

# Dual fluorescence and intramolecular charge transfer in a bulky electron donor–acceptor system. *N,N*-Dimethylanilino-*o*-bis-pyrazolopyridine

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## Abstract

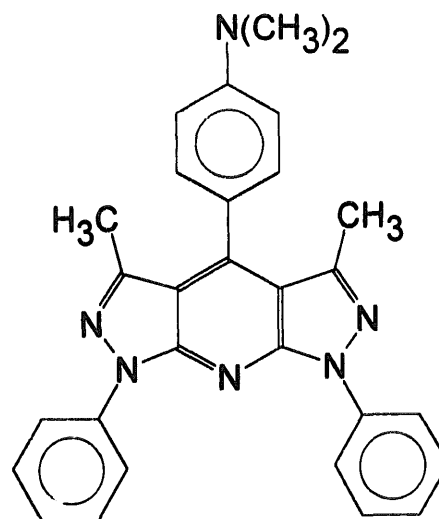
The photophysical properties of 4-(4'-*N,N*'-dimethylaminophenyl)-1,7-diphenyl-3,5-dimethyl-bis-pyrazolo-[3,4-*b*;4',3'-*e*]pyridine (DMA-DMPP), highly emissive in non-polar solvents and composed from a dimethylanilino electron donor and a bulky electron acceptor, have been investigated. The position of the fluorescence maximum as well as the fluorescence quantum yield and the radiative decay rate are strongly solvent polarity dependent; the magnitude of this effect becomes dramatically larger as the solvent polarity exceeds that of 1-chlorobutane. In protic solvents dual fluorescence is observed. In accordance with theoretical calculations the results are explained in terms of a polarity induced change in the energetic ordering of two emissive states of largely different charge transfer character.

**Keywords:** Electron transfer; Intramolecular charge transfer; Fluorescence; Solvent effects; Donor–acceptor systems; Excited states

## 1. Introduction

Photoinduced intramolecular electron transfer plays a key role in the photophysics of electron donor (D)–electron acceptor (A)  $p/\pi$  conjugated systems connected formally by a single bond. The molecular structure of their charge transfer excited states is the object of numerous discussions for more than 20 years. One of the best known and also widely accepted proposal for such a system is the so-called TICT (twisted intramolecular charge transfer) state model [1–3], which proposes the primarily excited molecule to undergo relaxation to an intramolecular charge transfer state, characterized by a minimal overlap between the donor and acceptor orbitals (zero overlap rule [4]) and almost full electron transfer. The zero overlap of the orbitals is achieved by a twist about the single bond connecting the donor and the acceptor moieties.

The perpendicular geometry was questioned recently as an inherent precondition to obtain intramolecular charge transfer in such D–A systems [5,6]. For bulky  $\pi$  donor and acceptor systems as, e.g. 9-(4-dimethylaminophenyl)-anthracene or 9,9'-bianthryl, the D–A conformation in the fluorescing charge transfer excited state was postulated to become more coplanar than in the ground state [5,6].



DMA-DMPP

In the present article we report the photophysical properties of the recently synthesized compound 4-(4'-*N,N*-dimethylaminophenyl)-1,7-diphenyl-3,5-dimethyl-bis-pyrazolo-[3,4-*b*;4',3'-*e*]pyridine (DMA-DMPP, see formulae), a *N,N*-dimethylaniline derivative with a strong and bulky electron acceptor unit in para position. This compound with large  $\pi$ -electron donor and acceptor subsystems, non-

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coplanar because of sterical hindrance, is a suitable object to check the validity of the TICT model for large D–A molecules.

## 2. Experimental

DMA-DMPP was synthesized and purified according to the procedure given elsewhere [7]. The solvents used were generally of spectroscopic grade (Uvasol Merck, Darmstadt, Germany). Absorption spectra were measured with a Shimadzu or Hitachi U3300 spectrophotometer. Fluorescence measurements were either performed using a unit and procedure described previously [8–10] or a luminescence spectrometer LS 50B (Perkin Elmer). Time correlated single photon counting was used to obtain the fluorescence decay profiles. The experimental setup and the deconvolution procedure was described elsewhere [10]. Plots of weighted residuals and of the autocorrelation function, values of reduced  $\chi^2$  and mean errors were used to judge the quality of the fit [11].

