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Conformations and Electronic Structures of Dibenzylideneacetone

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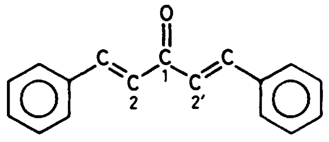
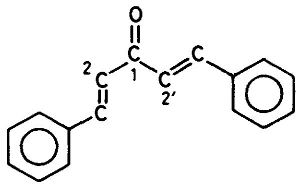
The u.v. absorption spectra of dibenzylideneacetone (DBA) have been measured in various media (cyclohexane, ethanol, ethanol–methanol, and a polyethylene matrix) at room temperature and at 101 K. The results (and those calculated by the PPP method) indicate that DBA assumes a twisted *cis,cis*-conformation at room temperature in the polyethylene matrix, and a near planar one at low temperature. The torsion angles around the two single bonds between the olefin and the carbonyl group are estimated to be about 22° at room temperature. The effects of light irradiation on the structure of DBA have also been examined. The polarization of each band in the polarized absorption spectrum has been ascertained: *e.g.* the first $\pi^* \longleftarrow \pi$ band of the planar *cis,cis*-conformer at 351 nm is polarized along the long molecular axis. MINDO/2 calculations have also been performed to elucidate the equilibrium conformations for the free molecule.

1,5-Diphenylpenta-1,4-dien-3-one (dibenzylidenacetone, DBA) is used as a ligand in metal complexes.[1,2] DBA might be expected to exist as several isomers, differing in conformation about the carbonyl–carbon single bonds. Recently, Tanaka, Yamada, and Kawazura have studied the conformations of DBA by proton n.m.r. spectroscopy and by an INDO molecular orbital method.[3] According to them, the major conformation is *cis,cis* and the minor one *cis,trans*; the *trans,trans*-conformer is not found at a room temperature.

There are several literature reports on the conformations of DBA in solution and in some metal complexes;[1,2] however, it seems that little is known about the electronic structures and absorption spectra of DBA. In this investigation, we have measured u.v. absorption spectra in various media at various temperatures, and also the polarized absorption spectrum. To obtain detailed knowledge of conformations and to assign the electronic transitions, PPP and MINDO/2 calculations have also been performed.



cis, cis – conformer



cis, trans – conformer

Experimental

Materials.—The commercially available DBA (Tokyo Kasei Co. Ltd.) was recrystallized twice from cyclohexane. Ethanol (Guaranteed Reagent Wako Pure Chemical Industries, Ltd.) was used without further purification. Cyclohexane was purified by distillation and column chromatography (silica gel). The commercially available polyethylene film (0.1 mm in thickness, Okura Kogyo Co. Ltd.) was soaked in cyclohexane to remove impurities.

Preparation of the Sample Film.—The polyethylene film was saturated with cyclohexane and was then soaked in the sample solution (solvent cyclohexane) to adsorb the sample molecules. The sample concentration in the film (0.1 mm thick) was about 2.8×10^{-2} mol l^{-1}. In order to orient the adsorbed molecules, the film was stretched mechanically at about 60 °C. The stretched sample film thus obtained was used for the measurement of the polarized absorption spectrum.

Measurements.—The solution and polarized absorption spectra were recorded with a Shimadzu UV-360 type spectrophotometer equipped with a cryostat and a Rochon-type polarizer.[4]

MO Calculations.—Molecular orbital calculations were carried out by a modified PPP method, in which interactions between the non-bonding electrons and π-electrons were taken into account through the electron repulsion terms. The semiempirical parameters used are the same as described elsewhere.[5,6] The one- and two-centre electronic repulsion integrals $(nn|\pi\pi)$ between the n and π electrons are estimated by the equation $(nn|\pi\pi) = (rr|ss)\mathrm{F}$, where $(rr|ss)$ is the electron repulsion integral obtained from the Pariser–Parr approximation, and F is a semiempirical parameter determined from comparison of calculated and observed $\pi^* \longleftarrow n$ transition energies of benzaldehyde and terephthalaldehyde (the value of F thus obtained is 0.45).

