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Theoretical Considerations of Lower Excited States of *trans*-Polyene Carbaldehydes. I. Electronic Structure and Oscillator Strength of π-π^* Transition

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The lower n,π^* and π,π^* excited state energies of four *trans*-polyenecarbaldehydes, acrolein, 2,4-pentadienal, 2,4,6-heptatrienal, and 2,4,6,8-nonatetraenal, were calculated within the framework of the conventional P-P-P SCF-MO-CI method and then discussed. Also, the oscillator strength for the π-π^* transition was obtained in terms of the dipole length and the dipole velocity.

So far systematic studies of the electronic properties of polyenecarbaldehydes have been relatively rare. Among them, only two compounds, acrolein,[1-4] which is a fundamental molecule of this series, and retinal[5-10] which corresponds to 2,4,6,8,10-dodecapentaenal in the skeletal structure of the π-electron system, have been well studied both experimentally and theoretically in terms of their electronic properties. The purpose of this investigation was to study theoretically the properties of the lower electronic states of certain *trans*-polyenecarbaldehydes, that is, acrolein, 2,4-pentadienal, 2,4,6-heptatrienal, and 2,4,6,8-nonatetraenal. In this series we want to discuss the following three subjects from a theoretical point of view; (i) the electronic structure of the lower n,π^* and π,π^* states of *trans*-polyenecarbaldehydes and their oscillator strengths for π-π^* transition, (ii) their emission spectra, and (iii) their triplet-triplet transition and oscillator strength.

In this investigation the lower n,π^* and π,π^* excited-state energies of four *trans*-polyenecarbaldehydes were calculated within the framework of the conventional P-P-P SCF-MO-CI method[11,12] and then discussed. Also, their oscillator strengths for the π-π^* transition were obtained in terms of the dipole length and the dipole velocity.[13-15] These results were then compared with the experimental values.

Method of Calculation

Electronic Structure. The following numerical values[16] were assumed for the skeletal structure of the four polyenecarbaldehydes in the present paper: 1.36 Å for the carbon double bond, 1.46 Å for the single bond, and 1.22 Å for the carbonyl group. Moreover, the value of 120° was assigned to the ∠CCC and ∠CCO bond angles. *Only the trans and planar skeletal structures were taken into account.*

All the calculations were carried out within the framework of the general semi-empirical SCF-MO-CI method,[11,12] and the Pariser-Parr approximation[11] was used for the π-electron repulsion integrals, with $Z_C=3.25$ and $Z_O=4.55$. All the penetration terms were neglected. The resonance integral for the nearest neighbor carbon atom was treated as a parameter, and the values of -2.50 and -2.30 eV were used for the carbon double and single bonds respectively. The resonance integral value for the carbonyl group was obtained by means of Kon's equation,[17] and the value of -2.67 eV was used for all the polyenecarbaldehydes. The n,π^* and π,π^* state energies were calculated including all singly-excited configurations.

On the other hand, Sidman[18] carried out n,π^* state energy calculations for the several carbonyl molecules within the framework of the P-P-P SCF-MO-CI method. He assumed that the energy of the *n*-orbital of the carbonyl molecule is constant, and -10.50 eV was assigned to the *n*-orbital energy of carbonyl molecule. In this paper, the *n*-orbital on the oxygen atom is assumed to be a 2pπ atomic orbital,[19] and its energy, ε_n, was calculated by means of the following equation:[19,20]

$$\varepsilon_n = U_n + \sum_{\mu \neq o}(P_{\mu\mu}-1)\gamma_{\mu n} + (P_{oo}-1)(\gamma_{no}-\delta_{no}/2) \qquad (1)$$

The two one-center integrals concerning the oxygen atom, γ_{no} and δ_{no}, represent $\langle n_O\pi_O|r_{12}^{-1}|n_O\pi_O\rangle$ and $\langle n_O\pi_O|r_{12}^{-1}|\pi_O n_O\rangle$ respectively. The value of 12.865 eV[18] was used for the former integral, while the value of 0.903 eV[21] was assigned to the latter one. The $\gamma_{\mu n}$ is a two-center atomic repulsion integral between the π-electron of the carbon atom, μ, and the *n*-electron of the oxygen atom. The $\gamma_{\mu n}$ was calculated by means of the usual Pariser-Parr approximation.[11] U_n is treated as a parameter for the *n*-electron orbital energy. The calculated n,π^* singlet state energy of acrolein was adjusted to the corresponding observed value for acrolein by means of parameter, U_n, and the value of -15.25 eV was assigned to it. In a previous paper,[19] the value of -14.75 eV[22] was used for U_n, but this value brought about a lower value in the n,π^* singlet-state energy than the value observed in the case of the P-P approximation.

