185\ \chi_6 + 0.31234\ \chi_7 + 0.35580\ \chi_8$

$-14.57123\ \varphi_2 =$
$0.71105\ \chi_1 + 0.45578\ \chi_2 - 0.02874\ \chi_3 - 0.16431\ \chi_4 - 0.26712\ \chi_5 - 0.30589\ \chi_6 - 0.26170\ \chi_7 - 0.15953\ \chi_8$

$-12.11845\ \varphi_3 =$
$0.13435\ \chi_1 + 0.02285\ \chi_2 - 0.25176\ \chi_3 - 0.56914\ \chi_4 - 0.29456\ \chi_5 + 0.27578\ \chi_6 + 0.57755\ \chi_7 + 0.31262\ \chi_8$

$-12.05362\ \varphi_4 =$
$0.24442\ \chi_1 + 0.02381\ \chi_2 - 0.49834\ \chi_3 - 0.00251\ \chi_4 + 0.48448\ \chi_5 + 0.47788\ \chi_6 + 0.00000\ \chi_7 - 0.47776\ \chi_8$

$-1.43621\ \varphi_5 =$
$-0.36987\ \chi_1 + 0.47637\ \chi_2 + 0.41637\ \chi_3 - 0.34619\ \chi_4 - 0.13014\ \chi_5 + 0.44474\ \chi_6 - 0.21688\ \chi_7 - 0.28511\ \chi_8$

$-0.64024\ \varphi_6 =$
$0.02450\ \chi_1 - 0.02847\ \chi_2 - 0.02033\ \chi_3 - 0.47797\ \chi_4 + 0.52382\ \chi_5 - 0.04837\ \chi_6 - 0.47438\ \chi_7 + 0.51764\ \chi_8$

$0.53306\ \varphi_7 =$
$-0.38261\ \chi_1 + 0.64278\ \chi_2 - 0.33373\ \chi_3 + 0.04843\ \chi_4 + 0.266021\ \chi_5 - 0.41844\ \chi_6 + 0.28216\ \chi_7 + 0.03536\ \chi_8$

$2.72601\ \varphi_8 =$
$0.09939\ \chi_1 - 0.22057\ \chi_2 + 0.44430\ \chi_3 - 0.38839\ \chi_4 + 0.37065\ x_5 - 0.36833\ \chi_6 + 0.38561\ \chi_7 - 0.41410\ \chi_8$

Table II. Calculated lower transition energies of n-π and π-π transitions of benzaldehyde without configuration interaction

Electronic transition	Orbital jump	Transition energy, eV.	Electronic transition	Orbital jump	Transition energy, eV.
$^1A'$-$^3A''$	n-5	5.465	$^1A'$-$^1A''$	n-5	5.698
	n-6	8.696		n-6	8.697
	n-7	6.860		n-7	7.110
	n-8	11.498		n-8	11.515
$^1A'$-$^3A'$	4-5	4.358	$^1A'$-$^1A'$	4-5	5.674
	3-5	4.644		3-5	5.822
	4-6	4.657		4-6	6.124
	3-6	4.395		3-6	6.215
	4-7	6.654		4-7	7.516
	3-7	7.066		3-7	7.649
	2-5	6.674		2-5	8.007

$$M^r_{0i} = \int \psi_0 r \psi_i \mathrm{d}v \quad (r = x, y, z)$$

where ψ_i is expressed approximately by a linear combination of singly-excited configuration functions. The oscillator strength, f,[8] is given by:

$$f = 1.085 \times 10^{11} \times \omega_{0i} \sum_r M^r{}_{0i}{}^2,$$

where ω_{0i} is the frequency of the transition in cm^{-1}.

Results

State Energies without Configuration Interaction.—The SCF-MO's and the MO energies so obtained are listed in Table I. The π-π transition energies in singlet and triplet states are calculated from the above equation; the n-π transition energies are also calculated by the Pariser-Parr method using the above SCF-MO's. In Table II, we show all the energies of n-π transitions and the lower lying energies of π-π transitions.

