CHEMISTRY LETTERS, pp. 99-102, 1981.

EXCIMER OF CONFORMATIONALLY FLEXIBLE MOLECULES: DIETHYL *p*-PHENYLENEDIACRYLATE AND METHYL 4-(β-METHOXYCARBONYLVINYL)-α-CYANOCINNAMATE

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Conformationally flexible molecules of diethyl *p*-phenylenediacrylate (1) and methyl 4-(β-methoxycarbonylvinyl)-α-cyanocinnamate (2) exhibit excimer emission in concentrated solutions. The excimer of 1 is formed via excitation of the ground state aggregates of 1. In crystalline state, only 2, which has the crystal structure of B-type in Stevens' classification, being different from the crystal structure (A-type) of 1, gives excimer emission. The stack-type structure is proposed for the excimers of 1 and 2.

It is well known that excimers are formed as an intermediate in the photodimerization of some aromatic and olefinic compounds.1) For conformationally flexible molecules such as stilbene and cinnamic acid, excimer fluorescence has not been observed in solution.2,3) In the previous paper,4) it was reported that a flexible molecule, diethyl *p*-phenylenediacrylate (1) showed the excimer emission in concentrated acetonitrile solution. The purpose of the present work is to confirm the excimer emission of 1 and to discuss the structure of the excimer. Excimer emission of another conformationally flexible molecule, methyl 4-(β-methoxycarbonylvinyl)-α-cyanocinnamate (2) is reported.

Compounds 1 and 2 were prepared according to the methods described in the previous papers.5,6) Solvents used were of commercially available spectrograde. Solutions were carefully deaerated by bubbling dry argon gas. The fluorescence spectra were measured by using frontal method on a Hitachi MPF 2A fluorescence spectrophotometer connected with a Haake thermoregulator. The spectra of crystals were measured as KBr disks.

The fluorescence spectra of 1 in acetonitrile were measured at various concentration from 10^{-3} to nearly saturated solution of 0.5 mol/l at 25°C (Fig. 1). There appears a structureless broad emission band of the excimer around 455 nm at 0.1 mol/l or higher concentrations, in addition to a molecular emission at 365 nm. The energy difference between the original and the newly observed emission bands is about 5500 cm^{-1} and this value agrees well with those reported for the characteristic red-shift between the

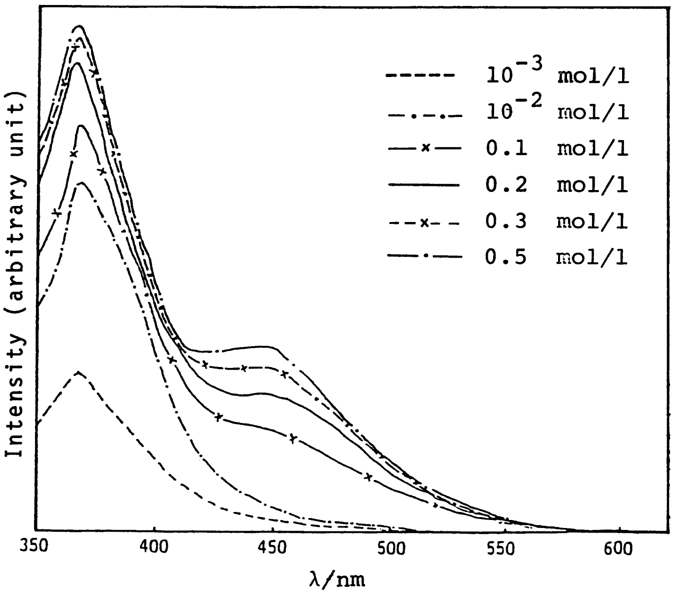

Fig. 1. Fluorescence spectra of various concentrations of 1 in acetonitrile at 25°C. Excitation at 335 nm.

molecular and excimer fluorescence of planar aromatic compounds such as pyrene and naphthalene.$^{7)}$ Besides in acetonitrile, excimer emission of 1 was also observed in various solvents such as benzene and chloroform.

The temperature dependence of the excimer emission of 1 was studied at temperatures between 10 and 65°C (Fig. 2). The isoemissive point was observed at near 395 nm. The excimer emission decreases and molecular emission increases when the temperature is raised. The enthalpy (ΔH_a) and entropy (ΔS_a) of the photoassociation and the ground state destabilization energy (E_r) were measured in acetonitrile and benzene solutions by the method of Stevens,$^{8)}$ and compared with those for typical planar aromatic compounds in Table 1. The ΔH_a and ΔS_a values obtained are smaller than those of the planar aromatic compounds, indicating that molecules of 1 in the excimer configuration are bound less tightly than the planar aromatic compounds. It is also shown in the table that the excimer binding energy of 1 in the non-polar solvent is weaker than in the polar solvent.

