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Photoinduced intramolecular charge transfer and internal conversion in molecules with a small energy gap between S_1 and S_2. Dynamics and structure

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Abstract

A discussion is presented of the fast excited state intramolecular charge transfer (ICT) and dual fluorescence observed with several 4-aminobenzonitriles. The occurrence or absence of this ICT reaction is shown to be determined by the magnitude of the energy gap $\Delta E(S_1,S_2)$ between the two lowest excited states. The strong decrease of the ICT efficiency in the series P8C to P3C of 4-aminobenzonitriles in which the amino nitrogen atom is part of a three- to eight-membered heterocyclic ring, is attributed to the increase with decreasing ring size of the barrier for the configurational change of the amino nitrogen from pyramidal to planar, which is considered to be an important reaction coordinate in the ICT process. Dual fluorescence does not occur with P3C nor with P4C in diethyl ether. Application of a pressure of 6000 bar leads to a threefold increase of the CT/LE fluorescence quantum yield ratio for the 4-(dialkylamino)benzonitrile DMABN (methyl) in diethyl ether, whereas this ratio only slightly increases for DDABN (*n*-decyl) in *n*-hexane. This difference is attributed to the increase of the solvent dielectric constant with pressure, which effect is much larger for diethyl ether than for *n*-hexane. These results mean that a large amplitude motion does not occur during the ICT reaction of DMABN and DDABN, in accordance with the model of planar intramolecular charge transfer for dual fluorescence. Dual fluorescence is observed with the rigidized aminobenzonitrile NMC7, showing that a full perpendicular twist of the amino group is not essential for the CT state. 1-(Dimethylamino)naphthalene (1DMAN) undergoes a fast thermally activated internal conversion (IC), for which the activation energy increases with solvent polarity. This IC reaction depends on the magnitude of the $\Delta E(S_1, S_2)$ energy gap and is similar in this respect to the ICT reaction of DMABN. © 1997 Elsevier Science S.A.

Keywords: Intramolecular charge transfer; Photostationary fluorescence; Time-resolved fluorescence; Dual fluorescence; Pressure dependence; Internal conversion; Aminobenzonitriles; Aminonaphthalenes

1. Introduction

With 4-(dimethylamino)benzonitrile (DMABN) [1–8] and a series of 4-(dialkylamino)benzonitriles, having alkyl groups ranging from ethyl (DEABN) to *n*-decyl (DDABN) [8], dual fluorescence is observed in a variety of solvents, even in nonpolar alkanes such as cyclohexane and *n*-hexane [8]. Dual emission in alkane solvents has also been found with alkyl esters of 4-(dialkylamino)benzoic acid [2,3,9–11]. These observations show that a polar solvent is not necessary for the appearance of ICT in these systems.

An unusually large number of different mechanisms for the photophysics of DMABN have appeared in the literature since the discovery of its dual fluorescence around the year 1960 [12]. The original model of Lippert [12], treating the phenomenon as a solvent polarity induced reversal of the two lowest excited states (^1L_b and ^1L_a) occurring after excitation, was superseded in the years between 1973 and 1977 by the 'twisted intramolecular charge transfer' (TICT) model [13,14]. In this TICT model [1–4] it is proposed that in the CT state of DMABN the dimethylamino group is twisted in a plane perpendicular to that of the phenyl ring, leading to a practically complete electronic decoupling: the principle of minimum overlap [3].

A variety of alternative models were proposed to explain the dual emission of DMABN [15]. There was generally a valid experimental reason for the introduction of the alternative reaction mechanisms. The proton transfer model advocated by Kosower [15]b, for example, was based on the interesting observation that the CT/LE fluorescence intensity ratio for DMABN is considerably larger in deuterated ethanol C_2H_5OD than in normal ethanol. Similarly, the model based

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on specific solute–solvent interactions proposed by Varma [15]c originated from experiments showing the strong influence of small amounts of polar solvents added to non-polar alkane solutions of DMABN, its effect outweighing by far the bulk properties of the medium such as the polarity.

Whereas Lippert's model was concerned with the nature and molecular properties of excited state levels, the TICT hypothesis is defined in terms of the molecular structure of the final equilibrated CT state. Other mechanisms, such as our 'planar intramolecular charge transfer' (PICT) model [6,7] in which the CT state is considered to be planar, likewise make a statement on the molecular structure of the final CT state, and do not directly identify the detailed pathway nor the reaction dynamics of the ICT reaction from the ground state S_0 via the locally excited state LE to the equilibrated CT state. As the number of experimental methods enabling a direct determination of excited state configurations, such as time-resolved infrared [16] and resonance Raman spectroscopy, is still rather limited, it is not too surprising that the question of the molecular structure of the CT state of DMABN has not yet been settled.

In our studies of the photophysics of DMABN and related molecules a rotation around the *N*-phenyl bond was not found to be needed to explain the experimental observations. Instead, a change in the configuration of the amino nitrogen from pyramidal towards planar was invoked as an important reaction coordinate [6,7,17–19]. This was based on our finding that in a series of 4-(amino)benzonitriles in which the amino nitrogen is part of a heterocyclic ring the ICT efficiency strongly decreases when the ring size becomes smaller. It was hence concluded that the decrease in ring size is connected with an important ICT reaction coordinate: the change in molecular configuration of the amino nitrogen from pyramidal (S_0) towards planar (CT). In support of our conclusion that a large amplitude motion does not take place in DMABN on the reaction pathway from LE to CT, it should be noted that an influence of solvent viscosity on the ICT reaction of DMABN has not been observed [20].

