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Theoretical Consideration on the Electronic Structures of *trans*- and *cis*-Isomers of Acrolein and 2,4-Pentadienal

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In the previous paper[1] an approach to n,π^*-state energy calculation was presented and the electronic structures of lower n,π^* and π,π^* states of several carbonyl molecules in the planar *trans* form were studied within the framework of the SCF–MO–CI approximation. Theoretical considerations suggest the possibility of the existence of *cis*-acrolein,[2] but its existence is not experimentally clear. Generally, no experimental evidence of the *cis*-form is known for such short polyene aldehydes as acrolein and pentadienal, but such longer ones as retinal, which corresponds to 2,4,6,8,10-dodecapentaenal in the π-electron system, have several *cis*-isomers.[3] In the case of retinal, its isomers play an important role in the vision mechanism of rhodopsin, and they have specific features in their optical behavior;[4] nevertheless, theoretical consideration of the electronic structure of *cis*-isomers of polyene aldehyde is still scarce. Therefore, it is of interest to make clear the electronic structure of *trans*- and *cis*-isomers of polyene aldehydes. The UV spectra of the conjugated enones and dienones have been well studied, and the empirical correlations of the UV absorption with the structure have become evident.[5,6] However, the band position of the n,π^* absorption spectrum for such a conjugated system as *trans*- and *cis*-polyene aldehydes is still unclear. In this paper the band positions of n,π^* and π,π^* states for *trans*- and *cis*-forms of acrolein and 2,4-pentadienal were studied by the same approach as was developed previously within the framework of the Pariser-Parr-Pople SCF–MO–CI method.[7,8] The P-P-type two-center repulsion integral[7] was used for the calculation of the π-electron system. The Mataga-Nishimoto approximation[9] was adopted for two-center repulsion integrals between n and π electrons.

In the previous paper[1] the value of -14.75 eV[10] was used for the parameter, U_n, in Eq. (7) corresponding to the n-orbital energy calculation. In this paper the value of -14.60 eV will tentatively be used for the U_n parameter in order to improve the calculated n,π^*-state energy.

The following numerical values[11] were used for the skeletal structures of acrolein and 2,4-pentadienal; 1.34 Å for the carbon double bond, 1.46 Å for the single bond, and 1.22 Å for the carbonyl group. The value of 120° was assigned to the C–C–C and C–C–O bond angles. All the calculations were carried out on the assumption of a planar structure for the present molecules.

Results and Discussion

The calculated results are listed in Table 1.

The intense absorption spectrum of acrolein is observed at 5.96 eV (208 nm), while the weak absorption band is observed at 3.71 eV (334 nm),[12] in an n-hexane solution. These observed values are assigned to the lowest π,π^* and n,π^* singlet states of acrolein.[12] These state energies correspond to the present calculated values, 5.960 eV (208 nm, $f=0.803$) for the π,π^* singlet state energy and 3.767 eV (329 nm) for the n,π^* singlet state energy.

On the other hand, the theoretical π,π^* and n,π^* singlet state energies of *cis*-acrolein are 5.608 eV (221 nm, 0.381) and 3.800 eV (326 nm). These results suggest that the π,π^* singlet state of *trans*-acrolein is higher than that of *cis*-acrolein and that the intensity of the former is larger than that of the latter. Those theoretical results correspond well with the observed results of the conjugated enones (from a to d)[13] shown in Fig. 1. The location of the n,π^* singlet state of

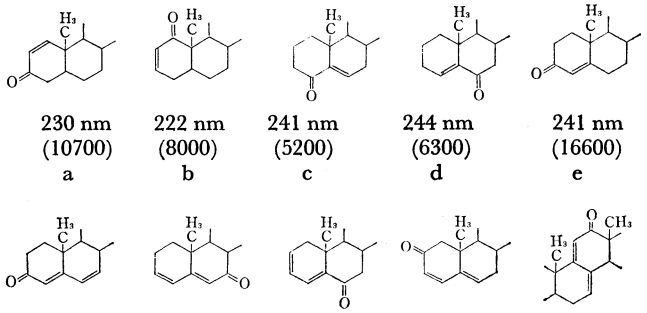

Fig. 1. Conjugated enones and dienones with the values of λ_{max} and intensities of their UV.[13]

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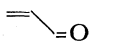
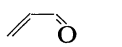
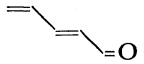
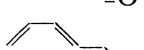
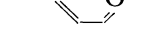
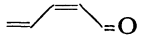
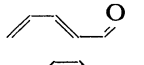
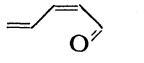
TABLE 1. CALCULATED LOWEST SINGLET AND TRIPLET STATE ENERGIES AND f NUMBERS OF *trans*- AND *cis*-ISOMERS OF ACROLEIN AND 2,4-PENTADIENAL WITH THE OBSERVED VALUES

