Electronic Spectra of Biphenyl and Fluorene

Toshihiko Hoshi, Hiroyasu Inoue*, Junko Shiraishi, and Yoshie Tanizaki**
Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University, Megurisawa-cho, Setagaya-ku, Tokyo
**Department of Applied Chemistry, Faculty of Technology, Kanagawa University, Kanagawa-ku, Yokohama*
***Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Meguro-ku, Tokyo*

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The ultraviolet absorption spectrum of diprotonated-2,7-diaminofluorene has been divided into two components polarized along the long and the short axes of the molecule by using the results of the dichroic spectra in the stretched PVA sheet. By a comparison of the experimental results with those calculated by means of a semi-empirical LCAO-ASMO-SCF-CI approximation including a variable β method the assignment of the absorption bands has been made. It has been found that the compound has five absorption bands above 210 mμ. The existence of the additional 300 mμ band of fluorene has been explained theoretically by increasing the ionization potentials of the 9- and 10-carbon atoms by 3 eV from the usual value (11.42 eV).

Biphenyl shows a structureless intense absorption band at 247 mμ in a non-polar solvent. On the other hand, fluorene, which is formed by bridging a methylene group at the 9- and 10-carbon atoms of biphenyl, has a band with a well-defined fine structure at about 300 mμ in addition to the 261 mμ band, which corresponds to the 247 mμ band of biphenyl.

Many theoretical and experimental investigations of the electronic spectrum of biphenyl have been published. For instance, Gondo[1] has calculated the electronic transition energies of biphenyl, in which the effects of twisting the 1–1′ bond in biphenyl are taken into account. Berlman and Steingraber[2] have determined the fluorescence lifetime of biphenyl and found a hidden band on the longer-wavelength side of the intense 247 mμ band.

On the other hand, only a few papers have reported on the spectrum of fluorene. Momicchioli and Rastelli[3] have calculated the transition energies and oscillator strengths for fluorene by the method of PPP with variable electronegativity, taking into account the small shortening of the 1–1′ distance and slight parameter changes.

In this paper, the absorption spectrum of diprotonated-2,7-diaminofluorene above 220 mμ has been divided into two kinds of absorption curves which are polarized along the short axis (C_2-axis) and the long axis of the molecule, by using the results of the dichroic spectra in the stretched PVA sheet.[4] We call these divided absorption curves "divided spectra." Using the divided spectra, we have determined a number of the absorption bands and the polarization directions. Furthermore, semi-empirical LCAO-ASMO-SCF-CI calculations including a variable β approximation for the above compound have been made. By a comparison of the experimental and the calculated results, the assignment of each band has been clarified.

Experimental

Materials. Diprotonated-2,7-diaminofluorene was used in place of fluorene, because the saturated concentration of fluorene in a PVA sheet was too small for the dichroic spectra to be measured. Since the absorption spectrum of diprotonated-2,7-diaminofluorene is almost identical with that of fluorene, the results obtained from the former can be regarded as representing the results from the latter.

The 2,7-diaminofluorene used here was obtained commercially and was purified by repeated recrystallizations from alcohol. The PVA powder used for the preparation of the sheets was a commercial product (mean degree of polymerization=1500, Nippon Gosei Co., Ltd., NM-14); it was used without further purification.

Measurements. The dichroic spectra using stretched PVA sheets were determined by a method described elsewhere.[5]

Divided Spectra. The method of obtaining the divided spectra has already been described[5]; that is, the relation between R_d and R_s is represented by:

$$2r^2 = \frac{2(T-1)+(T+1)R_d}{2T+(T-1)R_d} \tag{1}$$

where

$$T = \frac{R_s{}^2}{(R_s{}^2-1)}[1-\{\pi/2-\tan^{-1}(R_s{}^2-1)^{-1/2}\}(R_s{}^2-1)^{-1/2}]$$

R_d is the dichroic ratio ($R_d = D_{//}/D_{\perp}$), R_s is the stretching ratio of the PVA sheet, and r is a parameter whose inverse cotangent, $\cot^{-1}r$, indicates the angle between a transition moment and the orientation axis of a molecule.

In the case of a planar molecule having at least one C_2 symmetry axis, the absorption spectrum is divided into two kinds of absorption curves whose transition moments are parallel (x) and perpendicular (y) to the symmetry axis by the use of the dichroic spectra.

