Excited States Dipole Moments and Fluorescence Behaviour of Some Derivatives of Dimethylaminobenzonitrile

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Two sterically hindered derivatives of dimethylaminobenzonitrile (DMCA) have been synthesized and the dipole moment μ_A of their fluorescent excited state has been determined in differently polar solvents. Its value increases with solvent polarity up to a limiting value of $(50 \pm 2.5) \cdot 10^{-30}$ Cm. The results are discussed with reference to the twisted intramolecular charge transfer (TICT) state formation in the class of molecules related to DMCA.

1. Introduction

4-Cyano-N,N-dimethylaniline (= dimethylaminobenzonitrile = DMCA) and a considerable number of its derivates show two distinctly different fluorescence bands, with several there-of simultaneously observed in medium polar solvents. Since the first observation and explanation of this phenomenon by Lippert [1] a lot of work has been done putting forward some alternative models for its explanation. All the history is well presented in the latest reviews [2–5]; hence only the two most important models by Lippert [1] and Grabowski [2, 6] are briefly introduced here. In 1962 Lippert thought that a solvent polarity induced version of a non-polar B-state and a highly polar A-state accounts for the two distinct fluorescence bands of DMCA: the A-fluorescence in polar solvents, the B-fluorescence in non-polar solvents, and both emissions in medium polar solvents. Because of some interferring obervations, in 1976 Rotkiewicz, Grellmann and Grabowski presented the model later on called the "twisted intramolecular charge transfer (TICT)" state model [6], in which the dimethylamino and the benzonitrile subunit's planes are assumed to be parallel in a non-polar B-state but orthogonal in a polar A-state.

Many model compounds have been synthesized that fix the two subunits, or at least hinder the rotation around their bond. From the work of Grabowski's and Rettig's groups as well as from dipole moment measurements [7–9] on excited states of DMCA and related compounds it is obvious that a combination of both models describes best the observed effects. Considering the dipole moment measurements, the role of polarizability effects seems not yet to be clear [7–9], since from more detailed investigations on the related compound 4-(9-anthryl)-N,N-dimethylaniline and some of its derivates comes evidence, that polarizability effects can be neglected as compared to dipole moments, with this group of compounds. This is best seen with the compound 4-(9-anthryl)-2,3,5,6,N,N-dimethylaniline [10–12], in which case an anthracene-like fluorescence is superimposed on a CT-fluorescence, the intensity ratio of both being strongly solvent dependent. This solvent dependence can be interpreted by solvent reaction field induced moments, that is polarizability, or more simply by two or more differently polar emitting states.

For the sake of simplicity, in this communication a fluorescing polar CT state is called an A-state, as less polar second emitting state a B-state, regardless what the nature of the state is.

Now return to the group of dimethylaminobenzonitrile derivates. With the strongly sterically hindered molecule 4-cyano-2,6,N,N-tetramethylaniline (TetraMCA), for example, the polarizability could be determined in the A-state, which was assumed to solely contribute to the observed fluorescence. But if there would be some amount of B-fluorescence hidden under the total fluorescence, this could well pretend polarizability effects, even if there are none at all. The situation might even be more complicated if one takes into account that methyl groups might be abstracted from the dimethylamino group or even from the phenyl ring by photochemistry, thus most probably

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leaving a related compound that only emits B-fluorescence. Hence, the two compounds 4-cyano-2,N,N-trimethylaniline (TriMCA) and 4-cyano-2,3,5,6,N,N-hexamethylaniline (HMCA) have been synthesized and examined in some detail, in a more elaborate apparatus than used in [8] and described in [13]. No big differences should be expected from the results from measurements of excited state dipole moments and polarizabilities of these two compounds, when compared to TetraMCA, if a simple one state (TICT state) model is applicable, but perhaps some differences, if two (or even more) states contribute to an overall measured average excited state dipole moment.

