Theoretical Considerations of Lower Excited States of *trans*-Polyenecarbaldehydes. II. Radiative and Nonradiative Properties

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The spin-orbit coupling energies between the lowest $^1(n,\pi^*)$ and $^3(\pi,\pi^*)$ states, and between the lowest $^1(\pi,\pi^*)$ and $^3(n,\pi^*)$ states, for the four polyenecarbaldehydes were calculated using the results calculated within the framework of the conventional P–P–P SCF–MO–CI method. In the present paper, the general properties of the emission spectra of polyenecarbaldehyde are theoretically considered using the calculated results for the spin-orbit coupling energy and their lower electronic structure.

In a previous paper,1) the electronic structures of the lower n,π^* and π,π^* states of planar *trans*-polyenecarbaldehydes (acrolein, 2,4-pentadienal, 2,4,6-heptatrienal, and 2,4,6,8-nonatetraenal) and their oscillator strengths for the π-π^* transition were studied within the framework of the conventional P–P–P SCF–MO–CI method and then discussed. We can not even tentatively discuss the overall features of the emission property of polyenecarbaldehydes, however, because experimental data on the emission spectra of polyenecarbaldehyde are relatively rare except for acrolein2) and for retinal,3) which corresponds to 2,4,6,8,10-dodecapentaenal in the skeletal structure of the π electron system. In this investigation, the general features of their radiative and nonradiative properties will be discussed theoretically, using the previous results.1)

Method of Calculation

When a single-electron operator is used for the spin-orbit Hamiltonian, the coupling of the n,π^* and π,π^* states is as follows:

$$\beta\langle n\pi^*|\pi\pi^*\rangle = \pm(\hbar e^2/4m^2c^2)\langle\pi|H_o|n\rangle \tag{1}$$

where H_O is the orbital part of the spin-orbit coupling operator for molecular systems.4)

$$H_o = (e^2/2m^2c^2)\sum_\lambda\sum_i Z_\lambda^* l_i/r_{i\lambda}^3 \tag{2}$$

where Z_λ^* is the Slater effective charge of the nucleus, λ; $r_{i\lambda}$, the distance of the electron, i, from the nucleus, λ and l_i, the orbital moment of the i electron. $<\pi|$ and $<n|$ are the wavefunctions of the π- and n-electrons respectively for the ground state. $<\pi|$ has already been obtained by means of the P–P–P SCF–MO–CI method, and $<n|$ has been assumed in the previous paper1) to be 2p-type atomic orbital localized on the oxygen atom of the carbonyl group. If we neglect all the two-center integrals, the spin-orbit coupling energy between the n,π^* and the π,π^* states is represented by Eq. (3):

$$\beta\langle n\pi^*|\pi\pi^*\rangle = \pm i(\hbar^2e^2/4m^2c^2)(Z_o^{*4}c_o/3n_o^{*3}a_H^3) \tag{3}$$

where Z_O^* corresponds to the effective nuclear charge of the 2p atomic orbital of the oxygen atom and c_O, to the coefficient of the 2pπ-AO of the oxygen atom of the π-MO; n_O^* is the effective principal quantum number of the n electron, and a_H is the Bohr radius (0.529 Å). In the present calculation the numerical values of $Z_O^*=4.55$ and $n_O^*=2$ were used. When $\alpha=\pm i(\hbar^2e^2Z^{*4}/12m^2c^2n_O^{*3}a_H^3)$ is substituted into Eq. (3), the absolute value of the square of Eq. (3) may be represented as follows:

