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Polarized Electronic Absorption Spectra and Assignment of Fluorene and Biphenyls

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The divided electronic spectra polarized parallel to the long and short axes of molecules of biphenyl, THP (4,5,9,10-tetrahydropyrene), fluorene, and DHPH (9,10-dihydrophenanthrene) were determined by dichroism analysis using the stretched PVA film method. The experimental results are in good agreement with the ones calculated by the LCAO MO SCF CI method. Every compound has a very weak absorption ($f \approx 10^{-4}$) as the first band in the region of 32000—35000 cm^{-1}, which is electronically allowed and polarized parallel to the short axis. The intense band (34000—44000 cm^{-1}) of biphenyl consists of a relatively strong (39100 cm^{-1}) band and a weak (40500 cm^{-1}) band: the former is polarized parallel to the long axis and the latter to the short. Both fluorene and DHPH show five well corresponding electronic bands in the region below 45000 cm^{-1}.

The assignment of the electronic spectrum of fluorene has been studied[1-5] from the viewpoint of a biphenyl derivative. For fluorene itself, there have been few studies done in terms of the three fundamental factors: the transition energy, the polarization direction, and the oscillator strength. The agreement between the calculated and experimental results seems especially unsatisfactory for the very weak first band. On the other hand, there are a great many studies for the biphenyl spectrum, both theoretical and experimental.[6-11] These studies may be grouped into two types: the comformation and the assignment. From the conformational study, the dihedral angle of the biphenyl has been determined in crystal state (0°), in solution (20—30°) and in vapor ($\approx$45°). As for the assignment of the biphenyl spectrum, however, no detailed experimental study in terms of the above three factors has yet been made.

In the present study, we determined the polarized absorption spectra of biphenyl, fluorene, 9,10-dihydrophenanthrene, and 4,5,9,10-tetrahydropyrene[12] in the stretched PVA [poly(vinyl alcohol)] film, and divided the spectra into two components, which are polarized along the long and short axes of the molecule, by means of the dichroism analysis.[13] And then, comparing the component spectra with the calculated results, we assigned the spectra of fluorene and the biphenyl with respect to the three fundamental factors stated above.

Experimental

Material. Commercially available biphenyl (E.P.: extra pure reagent, >99% G.C.), fluorene (U.P.: ultra pure reagent, zone refined), 9,10-dihydrophenanthrene (G.R.: guaranteed reagent; abbrev. DHPH), and 4,5,9,10-tetrahydropyrene (G. R.: abbrev. THP) were obtained from Tokyo Kasei Kogyo Co., Ltd. Biphenyl was purified by repeated recrystallization from water containing ethanol. THP was furthermore refined using a special treatment at Tokyo Kasei Kogyo Co., Ltd., at our request. PVA powder, which was used for the preparation of film, was obtained commercially (Koso Chemical Co., Ltd.) and was used without further purification.

Polarized Spectra. The polarized absorption spectra of samples in the stretched PVA films were measured with a Shimadzu QV-50 Spectrophotometer equipped with a calcite polarizer of the Glan-Thompson type and a rotation apparatus for the polarizer.

The method of dichroism analysis using the stretched PVA film has already been reported.[13] The notations cited here are as follows: R_S is the stretch ratio of the PVA film, $D_{\parallel}$ and $D_{\perp}$ are the optical densities of the sample in a stretched film for the incident light polarized parallel and perpendicular to the stretching direction, respectively, and R_d is the dichroic ratio and is defined as $D_{\parallel}/D_{\perp}$. The orientation angle θ, which was computed theoretically using the R_S and R_d values, is indicated along the R_d curve in the figure. It means the angle of the transition moment with respect to an orientation direction associated with the molecular axis.

We divided the absorption spectrum observed in the nonstreched PVA film into the component spectra along the long and short axes of the molecule, according to the method already described.[13] In the present case, we chose the angle for the greatest R_d value as the orientation angle of the long axis transition, since the sum of the apparent orientation angles for the maximum and minimum R_d values is smaller than a right angle. [The reason for such a selection has been described in detail in Refs. 12 and 13.]