The ground state configuration of DMA-DMPP was obtained from AM1 calculations in the MOPAC 6.0 release [12]. For this geometry excited state energies, transition moments, and the change in the charge distribution were obtained from INDO/s calculations, including configuration interaction constructed from the 40 lowest singly excited conformation [13].

## 3. Results and discussion

The absorption and fluorescence spectra of DMA-DMPP in various solvents are depicted in Fig. 1.

The absorption spectrum is polarity dependent: the absorption coefficient of the lowest band increases and that of the

second band decreases with increasing solvent polarity. Spectral shifts of the maxima are small but the low energy edge of the lowest band shifts strongly bathochromically. Most of these changes occur in solvents of middle polarity, as the variation between solutions in hexane and 1-chlorobutane is much larger than that between the latter solvent and acetonitrile. Spectra obtained either in acetonitrile or in ethanol are not discernible. Polarity effects depend thus mainly on the polarity function  $\Delta f = (D - 1)/(2D + 1) - (n^2 - 1)/(2n^2 + 1)$ , independent of hydrogen bonding properties. Such a polarity dependent absorption spectrum was not observed for related compounds in which the 4'-dimethylaminophenyl donor is replaced by phenyl or 4'-nitrophenyl groups. Their absorption spectra resemble closely that of DMA-DMPP in hexane but exhibit insignificant solvent polarity dependence. This increase in the absorption coefficient is most probably due to an admixture of a higher, very polar singlet state whose energy is lowered or gains intensity in polar solvents.

The fluorescence of DMA-DMPP is very sensitive to the solvent, as the spectral position and the quantum yield is strongly solvent dependent.  $Q_f$  is large (0.78 in hexane) in nonpolar solvents, but decreases in polar ones (e.g. 0.26 in acetonitrile) and becomes small in hydroxylic solvents (e.g. 0.017 in methanol). For more details see Table 1. In non-hydroxylic solvents, where the quantum yield is high ( $>0.2$ ), only a single fluorescence band is observed, which shifts strongly bathochromically, as the solvent polarity increases. This indicates a large increase in the permanent dipole moment upon excitation. In alcohols, however, dual fluorescence appears. This might be due to the low intensity of the long wavelength emission, which is strongly quenched in hydroxylic solvents, and its good separation from the primarily excited band.

The appearance of dual fluorescence is also documented for hexane binary mixtures with ethanol (see Fig. 2): as the

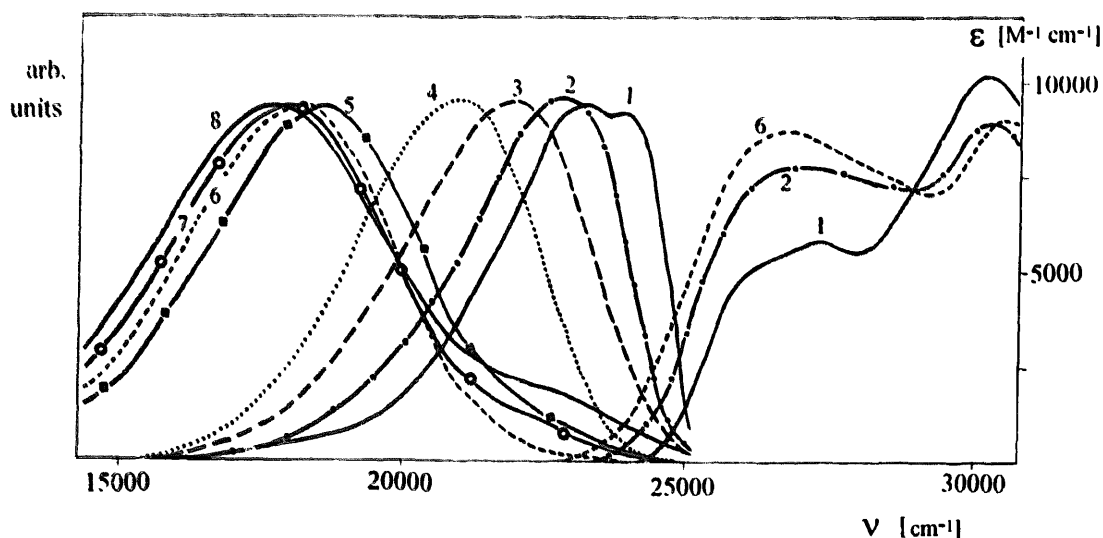


Fig. 1. Absorption and corrected fluorescence spectra of DMA-DMPP in different solvents: hexane (1), 1-chlorobutane (2), dichloromethane (3), tetrahydrofuran (4), 1-butanol (5), acetonitrile (6), 1-propanol (7), ethanol (8).