$$|\beta\langle n\pi^*|\pi\pi^*\rangle|^2 = |\alpha|^2c_o^2 \tag{4}$$

The absolute value of α for the oxygen atom is equal to 52.2 cm^{-1}. The calculation of the spin-orbit interaction matrix element between $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ states or $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states is not as easy as the calculation of the spin-orbit interaction matrix element between the different configurations. However, it is known that this quantity is much smaller than the corresponding one with a different configuration because of the lack of the contribution from the one-center term in the spin-orbit interaction matrix element. Here, this quantity is assumed to be of the order of 1 cm^{-1}.5) Thus, the spin-orbit coupling between the two states with different configurations is more important than that between those with the same configuration; the former energy may be several orders of magnitude greater than the latter one. Therefore, the efficiency6) of the intersystem crossing process, $^1(\pi,\pi^*)\rightsquigarrow{}^3(n,\pi^*)$ or $^1(n,\pi^*)\rightsquigarrow{}^3(\pi,\pi^*)$, is larger than that for the $^1(\pi,\pi^*)\rightsquigarrow{}^3(\pi,\pi^*)$ or $^1(n,\pi^*)\rightsquigarrow{}^3(n,\pi^*)$ process.

On the other hand, the energy separation between the lowest π,π^* singlet state, S_1, and the n,π^* triplet state, T_{n,π^*}, decreases, whereas the corresponding one between the n,π^* singlet state, S_{n,π^*}, and the lowest π,π^* triplet state, T_1, increases1) as the molecular size increases. Therefore, the $S_{n,\pi^*}\rightsquigarrow T_1$ process plays a more important role in the radiationless deactivation of acrolein than does the $S_1\rightsquigarrow T_{n,\pi^*}$ process, but the situation is reversed as the molecular size increases. In order to ascertain the relation between the spin-orbit interaction energy and the energy separation of the two states concerning the radiationless process, the conversion time for the radiationless process was estimated using the Robinson-Frosch equations, (5) and (6):7)

$$k = 0.71\times10^{12}\times\beta_{ij}^2\times S_{ij} \tag{5}$$

$$S_{ij} = \exp(-0.25\times E_{ij}^{0.4}) \tag{6}$$

where β_{ij} is the matrix element of [the interaction operator between i and j states, and where S_{ij} corresponds to the over-all vibrational factor in their paper.7) The conversion time can, then, be represented by Eq. (7):

$$\tau_{1/2} = \ln 2/k \qquad (7)$$

As Eqs. (5) and (6) were developed for aromatic compounds,[7] the application of these equations to polyenecarbaldehydes might not be justified. The critical comparison of the numerical values might be impossible, but the order-of-magnitude consideration may be useful for the discussion of the intersystem crossing process.

Results and Discussion

The absolute value of the square of the operator matrix elements for the spin-orbit coupling between S_{n,π^*} and T_1, and for that between S_1 and T_{n,π^*}, of the present four molecules and the conversion time were calculated by means of Eqs. (4) and (7), respectively. The calculated results are presented in Table 1. The square of the spin-orbit interaction between S_{n,π^*} and T_1, and/or S_1 and T_{n,π^*}, decreases rapidly with an increase in the number of atoms in the conjugated system. The calculated energy values[1] for the singlet and triplet states are plotted in Fig. 1.

In order to discuss the radiative and nonradiative processes of the excited states of polyenecarbaldehyde, we classified the electronic structures of their lower excited states into the following four groups (see also Fig. 2 for a schematical diagram). Acrolein, whose lowest excited singlet and triplet states are of an n,π* character, was assigned to *Group* (1), and the remaining three polyenecarbaldehydes, to *Group* (2), for which the lowest excited singlet state is of an n,π* character, while the lowest excited triplet state is of a π,π* character. Although the assignment of nonatetraenal to *Group* (2) may be controversial in that its lowest singlet π,π* state was calculated to be a little lower than the lowest n,π* singlet state, the lowest π,π* singlet state of nonatetraenal is estimated to be higher than its n,π* singlet state on the basis of the experimental results for retinals,[3] as has been discussed in the previous paper.[1] Some polyenecarbaldehydes with longer skeletal chains than nonatetraenal, *e.g.*, dodecapentaenal, were assigned to *Group* (3), for which both the lowest singlet and triplet states of the molecule are of a π,π* character; other, longer polyenecarbaldehydes whose lowest n,π* triplet states are higher in energy than their lowest singlet π,π* states were assigned to *Group* (4).