Evidence has been presented that for dual fluorescence and ICT to appear in molecules such as DMABN two requirements should be fulfilled [6–8,18]: (a) a relatively small energy gap $\Delta E(S_1, S_2)$ between the two lowest excited singlet states and (b) an energy barrier for the change in configuration of the amino group from pyramidal towards planar that is small enough to allow the ICT reaction to occur within the fluorescence lifetime of the locally excited (LE) state of the aminobenzonitrile. It has been suggested that vibronic coupling between S_1 and S_2 is an essential element in the ICT reaction [7,17–19]. Such a coupling clearly depends on the magnitude of $\Delta E(S_1, S_2)$. Further, the change in the molecular configuration of the amino group will be an important reaction coordinate in the ICT process of the dual fluorescent 4-(amino)benzonitriles. With electron donor/acceptor-substituted naphthalenes ICT has been observed when the energy gap $\Delta E(S_1, S_2)$ is sufficiently small for vibronic coupling to take place, such as with 1-dimethylamino-4-cyanonaphthalene [7,18]. In the first publication on the dual fluorescence of DMABN in 1961 [12] Lippert already pointed out that the presence of a small energy gap $\Delta E(S_1, S_2)$ is directly correlated with the appearance of dual fluorescence in 4-aminobenzonitriles. For instance, in the group of the 1,4-donor(D)/acceptor(A) benzenes dual fluorescence is not observed for 4-methoxybenzonitrile with $D = OCH_3$ and $A = CN$ or 4-nitro-*N,N*-dimethylaniline with $D = N(CH_3)_2$ and $A = NO_2$, which molecules have a considerably larger energy gap $\Delta E(S_1, S_2)$ than DMABN.

On the basis of the absence of a linear correlation between the maximum of the CT emission band $h\nu^{max}(CT)$ and the redox potentials of the electron donor (D) and acceptor (A) subunits in DMABN and other dual fluorescent 4-aminobenzonitriles, it has been concluded that a strong electronic coupling exists between the amino and benzonitrile subunits [6,7,18], in clear contradiction of the principle of minimum overlap of the TICT model [3,21]. DMABN can clearly not be treated as a D (NR_2) and an A (CN) group separated by a phenyl ring playing the role of an inert molecular spacer. The photophysics of DMABN has been shown to be clearly different from that of inter- and intramolecular exciplexes, 9,9'-bianthryl, 6-cyanobenzoquinuclidine (CBQ) and intramolecular donor/acceptor systems such as 9-(*N,N*-dimethylanilino)anthracene [6,7].

In the present paper it is proposed that the onset of vibronic coupling caused by the proximity of the two lowest singlet excited states leads to specific photophysical processes, such as the photophysics governing the ICT and dual fluorescence in DMABN and other 4-aminobenzonitriles. A second example to be treated here of the possible influence of vibronic coupling in a system with a small energy gap between the S_1 and S_2 states, is the fast thermally activated internal conversion observed with 1-(dimethylamino)naphthalene (1DMAN) in nonpolar solvents such as *n*-pentane. With 4-(methylamino)3,5-dimethylbenzonitrile (MHD) similar observations were made [22].

2. Experimental section

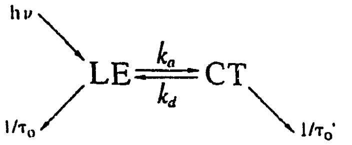
The fluorescence spectra were measured by using a quantum-corrected Shimadzu 5000PC spectrophotometer. Fluorescence quantum yields were determined using quinine sulfate in 1.0 N H_2SO_4 as a standard ($\Phi = 0.546$ at 25 °C) [23]. The picosecond time-correlated single-photon counting (SPC) data were obtained with a system described before [5,8] or with a picosecond laser system consisting of a mode-locked titanium–sapphire laser (Coherent, MIRA 900-F) pumped by an argon ion laser (Coherent, Innova 415). The analysis of the fluorescence decays was carried out by using the method of modulating functions [24]. The pressure equipment was built following the design provided by Schwarzer of this Institute [25]. The synthesis of the compounds discussed here has been described previously [5,8] or will be reported separately. For all compounds HPLC was used as the last purification method and the solvents were purified by chromatography just prior to use. The solutions were deoxygenated by nitrogen bubbling or by employing the freeze–pump–thaw method.

3. Reversible ICT reaction with DMABN

3.1. ICT stabilisation enthalpy $-\Delta H$

From the double exponential fluorescence response functions of the LE and CT states of DMABN in solvents such as toluene [5] and diethyl ether [7,18] it has been concluded that the ICT reaction of DMABN in these solvents is reversible and can be described by Scheme 1. This scheme is composed of the forward (k_a) and backward (k_d) reaction rate constants as well as the (reciprocal) lifetimes of the LE($1/\tau_0$) and the CT ($1/\tau_0'$) state.

By measuring the decay times τ_1 and τ_2 of the double exponential fluorescence decay function $i(\text{LE}) = A_{12}\exp(-t/\tau_2) + A_{11}\exp(-t/\tau_1)$ and also their amplitude ratio $A = A_{12}/A_{11}$, the rate constants k_a and k_d can be determined [5,8]. From such measurements carried out with DMABN in toluene or diethyl ether [5–8] as a function of temperature, the activation energies E_a and E_d of the ICT rate constants in Scheme 1 have been determined. It was found from these data that the ICT stabilisation enthalpy $-\Delta H(=E_d - E_a)$ is relatively small: 6 kJ mol^{-1} in toluene and 15 kJ mol^{-1} in diethyl ether. It should be noted, however, that these values for ΔH have been determined with the assumption that the ICT stabilisation enthalpy does not depend on temperature. The validity of this assumption is questionable [26] in view of the temperature dependence of the dielectric constant ϵ_r and the refractive index n_D of the solvents toluene and diethyl ether [27]. The ΔH values reported here have, therefore, an approximate character.