All singly excited configurations (including $\pi^* \longleftarrow n$) were taken into account in the CI calculations.

Results and Discussion

Ultraviolet Absorption Spectra.—Figure 1 shows the absorption spectra of DBA in cyclohexane and in ethanol at room temperature. The spectrum in cyclohexane consists of two

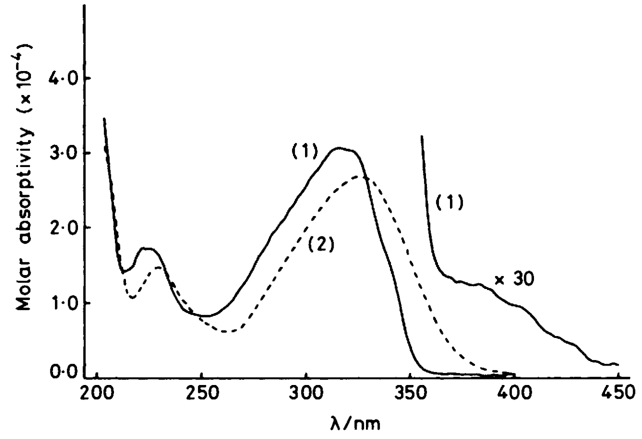


Figure 1. Absorption spectra of DBA in (1) cyclohexane and (2) ethanol at a room temperature

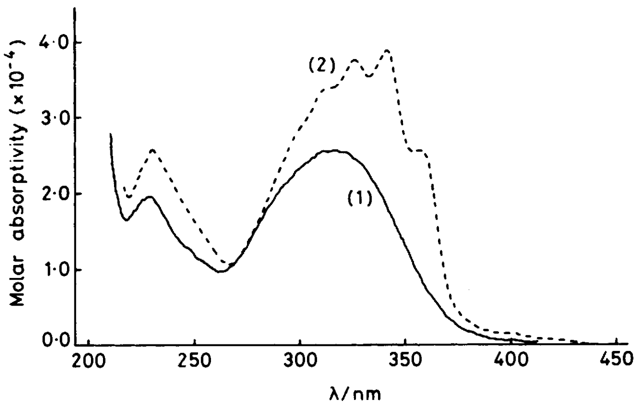


Figure 2. Absorption spectra of DBA in 1:1 methanol–ethanol at (1) room temperature and (2) 101 K

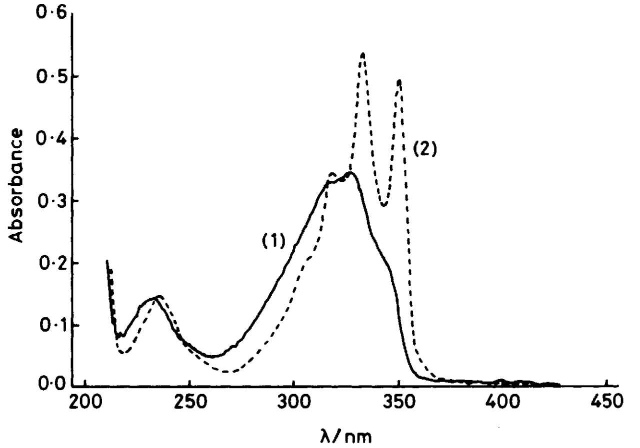


Figure 3. Absorption spectra of DBA in polyethylene matrix at (1) room temperature and (2) 101 K

structureless bands at 229 and 320 nm, and a weak band with fine structure in the region 370—450 nm. In the spectrum of the ethanolic solution, the bands corresponding to the first two in cyclohexane appear at 230 and 326 nm, but there is no absorption corresponding to the weak 370—450 nm band. From this, it is clear that the 229 and 320 nm bands are due to $\pi^* \longleftarrow \pi$ transitions, and the 370—450 nm band to the $\pi^* \longleftarrow n$ transition.