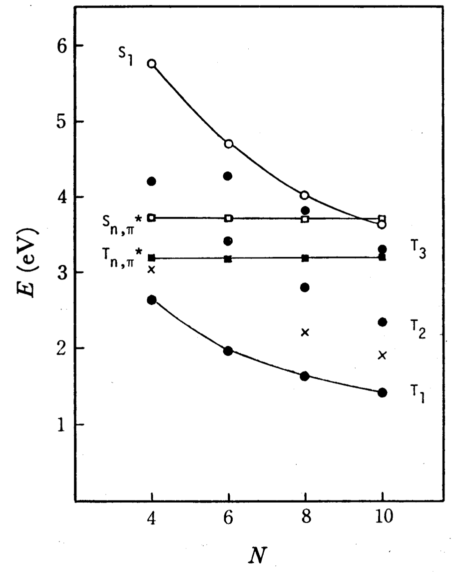

Fig. 1. Calculated lowest n,π* and π,π* state energies of *trans*-polyenecarbaldehydes.
N corresponds to the number of atom in the conjugated system of polyenecarbaldehyde. × corresponds to the observed value for the lowest π,π* triplet state energy (see Ref. 1).

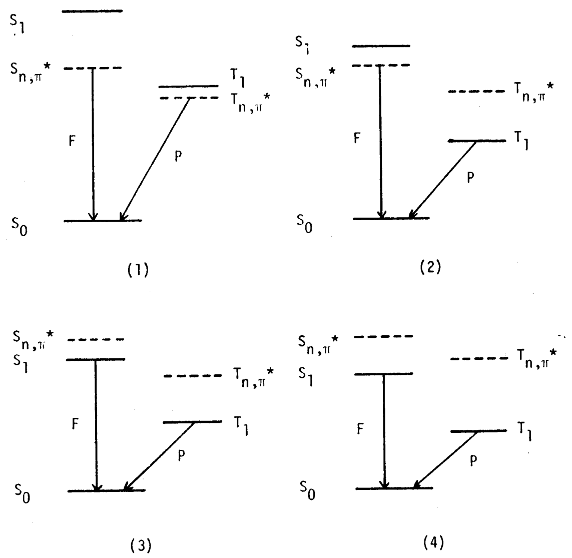

Fig. 2. Schematic energy level diagrams of polyenecarbaldehydes: (1), (2), (3), and (4) correspond to group (1), group (2), group (3), and group (4) (see text).

The general features of radiative and nonradiative properties for each case may be described as follows:

(i) *Group* (1). The observed electronic structure of the lower-lying excited states of acrolein is different in the order of T_{n,π^*} and T_1 states from the calculated

Table 1. Calculated values for the absolute square of spin-orbit coupling energy and conversion time[a] between S_{n,π^*} and T_1, or between S_1 and T_{n,π^*} of *trans*-polyenecarbaldehydes (in cm^{-2} and s)

	Acrolein	2,4-Pentadienal	2,4,6-Heptatrienal	2,4,6,8-Nonatetraenal
$\lvert\langle S_{n,\pi^*}\lvert H_{SO}\rvert T_1\rangle\rvert^2$	650	280	150	90
$\lvert\langle S_1\lvert H_{SO}\rvert T_{n,\pi^*}\rangle\rvert^2$	430	210	130	80
$\tau(S_{n,\pi^*}\rightsquigarrow T_1)$	3.4×10^{-12}	3.1×10^{-10}	1.4×10^{-9}	3.7×10^{-9}
$\tau(S_1\rightsquigarrow T_{n,\pi^*})$	3.0×10^{-9}	2.1×10^{-10}	4.0×10^{-11}	0.7×10^{-11}

a) The conversion time was obtained by Eq. (7) in text.

results shown in Fig. 1. The lowest triplet is T_{n,π^*}, lying at 3.01 eV,[8,9] while the next triplet state is of a π,π^* character, lying at 3.05 eV.[10] As the separation between the two states is very small, the lowest n,π^* state may be mixed with the lowest triplet π,π^* state by the vibronic coupling. Excitation to the lowest S_{n,π^*} state may result in fluorescence, internal conversion to S_0, and/or intersystem crossing to the T_1 state. The experimental results[2] for acrolein showed that the fluorescence is very weak ($\Phi_F(77\ K)=0.007$) and of an n,π^* character; the phosphorescence is also very weak ($\Phi_P(77\ K)=4\times10^{-5}$).