Scheme 1.

3.2. Red shift of the CT emission: potential energy diagrams

The CT emission in the fluorescence spectrum of DMABN and other 4-(dialkylamino)benzonitriles is strongly red shifted with respect to the LE band, see Fig. 1(a). This is the case in cyclohexane [8], toluene [5,7] and acetonitrile [6], irrespective of solvent polarity. From the energy $h\nu^{max}$(CT) of the CT emission maximum and the energy difference ΔE(LE) between the LE and the ground state (Fig. 1(a)), the energy δE_{rep}(CT) of the Franck–Condon (FC) ground state reached during the CT fluorescence can be obtained, by using Eq. (1) [6].

$$\delta E_{rep}(\text{CT}) = \Delta E(\text{LE}) - (-\Delta H) - h\nu^{max}(\text{CT}) \qquad (1)$$

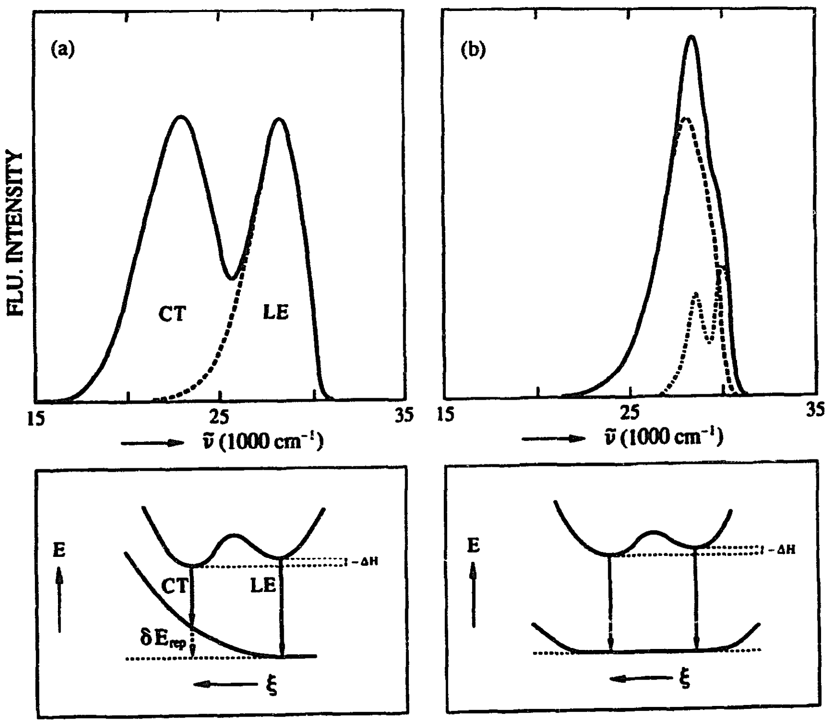


Fig. 1. Stylized fluorescence spectra (upper part) drawn according to (a) the shape of the fluorescence spectrum of (a) 4-(dimethylamino)benzonitrile (DMABN) in diethyl ether at −50 °C and (b) the LE component of 4-(diethylamino)benzonitrile (DEABN) in toluene at −92 °C [26]. Both spectra have been subtracted with the LE spectrum of 4-(methylamino)benzonitrile (MABN) obtained under similar conditions. In the lower part of the figure, potential energy diagrams are depicted for situations with relatively small values of the ICT stabilisation enthalpy $-\Delta H$, for (a) a considerable and (b) a negligible magnitude of the CT ground state repulsion energy ΔE_{rep}.

It then follows that the factor $\delta E_{\mathrm{rep}}(\mathrm{CT}) - (-\Delta H)$, which determines the red shift of the CT emission (Eq. (1)), is strongly dominated by $\delta E_{\mathrm{rep}}(\mathrm{CT})$. With DMABN in toluene, as an example, $\delta E_{\mathrm{rep}}(\mathrm{CT}) = 79$ kJ mol^{-1} to be compared with $\Delta H = -6$ kJ mol^{-1} [5]. It is clear, therefore, that the reason that the CT emission of DMABN and related molecules can easily be identified in the fluorescence spectrum is predominantly caused by the large value of the repulsion energy $\delta E_{\mathrm{rep}}(\mathrm{CT})$. In molecules for which $\delta E_{\mathrm{rep}}(\mathrm{CT})$ is small, see Fig. 1(b), it would be difficult to establish from an analysis of the fluorescence spectrum whether such a compound is dual fluorescent or not.

The magnitude of the ground state repulsion energy $\delta E_{\mathrm{rep}}(\mathrm{CT})$ reflects the configurational changes that have occurred in the molecule DMABN and its immediate solvent environment during the ICT reaction from the S_0 ground state to the equilibrated CT state. Two contributions to $\delta E_{\mathrm{rep}}(\mathrm{CT})$ can be distinguished in principle: firstly, the reorganisation of the solvent molecules, induced by the increase in the dipole moment of DMABN from 6.6 D in the ground state to 17 D in the CT state [8]; secondly, changes in the molecular configuration of DMABN such as bond lengths and bond angles, due to the increase in charge separation when going from S_0 to CT.

