2516 © 1982 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **55**, 2516—2520 (1982) [Vol. 55, No. 8

The Influence of Molecular Conformation on the Electronic Relaxation Processes. Biphenyl in Solution

Tsuneo Fujii,* Shigeru Komatsu,† and Satoshi Suzuki
Department of Industrial Chemistry, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380

(Received January 20, 1981)

The fluorescence spectra of biphenyl in an isopentane and methylcyclohexane mixture, in propylene glycol, and in glycerol have been observed as a function of temperature and excitation wavelength. The temperature dependence of the fluorescence spectra is interpreted in terms of the intramolecular geometric relaxation. The fluorescence spectra of biphenyl have been observed in various solvents at room temperature. The Ham effect was found in the biphenyl fluorescence.

The influence of molecular structure on photophysical processes has been investigated by several authors. Lim and Chakrabarti have studied the phosphorescence lifetimes and polarization of various aromatic amines and of phenoxide ion.1) Kasha and Rawls have studied the phosphorescence lifetimes of twisted anilines.2) They suggested that the enhanced spin-orbit coupling in heteroaromatic molecules should be attributed to the pseudo non-bonding character of the lone-pair electrons of the substituent. Huber *et al.* showed that the rate constant of $S_1 \rightarrow T_i$ intersystem-crossing, k_{TM}, and the radiative rate constant of $T_1 \rightarrow S_0$ decrease rapidly on going from diphenylamine to 9,10-dihydroxyacridine (acridan) and carbazole, while the radiative rate constant of $S_1 \rightarrow S_0$ is only slightly altered.3)

The influence of molecular conformations on electronic relaxation processes is an interesting problem in photophysics. Two benzene rings of biphenyl are connected with a C–C single bond and vibrate torsionally around the C–C bond. It was reported that the planes of the two benzene rings of biphenyl are inclined at an angle of 20—40° in the ground state, while they are inclined at an angle of 0—20° in the excited states.4–8) Electronic excitation and deexcitation processes of biphenyl inevitably include conformational changes.

Hughes *et al.* and Naqvi *et al.* studied the excitation-wavelength dependence of the fluorescence spectra of biphenyl9) and polyphenyls,10) but little attention has been directed to the effect of conformation on the electronic relaxation processes.

The preceding paper11) presented the excitation-wavelength dependence of the fluorescence and phosphorescence quantum yields and of the phosphorescence lifetime of biphenyl in propylene glycol and discussed the influence of molecular conformations on the rate constants of the radiative and radiationless processes of biphenyl. It was shown that the intramolecular geometric relaxation12) plays an important role in the temperature dependence of the photophysical processes of biphenyl.

This paper presents the experimental findings of the influence of solvent, temperature, excitation wavelength, and viscosity on the fluorescence spectra of biphenyl. The difference of the distribution of conformers in the ground and excited states of biphenyl satisfactorily explains the observed spectral changes.

Experimental

Biphenyl was purified by repeated recrystallizations from ethanol and passed 1000 times through a zone refiner. Methanol (Wako Pure Chemical Industries, Inc., Luminasol grade) and acetonitrile (Wako, Spectrosol grade) were used without further purification. Cyclohexane, isopentane, methylcyclohexane, glycerol, propylene glycol (Wako, JIS S grade), and ethanol (Wako, Super special grade) were dehydrated by the use of molecular sieves 3A and passed through a silica-gel column. Isopropyl alcohol, *N*-methylformamide, and tetrahydrofuran (Wako, JIS S grade) were used without further purification. The absorption and emission spectra were recorded on a Hitachi EPS-3 recording spectrophotometer and a Hitachi MPF-2A fluorescence spectrophotometer respectively. The concentrations of the sample solutions used in fluorescence measurements at room temperature are less than 10^{-3} mol dm^{-3} and the solutions were not degassed. The degree of polarization, *P*, was measured by the method of photoselection.13,14) The temperature of solutions was varied from 77 to 300 K by the use of a metal cryostat (Torisha Laboratory, Ltd.).

