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Molecular Interactions through Carbonyl Groups. Dimerizations of Dibenzylideneacetone and Dicinnamylideneacetone at Low Temperature

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From the UV spectral data together with the MO calculated results, it has been suggested that dibenzylideneacetone or dicinnamylideneacetone forms a noncentrosymmetric dimer in a nonpolar matrix at low temperature. The dimerizations occur through interactions between carbonyl groups.

In a previous paper, it has been reported that 1,5-diphenylpenta-1,4-dien-3-one (dibenzylideneacetone; DBA) takes a twisted conformation at room temperature in a polyethylene (PE) film or an ethanol-methanol mixed solvent, but the conformation changes into a planar one at low temperature (101 K).[1)] In this paper, we report the interaction between DBA or 1,9-diphenylnona-1,3,6,8-tetraen-5-one (dicinnamylideneacetone; DCA) molecules in a nonpolar solvent such as a 1:1 mixture of methylcyclohexane and isopentane (MP) at low temperatures.

Figure 1 shows UV absorption spectra of DBA in MP at various temperatures. The first band is shifted to the red with decrease in temperature. The spectrum I resembles well with that observed in the PE film at room temperature, indicating that the spectrum I is due to the twisted conformer of DBA, in which the two styryl groups are not in coplanar.[1)] The first band of the spectrum II has a peak at 330.5 nm and three shoulders at 347 nm, 321 nm, and 283 nm. Comparison of the above mentioned bands and those observed in the PE film at 101 K[1)] suggests that the spectrum II may be due to a mixture of planar and twisted conformers of DBA, and that the shoulder around 347 nm (II in Fig. 1) may be regarded as the 0-0 transition of the first band of the planar conformer. With further decrease in temperature from 148 K to 101 K, the first band is shifted to the red (330.5 nm → 339 nm) and is broadened (spectrum III). These spectral changes have not been obtained in the PE film, in which guest molecules are considered to be dispersed monomolecularly. Thus, the observed spectral changes from II to III in Fig. 1 may be interpreted as due to interaction between planar DBA molecules

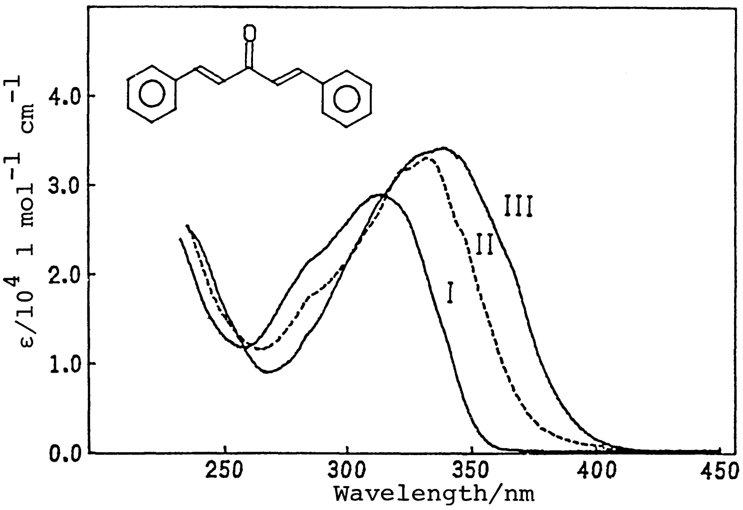

Fig. 1. The absorption spectra of dibenzylideneacetone (DBA) in a 1:1 mixed solvent of methylcyclohexane and isopentane (MP) at room temperature (I), 148 K (II) and 101 K (III).
ε: Molar absorptivity.

or a dimer formation. In polar media such as a 1:1 methanol-ethanol mixed solvent, the formation of dimer between DBA molecules is not observed, probably because of strong solvent-solute interactions. Such dimerization was recognized for formaldehyde in low temperature-argon and -nitrogen matrices.[2,3)]