4. Requirements for the occurrence of dual fluorescence with aminobenzonitriles

4.1. $S_1(^1L_b)$ and $S_2(^1L_a,CT)$: large energy gap $\Delta E(S_1,S_2)$

The conditions required for the occurrence of dual fluorescence in DMABN and related D/A-substituted molecules have been discussed on the basis of the level ordering of the ^1L_b and (^1L_a,CT) states and the magnitude of the energy gap $\Delta E(S_1, S_2)$, as depicted in Fig. 2 [7,18,19]. Four level orderings of S_1 and S_2 are considered in Fig. 2, two each for either ^1L_b or (^1L_a,CT) as the lowest excited state S_1. With 4-(methylamino)benzonitrile (MABN) and 4-aminobenzonitrile (ABN) no dual fluorescence and ICT is observed, even not in strongly polar solvents such as acetonitrile [5,8,28]. This has been attributed to the relatively large energy gap $\Delta E(S_1, S_2)$, preventing the vibronic coupling between S_1 and S_2, which is thought to take place during the ICT reaction [7,17,28]. The absence of ICT in MABN is not due to specific molecular properties of the NH(CH_3) group [5], as dual fluorescence is readily observed in 4-(methylamino)-3,5-dimethyl-benzonitrile (MHD) [28].

4.2. (^1L_a,CT) as the lowest excited singlet state: dual fluorescence with M4D

As compared with DMABN, a reversal of the molecular nature of the two lowest excited states has taken place with 4-(N-azetidinyl)-3,5-dimethyl-benzonitrile (M4D), the level ordering now being $S_1(^1L_a,\mathrm{CT})$ and $S_2(^1L_b)$ [7,19], see Fig. 2. A similar situation occurs with 4-(dimethylamino)-3,5-dimethyl-benzonitrile (MMD). This state reversal has been deduced from a detailed analysis of the absorption spectra of M4D and MMD [22]. In the case of MMD the change in the level ordering has already been reported, based on MCD spectra [29].

M4D in diethyl ether is dual fluorescent, see Fig. 3, where the CT and LE emissions in the spectrum of M4D at 20 and −110 °C are shown. Apart from the state reversal mentioned above, the energetic situation is similar to that of DMABN, with a relatively small energy gap $\Delta E(S_1, S_2)$ (Fig. 2). From the fact that dual fluorescence is observed with DMABN as well as with M4D, irrespective of the molecular nature of the lowest excited state, it is concluded that the proximity of the S_1 and S_2 states is indeed an important factor for the occurrence of ICT and dual fluorescence in 4-aminobenzonitriles. Dual fluorescence apparently only appears when $\Delta E(S_1, S_2)$ is sufficiently small to make vibronic coupling possible.

The LE and CT fluorescence response functions of M4D in diethyl ether are double exponential, as seen in Fig. 4, where a global analysis of the functions at 20 °C is presented. From the very short decay time τ_2 of 2 ps an ICT rate constant

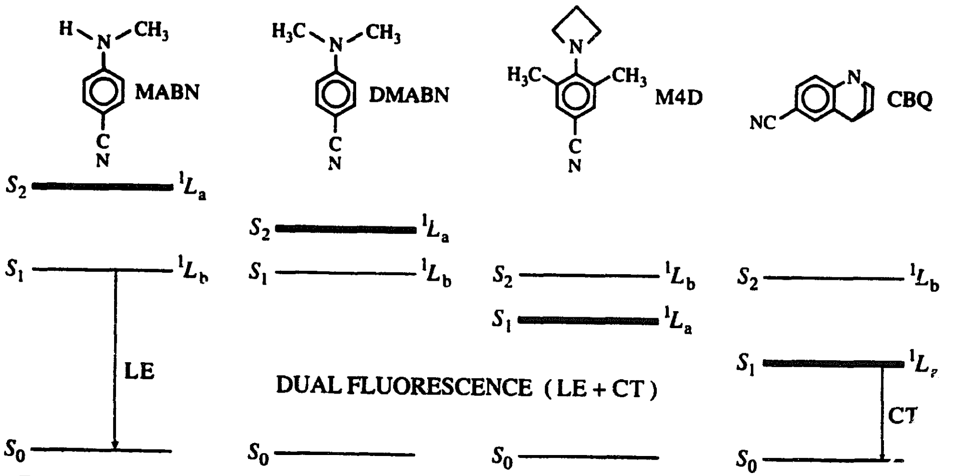


Fig. 2. Different level ordering of the two lowest excited states ^1L_b and (^1L_a,CT) for 4-aminobenzonitriles.

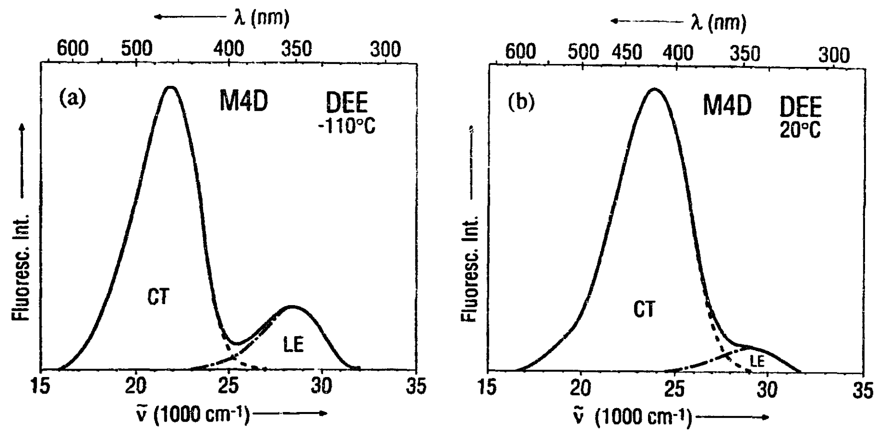


Fig. 3. Fluorescence spectra of 4-(*N*-azetidinyl)-3,5-dimethyl-benzonitrile (M4D) in diethyl ether at (a) − 110 °C and (b) 20 °C. The CT and LE emission bands are separated by taking the shape of the spectrum of 4-(methylamino)benzonitrile (MABN) for the LE state.

