

# Excimeric Emission and Photochemical Behavior of *p*-Phenylenediacyric Acid (*p*-PDA) and its Diethyl-Ester (*p*-PDAEt)

EL-ZEINY M. EBEID and SAMY A. EL-DALY

*Chem. Dept., Faculty of Science, Tanta Univ., Tanta-Egypt*

MASAKI HASEGAWA

*Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-Ku, Tokyo 113 Japan*

(Received July 15, 1985)

*p*-Phenylenediacyric acid (*p*-PDA) displays excimeric emission in concentrated solutions (concentration *ca.* 0.5 M) in dimethylsulphoxide (DMSO). The excimeric emission maximum is red shifted by *ca.* 5200  $\text{cm}^{-1}$  compared with molecular emission maximum. The fluorescence quantum yields of *p*-PDA has been measured in DMSO ( $\phi_f = 0.09$ ,  $\lambda_{ex} = 337 \text{ nm}$ ) and in cetyltrimethylammonium chloride (CTAC) cationic micelles that show remarkable solubilization of *p*-PDA.

The solution photoreactivity of *p*-PDA is wavelength dependent. In dilute DMSO solutions, 365 nm and 310 nm light causes *p*-PDA consumption giving a photoproduct of maximum absorption at *ca.* 265 nm. A back photoreaction is induced by 254 nm light. The photochemical quantum yields ( $\phi_c$ ) of the forward photochemical reaction have been measured as a function of temperature and the activation energy was evaluated as  $E_a = 9 \text{ kJ mol}^{-1}$  suggesting a unimolecular photoisomerization process.

Emission from crystalline *p*-PDA has also been reported. The emission maximum is red shifted from molecular emission maximum by *ca.* 3250  $\text{cm}^{-1}$ .

The energy transfer in the system diethyl-*p*-phenylenediacyrylate (*p*-PDAEt)-1,4-bis( $\beta$ -pyridyl-2-vinyl)benzene(P2VB) has been studied. Triplet states formation mechanism is proposed.

## INTRODUCTION

There is a growing interest in studying the photochemical and photo-physical behavior of diolefinic compounds. Some diolefins are reported as blue laser dyes<sup>1</sup> e.g., 1,4-bis ( $\beta$ -pyridyl 2 vinyl)benzene(P2VB) and 2,5-distyrylpyrazine (DSP). Some others, yet conformationally flexible, form excimers in concentrated solutions<sup>2</sup> e.g., diethyl *p*-phenylenediacylate (*p*-PDAEt) and methyl 4-( $\beta$ -methoxycarbonyl-vinyl)- $\alpha$ -cyanocinnamate in acetonitrile solutions.

The solution photochemical reactivity of many diolefins has been reported earlier<sup>3-6</sup> with the feasibility of both unimolecular isomerization and bimolecular oligomerization reactions depending on the reaction conditions e.g. concentration and irradiation wavelength.

In the present communication, we report the excimeric phenomenon, emission characteristics and photochemical reactivity of (*p*-PDA) that is characterised by relatively higher fluorescence quantum yield compared with its diethyl ester (*p*-PDAEt) in various media. We also report the energy transfer in the two diolefins (P2VB + *p*-DAEt).

## EXPERIMENTAL

*p*-PDA was prepared as described by Suzuki *et al.*<sup>7</sup> The material was recrystallized twice from ethanol. Emission spectra were measured using a Shimadzu RF 510 spectrofluorophotometer, UV-spectra were measured using a Unicam SP 8000 spectrophotometer.

