π Electronic Structure of Cinnamaldehyde

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In two previous papers[1,2] we studied the electronic structure of the acrolein molecule. This molecule has an intense absorption band of (π, π^*) type in the region near 2000 Å, which was assigned to an intramolecular charge transfer band by Nagakura[3]. Cinnamaldehyde is regarded as a derivative of acrolein, in which a hydrogen atom is substituted by a phenyl group. From this point of view the comparison of the spectra of acrolein and cinnamaldehyde may be interesting.

The absorption spectrum of cinnamaldehyde was measured in *n*-hexane solution in the 2000∼3000 Å region. Molecular orbital calculation was made for the π electronic structure of the cinnamaldehyde molecule with a view to understanding its absorption band, as there has scarcely been any theoretical work done on the electronic structure of this molecule.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of cinnamaldehyde and acrolein are shown in Fig. 1.

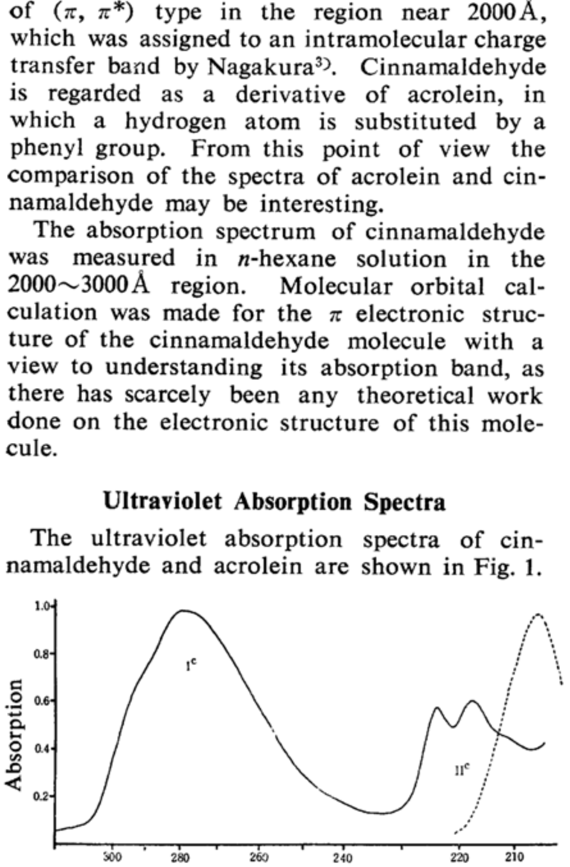

Fig. 1. Ultraviolet absorption spectra of cinnamaldehyde and acrolein.

Solid line: cinnamaldehyde in *n*-hexane
Broken line: acrolein in *n*-hexane

The spectra of these molecules were measured with a Hitachi self-recording quartz spectrophotometer of type E. P. S. The solvent was *n*-hexane carefully purified by the method of Weissberger and Proskauer[4]. It appears that the cinnamaldehyde band is displaced to the red with respect to the acrolein band, owing to the extension of conjugation within the molecule. In order to ascertain that the transition in cinnamaldehyde corresponding to the absorption in the 2000 Å region is of the $\pi-\pi^*$ type, the effect on the spectrum of changing the solvent from *n*-hexane to ethanol was also studied.

Calculation of Energy Levels

Although the methods of Pariser and Parr[5] and others simplify the calculation of molecular energy levels in very ingenious ways, it is still not easy to apply the theory to a molecule such as cinnamaldehyde. In the present calculation the MO's of cinnamaldehyde were obtained by the simple LCAO-MO method and we took account of the interaction of electrons by including configuration interaction to some extent[6]. As the molecular dimension of cinnamaldehyde is not known, we relied on the structure inferred from the result of the electric dipole moment value by Bently et al.[7] The molecular structure is shown in Fig. 2, but in our calculation a somewhat more simplified model was used. Actually cinnamaldehyde has not C_{2v} symmetry, but the orbitals obtained in our approximation are what would be found if C_1-C_7=C_8-C_9=O was linear. Thus the cinnamaldehyde MO's may be said to resemble those with C_{2v} symmetry. The MO's of cinnamaldehyde were obtained by the simple LCAO-MO method with neglect of overlap integrals. The Coulomb integral α_o and the resonance integral β_{co} are expressed as

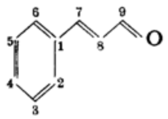

Fig. 2. Cinnamaldehyde.