2. Experimental

2.1 Experimental Method

Electric dipole moments have been determined by integral electro optical emission measurements (IEOEM). This method is described in detail in [13, 14] on the basis of the theory given in [15] for spectrally resolved electro optical emission measurements (EOEM). It was applied and checked thoroughly in some publications, e.g. in [16]. The main effect is due to the orientational anisotropy which is induced in a solution of polar species by a modulated external electric field and which then is probed by measuring the emitted fluorescence light through a linear polarizer.

For the molecules discussed in this communication, explicit polarizability and transition polarizability effects can be neglected compared to the dipole moment terms. Whether implicit polarizability effects induced in solution by the reaction fields have to be taken into account finally will be shown in the discussion section.

With these suppositions follows that the fluorescence photon current $p^E(\Phi)$ observed from solutions in an external electric field E is dependent on the square of E and on the angle Φ between the direction of E and the polarization direction given by an analyzing polarizer,

$$p^E(\Phi) = p^{E=0}\,[1 + X_M(\Phi)\,E^2]. \tag{1}$$

If only one species M fluoresces, $X_M(\Phi)$ is related through a suitable model [17] to the fluorescent excited state's dipole moment. If the A and B-states of the class of molecules considered in this paper both fluoresce with intensities I_A and I_B, a measured value $X_M(\Phi)$ is the sum of amounts due to these two pure states [14]

$$X_M(\Phi) = [X_A(\Phi) + q\,X_B(\Phi)]/(1+q), \tag{2}$$

where

$$q = I_B/I_A, \tag{3}$$

and where $X_A(\Phi)$ and $X_B(\Phi)$ are related to the A and B state's dipole moment.

As the detailed theory [15, 17] shows, one linear combination of the $X(\Phi)$ is most important for the evaluation of dipole moment values:

$$\chi_{3i} = 6\,X_i(\Phi=0^\circ) - 18\,X_i(\Phi=90^\circ) \tag{4}$$

where i = A, B or M.

Combination of (4) and (2) yields

$$X_{3A} = X_{3M} + q\,(X_{3M} - X_{3B}). \tag{5}$$

Thus, if $q=0$ or if no B-fluorescence is observed, the pure A state value X_{3A} is equal to the measured value X_{3M}.

For the compounds discussed here follows from the theory [15, 17] and with the symmetry of the fluorescing states

$$X_{3A} = 2\,f_e^2\,\mu_A^2/(kT)^2, \tag{6}$$

$$X_{3B} = 2\,f_e^2\,\mu_B^2/(kT)^2 \tag{7}$$

with

$$\mu_A = (1 - f\,\alpha_A^0)^{-1}\,\mu_A^0, \tag{8}$$

$$\mu_B = (1 - f\,\alpha_B^0)^{-1}\,\mu_B^0. \tag{9}$$

μ^0 and α^0 are the permanent dipole moment and the polarizability of the free molecule in the A and B-state, respectively. f_e and f are defined according to Onsager's model [18] as introduced to the electro optical methods by Liptay [19, 20]:

$$f_e = 3\,\varepsilon/(2\,\varepsilon + 1), \tag{10}$$

$$f = (2\,\pi\,\varepsilon_0\,a^3)^{-1}\,(\varepsilon - 1)/(2\,\varepsilon + 1), \tag{11}$$

where "a" is Onsager's parameter in spherical approximation, approximately equal to the radius of a sphere circumscribing the solute molecule. ε is the relative permittivity of the solvent and ε_0 the permittivity of the vacuum.

According to the formalism sketched above, the experiment proceeds as follows:

$X_M(\Phi)$ is measured for $\Phi=0^\circ$ and $\Phi=90^\circ$, according to (1), observing the field dependence of the photon current. This is done in an experimental set-up described in detail in [13].

Then X_{3M} is calculated according to (4).

The further procedure depends on whether only A-state fluorescence is observed of B-state fluorescence can be detected or has to be assumed but perhaps is hidden under the dominant A-state fluorescence. The respective implications will be discussed in the discussion section.