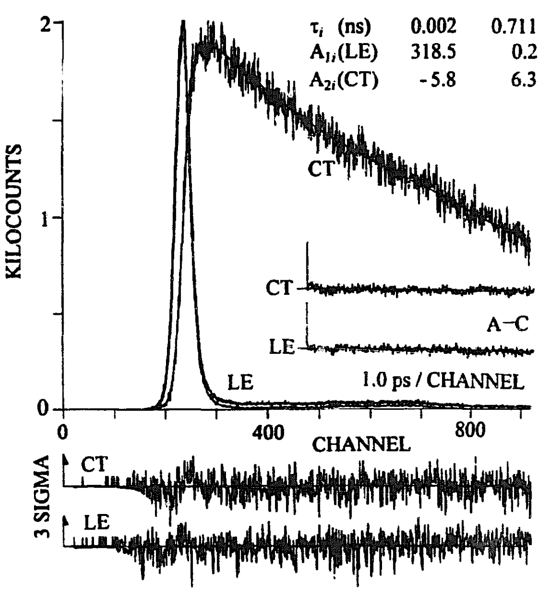


Fig. 4. Fluorescence response functions of the LE and CT emission of 4-(*N*-azetidinyl)-3,5-dimethyl-benzonitrile (M4D) in diethyl ether at 20 °C. The decay times (τ_2, τ_1) and their pre-exponential factors A_{2i} (CT) and A_{1i} (LE) are given. The LE and CT decays were analyzed simultaneously (global analysis [24]). The decays were obtained by using picosecond laser excitation at 296 nm. The weighted deviations, expressed as σ (expected deviations) and the autocorrelation functions *A–C* are indicated.

k_a (Scheme 1) of 5×10^{11} s^{-1} can be calculated [5,8] [1]. It is of interest to note that this value of k_a is considerably larger than the 2.3×10^{10} s^{-1} obtained for DMABN in diethyl ether at 20 °C [7]. Although it has been shown here that the observation of dual fluorescence does not depend on the nature of the lowest excited state, it is clear that the increased CT character of the S_1(^1L_a,CT) state of M4D as compared with the S_1(^1L_b) state of DMABN has made the ICT process considerably faster. This may be related to the molecular nature of the (^1L_a,CT) state, which is more polar than (^1L_b) and therefore perhaps more closely related to the final equilibrated CT state of the aminobenzonitriles.

With CBQ, having a larger energy gap between S_1 and S_2 than M4D [7,18], see Fig. 2, only a single CT emission band without an LE component is observed. This absence of dual emission is similar to the observation, described in Section 4.1., that only an LE emission is found with MABN. In both cases the lack of dual emission is attributed to the large energy gap $\Delta E(S_1,S_2)$, which prevents vibronic coupling between S_1 and S_2, see Fig. 2.

5. P3C to P8C: an important ICT reaction coordinate

In the series of 4-aminobenzonitriles 4-(*N*-aziridinyl)-benzonitrile (P3C) to 4-(*N*-octahydroazocinyl)benzonitrile (P8C), in which the amino nitrogen is part of a three- to eight-membered heterocyclic ring, the CT/LE fluorescence quantum yield ratio Φ'(CT)/Φ(LE), and also the forward ICT reaction rate constant k_a (Scheme 1), strongly decreases with decreasing ring size. This behaviour has been observed in several solvents of different polarity such as acetonitrile and diethyl ether [7,17–19]. Whereas the fluorescence of 4-(*N*-azetidinyl)benzonitrile (P4C) in diethyl ether only consists of a single LE emission band, dual fluorescence is found with this compound in the more polar solvent acetonitrile. From measurements of the double exponential LE and CT fluorescence decays of the molecules P4C to 4-(*N*-hexahydroazepinyl)benzonitrile (P7C) in acetonitrile it was shown that the activation energy E_a of the forward ICT reaction (k_a) increases when the amino ring becomes smaller, from 4.7 kJ mol^{-1} for P7C to 13.5 kJ mol^{-1} for P4C [7]. This increase in E_a has been attributed to the increase of the energy involved in the change of the configuration of the amino nitrogen from pyramidal towards planar. This interpretation is based on the results from dynamic NMR measurements, which show that in the series *N*-methylhomopiperidine (M7N) to *N*-methylaziridine (M3N) the amino

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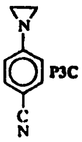
[1] When $\tau_2 \ll \tau_1$, as in Figs. 4 and 8, the rate constants of the forward (k_a) and backward (k_d) ICT reactions can be determined in an approximate manner from $k_a + k_d \approx 1/\tau_2$ and $k_a/k_d = A_{12}/A_{11}$. Using this procedure in the case of M4D (Fig. 3) the values $k_a = 5.0 \times 10^{10}$ s^{-1} and $k_d = 3.14 \times 10^8$ s^{-1} result, in excellent agreement, obvious in this case with a large value for A_{12}/A_{11}, with the outcome of a full analysis, with $\tau_0 = 3.91$ ns at diethyl ether at 20 °C from MABN as the model compound (cf. Ref. [5]): 4.99×10^{10} s^{-1} (k_a) and 3.12×10^8 s^{-1} (k_d).

nitrogen inversion barrier increases with decreasing ring size from 28.5 kJ mol^{-1} for M7N to 79.5 kJ mol^{-1} for M3N [30]. The results presented here mean that in potentially dual fluorescent 4-aminobenzonitriles the configurational change of the amino nitrogen towards planarity is an important reaction coordinate for the ICT reaction.