On the other hand, it will be useful to refer to the spectra of testosterone and its derivatives, which contain conjugated systems similar to that of acrolein in their skeletal structures. Their lowest triplet states have been assigned as the π,π^* type, primarily on the basis of the lifetime of the phosphorescence and the separation of the onset of phosphorescence from the observed S_0—T_{n,π^*} excitation spectrum.[11,12] These quantum yields ranged from 0.2—0.3, but no fluorescence was reported. The fluorescences for these compounds are expected to be very weak due to the effective intersystem crossing from S_{n,π^*} to T_1 and the weak intensity of the n-π^* transition. The relationship[13] between the absorption intensity and the fluorescence lifetime of the molecule suggests that the radiative lifetime for the fluorescence with an n,π^* character may be much longer than the nonradiative lifetime for the intersystem crossing process from S_{n,π^*} to T_1 states.

The lowest triplet state of acrolein may be populated mainly *via* the $S_{n,\pi^*} \rightsquigarrow T_1 \rightsquigarrow T_{n,\pi^*}$ and $S_1 \rightsquigarrow T_{n,\pi^*}$, while the corresponding state of the above-mentioned keto steroid is populated *via* the $S_1 \rightsquigarrow T_{n,\pi^*} \rightsquigarrow T_1$ and $S_{n,\pi^*} \rightsquigarrow T_1$ processes. With respect to the efficiency of the lowest triplet population of the two compounds, the keto steroid may have an advantage, because the radiationless lifetime for the $S_{n,\pi^*} \rightsquigarrow T_1$ process is much shorter than that for the $S_1 \rightsquigarrow T_{n,\pi^*}$ process, as is shown in Table 1. The reason for the difference in the intensity of phosphorescence of the two compounds may be explained to some extent by the assumption that the following equation holds for the phosphorescence state of the two compounds:

$$[k(T_{n,\pi^*} \rightsquigarrow S_0)/k(T_{n,\pi^*} \rightarrow S_0)] \gg [k(T_1 \rightsquigarrow S_0)/k(T_1 \rightarrow S_0)] \qquad (8)$$

Where the $k(T_i \rightsquigarrow S_0)$ and $k(T_i \longrightarrow S_0)$ notations correspond to the rate constants for the nonradiative and radiative processes respectively from the lowest triplet to the ground state.

However, the above discussion is not enough to explain the difference in the Φ_P values for the two compounds. The difference in the Φ_P may be attributed to the twisting of the carbon-carbon double bond of acrolein[2] in the π,π^* triplet state and to the stability of the cyclic structure of testosterone. Although a restricted twisting is possible in testosterone and its derivatives, the twisting will not give rise to the *cis-trans* isomerization. Also, the intersystem crossing to the ground state is expected to be less than for acrolein because of the restricted twisting. Therefore, the quantum yield of phosphorescence may be considerably larger than for acrolein.

(ii) *Group* (2). There are some higher-lying π,π^* triplet states between the S_{n,π^*} and T_1 states. Accordingly, the radiationless deactivation processes from S_{n,π^*} by spin-orbit coupling include not only $S_{n,\pi^*} \rightsquigarrow T_1$, but also the $S_{n,\pi^*} \rightsquigarrow T_i$ (i-th π,π^* triplet state)$\rightsquigarrow T_1$ process. These processes may compete with the radiative process from S_{n,π^*}. The increase in the fluorescence for *Group* (2) may not be expected. In Table 1, the spin-orbit interaction matrix elements between S_{n,π^*} and T_1 or S_1 and T_{n,π^*} decrease with an increase in the molecular size, but the energy separation between S_1 and T_{n,π^*} decreases rapidly.