Results

Figure 1 shows the fluorescence spectra of biphenyl in isopentane (dielectric constant $\varepsilon = 1.843$ at 20 °C), isopropyl alcohol ($\varepsilon = 19.92$ at 25 °C), methanol ($\varepsilon = 32.70$ at 25 °C), and *N*-methylformamide ($\varepsilon = 182.4$ at 25 °C). The spectrum of biphenyl in isopentane shows a sharp vibrational structure but has no 0-0 band. The spectra observed in cyclohexane, in methylcyclohexane, and in an isopentane–methylcyclohexane mixture (3 : 1) are almost the same as those in isopentane. Biphenyl shows less sharp fluorescence spectra in ethanol, methanol, and isopropyl alcohol than in isopentane. The shoulder which is assigned to the 0-0 band is observed. The spectrum in *N*-methylformamide exhibits a diffuse vibrational structure and has an obvious 0-0 band. Spectra similar to that in *N*-methylformamide are observed in propylene glycol, glycerol, acetonitrile, and tetrahydrofuran. These findings indicate that the appearance of the 0-0 band depends on the solvent polarity and the spectral sharpness decreases with an increase in the dielectric constant of the solvent.

The temperature and excitation-wavelength dependence of the fluorescence spectra in an isopentane–

---

† Present address: Semiconductor Engineering Department, Semiconductor Division, Tokyo Shibaura Electric Co., Ltd., Kawasaki 210.

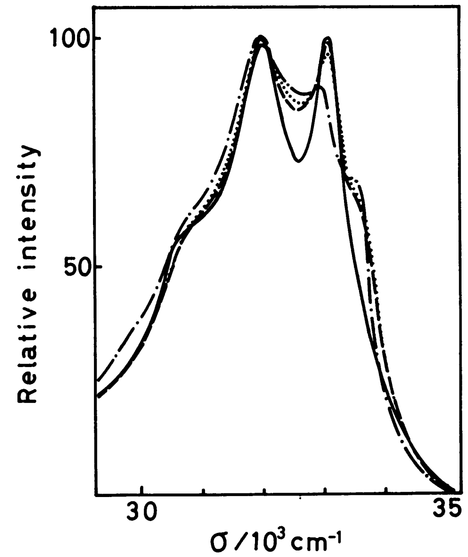

Fig. 1. The fluorescence spectra of biphenyl in isopentane (—┬—), isopropyl alcohol (------), methanol (······), and *N*-methylformamide (—·—) at room temperature. Excitation wavelength: 270 nm.

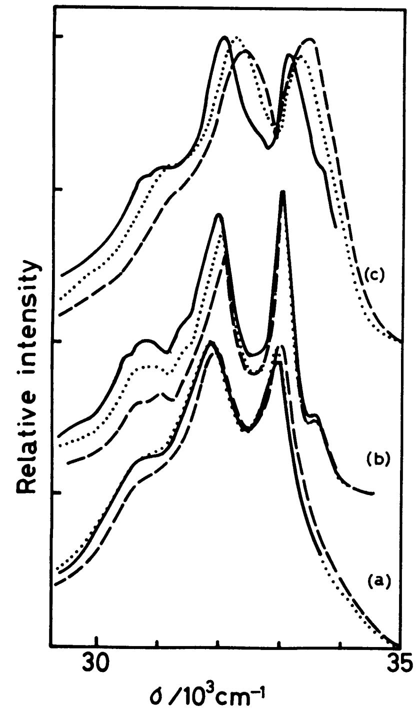

Fig. 2. The excitation-wavelength and temperature dependence of the fluorescence spectra of biphenyl in isopentane–methylcyclohexane mixture (3: 1).
a: 288 K, b: 128 K, c: 83 K. ------, ······, and —— correspond to the spectra excited at 250 nm, 270 nm, and 290 nm respectively.