Fluorescence quantum yields were measured relative to 9,10-diphenylanthracene<sup>8</sup> and light intensities were measured by ferrioxalate actinometry.<sup>9</sup>

## RESULTS AND DISCUSSION

Figure 1a shows the emission spectra of *p*-PDA. In dilute solutions (*ca.*  $10^{-5}$  M in methanol), the emission is relatively structured ( $\lambda_{ex} = 337$  nm) with a maximum at *ca.* 410 nm. In concentrated solutions (*ca.* 0.5 M in DMSO) the emission becomes broad, structureless and red shifted by about  $5200\text{ cm}^{-1}$ . The emission from concentrated

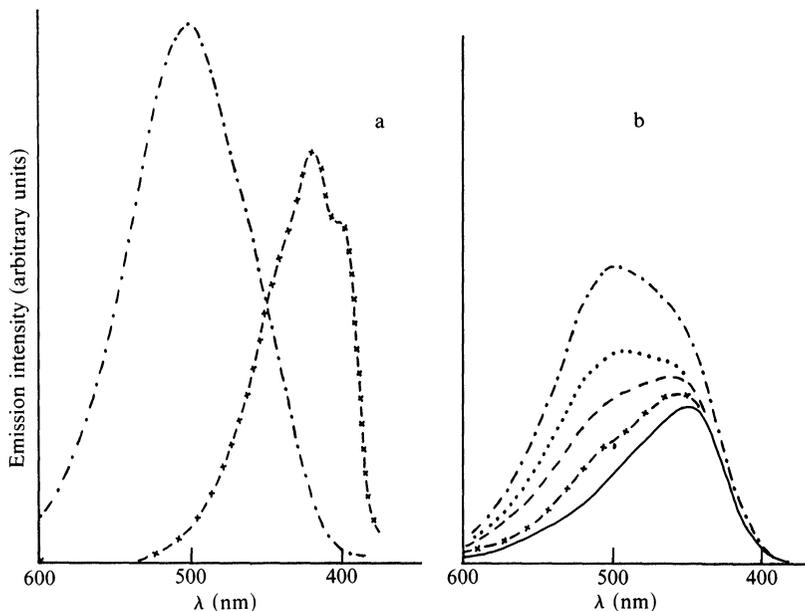


FIGURE 1 (a) The emission spectra ( $\lambda_{ex} = 330$  nm) of  $10^{-5}$  M methanolic (-x-x-x-) and 0.5 M DMSO-solution of *p*-PDA. (b) Effect of temperature on the excimeric emission of 0.5 M *p*-PDA in DMSO. Emission at 10°C (.....), 20°C (· · · · ·), 30°C (-----), 40°C (-x-x-x-) and at 60°C (——).

solutions is thus excimer-like and this behavior is similar to that reported for *p*-PDAEt<sup>2</sup> in acetonitrile. Figure 1b shows the temperature effect on the excimeric emission of *p*-PDA in DMSO. As the temperature is raised, the excimeric emission intensity decreases and the emission is blue-shifted towards molecular emission. This is attributed to the role of thermal energy in destabilizing excimeric species.<sup>10,11</sup>

*p*-PDA is characterized by higher fluorescence quantum yield values ( $\phi_f$ ) compared with its diethylester. Table I summarizes the  $\phi_f$  values of both compounds in DMSO.

Both *p*-PDA and PDAEt give no laser action upon pumping with nitrogen laser ( $\lambda_{ex} = 337.1$  nm). It seems that the excimer formation and the relatively low  $\phi_f$  values prohibits the laser activity of these two diolefins. *p*-PDA is sparingly soluble in water. The solubility increases significantly in cetyltrimethylammonium chloride (CTAC) solutions. Like many other fluorescers<sup>12-14</sup> both fluorescence intensities

TABLE I  
 $\phi_f$  values of *p*-PDA and *p*-PDAEt in DMSO

Compound	$\lambda_{ex}$	$\phi_f$
<i>p</i> -PDA	310	0.16
	320	0.13
	337	0.13
	365	0.09
<i>p</i> -PDAEt	337	0.03

and fluorescence quantum yields ( $\phi_f$ ) of *p*-PDA increase as the CTAC concentration increases (see Figure 2). The enhanced emission is correlated to the micellization of CTAC in aqueous media.