The experimental oscillator strength f^{exp} was determined from the divided spectra by the following formula:

$$f^{\text{exp}} = 4.32 \times 10^{-9} \int \varepsilon_\sigma \mathrm{d}\sigma,$$

where ε_σ is the molar extinction coefficient at wave number σ and the ε_σ value in ethanol was used instead of that in PVA, since it was confirmed experimentally that the ε_σ value in PVA is nearly equal to that in ethanol.

Calculation

In the MO calculation, the LCAO ASMO SCF CI method (PPP approximation[14,15]) was employed. The one- and two-center electron repulsion integrals were evaluated by the Pariser-Parr[14] and Nishimoto-Mataga equations.[16] Substituent effects of methylene groups were taken into consideration as the conjugative effect.[17] All the molecules were assumed to be planar and the geometry of THP is shown in Fig. 1(a) as the representative of the biphenyl. The C–C bond lengths in benzene rings were taken as 1.395 Å and the bond angles $\angle \text{CCC} = 120°$. Other bond lengths were taken as $(C_4\text{–}C_5) = (C_9\text{–}C_{10}) = 1.480$ and $(C{=}H_2) = 0.900$ Å. The resonance integrals were taken as $\beta(C_9\text{–}C_{10}) = \beta(C_{10}\text{–}C_{11}) = -2.00$, $\beta(C{=}H_2) = -5.30$, and $\beta(C{=}C) = -2.236$ eV. The geometry of fluorene shown in Fig. 1(b) was assumed as follows with reference to the crystal structure.[2] The C–C bond lengths in the six-

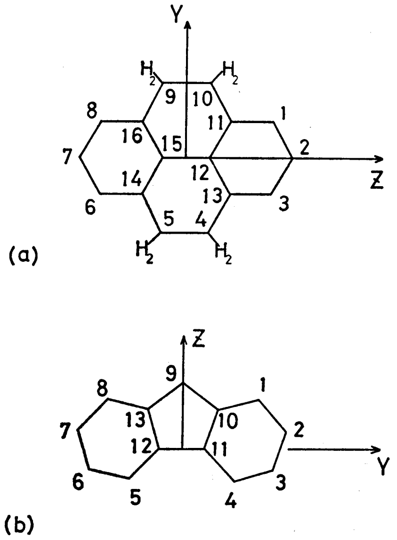

Fig. 1. Geometries of the THP (4,5,9,10-tetrahydropyrene) and fluorene molecules.

membered rings were taken as 1.400 Å and the bond angles ∠CCC=120°, and for the five-membered ring: $(C_{10}-C_{11})=(C_{12}-C_{13})=1.400$, $(C_{11}-C_{12})=1.480$, $(C_9-C_{10})=(C_9-C_{13})=1.460$ Å, and $\angle C_{10}C_{11}C_{12}=\angle C_{11}C_{12}C_{13}=108°$.

Results and Discussion

Dichroic Spectra and Divided Spectra. Figure 2 shows the dichroic spectra of biphenyl, fluorene, DHPH, and THP in the stretched PVA film. The spectra of these compounds are quite similar to one another, except that both the fluorene and DHPH spectra have additional bands at about 300 nm which are missing in those of biphenyl and THP.