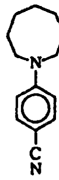

P3C


P4C


P5C


P6C


P7C


P8C

With P3C, the molecule with the smallest amino ring, for which we therefore expect the highest barrier for the configurational change from pyramidal to planar in the series P3C to P8C, dual fluorescence is not observed over an extended temperature range, neither in diethyl ether nor in acetonitrile (Fig. 5). The spectrum of P3C consists of a single LE emission band [19]. The fluorescence decay of P3C in diethyl ether as well as in acetonitrile (Fig. 5, at −40 °C) is single exponential, supporting our conclusion that an ICT reaction does not take place in this system owing to the magnitude of the activation energy E_a. Other factors, such as a large energy gap $\Delta E(S_1,S_2)$ and possibly insufficient electron donor strength of the aziridinyl group, can also negatively affect the ICT reaction.

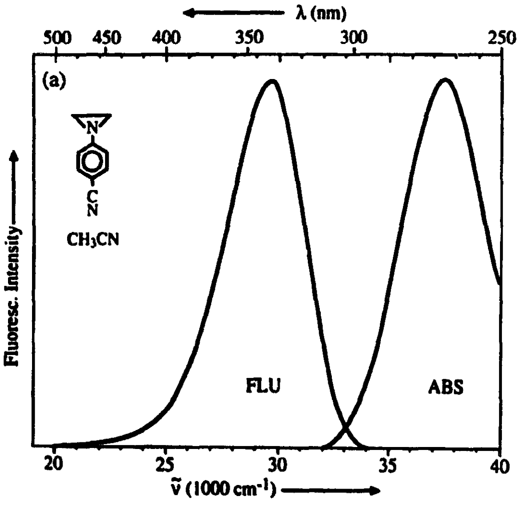


Fig. 5. (a) Fluorescence and absorption spectra of 4-(*N*-aziridinyl)-benzonitrile (P3C) in acetonitrile at 20 °C and (b) single exponential fluorescence response function of P3C in acetonitrile at −40 °C. See the caption of Fig. 4.

6. Pressure dependence of the ICT reaction of DMABN and DDABN: solvent viscosity and polarity

The fluorescence spectrum of DMABN was measured as a function of pressure in diethyl ether at around 20 °C. The spectra at 6000 bar and at normal pressure are shown in Fig. 6. The CT/LE fluorescence quantum yield ratio $\Phi'(\mathrm{CT})/\Phi(\mathrm{LE})$ strongly increases with pressure from 0.32 (1 bar) to 1.05 (6000 bar). Simultaneously, the CT emission maximum $h\nu^{\max}(\mathrm{CT})$ shifts to the red, from 23 800 to 22 800 cm^{-1}. The shape of the CT band and its width at half-maximum Δ(1/2) do not change.

Pressure measurements with 4-(di-*n*-decylamino)-benzonitrile (DDABN) in *n*-hexane at 20 °C, however, show a quite different behaviour. Here, the ratio $\Phi'(\mathrm{CT})/\Phi(\mathrm{LE})$ undergoes at most an increase of a few percent when the pressure is raised from 1 to 6000 bar and a shift of the CT maximum $h\nu^{\max}(\mathrm{CT})$ is not observed.

Upon increasing the pressure, the viscosity of *n*-hexane increases from 0.29 to 3.53 cP between 1 and 6000 bar [31]a and the dielectric constant ϵ_r changes slightly from 1.88 (1 bar) to 2.17 (6000 bar) [31]b, all data at 30 °C. The very small pressure dependence of the $\Phi'(\mathrm{CT})/\Phi(\mathrm{LE})$ ratio found with DDABN therefore means that an increase in sol-

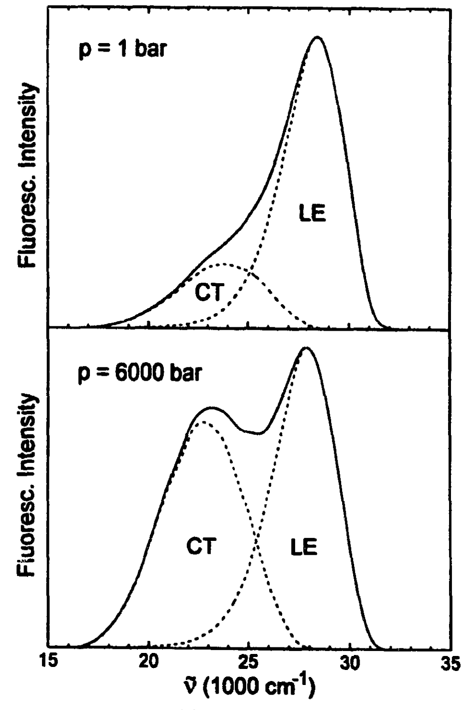


Fig. 6. Fluorescence spectra of 4-(dimethylamino)benzonitrile (DMABN) in diethyl ether at 20 ± 1 °C at 1 bar and at 6000 bar. The CT and LE emission bands are separated by taking the shape of the spectrum of 4-(methylamino)benzonitrile (MABN) for the LE state.

vent viscosity by a factor of 12 has practically no effect on the efficiency of the ICT reaction. It is therefore concluded that the substantial increase with pressure of the CT/LE fluorescence quantum yield ratio observed in the case of DMABN in diethyl ether cannot be attributed to the change in the viscosity of the solvent. It then follows that the increase in $\Phi'(\mathrm{CT})/\Phi(\mathrm{LE})$ must be due to the strong increase in the polarity of diethyl ether, for which the ϵ_r value, at 30 °C [31c], changes from 4.15 at 1 bar to 6.53 at 6000 bar. This increase of the solvent polarity with pressure is reflected by the red shift of $h\nu^{\max}(\mathrm{CT})$ mentioned above.