Table 1

Fluorescence maximum,  $\bar{\nu}_f$ , fluorescence quantum yield,  $Q_f$ , fluorescence lifetime,  $\tau_f$ , and natural fluorescence lifetime,  $\tau_f^0$ , of DMA-DMPP in various solvents at room temperature

	$\bar{\nu}_f$ ( $\text{cm}^{-1}$ )	$Q_f$	$\tau_f$ ( $\text{ns}^{-1}$ )	$\tau_f^0$ ( $\text{ns}^{-1}$ )
1 Hexane	23300	0.78	6.74	8.62
2 Benzene	22900	0.59	3.37	5.67
3 Diethyl ether	22900	0.27	4.20	15.7
4 1-Chlorobutane	22400	0.54	3.58	6.67
5 Tetrahydrofuran	20900	0.63	7.70	12.3
6 Dichloromethane	21100	0.60	6.30	10.5
7 Pentanol-1	18900	0.25	7.18	29.3
8 Butanol-1	18700	0.17	6.24	37.6
9 Cyclohexanone	19900	0.47	11.18	23.6
10 Propanol-1	18100	0.095	4.42	46.4
11 Ethanol	18000	0.066	3.60	54.7
12 Acetonitrile	18100	0.26	12.97	49.6
13 Methanol	17400	0.017	1.39	80.6
14 Dimethyl sulfoxide	17600	0.23	11.73	50.2
15 Propylene carbonate	17900	0.23	12.14	51.9

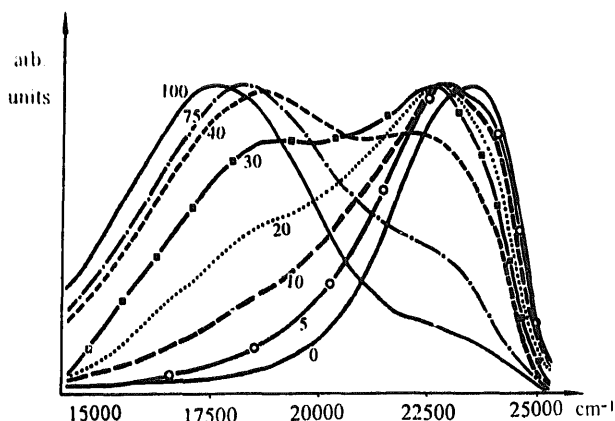


Fig. 2. Corrected fluorescence spectra of DMA-DMPP in hexane binary mixtures with ethanol. The composition is given in v/v % ethanol.

ethanol concentration is raised, long wavelength fluorescence grows in expense of the short wavelength emission. The spectra shown in Fig. 2 are normalized to equal height but it should be noted that the total quantum yield decreases concomitantly (see Table 1). Dual luminescence might mainly be influenced by bulk properties, as the photophysical properties vary uniformly with the composition of the binary mixture. In water as solvent,  $Q_f$  becomes smaller than 0.001. In this case, long wavelength fluorescence is almost totally quenched and only residual short wavelength, primary emission is observed.

A plot of the DMA-DMPP fluorescence maximum versus the solvent polarity function  $\Delta f$  shows a dramatic change in the slope in an intermediate polarity region near to  $\Delta f=0.2$  (see Fig. 3). This should indicate that the character of the emitting state changes from nonpolar to highly dipolar. A value of  $97 \times 10^{-30}$  Cm (29 D) was obtained for its dipole moment from the slope of a plot of  $\bar{\nu}_f$  versus  $(D-1)/(D+2)$  for solvents with larger polarity than 1-chlorobutane, using equation [14,15]

$$\bar{\nu}_f \approx \bar{\nu}_f^0 - \frac{1}{4\pi\epsilon_0} \cdot \frac{1}{hc\chi a^3} \cdot \bar{\mu}_m(\bar{\mu}_m - \bar{\mu}_n) \cdot \frac{D-1}{D+2} \quad (1)$$

and assuming  $a=760$  pm, and  $\chi=0.50$ .  $\bar{\nu}_f$  denotes the fluorescence maximum,  $a$  the cavity radius,  $\mu_n$  and  $\mu_m$  the dipole moments for the ground and the fluorescing state, respectively.  $\mu_n=20.6 \times 10^{-30}$  Cm (6.18 D) was derived from INDO/s calculations.