*p*-PDA solutions show a reasonable photoreactivity. Figure 3 shows the fractional fluorescence ( $\phi_f$ ) change of *p*-PDA in DMSO as a result of *uv*-irradiation ( $\lambda_{ex} = 310$  nm). A photostationary state is obtained after *ca.* 60% conversion. The photochemical change is thermally activated as shown in Figure 3. The energy of activation of the photochemical was evaluated by measuring the photochemical quantum yield ( $\phi_c$ ) at various temperatures. The results were then treated as follows:

The general expression is given as:

$$\phi_c = \frac{dC/dt}{dI/dt} \quad (1)$$

where  $C$  is the concentration in moles/litre and  $I$  is the light intensity in Einsteins. The term  $dC/dt$  represents the rate of the reaction

$$\frac{dC}{dt} = kC^n \quad (2)$$

where  $k$  is the rate constant and  $n$  is the order of the reaction.

From (1) and (2):

$$k = (\phi_c \cdot dI/dt) / C^n. \quad (3)$$

From the Arrhenius equation

$$k = A \exp -E_a/RT \quad (4)$$

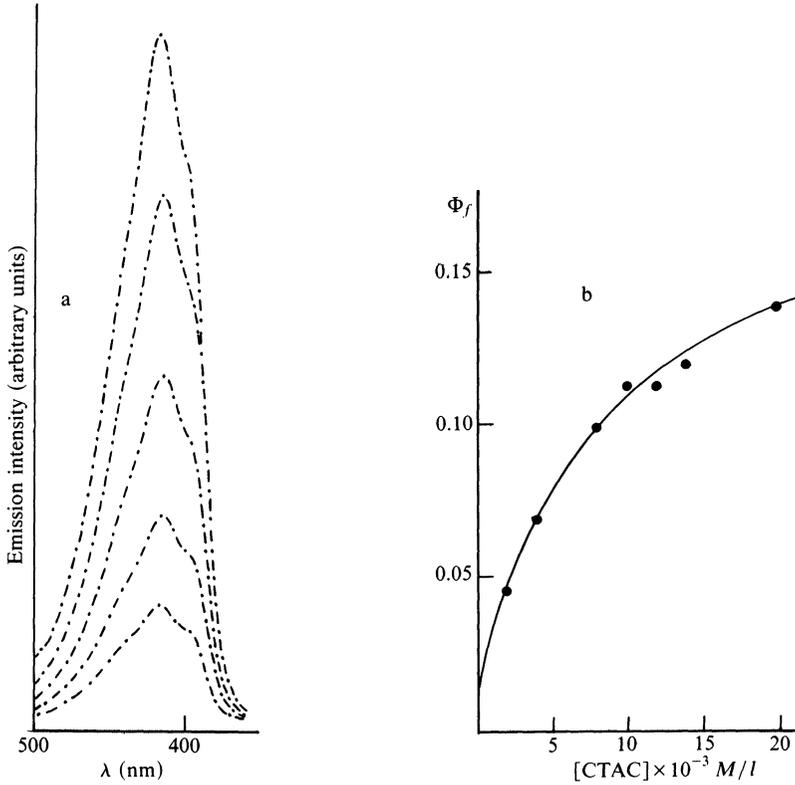


FIGURE 2 Effect of increasing CTAC concentration on the emission intensity (a) and emission quantum yields (b) of  $10^{-5} M$  *p*-PDA ( $\lambda_{ex} = 330$  nm) in aqueous medium. In (a) the CTAC concentrations as the intensity increases are 0,  $4 \times 10^{-3}$ ,  $1 \times 10^{-2}$ ,  $1.6 \times 10^{-2}$  and  $2.2 \times 10^{-2} M$ .

where  $A$  is the pre-exponential factor ( $A$  has its normal value of about  $10^{11} l \cdot mol^{-1} \cdot s^{-1}$ ),<sup>15</sup>  $E_a$  is the energy of activation,  $R$  is the gas constant, and  $T$  is the absolute temperature in Kelvins.