From Eq. (1), $R_{d\infty}$ is represented as:

$$R_{d\infty} = 2r^2 \tag{2}$$

where $R_{d\infty}$ is the dichroic ratio for stretching the PVA sheet to infinity. The observed optical density, D, in the unstretched PVA sheet and the ratio of D_x and D_y are given by:

$$D = D_x + D_y \tag{3}$$

$$\frac{D_x}{D_y} = \frac{2-R_{d\infty}\cot^2\varphi}{R_{d\infty}-2\cot^2\varphi} \tag{4}$$

where D_x and D_y are the optical densities whose transition moments are along the x- and y-axes respectively, and where φ is the angle between the x-axis and an orientation axis of a

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[1] Y. Gondo, *J. Chem. Phys.*, **41**, 3928 (1964).

[2] I. B. Berlman and O. J. Steingraber, *ibid.*, **43**, 2140 (1965).

[3] F. Momicchioli and A. Rastelli, *J. Chem. Soc., B*, **1970**, 1353.

[4] H. Inoue and Y. Tanizaki, to be published.

[5] Y. Tanizaki and S. Kubodera, *J. Mol. Spectry.*, **24**, 1 (1967).

molecule. Hence, by using Eqs. (2), (3), and (4), D can be divided into D_x and D_y.

Method of Calculation

The Pariser-Parr-Pople approximation[6] including a variable β method[7] was employed. The one-center repulsion integrals were obtained from the valence-state ionization potentials $I(r)$ and the electron affinities $A(r)$, $(rr|rr)=I(r)-A(r)$. The two-center repulsion integrals were evaluated by using the Nishimoto and Mataga equation, $(rr|ss)=14.397/(a_{rs}+R_{rs})$, where a_{rs} is a parameter determined from the equation:

$$14.397/a_{rs} = \{(rr|rr)+(ss|ss)\}/2.$$

The resonance integrals, β_{rs}'s, were adjusted at every iteration of the SCF calculations by means of the $\beta_{rs}=-1.84\ -0.51P_{rs}$ relation, where P_{rs} is the bond order of the r–s bond.

The valence-state ionization potential and the electron affinity for each carbon atom were taken as 11.42 eV and 0.58 eV respectively. The geometry and the numbering of the atoms used here are shown in Fig. 1.

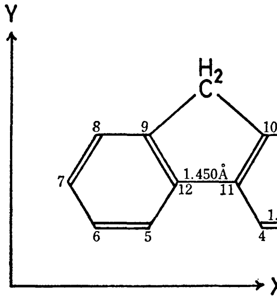

Fig. 1. Geometry of fluorene.

Results and Discussion

In Fig. 2 the absorption spectra of biphenyl, fluorene, and diprotonated-2,7-diaminofluorene are shown. As may be seen from this figure, the absorption curve of diprotonated-2,7-diaminofluorene is almost the same with that of fluorene; therefore, it seems reasonable to regard the results obtained from diprotonated-2,7-diaminofluorene as representing those of fluorene.

Biphenyl shows only one absorption maximum, at 257 mμ, above 210 mμ, whereas fluorene has an additional band at 300 mμ besides the 262 mμ band, which corresponds to the 247 mμ band of biphenyl. Figure 3 shows the "divided spectra" of diprotonated-2,7-diaminofluorene. From this figure, it is clear that the additional band at 300 mμ is polarized to the x-axis. The polarization of the intense 263 mμ band is along the x-axis, but a weak band polarized along the y-axis is hidden under this intense band. The absorption tail at around 220 mμ consists of two kinds of bands (x- and y-polarization). Thus, it may be concluded that fluorene has five absorption bands above 210 mμ.