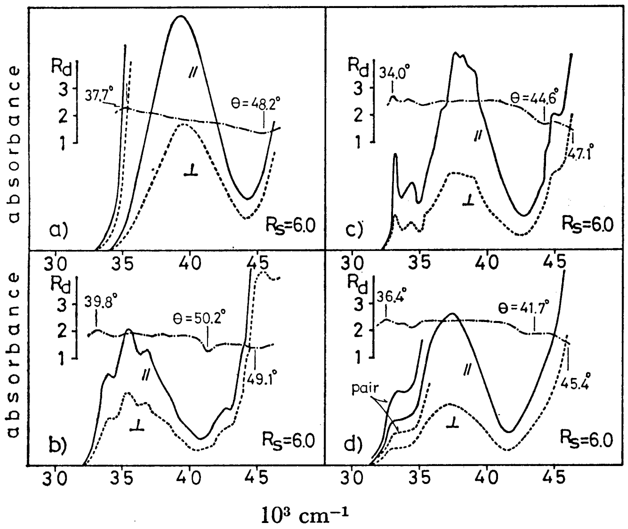

Fig. 2. Dichroic spectra and R_d curves for (a) biphenyl, (b) THP (4,5,9,10-tetrahydropyrene), (c) fluorene, and (d) DHPH (9,10-dihydrophenanthrene) in the stretched PVA films. The solid and broken lines indicate the absorbances ($D_{\parallel}$ and $D_{\perp}$) for the incident light polarized parallel and perpendicular to the stretching direction, respectively. R_d(chain line) is the dichroic ratio defined by $D_{\parallel}/D_{\perp}$.

The R_d curve of each compound has the maximum around the long wavelength side of the first absorption band and it clearly decreases toward longer wavelengths. The decrease of the R_d curve was confirmed by the dichroic spectra of the more concentrated sample films. This indicates that a weak band polarized parallel to the short axis is hidden in the longest wavelength region of the strong band polarized parallel to the long axis.

In order to reveal the two component spectra polarized parallel to the long and short axes of the molecule, we divided the spectra of the samples in the non-stretched PVA films. The divided spectra are shown in Fig. 3. The spectrum of THP shown in Fig. 3(b), which have already been reported,[12)] are reproduced for the comparison with those of other samples, especially with that of biphenyl.

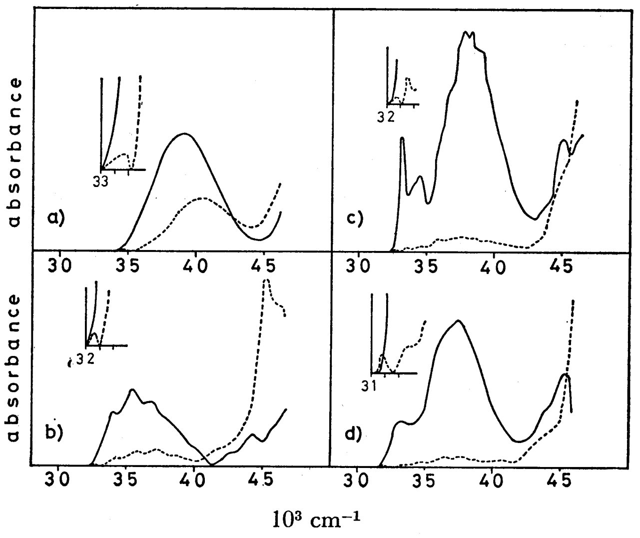

Fig. 3. Divided (component) spectra of (a) biphenyl, (b) THP (4,5,9,10-tetrahydropyrene), (c) fluorene, and (d) DHPH (9,10-dihydrophenanthrene) in the non-stretched PVA films. The solid and broken lines are long and short axis component spectra, respectively.

Figure 3(a) shows the component spectra of biphenyl. In the main absorption region of 34000—44000 cm^{-1}, there are two bands at 39100 and 40500 cm^{-1}: the former is polarized parallel to the long axis and the latter to the short. A very weak band polarized parallel to the short axis appears at 34600 cm^{-1}. In the region higher than 42000 cm^{-1}, two relatively strong bands exist, which are polarized perpendicularly to each other.

That the first absorption band (34000—44000 cm^{-1}) of biphenyl is composed of three electronic transitions has been inferred by Berlman from the investigation of the luminescence of biphenyl and its analogs.[10)] These three transitions may correspond to the 34600, 39100, and 40500 cm^{-1} bands of the present work. As for the position of the very weak band (34600 cm^{-1}) of biphenyl, there are many experimental data[7)] and most of them fall in the range 33000—34000 cm^{-1}.