It is reported that the major conformation of DBA is *cis,cis* and the minor one *cis,trans* at room temperature (from ^{1}H n.m.r. spectroscopy).[3] If this is the case, the u.v. absorption spectrum might be expected to show temperature dependence. We have therefore measured the spectrum of DBA at various temperatures. In Figure 2 are presented the spectra of a solution in ethanol–methanol (1:1) (giving a transparent matrix at a low temperature). In this solvent, a structureless band appears at 320 nm at a room temperature as in ethanol (Figure 1), but at low temperature (*e.g.* 101 K) the intensity is increased considerably and fine structure appears at 358.5, 342.0, 326.0, 312, and 300 nm; the 358.5 nm band may be assigned as O–O. Temperature dependences of the spectrum of DBA were also measured in a nonpolar medium (polyethylene matrix); the results are shown in Figure 3. The spectrum at room temperature is similar to that in cyclohexane; the location of the O–O band becomes better defined, as a shoulder around 346 nm. On the other hand, at low temperature, the bands are shifted to the red and appear at 351.0, 333.5, 320.0, and 303 nm.

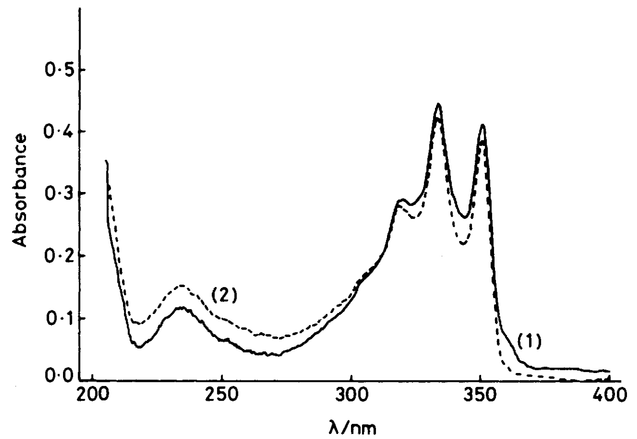


Figure 4. Effect of photoirradiation on the spectrum of DBA in the polyethylene film at 101 K: (1) before irradiation, (2) after 350 nm irradiation for 30 min

Generally a vibrational band becomes sharper at lower temperature, but the location of the band is almost invariant. In the present case, however, each band is shifted to the red significantly at low temperature. This suggests that the conformation of DBA is dependent on temperature. Usually a planar molecule gives an absorption or emission band with clearer fine structure than a nonplanar system. Therefore, the conformation of DBA giving the less structured band at room temperature can be considered to be nonplanar, *i.e.* twisted around the two single bonds between the olefinic and the carbonyl groups. On the other hand, it is considered that DBA assumes a near planar conformation at a low temperature, because the low-temperature absorption bands show a well defined fine structure. As already mentioned, the conformation of DBA is considered to be mainly *cis,cis* at room temperature.[3] The temperature dependence of the u.v. spectrum, however, shows that a planar *cis,cis*-conformation is not appropriate; a considerably twisted *cis,cis*-conformation must be taken into account. A planar *cis,cis*-conformation might be attained only at low temperature.

Effect of Light Irradiation.—In addition to the structured band with 0–0 transition at 351.0 nm and the broad band at 235 nm, a very weak band can be seen at 362.5 nm in the spectrum of DBA at 101 K [Figure 4, curve (1)]. This weak band disappears on irradiation at 350 nm, as shown in Figure 4 [curve (2)]. The positions of the other bands, however, are scarcely changed on irradiation. The weak band reappears when the sample film returns to room temperature. These experimental facts may be explained as follows. As already