Molecule		Sym	Singlet				Triplet	
			E_{cal}[a]	f_{cal}	E_{obs}	f_{obs}	E_{cal}	E_{obs}
trans-Acrolein		A'	5.960 (208)	0.803	5.96 (208)	0.10	2.935 (422)	3.05 (406)
		A''	3.767 (329)		3.71 (334)		3.255 (381)	3.01 (412)
cis-Acrolein		A'	5.608 (221)	0.381			2.969 (418)	
		A''	3.800 (326)				3.300 (376)	
2,4-Pentadienal	**A** 	A'	4.745 (261)	1.245	4.79 (259)	0.58[b]	2.048 (605)	
		A''	3.651 (340)		3.81 (325)		3.161 (392)	
	B 	A'	4.426 (280)	0.612			2.072 (598)	
		A''	3.661 (339)				3.172 (391)	
	C 	A'	4.603 (269)	0.859			2.098 (591)	
		A''	3.679 (337)				3.204 (387)	
	D 	A'	4.737 (262)	1.173			2.046 (606)	
		A''	3.650 (340)				3.162 (392)	
	E 	A'	4.376 (283)	0.595			2.120 (585)	
		A''	3.681 (337)				3.205 (387)	
	F 	A'	4.497 (276)	0.639			2.052 (604)	
		A''	3.657 (339)				3.189 (389)	
	G 	A'	4.312 (288)	0.382			2.056 (603)	
		A''	3.615 (343)				3.127 (396)	

a) eV in units; numbers in parentheses are in units of nm.
b) This f number corresponds to that of 2,4-hexadienal which was calculated from the data in Ref. 21.

cis-acrolein is a little bit higher than that of *trans*-acrolein, but there is no significant difference between the two n,π^* state energies; the difference may be within the range of accuracy of the present approximation.

The theoretical π,π^* triplet state energy of *trans*-acrolein, 2.935 eV is in good agreement with the observed value, 3.05 eV.[14] The corresponding value of *cis*-acrolein, 2.969 eV, is very close to that of *trans*-acrolein.

The calculated n,π^* triplet state energy of the *trans*-isomer, 3.255 eV, is still higher than the corresponding observed value, 3.01 eV,[15-17] although the present value is an improvement over the previous value, 3.405 eV.[1] According to the experimental results, the lowest triplet state of acrolein may be assigned to the n,π^* state, but both states are nearly degenerate. Therefore, the vibronic mixing of these states may be dominant.

The π,π^* singlet state of 2,4-pentadienal is observed at 4.79 eV (259 nm), and its n,π^* absorption spectrum is observed at 3.81 eV (325 nm), in an ethyl alcohol solution.[18] However, the n,π^* absorption spectrum of pentadienal appears at a shorter wavelength than that of acrolein, probably because of the solvent effect. The value of 4.79 eV may be assigned to the calculated π,π^* singlet state energy, 4.745 eV (261 nm, f=1.245), of the *trans*-isomer **A**. The calculated π,π^* singlet state energy and the oscillator strength of *trans*-pentadienal **A** are the largest of any other *cis*-isomers, as in the case of acrolein. This theoretical result is in harmony with the experimental results on the dienones (from f to j)[13] shown in Fig. 1. Figure 1 shows that the π,π^* singlet state and the intensity of *trans*-isomer are higher and larger than those of any *cis*-isomers. The calculated π,π^* singlet state energy and oscillator strength for the **D** isomer, 4.737 eV (262 nm) and 1.173, are larger than those of the **E** isomer, 4.376 eV (283 nm) and 0.595. Those results correspond well with the experimental results of the i or j and h compounds shown in Fig. 1.

The calculated n,π^* singlet energy of *trans*-2,4-pentadienal, 3.651 eV (340 nm), corresponds to the observed value, 3.81 eV (325 nm). The calculated n,π^* singlet state energies of *cis*-isomers lie within the range from 3.615 to 3.681 eV, as is shown in Table 1. It is interesting that there is no significant difference in the calculated n,π^* singlet state energy of *trans*- and *cis*-pentadienal isomers as there is in their π,π^* singlet state energy.

The calculated values of the π,π^* triplet state energies of pentadienal isomers lie within the range from 2.046 to 2.120 eV. The calculated lowest n,π^* triplet state energy of *trans*-pentadienal is 3.161 eV. The corresponding values of the *cis*-isomers range from 3.162 to 3.205 eV. These results suggest that the lowest π,π^* and n,π^* triplet states are almost constant in all the isomers.

The UV and optical rotatory dispersion curves of keto steroids containing *trans*- and *cis*-conjugated polyene aldehyde skeletal structures in their molecules may become experimental data for the comparison of the location of the n,π^* states of *trans*- and *cis*-isomers.

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However, the conjugated system of the keto steroid as a model compound of an acrolein or pentadienal isomer may be different from the present model assumed for an acrolein or pentadienal isomer because of some twisting around a certain single or double bond, because of some deviation from planarity, and because of the effect of the other parts of the keto steroid attached to the conjugated system. Especially, the comparison of the theoretical values of the acrolein and pentadienal isomers with the spectroscopic data of the corresponding keto steroids for the n,π^* singlet- and triplet-state energies and the π,π^* triplet energy should be done carefully, because there is no such significant difference in the energy states of *trans*- and *cis*-isomers with respect to the n,π^* states and the π,π^* triplet state respectively. Also, their n,π^*- and π,π^*-state energies are affected by the twisting of the single or double bond. The twisting about the single bond brings about a blue shift of the π,π^* state, while the double-bond twisting brings about a red shift.[2,3] The same theoretical result[19,20] is also obtained for the n,π^* state.

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