The calculated lifetime for the radiationless process, $\tau(S_1 \rightsquigarrow T_{n,\pi^*})$, becomes shorter and its process becomes important for the population of the lowest triplet state, T_1. The lowest triplet state for *Group* (2) is populated through the same processes for the keto steroid and the other two processes, $S_{n,\pi^*} \rightsquigarrow T_i \rightsquigarrow T_1$ and $S_1 \rightsquigarrow T_{n,\pi^*} \rightsquigarrow T_i \rightsquigarrow T_1$, but the latter two processes may be less efficient than the $S_{n,\pi^*} \rightsquigarrow T_1$ process. The present discussion shows that the efficiency of the population for the lowest triplet state of *Group* (2) may be worse than that of acrolein and the keto steroid. The phosphorescence for *Group* (2) may be expected to be very weak or not emissive if we take into account the twisting effect.

(iii) *Group* (3). The fluorescence has been observed for *trans*-retinal,[3] a model compound of *Group* (3), but no phosphorescence spectrum was observed at 77 K. The calculated value for the radiationless lifetime, $\tau(S_1 \rightsquigarrow T_{n,\pi^*})$, for nonatetraenal shows that the radiationless deactivation of the S_1 state becomes dominant. This result suggests that the excitation to the lowest singlet state, S_1, of *trans*-retinal may result in a rapid intersystem crossing to the T_{n,π^*} state before it fluoresces, as long as the lowest singlet state is of a π,π^* character. In a previous paper,[3] the fluorescence quantum yield of retinal was reported to be 0.71 (exciting at 440 nm at 77 K), but the value seems to be too large[14] in view of the above considerations and the comparison with the corresponding value of acrolein ($\Phi_F(77\ K)=0.007$). The previous calculation[3] showed that the *cis-trans* isomerization occurs in the lowest π,π^* singlet and triplet states. Its isomerization is one kind of radiationless deactivation process in the excited states. The experimental results for *trans*-retinal[3] suggest that such isomerization plays an important role in the emissibility of polyenecarbaldehyde. Therefore, the phosphorescence of *Group* (3) may be expected to be very weak or not emissive when we take the isomerization in the lowest triplet state into account.

(iv) *Group* (4). The fluorescence of *Group* (4) may become stronger than that of the other groups because of the decrease in the efficiency of the spin-orbit coupling for the $S_1 \rightsquigarrow T_1$ radiationless process resulting from the same configuration, although the internal conversion, $S_1 \rightsquigarrow S_0$, may increase. As the energy separation between S_1 and T_1 states decreases with an increase in the molecular size, the population of the T_1 state *via* the S_1 state may become relatively better in efficiency as the molecular length becomes larger.

As the lowest singlet and triplet states of *Group* (4) are all of a π,π^* character, β-carotene[15] and retinyl polyenes[16] may be model compounds for *Group* (4) in lower π electronic structures. These experimental results suggest that the fluorescence of *Group* (4) is much stronger than that of the other groups. In the case of β-carotene,[15] the phosphorescence was observed at 77 K, although it was weak. The conjugated system of the β-carotene is much longer than that of *trans*-retinal. Its energy separation between the S_1 and T_1 states was about 1000—1500 cm^{-1},[15] while the corresponding theoretical value of the model compound for *trans*-retinal was about 1600 cm^{-1}.[3] The delayed emission of β-carotene has been tentatively assigned to the S–T phosphorescence due to the thermal excitation.[15] This type of emission requires a small S–T energy separation. Therefore, such emission can not be expected for the small polyenecarbaldehyde in *Group* (4). As an increase in the conjugated system makes for a small S–T energy separation, there is a possibility that the phosphorescence may be detected for the longer polyenecarbaldehyde. However, the most important factor for the observation of the emission spectra is the twisting effect in the conjugated system of polyenecarbaldehyde through all the groups.

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