To explain the above mentioned spectral changes (spectrum II to III in Fig. 1), MO calculations have been performed, the method being described elsewhere.[4)] In the calculation the geometry of the dimer is assumed to be as shown below. The calculated first and second transition energies and oscillator strengths are presented in Table 1. For the dimer having C_{2h} symmetry (θ=0°), the first transition is computed to be forbidden, but this transition becomes allowed one when the two C=O axes are not parallel ($\theta \neq 0°$). The observed strong band at 339 nm is safely assigned to the calculated $S_2 \leftarrow S_0$ transition of the dimer from consideration of the band position and intensity. The band corresponding to the calculated $S_1 \leftarrow S_0$ transition may be superposed upon the lower energy side of the 339 nm band. If the above considerations are the case, similar phenomena may be observed in other organic carbonyl compounds which have analogous chemical structures with DBA. In order to assure this, we have treated dicinnamylideneacetone (DCA). The absorption spectra of DCA in the PE film at room temperature and 101 K are shown in Fig. 2. From the similar arguments described earlier for DBA,[1)] the spectrum I can be assigned to the twisted DCA molecule, and the spectrum II to the planar one. The 0-0 band of the first electronic transition of the twisted DCA is observed as a shoulder

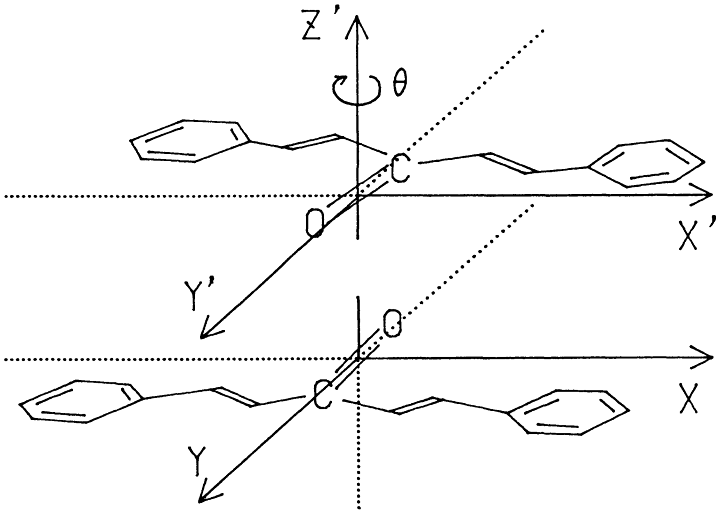

Table 1. The calculated $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transition energies and oscillator strengths of DBA and DCA dimers

		$S_1 \leftarrow S_0$		$S_2 \leftarrow S_0$		
	$\theta^{a)}$	Transition energy/nm	Oscillator strength	Transition energy/nm	Oscillator strength	Symmetry
	0°	336	forbidden	322	2.535	C_{2h}
DBA dimer	10°	336	0.02	322	2.512	C_2
	0°	387	forbidden	361	3.944	C_{2h}
DCA dimer	10°	386	0.028	361	3.916	C_2

a) θ is an angle between two C=O bond axes in the dimer.

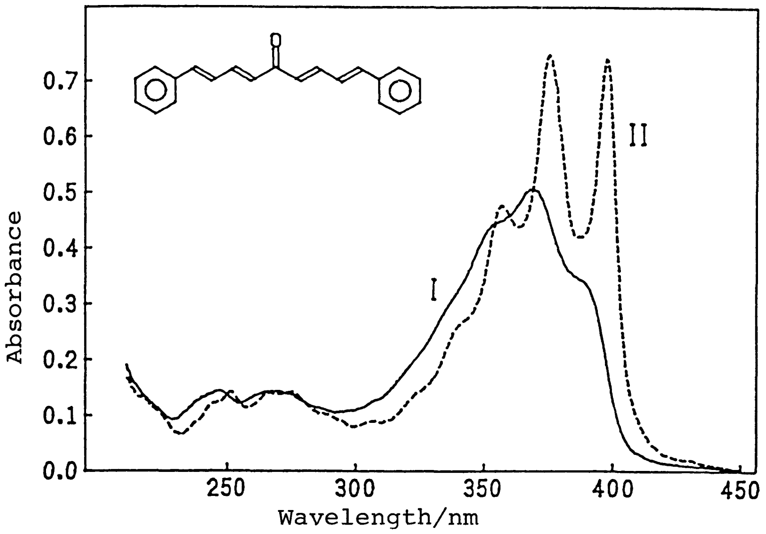

Fig. 2. The absorption spectra of dicinnamylideneacetone(DCA) in the PE film at room temperature (I) and 101 K (II).