Oscillator Strength of the π-π^* Electronic Transition. A. Transition Density: In MO theory, the transition probability is related to the transition density, ρ. In the absence of degeneracy, the transition density for an allowed singlet absorption from a closed-shell ground state to an upper state is given by:

$$\rho = \sqrt{2}\,\phi_i\phi_j \qquad (2)$$

where ϕ_i and ϕ_j are the molecular orbitals concerning an electron excitation. Expressing the molecular orbitals as linear combinations of atomic orbitals:

$$\phi_j = \sum_t c_{tj}\chi_t \qquad (3)$$

one gets the transition density matrix, ρ, in the atomic orbital basis with elements:

$$\rho_{st} = \sqrt{2}\, c_{si} c_{tj} \tag{4}$$

The transition moment becomes:

$$M = \sum_s \sum_t \rho_{st} m_{st} \quad \text{where } m_{st} = \langle \chi_s | r | \chi_t \rangle. \tag{5}$$

In an analogous manner, the transition gradient is:

$$D = \sum_s \sum_t \rho_{st} d_{st} \quad \text{where } d_{st} = \langle \chi_s | \text{grad} | \chi_t \rangle. \tag{6}$$

The oscillator strengths, f_1 and f_2, are given by Eqs. (7) and (8):

$$f_1 = 1.085 \times 10^{11} \nu M^2 \tag{7}$$

$$f_2 = 1.465 \times 10^5 D^2 / \nu \tag{8}$$

where ν is in wave number and where the integral is expressed in atomic units. In the present calculation, the f_1 oscillator strength is represented in terms of the conventional dipole length assuming a zero-differential overlap.

B. Transition Gradient Integral: In Cartesian coordinates in terms of the unit vectors, **i**, **j**, and **k**, the transition gradient integral between 2pπ atomic orbitals, a and b, is expressed by Eq. (9):

$$\langle a | \sum_j \nabla_j | b \rangle = (\mathbf{i} \cos x_{ab} + \mathbf{j} \cos y_{ab} + \mathbf{k} \cos z_{ab}) \nabla_{ab} \tag{9}$$

where cos x_{ab} is the direction cosine of the directed line connecting the atom a to the atom b with respect to the x axis. Similarly for y and z, ∇_{ab} is the absolute value of the $\langle x_a | \nabla | x_b \rangle$. The only component which contributes to the integral, ∇_{ab}, is the one directly along the bond from the atom a to the atom b, because of the symmetry of the 2pπ atomic orbital, the value of the intergral remains unchanged by reflection in the plane perpendicular to the orbital axis.

Let the molecule lie on the y z plane and let the 2pπ atomic orbital be along the x-axis. Then, the 2pπ atomic orbital of the q atom is:

$$\chi_q = (\mu_q^5/\pi)^{1/2} r \exp(-\mu_q r) \sin\theta \cos\phi \tag{10}$$

The μ_q corresponds to the Slater-μ-value of the orbital exponent of the q atom. In the present calculation, the values of 1.625 and 2.275 were used as the Slater-μ-values for the carbon and oxygen atoms respectively. The z axis is taken directly along the bond from the a atom to the b atom. The z component of the gradient primitive integral is:

$$\nabla_{ab} = \langle \chi_a | \partial/\partial Z | \chi_b \rangle \tag{11}$$

Then,

$$\nabla_{ab} = -\mu_b \langle \chi_a | z/r | \chi_b \rangle \tag{12}$$

The integral (12) was transformed into elliptical coordinates[23] after the substitution of the atomic orbital (10); it was evaluated as follows:

$$\nabla_{ab} = -\mu_b (R/2)^5 (\mu_a \mu_b)^{5/2} \{(B_1 - B_3)(A_4 - 2A_2 + A_0) + (B_4 - 2B_2 + B_0)(A_1 - A_3)\} \tag{13}$$