$$\alpha_o = \alpha + \delta_o \beta$$
$$\beta_{co} = \rho_{co} \beta$$

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[1] K. Inuzuka, This Bulletin, 34, 6 (1961).
[2] K. Inuzuka, ibid., 34, 729 (1961).
[3] S. Nagakura, *Mol. Phys.*, 3, 105 (1960).
[4] A. Weissberger and E. S. Proskauer, "Organic Solvents", Interscience Publishers, Inc., New York, N. Y. (1955).
[5] R. Pariser and R. G. Parr, *J. Chem. Phys.*, 21, 466, 767 (1953).
[6] H. Baba and S. Suzuki, ibid., 32, 1706 (1960).
[7] J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1947, 2957.

TABLE I. ORBITAL ENERGIES AND ORBITALS FOR CINNAMALDEHYDE

i	Symmetry	Orbital energy $(e_i-\alpha)/\beta$	Orbital ϕ_i
1	b_1	2.481	$0.0956\chi_1+0.0508(\chi_2+\chi_6)+0.0303(\chi_3+\chi_5)+0.0245\chi_4+0.1544\chi_7$ $+0.2644\chi_8+0.5374\chi_9+0.7751\chi_o$
2	b_1	2.100	$0.4826\chi_1+0.3928(\chi_2+\chi_6)+0.3423(\chi_3+\chi_5)+0.3260\chi_4+0.2593\chi_7$ $+0.1065\chi_8-0.0775\chi_9-0.1825\chi_o$
3	b_1	1.429	$0.3051\chi_1-0.0094(\chi_2+\chi_6)-0.3185(\chi_3+\chi_5)-0.4458\chi_4+0.5174\chi_7$ $+0.4171\chi_8+0.0126\chi_9-0.2515\chi_o$
4	a_2	1.000	$1/2(\chi_2+\chi_3-\chi_5-\chi_6)$
5	b_1	0.815	$0.4091\chi_1+0.2871(\chi_2+\chi_6)-0.1752(\chi_3+\chi_5)-0.4298\chi_4-0.2739\chi_7$ $-0.5158\chi_8-0.1237\chi_9+0.2555\chi_o$
6	b_1	−0.429	$0.1751\chi_1-0.2630(\chi_2+\chi_6)-0.0622(\chi_3+\chi_5)+0.2897\chi_4+0.5130\chi_7$ $-0.3310\chi_8-0.4883\chi_9+0.3580\chi_o$
7	a_2	−1.000	$1/2(-\chi_2+\chi_3-\chi_5+\chi_6)$
8	b_1	−1.117	$0.4721\chi_1-0.1815(\chi_2+\chi_6)-0.2694(\chi_3+\chi_5)+0.4824\chi_4-0.1870\chi_7$ $-0.1824\chi_8+0.4632\chi_9-0.2248\chi_o$
9	b_1	−1.650	$0.0747\chi_1+0.1169(\chi_2+\chi_6)-0.2675(\chi_3+\chi_5)+0.3243\chi_4-0.4061\chi_7$ $+0.5347\chi_8-0.4723\chi_9+0.2121\chi_o$
10	b_1	−2.129	$0.4909\chi_1-0.3811(\chi_2+\chi_6)+0.3204(\chi_3+\chi_5)-0.3010\chi_4-0.3218\chi_7$ $+0.2245\chi_8-0.1275\chi_9+0.0497\chi_o$

TABLE II. ENERGIES AND WAVE FUNCTIONS FOR LOWER EXCITED STATES OF CINNAMALDEHYDE

Symmetry	Excitation energy, eV.		Wave function	Oscillator strength
	calcd.	obs.		
B_2^-	4.10		$0.946V_{46}-0.326V_{57}$	0.000
A_1	4.11	4.41	V_{56}	0.806
B_2^+	5.50	5.53	$0.326V_{46}+0.946V_{57}$	0.337

where $\alpha=\alpha_c$ and $\beta=\beta_{cc}$. We adopted the values of the parameters $\delta_o=1.5$ and $\rho_{co}=2^{1/2}$ as given by Baba et al.6) Other Coulomb integrals were assumed to be equal to α. The resonance integrals except those of the benzene ring and carbonyl group, were calculated by the approximation generally adopted