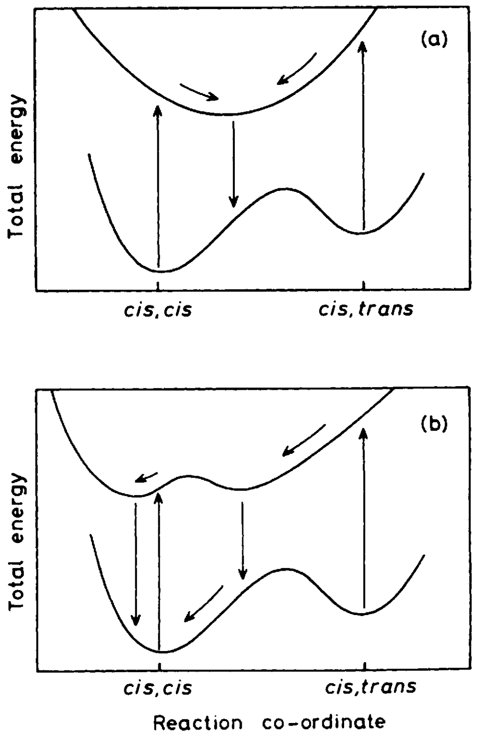


Figure 5. Assumed potential curves for the ground and excited states of DBA, for explaining photoisomerization

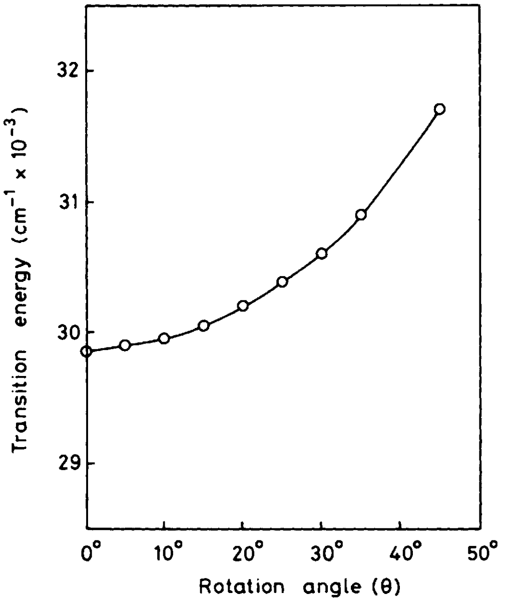


Figure 6. Changes in the calculated (PPP) transition energy corresponding to the observed first $\pi^* \leftarrow \pi$ band of DBA with respect to the rotation around the 1,2- and 1,2′-bond (θ)

pointed out, the DBA molecule is twisted significantly at room temperature. As the temperature is lowered, the molecule becomes planar; the major conformer is then a *cis,cis*-form and the minor one *cis,trans*-. The 0–0 band of the first $\pi^* \leftarrow \pi$ transition for the *cis,cis*-conformer is at 351.0 and that for the *cis,trans*- at 362 nm.

In order to confirm the foregoing assignment, that the 351.0 nm and the 362 nm bands are due to the 0–0 transitions of the *cis,cis*- and *cis,trans*-conformers, respectively, PPP MO calculations were performed. The first $\pi^* \leftarrow \pi$ transition energy for the *cis,cis*-conformer is computed to be 339 nm (29 500 cm^{-1}) and that for the *cis,trans* 342 nm (29 200 cm^{-1}). Since, in general, PPP calculation does not give accurate results, it is difficult to use these results for quantitative arguments. In the present calculation the semiempirical parameters used are the same for the two conformers (*cis,cis* and *cis,trans*), except for the torsion angle around the 1,2-bond. Therefore, the results may reflect only conformational differences, and one can discuss the conformation of the molecules qualitatively. The calculated results tend to support the interpretation of the present observation, *i.e.* the first $\pi^* \leftarrow \pi$ transition energy for the *cis,cis*-conformer is slightly higher than that for the *cis,trans*-. The photoinduced isomerization of the *cis,trans*- to the *cis,cis*-conformer may be explained by use of the potential curves shown in Figure 5. In Figure 5(a), the potential curve of the excited state is assumed to have a single minimum. The relaxed excited-state conformations derived from the *cis,cis*- and *cis,trans*-isomers can be considered identical, and the minimum in the excited-state potential curve is located in the *cis,cis*-side of the ground state, thus resulting in the isomerization already mentioned. In Figure 5(b), double minima, in the *cis,cis*-side of the ground state, are assumed. This diagram explains the observed photochemical behaviour.