Figures 3(c) and (d) show the component spectra of fluorene and DHPH, respectively. These are quite similar to each other except that the vibrational structure is revealed in the fluorene spectra. Both of the component spectra also show a very weak band at about 32000 cm^{-1}, which corresponds to those of biphenyl (34600 cm^{-1}) and THP (32800 cm^{-1}).

Popov *et al.*[5] determined the dichroic spectra of fluorene in the poly(vinyl butyral) film. The dichroism clearly shows an abrupt dropping toward the corresponding wavelength region of the weak band. This dropping suggests the existence of a hidden band of a short axis polarized transition, though they did not point it out.

Both of the component spectra of fluorene and DHPH have a band of long axis polarization in the region of 32000—35000 cm^{-1}. Since this band is missing in the biphenyl and THP spectra, it is considered as an additional characteristic band for fluorene and DHPH. The appearance of this band may have some relations with the partial loss of symmetry (D_{2h}—C_{2v}).[4]

Comparison of Experimental and Calculated Results. The experimental and calculated results are compared in Tables 1—4 for biphenyl, THP, fluorene, and DHPH, respectively. The first absorption bands of all the sample molecules are extraordinarily weak and have the polarization parallel to the short axis. The experimental oscillator strengths are the order of 10^{-4} and correspond well to the calculated ones. As for the intensity of this band of biphenyl, for instance, usually zero values of the oscillator strengths have been computed, except in the calculation by Momicchioli *et al.*[3] This could be attributed to a disregard of the off-diagonal terms of the transition density matrix.[18]

As is seen from Fig. 3, only biphenyl shows very smooth component spectra, while the other samples have fine structure or a shoulder. Therefore, we could estimate experimentally, all the 0-0 transition energies except for that of biphenyl. As is shown in Tables 2—4, the experimental energies agree well with the calculated ones for the allowed transitions lower than 45000 cm^{-1} of THP, fluorene, and DHPH. For the case of biphenyl (Table 1), however, the experimental energy (39100 cm^{-1}) of the main band (the second), for example, was considerably higher than the calculated one (36400 cm^{-1}, the third transition), because we had to take the energy at the band maximum as the experimental one.

We have already pointed out that the main intense band 34000—44000 cm^{-1}) of biphenyl (Fig. 3(a)) consists of two subbands. One (39100 cm^{-1}) of these, which is polarized parallel to the long axis, could be assigned as the third transition (36400 cm^{-1}) of the calculated results. But the other band, which is polarized to the short axis and has the maximum at 40500 cm^{-1}, cannot be assigned to any allowed transition calculated (Table 1). The calculated results shown in Table 1, however, have been obtained by assuming that biphenyl

TABLE 1. COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS FOR BIPHENYL (D_{2h})

Transtn. No.	Transition energy		Oscillator strength		Polarization		Symmetry
	Calcd 10^3 cm^{-1} (nm)	Obsd 10^3 cm^{-1} (nm)	Calcd[a)]	Obsd	Calcd	Obsd	
I	34.63 (289)	34.6 (289)	3.1×10^{-4}	6×10^{-5}	y	short	B_{2u}
II	35.09 (285)						B_{3g}
III	36.40 (275)	39.1 (256)	0.8471	0.293	z	long	B_{1u}
IV	46.50 (215)	[40.5] [247][b)]		[0.120][b)]		[short][b)]	B_{3g}
V	47.82 (209)						A_g
VI	48.85 (205)	>46	0.8868		y	short	B_{2u}
VII	48.87 (205)						A_g
VIII	49.66 (201)	>46	1.0832		z	long	B_{1u}

a) All terms of the transition density matrix were included. b) To be assigned as an allowed transition (B_3) provided that biphenyl belongs to the point group D_2.