methylcyclohexane mixture, propylene glycol, and glycerol are shown in Figs. 2, 3, and 4 respectively. Figure 2 shows that the fluorescence spectra in a hydrocarbon solvents are slightly dependent on the excitation wavelength at room temperature. The spectra at 128 K has the sharpest vibrational bands among the observed fluorescence spectra. At 83 K, the vibrational bands become wide again. The freezing point of isopentane is

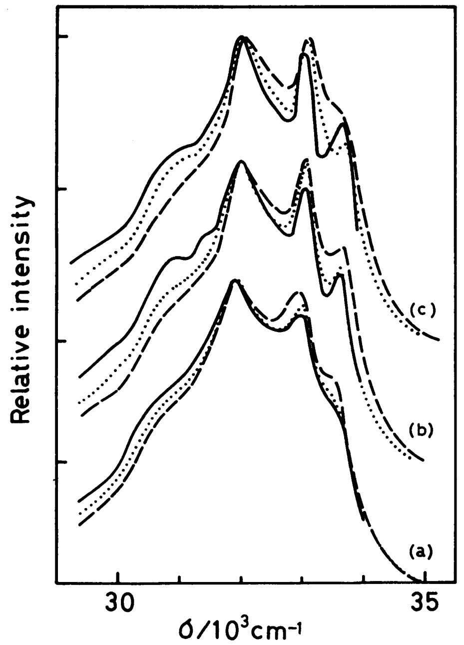

Fig. 3. The excitation-wavelength and temperature dependence of the fluorescence spectra of biphenyl in propylene glycol.
a: 291 K, b: 198 K, and c: 127 K. ------, ······, and —— have the same meaning as in Fig. 2.

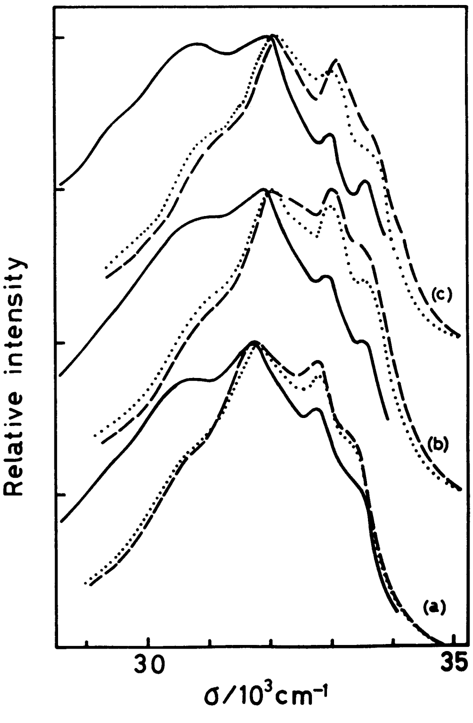

Fig. 4. The excitation-wavelength and temperature dependence of the fluorescence spectra of biphenyl in glycerol.
a: 287 K, b: 233 K, and c: 168 K. ------, ······, and —— have the same meaning as in Fig. 2.

113 K; the mixed solvent appears to be rigid at 83 K and fluid at 128 K. The broadening of the vibrational structure with lowering temperature from 128 K to 83 K can be related to the freezing of the solvent. The width of vibrational bands is broader at 173 K and 83 K than at 128 K. The width of vibrational bands increases with increasing the excitation energy. The individual vibrational bands observed at 83 K are displaced more to the blue than those observed at higher temperature. The increase in excitation energy also shifts the individual vibrational bands to the blue. Figure 3 shows that the 0-0 vibrational band is obvious in propylene glycol at room temperature. The excitation-wavelength dependence of the biphenyl fluorescence increases with lowering the temperature. Figure 4 shows that the excitation-wavelength dependence of biphenyl fluorescence is also obvious in viscous solvents such as glycerol even at room temperature.