From (3) and (4) and taking the logarithms

$$\ln \phi_c = \ln A + n \ln C - \ln \frac{dI}{dt} - \frac{E_a}{RT} \quad (5)$$

Assuming a constant incidence of light photons and that the photochemical quantum yields are measured over a narrow concentration

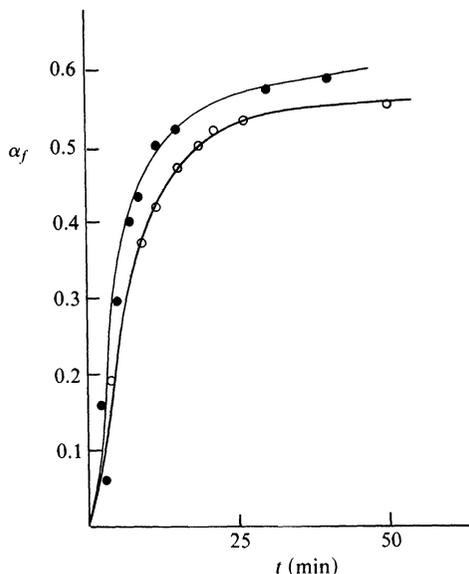


FIGURE 3 Fractional fluorescence change ( $\alpha_f$ ) as a result of irradiation ( $\lambda_{ex} = 310$  nm) of  $5 \times 10^{-6}$  M *p*-PDA in DMSO at 30°C (○) and 50°C (●).

change, the term  $(\ln A + n \ln C - \ln dI/dt)$  is presumed constant for a first approximation and relation (5) can be reduced to a modified Arrhenius form (6) where  $C'$  is a dimensionless constant;

$$\ln \phi_c = C' - E_a/RT. \quad (6)$$

Figure 4 shows a reasonable validity of Eq. (6) where a plot of  $\ln \phi_c$  vs.  $1000/T$  gives a straight line of slope  $= E_a/R$ . For *p*-PDA photochemical reaction in DMSO ( $\lambda_{ex} = 310$  nm)  $E_a = 9$  kJ mol<sup>-1</sup>. This value is within the expected diffusion-controlled energies of activation ( $E_a = 4$ – $13$  kJ mol<sup>-1</sup>).<sup>15</sup>

The photoreactivity of *p*-PDA is wavelength dependent. Figure 5a shows the changes in *uv*-visible absorption spectra of *p*-PDA as a result of *uv*-irradiation ( $\lambda_{ex} = 365$  or 310 nm). This results in the build up of new photoproduct absorbing at *ca.* 265 nm. Irradiation at shorter wavelength ( $\lambda = 254$  nm) gives a back photochemical reaction as shown in Figure 5b regenerating *p*-PDA monomer. There is a sharp isosbestic point at 290 nm in both forward and backward photo-

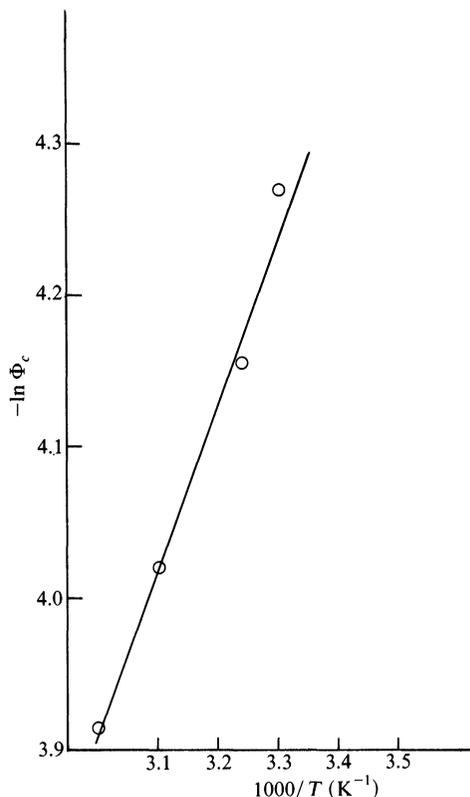


FIGURE 4 A plot of the modified Arrhenius relation (Eq. (6)) for the photochemical reaction of  $10^{-5}$  M *p*-PDA solutions in DMSO ( $\lambda_{ex} = 310$  nm).