The fluorescence maximum in aqueous solutions fits excellently to an extrapolation of the polarity dependence of  $\bar{\nu}_f$  at very low polarities ( $\Delta f < 0.2$ ) to the polarity of water. This supports the conclusion that in this environment only weak residual fluorescence from the non-polar, primarily excited state is observed, as the polar state is effectively quenched.

Also the fluorescence lifetimes obtained from a fit of the fluorescence decay profiles to a single exponential function in the nanosecond time regime are given in Table 1. No general trend can be deduced for the polarity dependence of  $\tau_f$ . Nevertheless, the natural lifetime  $\tau_f^0$  can formally be calculated, and its dependence on  $\Delta f$  is shown in Fig. 3.  $\tau_f^0$  values are nearly constant at low polarities but increase steeply at  $\Delta f > 0.2$ , concomitantly with the decrease of  $\bar{\nu}_f$ . This increase should most likely result from concurrent emissions originating from the primarily excited non-polar and the final polar excited state. This final state has, thus, a much

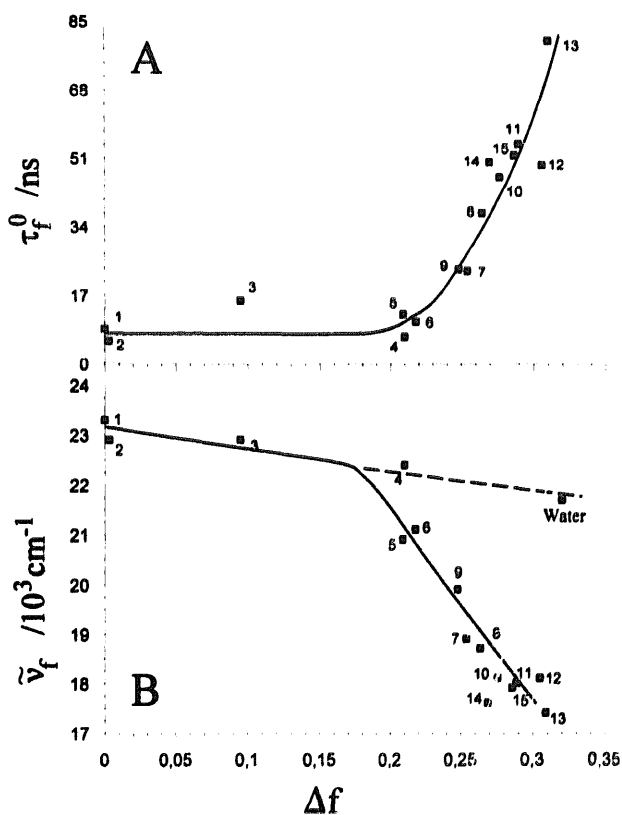


Fig. 3. Plot of the solvent shift of DMA-DMPP fluorescence maxima,  $\bar{\nu}_f$  (B), and of the natural fluorescence lifetime,  $\tau_f^0$  (A), versus the solvent polarity function  $\Delta f = (D-1)/(2D+1) - (n^2-1)/(2n^2+1)$ . The numbering of the solvent is given in Table 1.