State Energies with Configuration Interaction.—In large molecules, multiply-excited configurations should make negligibly small contributions to the lower excitation energies. In the present calculation we take account of a singly-excited configurations only. In the π-π transition, all calculations of singly-excited configurations were carried out by solving a 16th-order secular equation for each of the singlet and triplet states. Similarly, in the calculation of the n-π transition energies, four configurations were taken for each of the singlet and triplet states. The lower-lying state energies and their wave functions as obtained from these four secular equations are listed in Tables III and IV.

The charge densities, bond orders and free valences for the ground state of benzaldehyde

8) R. S. Mulliken and C. A. Rieke, *Rep. Progr. Physics*, **8**, 231 (1941).

TABLE III. WAVE FUNCTIONS FOR LOWER EXCITED STATES OF BENZALDEHYDE

State		1,5	1,6	1,7	1,8	2,5	2,6	2,7	2,8
$^1A'$:	1	0.00984	0.02225	0.00332	0.00722	−0.00860	0.08392	−0.02236	0.00337
	2	−0.07075	0.00642	−0.03639	−0.09112	0.00982	0.00455	0.10966	0.04908
	3	0.02130	−0.03858	−0.04084	−0.03677	−0.32492	0.01959	−0.19221	0.07438
	4	−0.07474	−0.04402	−0.04635	0.02088	−0.06519	−0.02728	−0.03255	−0.01553
$^3A'$:	1	0.00749	0.01132	−0.02712	0.18623	−0.14833	0.00827	−0.25505	−0.06783
	2	−0.21072	0.00186	−0.22530	−0.04296	−0.52528	0.04140	−0.40502	0.15213
	3	0.05002	−0.05493	0.03981	0.00174	0.09732	−0.03173	0.07221	−0.02230
	4	−0.13160	0.00587	−0.10258	0.02003	−0.36865	−0.00203	−0.18448	0.04268
State		3,5	3,6	3,7	3,8	4,5	4,6	4,7	4,8*
$^1A'$:	1	0.56986	−0.35767	−0.21659	−0.02446	−0.47200	−0.50474	0.11774	−0.01135
	2	0.45188	0.43795	−0.09676	0.00485	0.63454	−0.38581	−0.11522	0.02516
	3	−0.02911	0.65594	−0.13755	0.01896	−0.50889	−0.03055	−0.36635	−0.04586
	4	0.66851	0.03127	0.12750	0.06169	−0.03751	0.71660	0.02540	−0.00954
$^3A'$:	1	−0.39213	−0.44564	0.09045	0.00288	−0.63530	0.29510	0.14547	−0.01665
	2	0.00920	0.47292	−0.17087	0.00898	−0.26416	−0.23937	−0.24080	0.00953
	3	0.73377	0.15715	−0.23506	0.04310	−0.44048	0.33684	0.21658	−0.04559
	4	0.26821	−0.47089	−0.21056	0.01470	0.42672	0.42835	−0.30864	0.03004
State		*n*,5	*n*,6	*n*,7	*n*,8**				
$^1A''$:	1	0.78017	−0.06061	0.61279	−0.11027				
$^3A''$:	1	0.77119	−0.05880	0.62303	−0.11682				

* *i*, *j* represents a state excited from φ_i to φ_j.

** *n*, *j* represents a state excited from nonbonding orbital to φ_j.

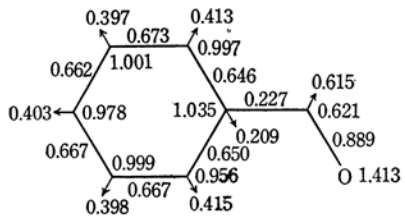

Fig. 2. Molecular diagram of benzaldehyde in the ground state.

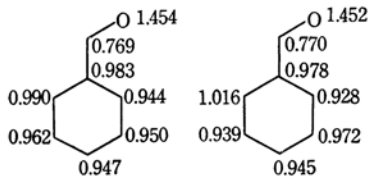

Fig. 3. π-Electron charge densities of benzaldehyde in excited state.
I: 1st excited state; II: 2nd excited state

are also shown in Fig. 2. The charge densities of the 1st and 2nd excited states are shown in Fig. 3.