chemical reactions. At such low *p*-PDA concentrations (*ca.*  $10^{-5}$  M) bimolecular reactions are unlikely to occur and the photoproduct is thought to be the cisphotoisomer. This is also consistent with the low energy of activation of  $9 \text{ kJ mol}^{-1}$ .

Crystalline *p*-PDA gives emission at 460 nm ( $\lambda_{ex} = 365$  nm) that is also red shifted compared with molecular emission by *ca.*  $3250 \text{ cm}^{-1}$  a value that is less than excimeric emission shift in concentrated solutions indicating the absence of such excimeric emission in crystalline *p*-PDA. This is expected from the idealized crystal structure that belongs to *A*-type of Steven's classification.<sup>11,16</sup>

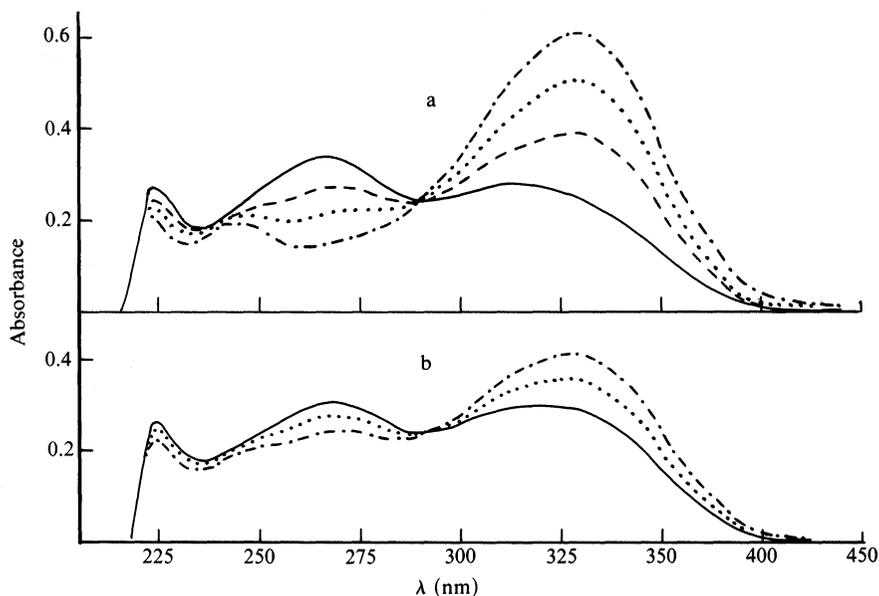


FIGURE 5 (a) The changes in UV-absorption spectra of  $10^{-5}$  M *p*-PDA methanolic solutions as a result of UV-irradiation ( $\lambda_{ex} = 365$  nm, irradiation using 310 nm light give similar behavior). Irradiation times are 0 (—), 6 (·····), 15 (----) and 75 minutes (— · — · —). (b) The effect of 254 nm light in inducing a back photochemical reaction. Starting with previously irradiated ( $\lambda_{ex} = 310$  nm) *p*-PDA solution (—), irradiation time using 254 nm light are 34 (·····) and 77 mins (----).

UV-irradiation ( $\lambda_{ex} = 365$  nm) of crystalline *p*-PDA results in an initial increase in the emission intensity at 460 nm (see Figure 6). This initial increase in emission intensity is attributed to the consumption of photoreactive excitation traps at early stages of UV-irradiation.