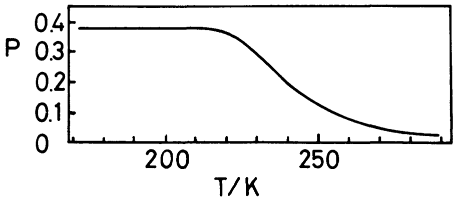

Fig. 5. The temperature dependence of the fluorescence polarization excited at 270 nm and monitored at the peak of 0-1 vibrational band.

The temperature dependence of P of the biphenyl fluorescence in propylene glycol is shown in Fig. 5. Figure 5 shows that the value of P of the biphenyl fluorescence reaches a maximum at 210 K in propylene glycol. The value of the fluorescence spectra for naphthalene derivatives also reaches a maximum at 210 K in the same solvent.[15]

Discussion

Effect of Molecular Conformations on the Fluorescence Spectra of Biphenyl. At high temperature, the fluorescence spectra of biphenyl in an isopentane–methylcyclohexane mixture are not dependent on the excitation wavelength and no 0-0 band is observed (Fig. 2). The spectrum observed at 128 K is more structured than that at 288 K and the 0-0 band becomes obvious. The spectrum at 83 K has more diffuse vibrational bands than those at 128 K.

The temperature and excitation-wavelength dependences in propylene glycol and glycerol are shown in Figs. 3 and 4. The spectral sharpness in the two solvents is different from that in hydrocarbon solvents but the energies of the individual vibrational bands are almost the same in these solvents. Figures 2—4 show that the temperature and viscosity of sample solutions, as well as the excitation wavelength, have an important effect upon the biphenyl fluorescence. This complex behavior may be interpreted in terms of the intramolecular geometric relaxation.[12]

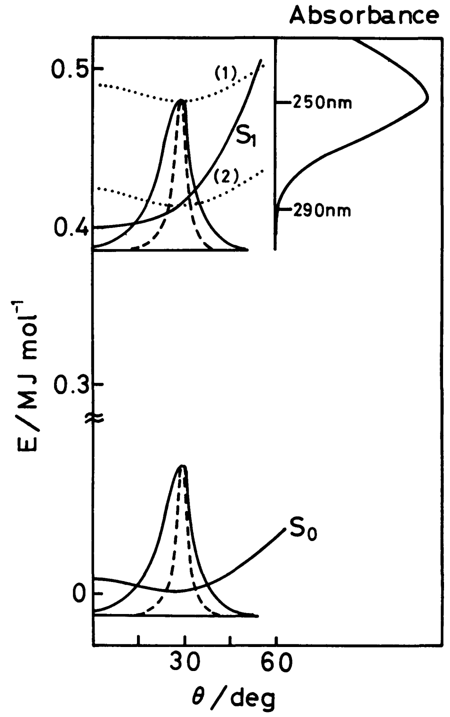

Fig. 6. A schematic potential energy curves of biphenyl for the angle of twist.
Curves (1) and (2) plot the potential curves which are higher in energy by an amount corresponding to 250 and 290 nm radiation respectively. Absorption and Boltzmann distribution at 300 K (——) and 77 K (······) are also indicated.