2.2 Compounds

2.2.1 4-cyano-2,N,N-trimethylaniline

This compound was first synthesized by Rotkiewicz et al. [21] in a five step process with an overall yield of 0.18%. The two step synthesis developed during this work started from commercially available 4-bromo-2-methylaniline (from ALDRICH), which was methylated [10] to give 4-bromo-2,N,N-trimethylaniline with 41% yield, after purification. The subsequent halogen cyanide exchange was done following the method reported previously [10] and gave TriMCA with 84% yield. Hence this two step synthesis with an overall yield of 34% offers a very convenient access to this compound. The spectroscopic characterization showed to be identical with that given in [21] for TriMCA.

2.2.2 4-cyano-2,3,5,6-hexamethylaniline

The preparation of this new model compound was performed analoguous to that sketched above. The reaction of 3.89 g (15 mmole) of 4-bromo-2,3,5,6,N,N-hexamethylaniline [10] with 2.69 g (35 mmole) Cu(I)-cyanide in 30 ml dimethylformamide (abs) and 2 ml pyridine (abs) yielded HMCA in excellent 85% yield, after purification.

Purification:
1. dry column chromatography
   stat. phase: silica, activity III
   mobile phase: toluene (abs)
2. sublimation: 0.2 Torr, bath temperature 60 °C

Purity test:
stat. phase: silica, alumina
mob. phase: toluene (abs)

mp: 66–67 °C

$C_{13}H_{18}N_2$

calcd: C: 77.18, H: 8.97, N: 13.85,
found: C: 77.29, H: 8.97, N: 13.85.

Molar mass: 202.3 g mole^{-1}.

EI-mass spectrum:
$203(M+1^+,11)$, $202(M^+,78)$, $201(M-1^+,44)$, $187(M^+-CH_3,100)$, $171(M-1^+-2CH_3,39)$, $158(M^+-44,8)$, $156(M-1^+-3CH_3,6)$, $143(M^+-44-CH_3,5)$, $141(M-1^+-4CH_3,2)$, $128(M^+-44-2CH_3,4)$, 116(10), 115(9), $91(C_7H_7^+,8)$, $77(C_6H_5^+,7)$, $65(C_5H_5^+,4)$, $44(CH_3-CH=NH_2^+,19)$, $39(C_3H_3^+,7)$.

IR (KBr): $\tilde{\nu}/\mathrm{cm}^{-1}$:
2990, 2965, 2920, 2800 (m, CH_3-aliphat.), 2240 (s, CN), 1565, 1470, 1445, 1405 (m, C=C aromat.), 1352 (m, CN-aromat. tert. amine), 1280, 1230, 1080 (ss), 1015, 925.

^{1}H-NMR ($CDCl_3$): δ/ppm:
2.17 (s, 6H, 3,5-CH_3), 2.42 (s, 6H, 2,6-CH_3), 2.81 (s, 6H, $-N(CH_3)_2$).

3. Experimental Results and Discussion

3.1 Electro Optical Emission Measurements

Table 1 shows the values for the experimental quantity $X_M(\Phi)$, determined for TriMCA and HMCA in various solvents. The relative standard error of the mean of 4 to 6 independent measurements is 8 to 10%. From these $X_M(\Phi)$, the values of $f_e^{-2} \cdot X_{3M}$ have been calculated according to (4). They are listed in Table 2 together with the dielectric constant ε of the used solvents.

Also shown in Table 2 is the excited A-state dipole moment μ_A, which was calculated with the assumption that only one state – the A-state – fluoresces. The standard error of the dipole moment values is about

Table 1. $X_M(\Phi)$ values, determined at 298 K with TriMCA and HMCA. All values are given in units of 10^{-20} V^{-2} m^2. The reproducibility of the X_M values is about 10%.