The UV-absorption of *p*-PDAEt (Figure 5a) reveals a remarkably strong absorption band at 320 nm that is close to the nitrogen laser line at 337.1 nm.<sup>1</sup> On the other hand, the recently reported 1,4-bis( $\beta$ -pyridyl-2-vinyl)benzene (P2VB) blue laser dye absorbs strongly at 380 nm which is the same emission region of *p*-PDAEt ( $\lambda_{ex} = 337.1$  nm). The energy transfer dye laser system (ETDL) consisting of (P2VB + *p*-PDAEt) has been studied. Despite the apparent higher energy of the first singlet absorption of *p*-PDAEt compared with P2VB, experimental study shows that *p*-PDAEt is an efficient quencher of P2VB emission. Figure 7 shows the Stern-Volmer plots of emission

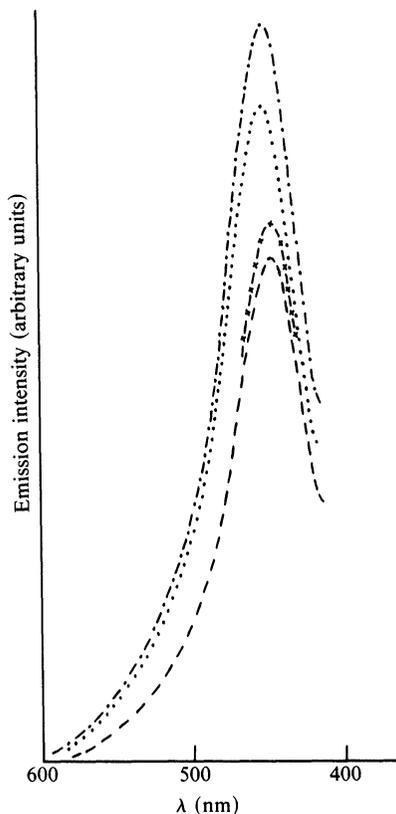


FIGURE 6 Effect of UV-irradiation ( $\lambda_{ex} = 365$  nm) on the emission spectra of *p*-PDA crystals. Irradiation times are 0 (-----), 5 (-x-x-x-), 20 (.....) and 25 mins (-.-.-).

quenching of PSVB using *p*-PDAEt as a quencher. Due to big differences in fluorescence quantum yields of *p*-PDAEt ( $\phi_f = 0.03$ ) and P2VB ( $\phi_f = 0.46$ ) there is no significant contribution in the emission of the fluorecser (P2VB) by the quencher (*p*-PDAEt). The Stern-Volmer plots are non-linear and are quadratic in the quencher concentration  $[Q]$ . This situation is frequently encountered when a reaction occurs from a triplet state and a quencher is employed which quenches both the triplet state and the singlet state from which the triplet state arises by intersystem crossing.<sup>17</sup> The half quenching concentration  $[Q]_{1/2}$  at

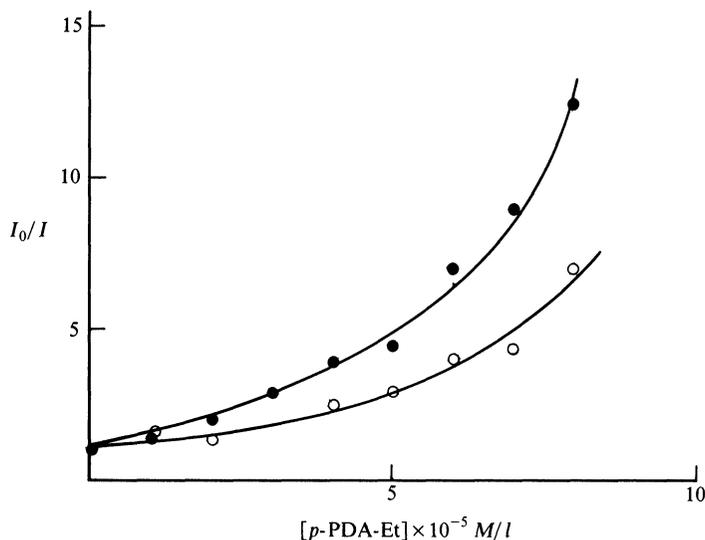


FIGURE 7 Stern-Volmer plots of emission quenching of P2VB ( $10^{-5}$  M) using *p*-PDAEt quencher in DMSO at 25°C (●), and 50°C (○).