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

were S_{rs} is the overlap integral between neighboring atom r and s, and S the overlap integral for benzene. In Table I the MO energies and orbitals of cinnamaldehyde are given. For the resonance integral values which are necessary for determining the energies of configurations the values given by Goodman and others8,9)

$$\beta(B_2)=2.98\text{ eV.}$$

$$\beta(A_1)=3.30\text{ eV.}$$

were used. The configuration interaction was considered between those configurations with lower energy and belonging to the same symmetry. The matrix element of the total Hamiltonian $\mathbf{H}$ between the configurations V_{ik} and V_{jl} is given by

$$\int V_{ik}^*\mathbf{H}V_{jl}\,dv=2[ki|jl]-[kl|ji] \qquad (i\neq j,\ k\neq l)$$

where

$$[ij|kl]=\int\phi_i^*(1)\phi_k^*(2)(e^2/r_{12})\phi_j(1)\phi_l(2)\,dv$$

MO's ϕ_i are obtained by the simple LCAO procedure neglecting differential overlap. The integral $[ij|kl]$ can be expressed in terms of atomic orbitals as

$$[pp|qq]=\int\chi_p^*(1)\chi_q^*(2)(e^2/r_{12})\chi_p(1)\chi_q(2)\,dv$$

For the integrals of this type we employed Pariser and Parr's results5). To avoid difficult calculation only the interaction between V_{46} and V_{57} belonging to the same symmetry is considered. In this way the value of the matrix element

$$\int V_{46}^*\mathbf{H}V_{57}\,dv=0.449\text{ eV.}$$

is obtained. If we assume that there is approximately no interaction between V_{56} and other configurations, the energy of the state represented by V_{56} is calculated directly. The energies of the states resulting from the interaction of V_{46} and V_{57} were obtained including the

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8) L. Goodman and H. Shull, *J. Chem. Phys.*, **27**, 1388 (1957).

9) E. G. McRae and L. Goodman, *J. Mol. Spectroscopy*, **2**, 464 (1958).

configuration interaction energy between them as given above. The oscillator strength, f, is calculated by the method described by Mulliken and Rieke[10],

$$f = 1.085 \times 10^{11} \times \omega \sum_r Q_r^2 \quad (r = x, y, z)$$

where ω is the frequency of the transition in cm^{-1} and Q_r is the transition moment defined by

$$Q_r = \int \Psi_i{}^* \, r \, \Psi_j \, \mathrm{d}v$$

Ψ_i is a state wave function. The results are shown in Table II.

Discussion

The electronic spectrum of cinnamaldehyde in *n*-hexane solution has three absorption peaks at about 280, 224 and 218 mμ (Fig. 1). Among these three peaks the one at 280 mμ is the strongest, having two weak shoulders near 293 and 300 mμ. In Fig. 3 the orbital energy level diagram of cinnamaldehyde is given with those of benzene and acrolein. From this figure the occupied levels 4, 5 and the vacant levels 7, 8 of cinnamaldehyde may be assigned to the degenerate levels 2, 3 and 4, 5 of benzene. The levels 3 and 6 of cinnamaldehyde may be assigned to the levels 2 and 3 of acrolein in ground and upper states, respectively. We assigned the band at 280 mμ (4.41 eV.) to the calculated value 4.11 eV. (A_1), because the value of calculated oscillator strength of A_1 state is much greater than that of $B_2{}^-$ state. Therefore, the band at 280 mμ corresponds to the transition from ϕ_5 to ϕ_6. In our experiment no band corresponding to the calculated value 4.10 eV. ($B_2{}^-$) was found. The reason why we could not find the band ($B_2{}^-$) may be explained by the interpretation that the band (A_1) of cinnamaldehyde is displaced to the longer wavelength side by the greater extension of conjugation and covers the band ($B_2{}^-$). This interpretation conforms with the result of our calculation and with the work of Thomas et al.[11]

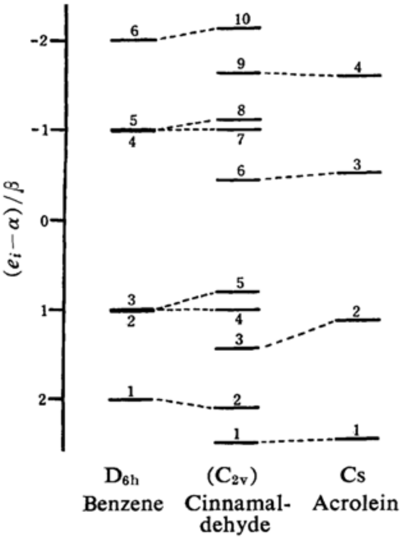

Fig. 3. Orbital energy level diagram.