TABLE 2. COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS FOR 4,5,9,10-TETRAHYDROPYRENE (THP) [D_{2h}]

Transtn. No.	Transition energy		Oscillator strength		Polarization		Symmetry
	Calcd 10^3 cm^{-1} (nm)	Obsd 10^3 cm^{-1} (nm)	Calcd[a)]	Obsd	Calcd	Obsd	
I	33.56 (298)	32.8 (305)	1.9×10^{-4}	4.4×10^{-4}	y	short	B_{2u}
II	34.03 (294)	[34.2] [292][b)]				[short][b)]	B_{3g}
III	35.03 (286)	33.9 (295)	0.7290	0.298	z	long	B_{1u}
IV	43.96 (228)						B_{3g}
V	45.90 (218)						A_g
VI	46.71 (214)	[41.4] [242][c)]	1.1858		y	short	B_{2u}
VII	47.28 (212)	[42.6] [235][c)]	1.1358		z	long	B_{1u}

a) See footnote a) in Table 1. b) To be assigned as an electronically forbidden band or an intensity borrowing band. c) In the previous paper, 45200 and 46000 cm^{-1} were used as the observed transition energies of VI and VII, respectively. (See Ref. 12).

Table 3. Comparison of calculated and experimental results for fluorene (C_{2v})

Transtn. No.	Transition energy Calcd 10^3 cm^{-1} (nm)	 Obsd$^{b)}$ 10^3 cm^{-1} (nm)	Oscillator strength Calcd$^{a)}$	 Obsd	Polarization Calcd	 Obsd	Symmetry
I	33.95 (295)	32.6 (307)	5.4×10^{-3}	1.0×10^{-4}	z	short	A_1
II	34.62 (289)	33.1 (302)	0.0600	0.0623	y	long	B_2
III	35.76 (280)	36.0 (278)	0.5636	0.377	y	long	B_2
IV	45.09 (222)	43.6 (229)	0.2466		y	long	B_2
V	46.71 (210)	45.0 (220)	0.0902		z	short	A_1
VI	48.42 (207)		0.7992		z		A_1
VII					y		B_2

a) See footnote a) in Table 1. b) An other broad weak band, which is considered to be an intensity borrowing band, was observed in the region of 33000—42000 cm^{-1}.

Table 4. Comparison of calculated and experimental results for 9,10-dihydrophenanthrene (DHPH) (C_{2v})

Transtn. No.	Transition energy Calcd 10^3 cm^{-1} (nm)	 Obsd$^{b)}$ 10^3 cm^{-1} (nm)	Oscillator strength Calcd$^{a)}$	 Obsd	Polarization Calcd	 Obsd	Symmetry
I	34.15 (293)	31.7 (315)	2.2×10^{-4}	2.0×10^{-4}	z	short	A_1
II	34.59 (289)	33.2 (301)	0.0063	0.0369	y	long	B_2
III	35.86 (279)	36.0 (278)	0.7731	0.296	y	long	B_2
IV	45.33 (221)	43.6 (229)	0.1035		y	long	B_2
V	46.54 (215)	44.0 (227)	0.2880		z	short	A_1
VI	48.15 (208)		0.7607		z		A_1
VII	48.52				y		B_2

a) See footnote a) in Table 1. b) See footnote b) in Table 3.

belongs to the point group D_{2h}. But, in order to explain the extra band at 40500 cm^{-1}, it is necessary to consider that the real biphenyl molecule in the PVA substrate has some non-zero dihedral angle, *i.e.*, it belongs to the point group D_2. Thus the $B_{3g}\leftarrow A_g$ transition in Table 1 should be altered to $B_3\leftarrow A$ transition which becomes an allowed transition. Moreover, strictly speaking, the statement "the polarization in the short axis direction" should be changed to "the polarization direction perpendicular to the long axis of molecule," because in dichroism analysis we cannot distinguish the difference in the two directions of the out of plane transition and the in-plane short axis transition. For that reason, the extra band (40500 cm^{-1}) of biphenyl can be explained as an allowed transition.

The other samples also show the respective extra bands in the region 33000—42000 cm^{-1}. However, the intensities are much weaker than the extra band of biphenyl. This may be attributed to some electronically forbidden transition or to intensity borrowing.

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