We can classify the processes of the intramolecular geometric relaxation of biphenyl into five categories. (1) Vibrational relaxation, (2) emission without geometric relaxation, (3) geometric relaxation along the angle of twist between the planes of two benzene units of biphenyl(θ), (4) emission from incompletely relaxed conformers, (5) emission from the completely relaxed conformers in the excited state. Process (3) is considered to be rate-determing. When solvent viscosity increases with lowering the temperature, process (3) is gradually prevented and process (4) gradually increases. At sufficiently low temperature, process (3) is prevented completely due to high viscosity of solvent and emission occurs only *via* process (2). Under such conditions emission emerges only from the conformers having the same conformation as in the ground state. Figure 6 illustrates such a situation. The ground- and excited-state potential curves as a function of θ and the Boltzmann distribution of conformational population were estimated from the calculations by Imamura and Hoffmann[6] and Golebiewski and Parczewski.[7] Curves (1) and (2) indicate the energy levels obtained by exciting the ground-state biphenyl with 250-nm and 290-nm radiations respectively. The potential curve of the ground state has two minimums at about $\theta = \pm 30°$, while that of the S_1 has a minimum at $\theta = 0°$. The energy required to excite biphenyl to the S_1 excited state is larger at large θ than at small θ. The 290-nm radiation excites only biphenyl whose θ is smaller than about 30°, while the 250-nm radiation makes it possible to excite all possible conformers of biphenyl in the ground state This leads to different distributions of conformers dependent on the excitation wavelength in the excited state and results in the fluorescence spectra being dependent on the excitation wavelength.

If process (3) is completed before emission, fluorescence emerges from the well-relaxed excited conformers. Under such conditions, a fluorescence spectrum independent of the excitation wavelength is expected to be observed. As the temperature decreases, the distribution about the equilibrium conformation becomes narrow due to the Boltzmann distribution law. This makes the fluorescence spectrum sharpen on lowering the temperature down to the freezing point of the solvent.

The fluorescence spectrum of biphenyl varies slightly with the excitation wavelength even at room temperature (Fig. 2). This implies that the fluorescence from the incompletely relaxed conformers can not be neglected at room temperature.

When process (3) is gradually hindered with decrease in temperature, biphenyl molecules tends to fluoresce from the imcompletely relaxed or unrelaxed conformers in the excited state. When process (3) in completely hindered, the distribution of excited conformers is the same as that of the ground-state conformers. The fluorescence under such conditions is the superposition of various fluorescences corresponding to different conformations and is broader than at higher temperature. Berlman also found that nonplanar conformers of polyphenyls show diffuse fluorescence spectra and planar conformers show structured ones.[16]

The above discussion is supported by the results in Fig. 2. The isopentane–methylcyclohexane mixture is fluid at 128 K and rigid at 83 K. Intramolecular geometric relaxation occurs effectively at 128 K and is prevented completely at 83 K. The features of the fluorescence spectra at 128 K are determined by the distribution of conformers which attain equilibrium fitting to the S_1 state, while those at 83 K are determined by a conformational distribution identical to that in the ground state. In addition to this, the potential curve for S_1 is steeper around $\theta=30°$ than that for S_0. As a consequence of these facts, biphenyl shows a more broad and blue-shifted fluorescence in an isopentane–methylcyclohexane mixture at 83 K than at 128 K. In the case of the fluorescence spectra in propylene glycol and glycerol, the solution is viscous to a certain extent even at room temperature. Since viscousness of the solvent prevents the complete intramolecular geometric relaxation of excited-state biphenyl even at higher temperature, the excitation-wavelength dependence of the biphenyl fluorescence in viscous solvents is larger than that in fluid solvents. The viscosity of the solvents such as propylene glycol and glycerol gradually increase with lowering the temperature; no drastic change with lowering the temperature is observed in these solvents, unlike the result for the isopentane–methylcyclohexane mixture (Figs. 3 and 4).

The above interpretation is also supported by considering the temperature dependence of the intersystem-crossing rate constants. The values of k_{TM} for biphenyl in propylene glycol by 250-nm and 290-nm excitations are almost the same in the temperature range from 303 to 200 K. There is a difference in the k_{TM} values based on the two excitations at 250 and 290 nm below 200 K.[11] These findings indicate that propylene glycol is completely rigid below 200 K against any molecular rotation including the relaxation along θ during the lifetime of the fluorescent state. The rigidity of propylene glycol is also confirmed by the result of Fig. 5. The P of the biphenyl fluorescence in the solvent reaches a maximum at 210 K. At the temperature below 200 K the distribution of conformers in the fluorescent state is the same as in the ground state. In conclusion, the effects of temperature, viscosity, and excitation-wavelength on biphenyl fluorescence can be interpreted by considering the intramolecular geometric relaxation.