Our conclusion that the solvent polarity and not the solvent viscosity is the determining factor for the ICT process and the dual fluorescence of 4-aminobenzonitriles such as DMABN, is in accord with previous studies [20] on the solvent polarity dependence of the photophysics of DMABN, which show that the ICT activation energy E_a decreases with increasing polarity.

The absence of a viscosity dependence of $\Phi'(\mathrm{CT})/\Phi(\mathrm{LE})$ for DDABN in n-hexane and the increase of this ratio with pressure for DMABN in diethyl ether makes the involvement of a large amplitude motion in the course of the ICT reaction unlikely. The observations can be understood, however, within the framework of our reaction mechanism [7,18], which identifies as the essential reaction coordinates the change in configuration of the amino nitrogen of the aminobenzonitriles from pyramidal to planar and the concomitant changes in bond lengths occurring between the ground state and the equilibrated CT state. Such changes are not expected to show a pronounced viscosity dependence.

7. NMC5, NMC6 and NMC7: blocking perpendicular twist

Two different structural arguments have been advanced as support for the TICT model proposed for aminobenzonitriles: (a) the photophysical behaviour of model compounds such as 1-methyl-6-cyano-1,2,3,4-tetrahydroquinoline (NMC6) and MMD, in which the rotation around the N-phenyl bond is affected [1–4] and (b) the presence of a linear correlation between the CT emission maximum and the redox potentials of the A and D subunits [21]. The last argument has been discussed in detail recently [6,7,18], the first one will be treated here.

The molecules 1-methyl-5-cyanoindoline (NMC5) and NMC6, in which the rotation around the N-phenyl bond is blocked, have played an important role as model compounds designed to investigate the validity of the TICT model. The finding that only LE emission is observed for these molecules, even in polar solvents such as acetonitrile, has been considered to support the hypothesis that the possibility of rotation around the N-phenyl bond is an essential requirement for the occurrence of dual fluorescence in aminobenzonitriles [1–4].

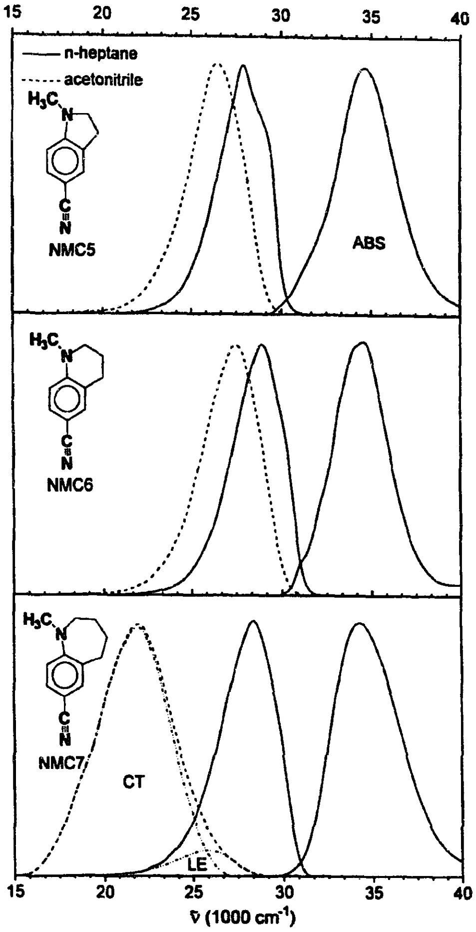


Fig. 7. Fluorescence and absorption (ABS) spectra of 1-methyl-5-cyanoindoline (NMC5), 1-methyl-6-cyano-1,2,3,4-tetrahydroquinoline (NMC6) and 1-methyl-7-cyano-2,3,4,5-tetrahydro-1H-1-benzazepine (NMC7) in n-heptane (———) and acetonitrile (- - -) at 25 °C. The fluorescence spectra of NMC5 and NMC6 consist of a single LE band in both solvents. The CT and LE abbreviations (see Scheme 1) in the fluorescence spectrum of NMC7 refer to acetonitrile. The emission spectrum of NMC7 in n-heptane predominantly consists of an LE band with a small admixture of a CT component at the red edge of the spectrum.

In Fig. 7 the fluorescence and absorption spectra of NMC5, NMC6 and 1-methyl-7-cyano-2,3,4,5-tetrahydro-1H-1-benzazepine (NMC7) in n-heptane and acetonitrile at 25 °C are presented. The fluorescence spectra of NMC5 and NMC6 in acetonitrile are red shifted relative to those in n-heptane, as a consequence of their excited state dipole moment μ_e of around 11 D [32]. The spectra only consist of a single LE band, which is similar in shape to the spectra of MABN and ABN [28] in the case of NMC6. There is no indication of the appearance of dual fluorescence and the fluorescence decays of NMC5 and NMC6 in n-heptane and acetonitrile are single exponential, see Table 1. These results are in agreement with previous spectral data obtained with NMC5 and NMC6 in a variety of solvents spanning the polarity scale over an extended temperature range [26,33].

For the seven-membered heterocyclic molecule NMC7 in acetonitrile, in contrast, a CT emission band dominates the fluorescence spectrum with a clearly larger Stokes shift for the CT than for the considerably weaker LE band (Fig. 7).