MO Calculations.—To obtain more detailed information on the structure of DBA, we have performed PPP and MINDO/2 calculations assuming various torsion angles around the 1,2- and 1,2′-bond. Changes in the transition energies (calculated by the PPP method) corresponding to the first $\pi^* \leftarrow \pi$ band of DBA with respect to the rotations around the 1,2- and 1,2′-bond (θ) are shown in Figure 6. The calculated first $\pi^* \leftarrow \pi$ transition energy increases with increasing rotation angles (θ). These results do not contradict the presence of the aforementioned conformers deduced from the spectral shift for the first $\pi^* \leftarrow \pi$ band (Figures 2 and 3). The energy separation between the 0–0 bands of the first $\pi^* \leftarrow \pi$ transitions for the twisted conformer to be stable at a room temperature and the planar one stable at low temperature (101 K) is approximately 400 cm^{-1}. From comparison of the observed and calculated energy differences for the $\pi^* \leftarrow \pi$ transitions, the torsion angle θ of the DBA molecule at room temperature in the polyethylene matrix is estimated to be about 22°.

It would be interesting to know the relation between the total energy and the torsion angle (θ). For this purpose the MINDO/2 calculation has been performed; the results are shown in Figure 7, in which the total energies are plotted against θ. As seen from the Figure, the total energy has a minimum value at θ = 80—90°. This value is not in agreement with that estimated from the spectral data for DBA in the polyethylene matrix (22°). This discrepancy might be explained as follows. The result obtained from the MINDO/2 calculation should correspond to the value for the isolated DBA molecule. The conformation estimated from the spectral data for DBA in the polyethylene matrix, however, is not regarded as that for the isolated molecule, since the DBA molecule in the matrix interacts with the host molecules. A similar phenomenon is observed with biphenyl: the angle between the phenyl groups is 0° in the crystal, 20° in solution, and 40° in the gas phase.[7,8]

Polarized Absorption Spectrum.—Figure 8 shows the polarized absorption spectrum of the planar *cis,cis*-DBA in the stretched polyethylene film at 101 K ($D_{\parallel}$ and $D_{\perp}$ are the absorbances measured with polarized light beams the electric vectors of which are parallel to and perpendicular to the direction of stretch of the film, respectively, and R_d is $D_{\parallel}/D_{\perp}$).

Table. Comparison of the observed and calculated results for dibenzylideneacetone (DBA)

	Transition energy (nm)		Intensity		Polarization[d]	
	Calc.	Obs.[a]	Calc. (f)[b]	Obs. (ε)[c]	Calc.	Obs.
$S_1(^1B_1)$[e]	403	*ca.* 450	Forbidden	*ca.* 80	*X*	*X*
$S_2(^1B_2)$	339	351	1.225	30 900	*Y*	*Y*
$S_3(^1B_2)$	301		0.001		*Y*	
$S_4(^1A_1)$	301		0.013		*Z*	
$S_5(^1A_1)$	300	*ca.* 300	0.136	*ca.* 3 000	*Z*	*Z*
$S_6(^1B_2)$	252	260 to 220	0.188	17 400	*Y*	
[$S_7(^1A_1)$	247		0.014		*Z*]	
$S_8(^1B_2)$	233		0.102		*Y*	
$S_9(^1A_1)$	232		0.279		*Z*	
$S_{10}(^1A_1)$	223		0.001		*Z*	

[a] Observed in the polyethylene matrix at 101 K. [b] Oscillator strength. [c] Molar absorptivity observed in cyclohexane. [d] *X* out-of-plane, *Y* long molecular axis, *Z* short molecular axis. [e] ^1n–π^*