which  $I = I_0/2$  is  $2 \times 10^{-5}$  M. Assuming a diffusion controlled quenching mechanism,  $k$  is in the order of  $10^8 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$  in DMSO solvent ( $\eta = 1.8$  poise) as calculated from the modified Debye equation.<sup>15</sup> Then

$$\frac{I_0}{I} = 2 = 1 + k[Q]_{1/2}.$$

Substituting for  $k$  and  $[Q]_{1/2}$ , the lifetime,  $T$  is in the range of milliseconds.

There are three arguments that the quenching of P2VB emission by *p*-PDAEt occurs mainly via triplet-states. These arguments are;

- (i) The first singlet electronic state of the quencher is of higher energy compared with that of the fluorescer.
- (ii) Stern-Volmer plots are quadratic in  $[Q]$ .<sup>17</sup>
- (iii) The half quencher concentration  $[Q]_{1/2}$  is low ( $2 \times 10^{-5}$  M) suggesting the involvement of triplets.<sup>15</sup>

Figure 7 shows that the quenching efficiency decreases as the temperature increases. This is not expected for diffusion controlled

quenching but is consistent with a significant contribution of static quenching.<sup>17</sup>

## References

1. E. M. Ebeid, M. M. F. Sabry and S. A. El-Daly, *Laser Chem.* **5**, 223(1985) and references therein.
2. M. Sakamoto, S. Huy, H. Nakanishi, F. Nakanishi, T. Yurugi and M. Hasegawa, *Chemistry Lett.* **99** (1981).
3. M. Hasegawa, *Adv. Polym. Sci.* **42**, 1 (1982) and *Chem. Rev.* **83**, 507 (1983) and references therein.
4. Y. Suzuki, T. Tamaki and M. Hasegawa, *Bull. Chem. Soc. Japan* **47**, 210 (1974).
5. E. M. Ebeid, M. H. Abdel-Kader and S. E. Morsi, *J. Chem. Soc. Faraday Trans. 1*, **78**, 3213 (1982).
6. E. M. Ebeid and S. H. Kandil, Submitted for publication.
7. F. Suzuki, Y. Suzuki, H. Nakanishi and M. Hasegawa, *J. Polym. Sci. A-1*, **7**, 2319 (1969).
8. J. V. Morris, M. A. Mahaney and J. R. Huber, *J. Phys. Chem.* **80**, 969 (1976).
9. I. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. London, Ser. A* **235**, 518 (1959).
10. J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley, New York, 1970).
11. B. Stevens, *Adv. Photochem.* **8**, 161 (1971).
12. M. Gratzel and J. K. Thomas, in: *Modern Fluorescence Spectroscopy* Vol. 2, ed. E. L. Wehry (Plenum Press, New York, 1976) Chap. 4.
13. C. R. Singletery and L. A. Weinberger, *JACS* **73**, 4574 (1951).
14. R. R. Alfano, S. L. Shapiro and W. Yu, *Opt. Commun.* **7**, 191 (1973).
15. E. F. Caldin, *Fast Reactions in Solutions* (Blackwell, Oxford, 1964).
16. H. Nakanishi, K. Ueno, M. Hasegawa and Y. Sasada, *Acta Cryst.* **B34**, 2209 (1978).
17. J. A. Bartrop and J. D. Coyle, *Excited States in Organic Chemistry* (John Wiley and Sons, 1975), p. 152.