Solvent	TriMCA		HMCA	
	X_M ($\Phi=0°$)	X_M ($\Phi=90°$)	X_M ($\Phi=0°$)	X_M ($\Phi=90°$)
Heptane	2210	− 710	2000	− 760
Cyclohexane	2240	− 680	1980	− 810
Decalin	2120	− 710	2080	− 890
Amylether	2920	−1350	2220	−1350
Butylether	3330	−1370	2600	−1470
n-Propylether	3720	−1560	2650	−1600
iso-Propylether	3920	−1810	3100	−2050
Dioxane	3110	−1460	2610	−1410
Fluorobenzene	3930	−1810	2830	−2210
Benzotrifluoride	4300	−1900	3520	−2360

Table 2. Values for $f_e^{-2} \cdot X_{3M}$ and μ_A for TriMCA and HMCA, calculated assuming only one emitting excited state A.

Solvent	ε	TriMCA		HMCA	
		$f_e^{-2} \cdot X_{3M}/$ $10^{-20}\,\mathrm{V}^{-2}\,\mathrm{m}^2$	$\mu_A/$ $10^{-30}\,\mathrm{C\,m}$	$f_e^{-2} \cdot X_{3M}/$ $10^{-20}\,\mathrm{V}^{-2}\,\mathrm{m}^2$	$\mu_A/$ $10^{-30}\,\mathrm{C\,m}$
Heptane	1.914	18400	39.4	18100	39.1
Cyclohexane	2.015	17800	38.8	18300	39.4
Decalin	2.160	17200	38.1	19200	40.3
Amylether	2.770	25900	46.8	23300	44.4
Butylether	3.060	26800	47.6	25200	46.2
n-Propylether	3.390	29500	50.0	26200	47.1
iso-Propylether	3.880	31800	51.8	31400	51.6
Dioxane	2.209*	30100	50.5	27500	48.3
Fluorobenzene	5.420	29800	50.2	30100	50.5
Benzotrifluoride	9.035	29700	50.1	31500	51.6

* Note that the microscopically effective dielectric constant of dioxane is around 5 to 6, well known from solvent shift measurements [17].

2 to $2.5 \cdot 10^{-30}$ C m relative to each other – about 5% absolute calibration error has to be added, if absolute values are to be compared with results from other independent methods.

The most striking observation is that the dipole moment μ_A of both compounds shows a solvent dependence that seems to level off at a dielectric constant of about $\varepsilon = 3.5$. Three effects are currently discussed that may account for this behaviour:

i) There is some amount of a fluorescence from a less polar B-state hidden under the strong A-fluorescence, in non-polar and medium polar solvents, the dipole moment of which may be assumed to be very roughly the same for the twisted and the planar compounds. Then, the ratio q in (3) would no more be zero and thus X_{3A} were to be calculated according to (5). Although X_{3B} could be taken in good approximation from the results from IEOEM on typical B-band emitting species like DMCA in cyclohexane to be roughly $6300 \cdot 10^{-30}\,\mathrm{V}^{-2}\,\mathrm{m}^2$ (equivalent to a B-state dipole moment $\mu_B = 19.3 \cdot 10^{-30}$ C m) a quantitative evaluation is not possible since q cannot be determined because both the A and B-fluorescence bands are too less structured to yield unambiguous results from a deconvolution procedure, if not an emission from a locally excited state within the bonzonitrile moiety, such a B-fluorescence, in principle could be emitted from a photochemical by-product like a related molecule where one or more methyl groups had been abstracted. This idea is supported by the observation that photochemical degradation preferentially showed up in non-polar solvents, where the measuring signals (means $X_M(\Phi)$ values) decreased after longer measuring times. On the other side, all efforts have been made to avoid photochemistry and to measure the signals immediately after illumination of the solutions. Since such a fluorescence is emitted at the blue edge of the A-fluorescence, it might be revealed by spectrally resolved electro optical emission measurements.