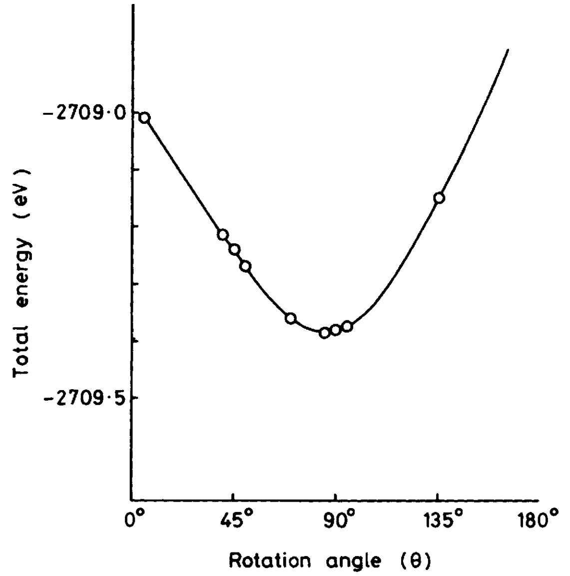


Figure 7. Changes in total energy, calculated by the MINDO/2 method, with respect to the torsion angle (θ)

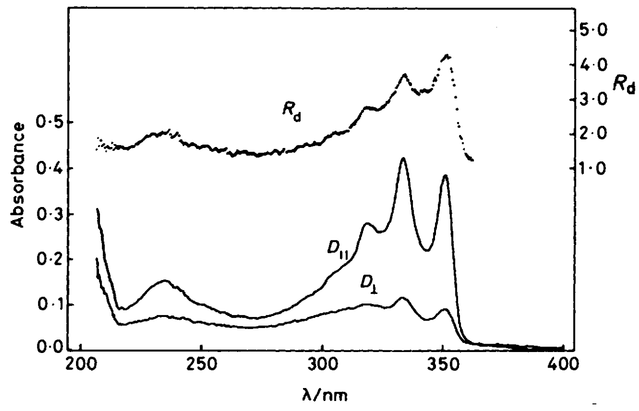


Figure 8. Polarized absorption spectrum of DBA in the stretched polyethylene film at 101 K after 350 nm irradiation

This polarized absorption spectrum can be regarded as that for the planar *cis,cis*-conformer, because the 362 nm band of the *cis,trans*-species is completely removed by the irradiation. Reliable R_d values for the $\pi^* \longleftarrow n$ band could not be obtained, because of its very low intensity. It is known that guest molecules in stretched polymer films are usually oriented with their long molecular axes inclined preferentially in the stretch direction.[9] The R_d value for the 0–0 band of the first $\pi^* \longleftarrow \pi$ transition is the largest, indicating that this transition is polarized along the long molecular axis (*Y* axis). The band in the wavelength region 220—260 nm shows mixed polarization, because the R_d values are intermediate ones. This means that the 220—260 nm band is not due to a single electronic transition. The observed results are compared with those calculated by the PPP method in the Table. The observed long-axis-polarized 351 nm band is clearly assigned to the $S_2 \longleftarrow S_0$ ($^1B_2 \longleftarrow {}^1A_1$) transition. The 220—260 nm band with mixed polarization can be interpreted as due to superimposition of three electronic transitions, $S_6(^1B_2) \longleftarrow S_0$ (the longer molecular axis, *Y*), $S_8(^1B_2) \longleftarrow S_0$ (*Y*), and $S_9(^1A_1) \longleftarrow S_0$ (the shorter axis, *Z*). According to the Table, the existence of a short-(*Z*) axis-polarized transition with intermediate intensity is expected around 300 nm. Careful inspection of the polarized absorption spectrum shows a weak shoulder around 300 nm in the $D_{\perp}$ curve. The R_d values of this shoulder are low, showing that this shoulder is polarized along the shorter (*Z*) molecular axis. Thus this band can be assigned to the calculated $S_5(^1A_1) \longleftarrow S_0$ transition.

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