In the case of $t=0$, Eq. (12) may be simplified as follows:

$$\nabla_{ab} = -\mu_b (p/5)(1 + p + p^2/3) \exp(-p) \tag{14}$$

where

$$p = (1/2)(\mu_a + \mu_b) R/a_0, \quad t = (\mu_a - \mu_b)/(\mu_a + \mu_b) \tag{15}$$

R is the bond distance between the a and b atoms, and a_0 is the Bohr radius (0.529 Å).

Results and Discussion

The calculated results of the π,π^* state energy and the oscillator strength of the present polyenecarbaldehydes are shown in Table 1, along with their calculated n,π^* state energies. The calculated values for the lowest singlet and triplet states are plotted in Fig. 1. The calculated n-π^* transition energies for the four *trans*-polyenecarbaldehydes from acrolein to 2,4,6,8-nonatetraenal are almost all the same. The present theoretical calculation suggests that the n,π^* singlet state is lower than the π,π^* singlet state from *trans*-acrolein to *trans*-2,4,6-heptatrienal, while the former state of *trans*-2,4,6,8-nonatetraenal is higher than its latter state. However, from the experimental fact about retinals,[7] the n,π^* singlet state of *trans*-2,4,6,8-nonatetraenal may be still lower than its π,π^* state. Judging from the experimental results[7] and the fact that the π-electronic structure of retinal is not exactly the same as that of the corresponding polyenecarbaldehyde because of the difference in the molecular structure between retinal and dodecapentaenal, the relative order of the n,π^* and π,π^* singlet states of dodecapentaenal may be critical. The n,π^* singlet state of a polyenecarbaldehyde larger than dodecapentaenal should be higher than its π,π^* singlet state.

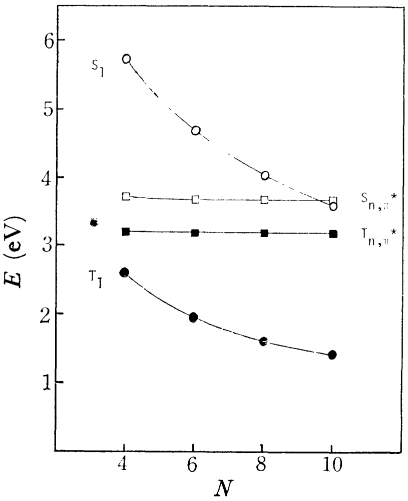

Fig. 1. Calculated lowest n,π^* and π,π^* state energies of *trans*-polyene aldehydes. N corresponds to the number of atom in the conjugated system of polyene aldehyde.

On the other hand, all the calculated n,π^* triplet states of the present molecules are higher than their π,π^* triplet states, though the experimental result for acrolein shows that the n,π^* triplet state, 3.01 eV,[4,24] is lower than the π,π^* triplet state, 3.05 eV.[3] The energy difference in acrolein between the n,π^* singlet and triplet states is about 0.7 and 0.5 eV in the experimental and theoretical values respectively. The energy difference between the two states depends on the one-center integral, $\langle n_O \pi_O | r_{12}^{-1} | \pi_O n_O \rangle$; the value of 0.903 eV[21] was assigned to that. To improve the present difference, a larger one-center integral value may be better. Plotnikov[25] used the value of 1.26 eV for this

Table 1. Calculated n,π^* and π,π^* singlet and triplet state energies of *trans*-polyenecarbaldehydes (in eV)