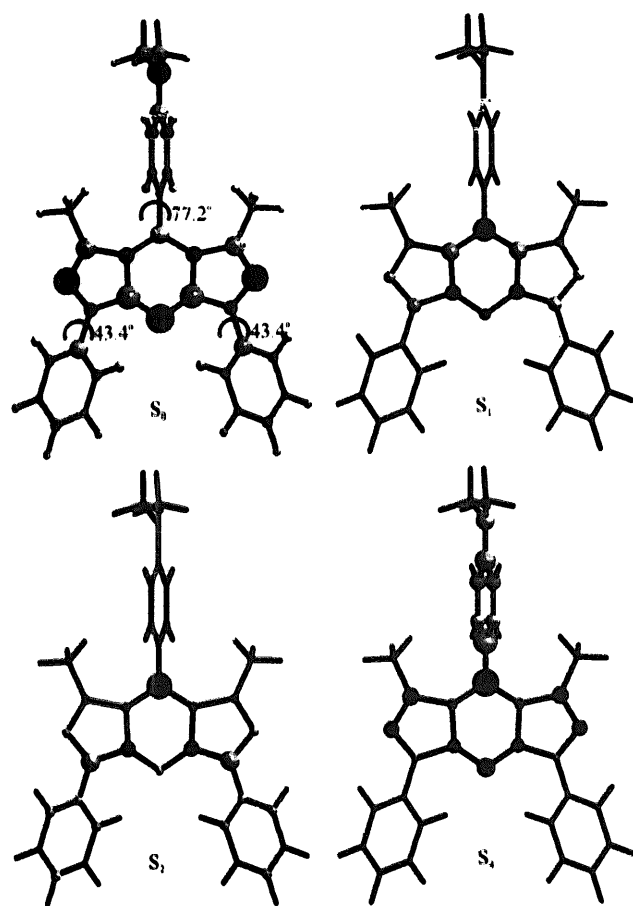


Fig. 4. Ball model of DMA-DMPP in the ground state, according to the AM1 calculations. For the excited states  $S_1$ ,  $S_2$  and  $S_4$ , the charge density obtained from INDO/s-CI is plotted. Black balls indicate an increase of negative charge in the excited state, while white ones show an increase of positive charge.

lower transition dipole for the respective radiative transition to the ground state.

The radiative lifetimes of fluorescence can be estimated from the absorption spectrum by the Strickler-Berg-equation [16]:

$$\frac{1}{\tau_f^0} = \frac{8\pi c}{N_L} \cdot \ln 10 \cdot n^2 \langle \bar{\nu}^{-3} \rangle^{-1} \int \epsilon(\bar{\nu}) d \ln \bar{\nu} \quad (2)$$

where  $n$  denotes the refractive index of the solvent. Assuming a Gaussian profile of the first absorption band this results in  $\tau_f^0 = 44$  ns for hexane solutions and 30 ns for acetonitrile. At least the value obtained in hydrocarbons is remarkably longer than that calculated from the photophysical data. The high fluorescence quantum yield and large transition dipole of the emitting state characterize it as a  $\pi, \pi^*$  state. The difference in the absorption and emission transition dipoles could indicate a geometrical rearrangement in the excited state, e.g. the molecule could become more planar upon excitation.

When the polarity of the solvent increases, another highly dipolar excited state becomes the lowest state, which is also strongly emissive in non-hydroxylic solvents, although

Table 2

Results of INDO/s-CI calculations on DMA-DMPP;  $\Delta E$  denotes the transition energy,  $f$  the oscillator strength, and  $\mu$  is the permanent dipole moment of the respective excited state

State	$\Delta E$ ( $\text{cm}^{-1}$ )	$f$	$\mu$ ( $10^{-30}$ Cm)
Ground	—	—	20.6
1	31920	0.037	15.6
2	32780	0.276	2.9
3	34853	0.042	27.6
4	35826	0.049	75.3

its transition dipole moment for fluorescence is much smaller.

The ground state geometry of DMA-DMPP was calculated by the semiempirical AM1 method and is shown in Fig. 4. The molecule is non-planar due to steric hindrance and the torsional angle between donor and acceptor planes is  $77^\circ$ . Also both phenyl groups are not coplanar with the bis-pyrazolopyridine subsystem and are twisted by  $44^\circ$ .

The sequence of the excited states obtained from INDO/s calculations are summarized in Table 2. Orbital plots are shown in Fig. 4. The three lowest excited states have only a small permanent dipole moment, and the transition to the second state should be the most intense. The fourth excited state,  $S_4$ , has a much larger permanent dipole moment orientated along the bond connecting the donor and the acceptor subunits. Its dipole moment is in excellent agreement with the experimental result from solvatochromic experiment. This state may become the lowest excited state in polar solvents. The energy barrier separating the two emitting states in alcohols, a necessary prerequisite to observe dual fluorescence, may be caused by avoided crossing along the reaction coordinate, which corresponds to structural and solvent reorganization.