It should be mentioned here about the electron distribution associated with ϕ_3, ϕ_5 and ϕ_6 of cinnamaldehyde. Table III shows the distribution of an electron occupying the MO's ϕ_3, ϕ_5 and ϕ_6 in terms of squares of coefficients of atomic orbitals. It seems that the excitation of an electron from ϕ_5 to ϕ_6 transfers the electronic charge from the benzene ring to the acrolein group. This suggests that the transition from ϕ_5 to ϕ_6 corresponds to an intramolecular charge transfer band. In the region of the band II^c there are two peaks at 224 and 218 mμ. Of these the 218 mμ peak is higher than the 224 mμ peak. There may arise a question as to whether or not the two main peaks constituting the band II^c reveal the vibrational structure of an electronic transition, or represent two different transitions. The frequency separation between them is 1230 in *n*-hexane and 1030 cm^{-1} in ethanol solutions, respectively, at room temperature. The change of 200 cm^{-1} is too great. It may be reasonable to interpret the two peaks as two different transitions. The band at 224 mμ (5.53 eV.) may be assigned to the calculated excitation energy 5.56 eV. ($B_2{}^+$), and may correspond to the A_{1g}-B_{2u} transition in benzene.

TABLE III. DISTRIBUTION OF AN ELECTRON IN MO'S ϕ_3, ϕ_5 AND ϕ_6

	ϕ_3	ϕ_5	ϕ_6
$C_1{}^2$	0.0931	0.1674	0.0307
$C_2{}^2$	0.0001	0.0824	0.0692
$C_3{}^2$	0.1015	0.0307	0.0039
$C_4{}^2$	0.1987	0.1848	0.0839
$C_7{}^2$	0.2677	0.0750	0.2631
$C_8{}^2$	0.1739	0.2660	0.1096
$C_9{}^2$	0.0002	0.0153	0.2385
$C_O{}^2$	0.0632	0.0651	0.1281

On the other hand, from the energy level diagram Fig. 3, we tentatively assign the band at 218 mμ (5.69 eV.) to a transition V_{36} which has the lowest energy among the transitions V_{36}, V_{58}, V_{47} and V_{48}. The transition energies for them are directly obtained from the

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[10] R. S. Mulliken and C. A. Rieke, *Rep. Progr. Phys.*, **8**, 231 (1941).

[11] J. F. Thomas and G. Branch, *J. Am. Chem. Soc.*, **75**, 4793 (1953).

orbital energies in Table I, this is, 1.858β, 1.932β, 2.000β, 2.117β. Since cinnamaldehyde has in reality no C_{2v} symmetry and the energies of these configurations are close to each other, the configuration interaction between them must be taken into consideration in order to ascertain the above assignment for V_{36}. For simplicity only the interaction is here considered between configurations of apparently the same symmetry type. Accordingly, the interaction between V_{36}, V_{58} and V_{47} is taken into consideration. The state energies for them were calculated including configration interaction. The results of the calculation are shown in Table IV. The calculated value for V_{36} is in good agreement with the observed value within present approximation. The calculated value 5.53 eV. for V_{36} conforms rather with the band at 224 mμ (5.53 eV.), but we may tentatively assign the transition from ϕ_3 to ϕ_6 to the band at 218mμ within the present approximation. Since the orbitals ϕ_3 and ϕ_6 of cinnamaldehyde correspond to the orbitals ϕ_2 and ϕ_3 of acrolein in Fig. 3, it may be said that the 218 mμ band corresponds to the transition in the substituent group.

TABLE IV. EXCITATION ENERGIES FOR LOWER EXCITED STATES OF CINNAMALDEHYDE

	$(m_i-m_j)\beta$ eV.	Including C. I.	Obs.
V_{36}	6.13	5.53	5.69
V_{58}	6.38	6.22	
V_{47}	6.60	7.37	

Summary

State energies of the cinnamaldehyde molecule are calculated by the simple LCAO-MO method, including configuration interaction and assuming the C_{2v} symmetry. The results of the calculation conform well with the observed absorption bands lying in the 2000～3000 Å region. In cinnamaldehyde the 280 mμ band is assigned to the intramolecular charge transfer band. The B_2^- band which we could not find in spectrum of cinnamaldehyde may be covered under the charge transfer band which is greatly shifted toward the red as the result of extension of conjugation. In the region of the band II^c two peaks at 224 and 218 mμ represent two different transitions, respectively. The former is assigned to the B_2^+ type transition and the latter to the transition in the acrolein group.

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