Molecule	Sym.	Singlet					Triplet	
		E_{calcd}	E_{obsd}	f_1	f_2	f_{obsd}	E_{calcd}	E_{obsd}
Acrolein								
1	A′	5.746	5.96[a)]	0.852	0.427		2.630	3.05[b)]
2	A′	7.351		0.063	0.018		4.187	
3	A′	8.006		0.048	0.016		7.572	
1	A″	3.720	3.71[a)]				3.207	3.01[c)]
2,4-Pentadienal								
1	A′	4.685	4.60[d)]	1.285	0.576	0.58[d)]	1.957	
2	A′	6.603		0.012	0.012		3.419	
3	A′	6.671		0.053	0.010		4.273	
1	A″	3.694	3.50[d)]				3.190	
2,4,6-Heptatrienal								
1	A′	4.039	4.06[e)]	1.688	0.708	0.86[e)]	1.616	2.2[f)]
2	A′	5.836		0.060	0.013	0.14	2.778	
3	A′	5.939		0.004	0.013		3.778	
1	A″	3.693					3.193	
2,4,6,8-Nonatetraenal								
1	A′	3.609	3.65[d)]	2.055	0.821		1.423	1.9[f)]
2	A′	5.298		0.049	0.019		2.336	
3	A′	5.401		0.012	0.018		3.264	
1	A″	3.694					3.197	

a) See Ref. 2. b) See Ref. 3. c) See Ref. 4. d) See Ref. 29. This f number corresponds to that of 2,4-hexadienal which was calculated from the data in Ref. 29. e) See Ref. 30. f) See Ref. 26.

integral in his calculation. The calculated n,π^* triplet states of the other molecules are higher than their π,π^* triplet states. This result seems reasonable in view of experimental results on acrolein and the n,π^* and π,π^* singlet-triplet energy separation.

Judging from the present results, the lowest triplet state of polyenecarbaldehyde may be said to be of the π,π^* character, but not of the n,π^* character except for the case of acrolein. The slope of the n,π^* state energy curves in Fig. 1 is nearly flat compared with that of the π,π^* state energy curves. This result suggests that the lowest n,π^* triplet state may also be higher than the lowest π,π^* singlet state from the polyenecarbaldehyde larger than nonatetraenal. The calculated π,π^* triplet state energies of the present molecules are not in good agreement with the observed values.[26] The energy difference between the calculated and observed values is within the range of about 0.5 eV. The theoretical values are lower than the experimental values.[26] A similar result was reported by Forster[27] in the triplet-state calculation of polyene by the SCF–MO method using the Mataga-Nishimoto approximation.[28] In his case, the calculated values range from 1.43 to 0.98 eV as the carbon chain varies from C_4 to C_{22}. We also have obtained the similar result that SCF-MO calculation using the Mataga-Nishimoto approximation gives lower values than the values calculated by means of the Pariser-Parr integral with respect to the triplet state of polyenecarbaldehyde. Figure 1 shows that the singlet-triplet splitting of polyenecarbaldehyde decreases in the n,π^* and π,π^* states as the number of the atom in the conjugated system increases.

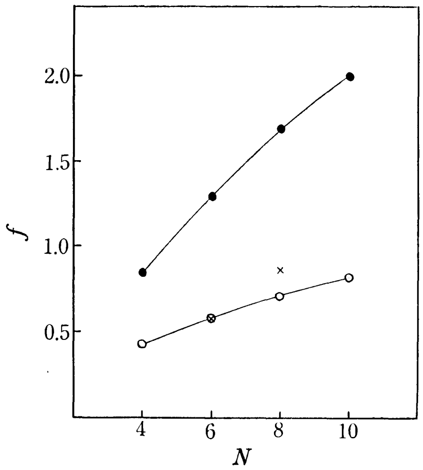

Fig. 2. Oscillator strength of the lowest π-π^* transition of *trans*-polyene aldehydes.
● corresponds to f_1, ○ to f_2, and × to f_{obsd}

The oscillator strengths, f_1, f_2, and f_{obsd}, are plotted in Fig. 2. The oscillator strengths calculated by means of Eq. (7) are larger than the observed values, and they increase rapidly as the number of the atom, N, increases. The ratio of f_1 to f_{obsd} is about 2.

On the other hand, the oscillator strengths calculated by means of Eq. (8) are smaller than the observed values, but the agreement between them is much better. The ratio of f_2 to f_{obsd} ranges from 0.8 to 1. The trend of the f_2 curve is closer to that of f_{obsd} than the trend of the f_1 curve in Fig. 2. Comparison with the both theoretical results suggests that the dipole-velocity treatment is better than the dipole-length method in the molecular orbital calculation of conjugated molecules as long as the point charge approximation is adopted to the calculation of the oscillator strength.

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