The critical concentration for the appearance of the excimer band for 1 is relatively high as compared with those of planar aromatic compounds. It seems that the excimer of 1 is formed by excitation of aggregates of 1 rather than excitation of isolated molecules of 1. Recently, excimer-type fluorescence from excited tetramer produced by the photoassociation of the excited dimer and the ground state dimer, was observed for 9-anthroic acid,$^{8)}$ and not from the usual bimolecular photoprocess of isolated molecules. Excitation spectra of 1 in acetonitrile were determined by monitoring the fluorescence emission at 365 and 455 nm. It was found that the molecular fluorescence appears most intensively when the excitation wavelength is 330 nm. This light corresponds to the maximum in the absorption spectra of 1. On the other hand, the excimer emission appears most intensively when

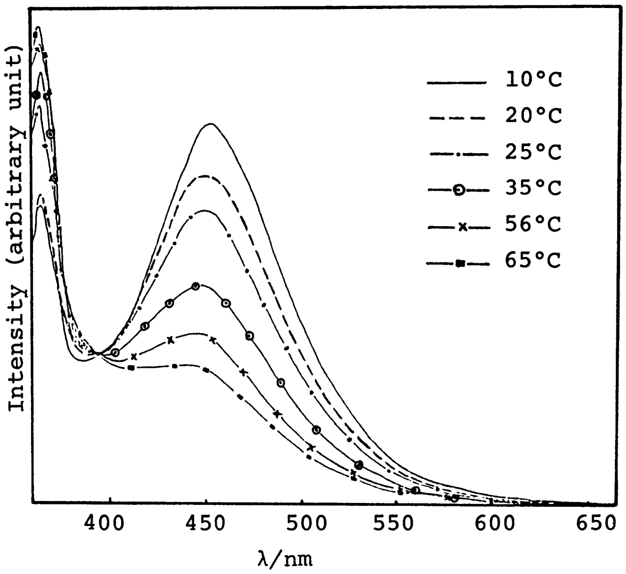

Fig. 2. Fluorescence spectra of 0.25 mol/l of 1 in acetonitrile at various temperatures. Excitation at 355 nm.

Table 1. ENTHALPIES, ENTROPIES AND GROUND STATE DESTABILIZATION ENERGIES FOR PHOTOASSOCIATION OF AROMATIC MOLECULES

	Solvent	ΔH_a kcal/mole	E_r kcal/mole	ΔS_a cal/mole deg	Reference*
Pyrene	Ethanol	9.2	7.9	-18.5	Stevens *et.al.* (1964)
	Paraffin oil	11.0	6.0	-20.0	Förster *et.al.* (1962)
Mesitylene	Mesitylene	2.8	8.1	-15.6	Birks *et.al.* (1968)
2-Methylnaphthalene	Ethyl ether	5.8	12.9	-21.0	Stevens *et.al.* (1964)
	Ethanol	5.1	12.9	-12.0	Selinger (1966)
1,6-Dimethylnaphthalene	Ethanol	4.6	9.4	-12.5	Selinger (1966)
	Heptane	6.2	7.8	-19.8	Birks *et.al.*(1966)
Diethyl *p*-phenylene-diacrylate (1)	Acetonitrile	5.2	10.6	-15.2	Present work
	Benzene	2.3	11.0	-7.3	Present work

* Taken from the review7) except for the present work.

the excitation wavelength is 355 nm. Fig. 3 compares the fluorescence spectra of 1 with the excitation wavelengths of 335 nm and of 355 nm. Attempts to identify the absorption maximum around 355 nm by the derivative spectrophotometry failed because the solution was too concentrated for accurate measurements.

The fluorescence spectra of another conformationally flexible aromatic diolefinic compound, 2, were studied in solution and in crystalline state. Fig. 4 shows that 2 exhibits the excimer emission both in concentrated solution and in crystalline state. Besides a broad structureless excimer band at near 490 nm, a very weak band of molecular fluorescence around 390 nm is observed in the fluorescence spectrum of crystalline 2, but the latter band becomes strong when measured in concentrated solution. The fine structured molecular fluorescence is observed when measured in EPA glass at -196°C. The crystal structure of 2 has been reported5) to belong to B-type of Stevens' classification.8) Molecules of 2 related by the translation of 3.955 A are piled up so that the molecules overlap heavily in the form of a stack.6) On the other hand, the fluorescence spectra of 1 in crystalline state were investigated for comparison. No excimer emission was observed neither at room temperature nor at liquid N_2 temperature. The crystal structure of