at 387 nm, and that of the planar one is found as a better defined peak at 397.5 nm. The absorption spectra of DCA in MP at various temperatures are shown in Fig. 3. The spectral changes observed for DCA are quite similar to the case of DBA (Fig. 1), and the spectra I, II,and III can be assigned to the twisted conformer, a mixture of the twisted and planar ones and the dimer of the planar molecules, respectively. In the case of the dimer of DCA, the 0-0 band of the first electronic transition is obviously observed at 460 nm in MP at 101 K (spectrum III in Fig. 3). The calculated results for the dimer of DCA are shown in Table 1. Although the calculated $S_1 \leftarrow S_0$ transition is forbidden for the dimer of a C_{2h} symmetry, the corresponding transition is allowed for the C_2-dimer, the transition energy and oscillator strength (f) being 386 nm and 0.028, respectively. The 385 and 460 nm bands for the dimer of DCA can be considered to be the 0-0 transitions which correspond to the calculated $S_2 \leftarrow S_0$ (361 nm, f=3.916) and $S_1 \leftarrow S_0$ (386 nm, f=0.028), respectively. The shoulders at 429 and 402 nm may be vibronic bands of the 460 nm band. Although a dimer shows a structureless band around room temperature, the first electronic band of DCA-

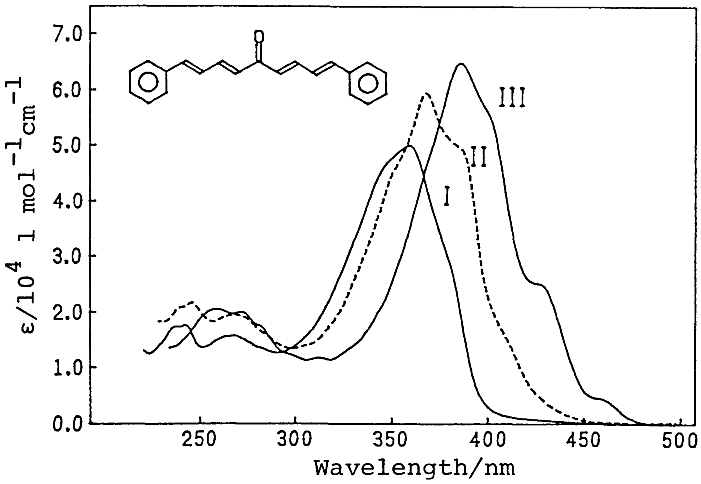

Fig. 3. The absorption spectra of dicinnamylideneacetone(DCA) in a 1:1 mixed solvent of methylcyclohexane and isopentane (MP) at room temperature (I), 184 K (II) and 101 K (III).
ε: Molar absorptivity.

dimer is somewhat structured because of being measured at low temperature, but each vibronic band is considerably broad compared with that of DCA-monomer given in Fig. 2(II).

Thus, the observed and calculated results for DBA and DCA indicate that these molecules form dimers in nonpolar fluid media such as MP at appropriately low temperatures. The dimer of DBA or DCA does not take a C_{2h}-conformation ($\theta=0$). Similar noncentrosymmetric dimer was reported for the case of formaldehyde at low temperature.$^{3)}$ According to the present MO calculations, the $S_1 \leftarrow S_0$ transition energy of the dimer of DBA or DCA is lower than that of the first $\pi\pi^*$ transition of the planar monomer and less intense, while the $S_2 \leftarrow S_0$ transition energy of the dimer is higher, and more intense. This is interpreted as follows. For the assumed conformation of the dimer, a pair of the monomer's transition moment, which is polarized along the long axis, is in a parallel alignment. For this parallel alignment of transition moments, the out-of-phase combination is stabilized to give the forbidden $S_1 \leftarrow S_0$ transition of the dimer and the in-phase one is destabilized to give the allowed $S_2 \leftarrow S_0$ transition. The above calculated results reproduce qualitatively the observed ones, indicating that the geometry of the dimer assumed here is considered to be reasonable.

Since very little informations are available concerning the dimerizations through carbonyl-carbonyl interactions, we are now investigating on the systems for many other organic carbonyl compounds.

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