A dimer emission as described in [22] for TriMCA at temperatures below 183 °C in non-polar solvents, if present at all at the measuring conditions at 298 °C, would behave similar to a B-state emission, in these electro optical measurements.

ii) The observed solvent dependence is due to reaction field (solvent polarity) induced moments, that is due to polarizabilities. If this holds true, a plot of $1/\mu_A$ against $(\varepsilon - 1)/(2\varepsilon + 1)$ should give a straight line, according to (8). Figure 1 shows the respective plot. The plot does not show at all a straight line with both compounds. Instead, the plots level off quite distinctly at medium polar solvents. Thus the solvent dependence of the measured values μ_A cannot be ascribed to polarizability effects. Earlier results for TetraMCA [8] had been explained by (relatively small) polarizability effects. With the present investigations, such minor effects could remain undetected due to a strongly solvent dependent amount of a perturbing emission from a less polar excited species, as discussed above. In good approximation, therefore, $\mu_A = \mu_A^\circ \approx 50 \cdot 10^{-30}$ C m, according to (8).

iii) There is A-state emission, only, and the measured value for X_M and thus for the observed dipole moment μ_A is considered as an average value, averaged over all rotational conformations around the substituted benzonitrile-dimethylamino group bond. Within the framework of the TICT model [2, 6], the most polar conformation should be the orthogonal position of these groups. If the average torsion angle around this bond is decreased by the interaction of the solute with polar solvents (narrowing of the potential

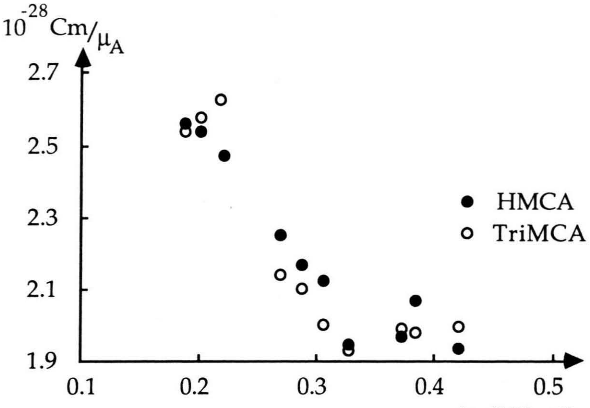

Fig. 1. $1/\mu_A$ plotted against the solvent function $(\varepsilon-1)/(2\varepsilon+1)$.

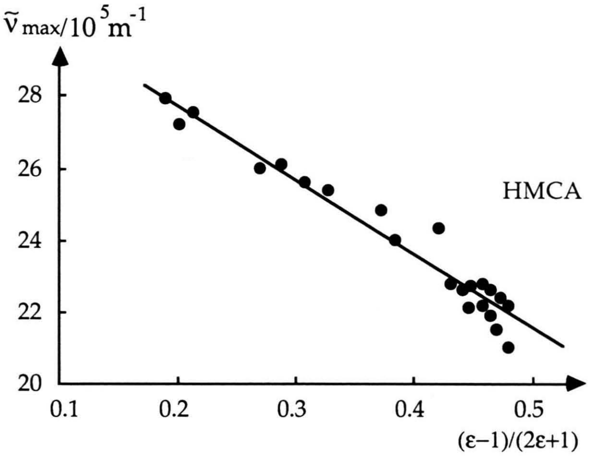

Fig. 2. Wavenumber $\tilde{\nu}_{max}$ of the fluorescence maximum of HMCA in different solvents plotted against $(\varepsilon-1)/(2\varepsilon+1)$.

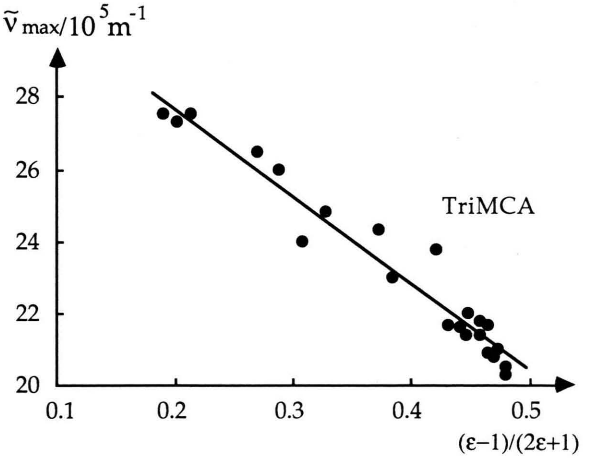

Fig. 3. Wavenumber $\tilde{\nu}_{max}$ of the fluorescence maximum of TriMCA in different solvents plotted against $(\varepsilon-1)/(2\varepsilon+1)$.

surface by solvent-solute interaction), a limiting value for μ_A should be expected, just as is found. Note that by the formalism such reaction field induced changes of a dipole moment may be treated as polarizability effects, but in this case then are not due to pure electronic polarizabilities of a rigid molecule!