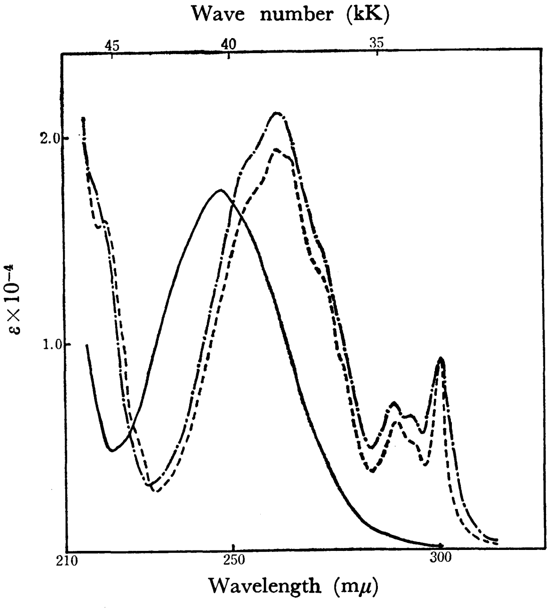

Fig. 2. Absorption spectra of biphenyl (——, in ethanol), fluorene (----, in ethanol), and diprotonated-2,7-diaminofluorene (—·—, in 80% ethanol).

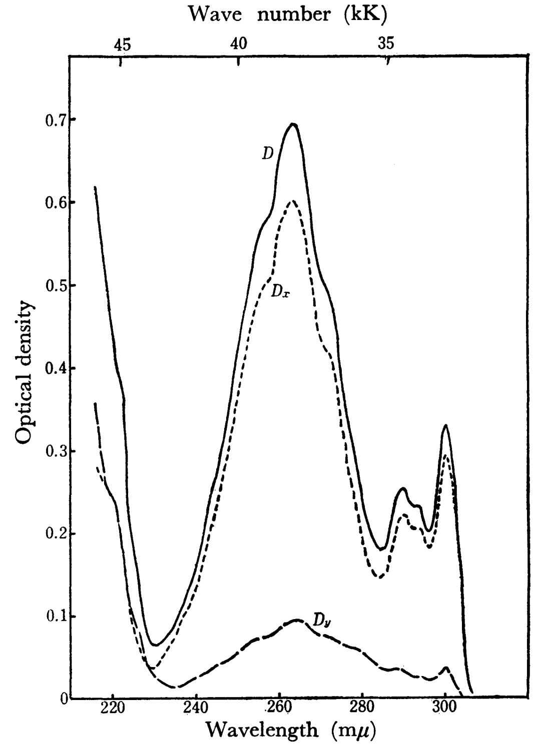

Fig. 3. Divided spectra of diprotonated-2,7-diaminofluorene.
D: The absorption spectrum in the non-stretched PVA sheet.
D_x: The x-component of D. D_y: The y-component of D.

According to Platt,[8] the additional 300 mμ band of fluorene may be interpreted as corresponding to the hidden band of biphenyl (^1L_b). This is not consistent with the present experimental results, because the ^1L_b band should be polarized to the short axis (y-axis) of the molecule. According to the calculated results obtained by Momicchioli *et al.*,[3] fluorene has five transitions below 6 eV; the lowest transition is of

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[6] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Proc. Phys. Soc.*, **68**, 81 (1955).

[7] K. Nishimoto and L. S. Forster, *Theoret. Chim. Acta* (Berlin), **3**, 407 (1965).

[8] J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).

TABLE 1. A COMPARISON OF THE EXPERIMENTAL AND CALCULATED RESULTS FOR FLUORENE ($I(9)=I(10)=14.42$ eV)

	Transition energy Calcd eV (mμ)	Transition energy Obsd eV (mμ)	Ocsillator sterngth Calcd	Polarization Calcd	Polarization Obsd	Symmetry
I	4.17 (297)	4.13 (300)	0.2982	x	x	B_1
II	4.25 (292)	4.71 (263)	0.0051	y	y	A_1
III	4.67 (266)	4.71 (263)	0.5389	x	x	B_1
IV	5.72 (217)	5.64 (220)	0.0781	y	y	A_1
V	5.83 (213)		0.1359	x	x	B_1

$^1A_1\rightarrow{}^1A_1$ while the other four transitions are of $^1A_1\rightarrow{}^1B_1$ type. These calculated results are also not sufficient to explain the results of the "divided spectra, since the polarizations of the four calculated transitions are along the x-axis (in the "divided spectra", two y-polarized bands are found); besides, the oscillator strength of the transition which may correspond to the 300 mμ band is too small. Therefore, in order to explain the results of the "divided spectra," we carried out MO calculations.