In aprotic polar solvents the experimental radiative lifetime of CT fluorescence (Table 1) is smaller than that in protic polar ones. Specific solvation effects might occur in hydroxylic solvents, but their influence upon CT-fluorescence is most likely small (see above and Fig. 2). This view might also be supported by the observation that its efficiency in pure alcoholic solvents is primarily determined by the length of the alkyl chain:  $\tau_f^0$  becomes longer with decreasing chain length of the alcohol and, in parallel, the charge-transfer fluorescence is strongly diminished. In aqueous solution only a high energy emission is observed. This enhanced non-radiative relaxation might indicate a change of the molecular geometry in the emitting CT state, and most probably donor and acceptor moieties become more perpendicularly orientated in highly polar, hydroxylic solvent. The emission probability is thus reduced due to the minimal orbital overlap. This is in some contrast to other intramolecular charge transfer systems with bulky electron acceptors [5,6], as a more coplanar conformation was proposed for the highly dipolar excited state.

#### 4. Conclusions

DMA-DMPP represents a molecular system composed of two large electron donor and acceptor subunits. This compound shows high fluorescence quantum yield in low polarity solvents ( $D < 10$ ), ascribed to emission from the non-dipolar, vertically excited  $\pi, \pi^*$ -state. As the solvent polarity increases, the energy of a highly dipolar charge transfer state is lowered and becomes, thus, emissive;  $Q_f$  decreases and  $\tau_f^0$  increases concomitantly. In protic, polar solvents dual fluorescence appears due to quenching of the long-wavelength band. A dipole moment of  $97 \times 10^{-30}$  Cm (29 D) can be obtained for the final charge transfer state, and this is in good agreement to the results of theoretical calculations: the fourth excited state ( $S_4$ ) lies  $\approx 50$  kJ mol $^{-1}$  (0.5 eV) above the  $S_1$ , and its calculated dipole moment is  $75.3 \times 10^{-30}$  Cm (22.6 D), in good agreement with the experimental value. The  $S_4$  becomes therefore the most probable lowest excited singlet state in polar solvents. It might be excited in a vertical absorption transition but relaxes most likely to an orthogonal donor-acceptor geometry, when the solvent polarity is high.

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#### References

- [1] K. Rotkiewicz, K.-H. Grellmann and Z.R. Grabowski, *Chem. Phys. Lett.*, **19** (1973) 315.
- [2] Z.R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D.J. Cowley and W. Baumann, *Nouv. J. Chim.*, **3/7** (1979) 443.
- [3] W. Rettig, in *Topics of Current Chemistry*, Vol. 169, Springer, Berlin, 1994, p. 254.
- [4] Z.R. Grabowski, K. Rotkiewicz and A. Siemiarczuk, *J. Lumin.*, **18/19** (1979) 420.
- [5] K.A. Zachariasse, Th. Van der Haar, U. Leinhos and W. Kühnle, *J. Int. Rec. Mats.*, **21** (1994) 501.
- [6] J. Herbich and A. Kapturkiewicz, *Chem. Phys.*, **158** (1991) 143; *Chem. Phys.*, **170** (1993) 221.
- [7] L. Hennig, J. Hofmann, M. Alva-Astudillo, G. Mann, *J. Prakt. Chem.*, **332** (1990) 351.
- [8] J. Jasny, *J. Luminesc.*, **17** (1978) 149.
- [9] G. Köhler, G. Kittel and N. Getoff, *J. Photochem.*, **18** (1982) 19; G. Köhler and K. Rotkiewicz, *Spectrochim. Acta*, **42A** (1986) 1127; K. Rotkiewicz and G. Köhler, *J. Luminesc.*, **37** (1987) 219.
- [10] G. Köhler, *J. Photochem.*, **35** (1986) 189; K. Rechthaler and G. Köhler, *Chem. Phys.*, **189** (1994) 99.
- [11] D.V. O'Connor and D. Phillips, *Time-correlated Single Photon Counting*, Academic Press, New York, 1984.
- [12] M.J.S. Dewar and W. Thie, *J. Am. Chem. Soc.*, **99** (1977) 4899.
- [13] J. Ridley and M. Zerner, *Theor. Chim. Acta*, **32** (1973) 111.
- [14] P. Suppan, *J. Photochem. Photobiol., A: Chem.*, **50** (1990) 293.
- [15] G. Köhler, P. Wolschann and K. Rotkiewicz, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **104** (1992) 197.
- [16] S.J. Strickler and R.A. Berg, *J. Chem. Phys.*, **37** (1962) 814.