The Ham Effect on the Fluorescence Spectra of Biphenyl. The symmetry-forbidden 0-0 band appears in the absorption spectra of benzene[17,18] and in the fluorescence spectra of pyrene.[19] The band is known as the Ham band. The MO calculations[5,6,20] and experimental findings[21] revealed that the lowest absorption band of biphenyl is symmetry-forbidden regardless of θ. It is seen from Fig. 1 that the appearance and the intensity of the 0-0 band of biphenyl fluorescence are related to the solvent polarity. The 0-0 band is also affected by the change of temperature. The lowering of temperature changes the solvent polarity, solvent viscosity, and the dispersion forces between biphenyl and solvent molecules. Figures 2—4 indicate that the 0-0 band becomes obvious with lowering the temperature. It is therefore concluded that the intensity change of the 0-0 band of biphenyl fluorescence in various solvents is attributable to the Ham effect.

References

1) E. C. Lim and S. K. Chakrabarti, *Chem. Phys. Lett.*, **1**, 28 (1967); *J. Chem. Phys.*, **47**, 4726 (1967).

2) M. Kasha and H. R. Rawls, *Photochem. Photobiol.*, **7**. 561 (1968).

3) J. E. Adams, W. W. Mantulin, and J. R. Huber, *J. Am. Chem. Soc.*, **95**, 5477 (1973); J. R. Huber and J. E. Adams, *Ber. Bunsenges. Phys. Chem.*, **78**, 217 (1974); H. J. Haink and J. R. Huber, *Chem. Phys. Lett.*, **44**, 117 (1967).

4) H. Suzuki, *Bull. Chem. Soc. Jpn.*, **32**, 1340 (1959).

5) Y. Gondo, *J. Chem. Phys.*, **32**, 3928 (1964).

6) A. Imamura and R. Hoffman, *J. Am. Chem. Soc.*, **90**, 5379 (1968).

7) A. Golebiewski and A. Parczewski, *Z. Naturforsch., Teil A*, **25**, 1710 (1970).

8) A. d'Annibale, L. Lunazzi, A. C. Boicelli, and D. Nacciantelli, *J. Chem. Soc., Perkin Trans. 2*, **69**, 1396 (1973).

9) E. Hughes, Jr., J. H. Wharton, and R. V. Nauman, *J. Phys. Chem.*, **75**, 3097 (1971).

10) K. R. Naqvi, J. Donatsch, and U. P. Wild, *Chem. Phys. Lett.*, **34**, 285 (1976).

11) T. Fujii, S. Suzuki, and S. Komatsu, *Chem. Phys. Lett.*, **57**, 175 (1978).

12) M. A. El-Bayoumi, *J. Phys. Chem.*, **80**, 2259 (1976).

13) A. C. Albrecht, *J. Mol. Spectrosc.*, **6**, 84 (1961).

14) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).

15) S. Suzuki, T. Fujii, A. Imai, and H. Akahori, *J. Phys. Chem.*, **81**, 1592 (1977).

16) I. B. Berlman, *J. Phys. Chem.*, **74**, 3084 (1970).
17) J. S. Ham, *J. Chem. Phys.*, **21**, 756 (1953).
18) M. Koyanagi, *J. Mol. Spectrosc.*, **25**, 273 (1969).
19) A. Nakajima, *Bull. Chem. Soc. Jpn.*, **44**, 3272 (1971).
20) A. Gamba, G. F. Rantardine, and M. Simonetta, *Spectrochim. Acta*, **28A**, 1877 (1972).
21) R. M. Hochstrasser, R. D. McAlpine, and J. D. Whiteman, *J. Chem. Phys.*, **58**, 5078 (1973).