Commonly, there are two concepts for interpreting the effects of a methylene group on the π-electron system; one is that of hyperconjugation, and the other, an inductive concept. In the present paper, the effects of the methylene group in fluorene were treated as inductive; we calculated the state energies and the excited-state wave functions, increasing the ionization potentials of the carbon atoms at the 9 and 10 positions of biphenyl.[9] The results of the calculations are shown in Fig. 4. The results when the ionization potentials of the two carbon atoms are 14.42 eV agree well with those of the "divided spectra." The results calculated for biphenyl are also shown in Fig. 4a. In this case, four forbidden transitions are found at 34.1 kK (293 mμ), 34.5 kK (290 mμ), 45.8 kK (218 mμ), and 46.4 kK (216 mμ). A weak absorption band corresponding to the forbidden transition at 34.1 or 34.5 kK has been observed at 33.6 kK (298 mμ) in crystal and in solution at low temperatures.[10–13]

The four forbidden transitions of biphenyl become allowed transtions when the ionization potentials of the carbon atoms at the 9 and 10 positions are increased, and the four forbidden transitions at 34.1, 34.5, 45.8, and 46.4 kK are changed to the y-, x-, x-, and y-polarized transitions respectively. This may be due to the fact that, when the ionization potentials are increased, the symmetry of the π-electron system of biphenyl skeleton is reduced from D_{2h} to C_{2v}, in which the biphenyl skeleton is assumed to be a plane. By assuming that the two benzene rings of biphenyl are not coplanar, the symmetry of the π-electron system is also reduced from D_{2h} to D_2; however, Gondo[1] has indicated that the forbidden transitions of biphenyl are not changed into allowed transitions by this treatment.

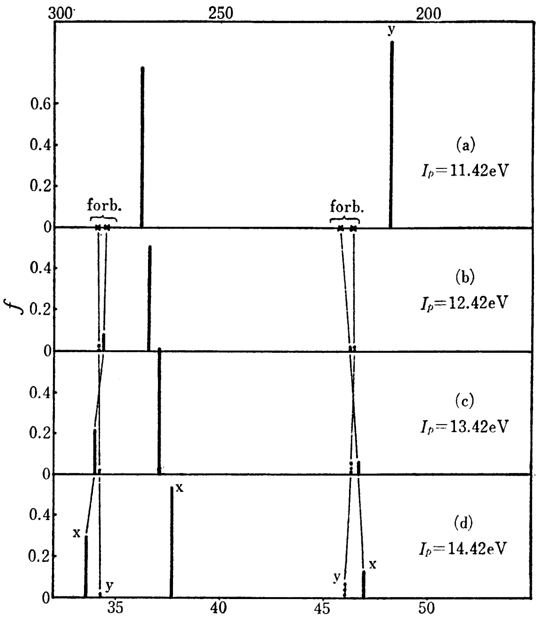
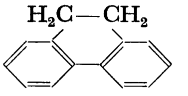
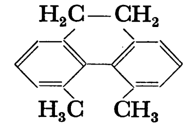


Fig. 4. Changes in the transition energies of biphenyl for the variation of the ionization potentials of the 9- and 10-carbon atoms.



9,10-dihydrophenanthrene



4,5-dimethyl-9,10-dihydrophenanthrene

Mislow *et al.*[14] have observed an additional band at 300 mμ in the case of 9,10-dihydrophenanthrene, as in the case of fluorene. This may be explained just as in the case of fluorene. However, the additional 300 mμ band disappears upon the introduction of two methyl groups at the 4- and 5-carbon atoms of 9,10-dihydrophenanthrene.[14] This may be attributed to the fact that the approximate symmetry of the π-electron system again becomes D_{2h} (4,5-dimethyl-9,10-dihydrophenanthrene) from C_{2v} (9,10-dihydrophenanthrene) upon the introduction of the two methyl groups.

In Table 1 the calculated results of fluorene ($I(9)=I(10)=14.42$ eV) are summarized and compared with the results of the "divided spectra."

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[10] A. R. Deb, *Indian. J. Phys.*, **27**, 305 (1953).

[11] R. Coffman and D. S. McClure, *Can. J. Chem.*, **36**, 48 (1958).

[12] D. S. McClure, *ibid.*, **36**, 59 (1958).

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