Finally, the result from IEOEM is that at least in medium polar and polar solvents both compounds emit from a polar state, the dipole moment μ_A° of which is $(50 \pm 2.5) \cdot 10^{-30}$ C m. This value can be compared to the dipole moment of the TICT state of DMCA, which was reported to be $55 \cdot 10^{-30}$ C m, in dioxane [7], and to the primary results reported in [9] from a quite different method to determine excited state dipole moments. The good agreement then supports the idea of a TICT state forming process after excitation in those related molecules that are not sterically hindered, like DMCA.

3.2 Solvent Shift Measurements on the A-Fluorescence

From electro optical investigations it was shown in the previous section, that polarizability effects are at least small enough to be neglected, that is all terms like $(1 - f\,\alpha_A^\circ)$ are approximately equal to one, in all solvents. Then, the wavenumber $\tilde{\nu}_{max}$ of the maximum of the (predominantly A-type) fluorescence should be a linear function of the solvent parameter $(\varepsilon-1)/(2\varepsilon+1)$, if solvents with very high or very low refractive indices are disregarded [19, 23]:

$$\tilde{\nu}_{max} = \text{const} - (2\,h\,c\,\pi\,\varepsilon_0)^{-1}\,[\mu_A^\circ(\mu_A^\circ - \mu_g^\circ)/a^3] \cdot (\varepsilon-1)/(2\varepsilon+1), \tag{12}$$

where μ_g° is the Frank-Condon ground state dipole moment.

It might be argued that in case i) the determination of $\tilde{\nu}_{max}$ may be erroneous in non-planar solvents due to the perturbance by a B-fluorescence, whatever its nature. With the aforementioned dipole moment of a B-state, with that of the A-state and with the value $f_e^{-2} \cdot X_{3M}$ from Table 2 measured in cyclohexane, q can be calculated from (5) and using (6) and (7) to be

Table 3. Results from the solvent shift of the (A)-fluorescence of TriMCA and HMCA.

	TriMCA	HMCA
$\mu_A^\circ(\mu_A^\circ - \mu_g^\circ)\,a^{-3}/10^{-30}$ C^2 m^{-1}	26.9 ± 0.5	22.9 ± 0.6
$a^3/10^{-30}$ m^3	60 ± 4	86 ± 6

about 0.9, in cyclohexane. The same procedure yields $q < 0.2$, from amylether to more polar solvents. Hence, only the fluorescence maximum in the most non-polar solvents should perhaps be erroneous in that sense that its maximum could have been taken at too short wavelengths. The same holds in cases ii) or iii) from similar arguments. Hence, from a plot of $\tilde{\nu}_{\max}$ against $(\varepsilon - 1)/(2\,\varepsilon + 1)$ the term $\mu_A^\circ(\mu_A^\circ - \mu_g^\circ)/a^3$ can be determined from the slope of a straight regression line according to (12). Figures 2 and 3 show the respective plots. Table 3 compiles the results from the regression analysis, together with the cube of the cavity parameter a, which results if $\mu_A^\circ = 50 \cdot 10^{-30}\,\mathrm{C\,m}$ is taken from the results in the previous section and the Franck-Condon ground state dipole moment μ_g° equal to that of the equilibrium ground state as determined in [24] to be $19.3 \cdot 10^{-30}\,\mathrm{C\,m}$.

The resultant values for a^3 are in very good agreement with those estimated from bond lengths and Van-der-Waals radii to be $60 \cdot 10^{-30}\,\mathrm{m}^3$ for TriMCA and $72 \cdot 10^{-30}\,\mathrm{m}^3$ for HMCA.