Discussion

Since benzaldehyde has the symmetry C_s, all the electronic transitions are symmetry-allowed.

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

State		Calculated		Experimental	
		E, eV.	*f*	*E*, eV.	*f*
$^1A'$:		0	0	0	0
	1	4.771	0.017	4.50[a]	0.026[a]
	2	5.032	0.066	5.32[a]	0.29[a]
	3	6.313	1.02	6.36[b,c]	0.45[b,c]
	4	6.794	0.88		
$^3A'$:	1	3.273			
	2	3.937			
	3	4.223			
	4	4.402			
$^1A''$:	1	3.860		3.34[d,e]	0.55 $\times 10^{-3}$ [d]
$^3A''$:	1	3.370		3.22[d]	1.8 $\times 10^{-7}$ [d]

a) Ref. 9, b) Ref. 10, c) Ref. 11, d) Ref. 13, e) Ref. 12

The π-electronic states belong to the irreducible representation, A′, of the symmetry group C_s, while the n–π single excitation belongs to the symmetry type A″, since the symmetry of the n orbital is a″. Therefore, the transition moment is perpendicular to the molecular plane, that is, parallel to the y axis.

Benzaldehyde has four absorption bands in the region from 400 to 190 mμ. In a previous

paper,[1] we tried to assign these absorption bands using the C_{2v} model with Hückel MOs. The results for state energies and oscillator strengths in the present calculation are listed in Table IV, along with the observed values. From these results, the band at 285 mμ (4.50 eV.)[9] corresponds to the calculated energy of 4.771 eV. The bands at 233 mμ (5.32 eV.)[9] and 195 mμ (6.36 eV.)[10,11] are correlated with the state energies, 5.032 and 6.313 eV. respectively. On the basis of the above correspondence, they may be assigned to $^1A'$–$^1A'$ transitions. The calculated energy values are in good agreement with the observed values, as compared with the previous values,[1] but the calculated values of the oscillator strengths of the first and second transitions are smaller than the observed values.

The electronic transition at 26929 cm^{-1} (3.34 eV.)[12] corresponds to the calculated energy of 3.860 eV. Therefore, the transition may be assigned to $^1A'$–$^1A''$. This calculated value should be compared with the previous value (3.614 eV.). The calculated state energy, 3.370 eV., is the lowest of the n, π state energies and corresponds to $^1A'$–$^3A''$. This value is correlated with the S−T absorption band at 25195 cm^{-1} (3.22 eV.)[13] and should be compared with the previous value (3.124 eV.). On the other hand, the calculated values for the π,π triplet states are lower than the previous values;[1] however, no experimental data are available.

The reactivity indices for the ground state are shown in Fig. 2. The charge density of the meta position is higher than those of the ortho and para positions. This result indicates a tendency of the carbonyl group to meta orientation for electrophilic reagents, in accordance with the previous calculation.[1] The high-charge densities of ortho positions suggest that they also have a high reactivity for electrophilic reagents. The free valence in carbon atoms is the highest at the carbon atom 2, as is shown in Fig. 2. This suggests that position 2 is reactive in the case of radical reaction, as has been observed in the photo-oxidation reaction of benzaldehyde. The charge densities in two lower excited states are shown in Fig. 3. These results are very different from those of the previous calculations.[1]

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11) H. B. Klevens and J. R. Platt, Technical Report, Laboratory of Molecular Structure and Spectra, University of Chicago, Chicago (1953—1954).
12) S. Imanishi, K. Semba, M. Ito and T. Anno, This Bulletin, **25**, 150 (1952).
13) Y. Kanda, Private Communication.

Summary

The state energies, charge densities, bond orders and free valences of benzaldehyde have been elucidated by the use of the SCF-MO method with a model of C_s symmetry, including interactions of all the singly-excited configurations. In the singlet state, the numerical values of state energies are more reliable than the previous results, which were derived from the C_{2v} model by the use of Hückel MO. In the triplet state, however, the numerical values of state energies seem to be lower than the previous results.

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