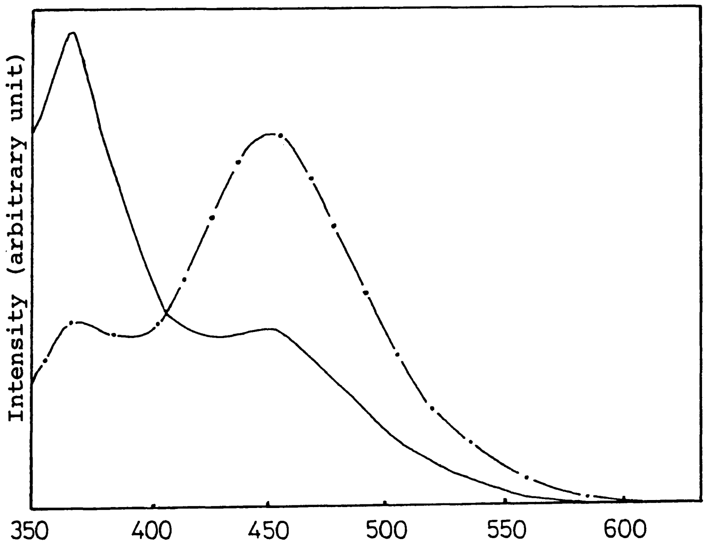

Fig. 3 Fluorescence spectra of 0.5 mol/l of 1 in acetonitrile at 25°C. Excitation at 335 nm, ——— ; excitation at 355 nm, —·— .

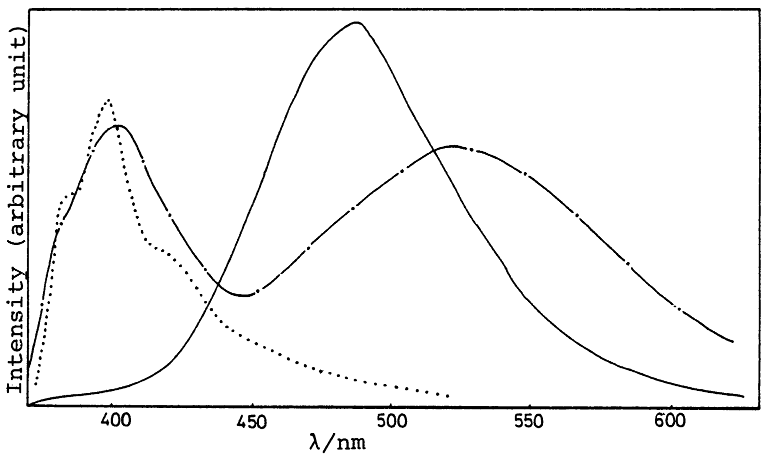

Fig. 4. Fluorescence spectra of 2 under various conditions. Excitation at 370 nm. 10^{-5} mol/l in EPA glass at -196°C, ... ; 0.3 mol/l in chloroform at 25°C, —·— ; in crystalline state at 25°C, ——.

1 belongs to A-type of Stevens' classification and molecules of 1 are piled up displacing in the direction of molecular long axis by about half a molecule.10) Therefore, the most probable structure of the excimers of 1 and 2 in concentrated solutions must be of stack-type as the structure of excimer of 2 in crystalline state. Recent finding, that the main photoproduct of 1 by irradiation of light of $\lambda > 350$ nm in concentrated solutions, is the 1,2-dimer of mirror symmetry,11) supports the proposed stack-type excimer structure for 1 in concentrated solutions.

One of the authors, S. H., wishes to express his thanks to a Grant for Foreign Student from the Ministry of Education.

References and Notes

1) M. D. Cohen, E. Elgavi, B. S. Green, Z. M. J. Ludmer, and G. M. J. Schmidt, *J. Am. Chem. Soc.*, 94, 6776 (1972), and references cited therein.
2) M. D. Cohen, B. S. Green, Z. Ludmer, and G. M. J. Schmidt, *Chem. Phys. Lett.*, 7, 486 (1970).
3) Excimer of stilbene was reported in squalane by thermoluminescence study, see B. Brocklehurst, D. C. Bull, M. Evans, P. M. Scott, and G. Stanney, *J. Am. Chem. Soc.*, 97, 2977 (1975).
4) F. Nakanishi, H. Nakanishi, and M. Hasegawa, *Nippon Kagaku Kaishi*, 1575 (1976).
5) F. Suzuki, Y. Suzuki, H. Nakanishi, and M. Hasegawa, *J. Polym. Sci. A-1*, 7, 2319 (1969).
6) H. Nakanishi and Y. Sasada, *Acta Cryst.*, B34, 332 (1978).
7) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, 1970, p.352, p.356.
8) B. Stevens, *Adv. Photochem.*, 8, 161 (1971), and references cited therein.
9) S. Suzuki, T. Fujii, N. Yoshiike, S. Komatsu, and T. Iida, *Bull. Chem. Soc., Jpn.*, 51, 2460 (1978).
10) H. Nakanishi, K. Ueno, M. Hasegawa, and Y. Sasada, *Acta Cryst.*, B34, 2209 (1978).
11) S. Sakamoto, S. Huy, H. Nakanishi, F. Nakanishi, and M. Hasegawa, the 40th Autumn Meeting of Jap. Chem. Soc. and Other Related Societies, October, 1979, Fukuoka. Preprints II, p.457. Data to be published.

(Received October 9, 1980)