3.3 Final Remarks

It has been shown in the foregoing chapters that the experimentally determined solvent polarity dependence of the excited state dipole moment of the two investigated compounds can be understood by a solvent polarity dependent average torsional angle around the phenyl to dimethylamino group bond. If this angle gets smaller with increasing solvent polarity the experimental value for μ_A in polar solvents would resemble best the dipole moment of a TICT state. The respective value of about $50 \cdot 10^{-30}\,\mathrm{C\,m}$, if used to evaluate the results from solvent shift measurements, the yielded quite reasonable values for a^3 for both compounds. This consistent result in turn strongly supports the interpretation of the observed fluorescence as essentially due to the emission from a TICT state in the case of the presented molecules where the dimethylamino group is forced to a position more or less orthogonal to the phenyl plane.

Acknowledgements

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[1] E. Lippert, W. Lüder, and H. Boss, in Adv. Mol. Spectrosc., A. Mangini, Ed., Pergamon Press, Oxford 1962, p. 443.
[2] Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley, and W. Baumann, Nouv. J. Chim. **3,** 443 (1979).
[3] W. Rettig, Angew. Chem. **98,** 969 (1986); Angew. Chem. Int. Ed. Engl. **25,** 971 (1986).
[4] E. Lippert, W. Rettig, V. Bonacic-Koutecky, F. Heisel, and J. A. Miehe, Adv. Chem. Phys. **68,** 1 (1987).
[5] W. Rettig, in: Modern Models of Bonding and Delocalization, J. F. Liebman and A. Greenberg, Eds. VCH Publishers, New York 1988, Chapter V.
[6] K. Rotkiewicz, K.-H. Grellmann, and Z. R. Grabowski, Chem. Phys. Lett. **19,** 315 (1973).
[7] W. Baumann, Z. Naturforsch. **36a,** 868 (1984).
[8] H. Bischof, W. Baumann, N. Detzer, and K. Rotkiewicz, Chem. Phys. Lett. **116,** 180 (1985).
[9] R. J. Visser, P. C. M. Weisenborn, C. A. G. O. Varma, M. P. de Haas, and J. M. Warman, Chem. Phys. Lett. **104,** 38 (1984).
[10] N. Detzer, W. Baumann, B. Schwager, J.-C. Fröhling, and C. Brittinger, Z. Naturforsch. **42a,** 395 (1987).
[11] W. Baumann. B. Schwager, N. Detzer, T. Okada, and N. Mataga, J. Phys. Chem. **92,** 3742 (1988).
[12] T. Okada, N. Mataga, W. Baumann, and A. Siemiarczuk, J. Phys. Chem. **91,** 4490 (1987).
[13] W. Baumann and H. Bischof, J. Mol. Structure **84,** 181 (1982).
[14] W. Baumann and H. Bischof, J. Mol. Structure **129,** 125 (1985).
[15] W. Baumann and H. Deckers, Ber. Bunsenges. Phys. Chem. **81,** 786 (1977).
[16] H. Bischof and W. Baumann, Z. Naturforsch. **40a,** 874 (1985).
[17] W. Baumann, in: Physical Methods of Chemistry, Vol. III B, B. W. Rossiter and J. F. Hamilton, Eds., John Wiley & Sons, New York 1989, p. 45.
[18] L. Onsager, J. Amer. Chem. Soc. **58,** 1486 (1936).
[19] W. Liptay, in: Excited States, Vol. 1, E. C. Lim, Ed., Academic Press, New York 1974.
[20] W. Liptay, Z. Naturforsch. **20a,** 272 (1965).
[21] K. Rotkiewicz, , Z. R. Grabowski, A. Krówczynski, and W. Kühnle, J. Luminesc. **12/13,** 877 (1976).
[22] K. Rotkiewicz, H. Leismann and W. Rettig, J. Photochem. Photobiol. A, **49,** 347 (1989).
[23] W. Liptay, Z. Naturforsch. **20a,** 1441 (1965).
[24] J.-C. Fröhling, K. Rotkiewicz, and W. Baumann, unpublished results.