Table 1

Decay times τ_1 and τ_2 and their amplitude ratio A_2/A_1, fluorescence quantum yield Φ for LE and CT and LE radiative rate constant k_f of three rigidized aminobenzonitriles in acetonitrile at 25 °C. Excitation wavelength: 300 nm (NMC5 [a] and NMC6 [b]) and 320 nm (NMC7 [c])

	NMC5	NMC6	NMC7
τ_1 (ns)	4.19	2.87	6.46
τ_2 (ns)	–	–	0.014
A_2/A_1	–	–	10.6
Φ (LE)	0.23	0.26	0.01
Φ (CT)	–	–	0.13
k_f ($\times 10^7$ s^{-1})	5.4	2.6	–

[a] 1-methyl-5-cyanoindoline.

[b] 1-methyl-6-cyano-1,2,3,4-tetrahydroquinoline.

[c] 1-methyl-7-cyano-2,3,4,5-tetrahydro-1H-1-benzazepine.

The contribution of the CT emission to the overall fluorescence spectrum of NMC7 in *n*-heptane is much smaller than in acetonitrile. Such a polarity dependence is commonly observed with dual fluorescent aminobenzonitriles and can in the case of DMABN be ascribed to a strongly increased ICT back reaction k_d in nonpolar solvents [5,7,8]. The predominant CT character (Table 1) of the NMC7 fluorescence in acetonitrile [7,18,28] is supported by solvatochromic and time-resolved microwave conductivity (TRMC) experiments [32], showing that the dipole moment of the CT band of NMC7 is similar to that found for DMABN, for which a μ(CT) of around 17 D has been determined by TRMC measurements [8]. The excited state dipole moment of 11 D found for NMC6, mentioned above, is similar to that of MABN [8] and therefore supports the identification of its fluorescence band as originating from an LE state.

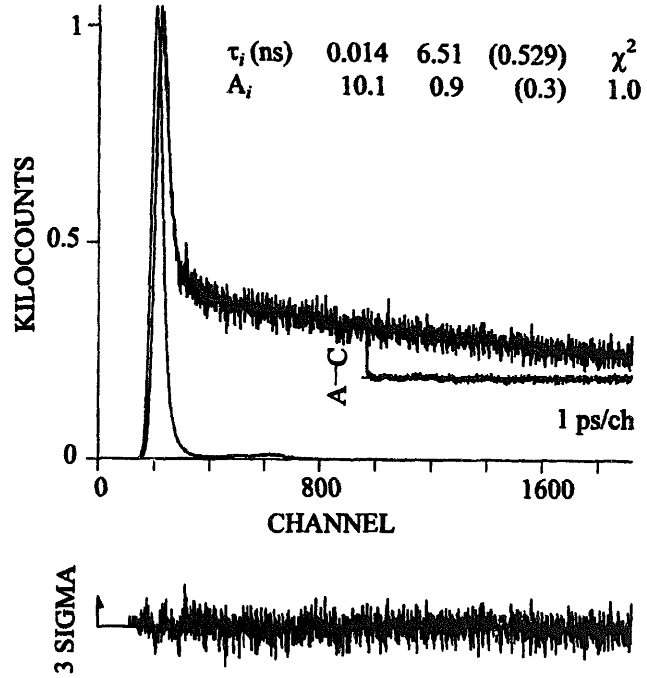


Fig. 8. Fluorescence response function of the LE emission of 1-methyl-7-cyano-2,3,4,5-tetrahydro-1H-1-benzazepine (NMC7) in acetonitrile at 20 °C. The decay times $\tau_2 = 0.014$ ns and $\tau_1 = 6.51$ ns as well as their pre-exponential factors A_i are given. The decay time in parentheses is attributed to an impurity. See the caption of Fig. 4.

The observation of dual fluorescence and ICT in the case of NMC7 indicates that the increased flexibility of its seven-membered heterocyclic ring, as compared with the smaller more rigid rings in NMC5 and NMC6, is sufficient to enable NMC7 to undergo an efficient ICT reaction. In acetonitrile a rate constant k_a of 7×10^{10} s^{-1} at 20 °C can be determined [5,7,8] [2] from the two decay times $\tau_2 = 14$ ps and $\tau_1 = 6.51$ ns together with their amplitude ratio $A_2/A_1 = 11.2$, obtained from the double exponential LE fluorescence decay curve shown in Fig. 8. For NMC7 in *n*-heptane at 20 °C the ICT reaction is considerably slower than in acetonitrile: $k_a = 2.6 \times 10^9$ s^{-1}, as similarly determined from the LE fluorescence decay data $\tau_2 = 72$ ps, $\tau_1 = 1.51$ ns and $A_2/A_1 = 0.20$, taking NMC6 in *n*-heptane as the model compound. These observations are another [20] example of the increase with polarity of the rate constant k_a.

8. Internal conversion in 1DMAN

8.1. Thermally activated internal conversion

The fluorescence quantum yield Φ as well as the fluorescence lifetime τ of 1-(dimethylamino)naphthalene (1DMAN) in an alkane solvent such as *n*-pentane at 25 °C have considerably smaller values than in the more polar solvents diethyl ether and acetonitrile, see Table 2 and also Fig. 9. The fluorescence decays are single exponential and no sign of dual fluorescence is detected. The values of Φ and τ of 1DMAN both increase with solvent polarity. The radiative rate k_f is not so strongly affected, decreasing by a factor of two between *n*-pentane and acetonitrile (Table 2). These

Table 2

Fluorescence quantum yield Φ, fluorescence decay time τ, radiative (k_f) and internal conversion (k_{IC}) rate constants and the internal conversion activation energy E_{IC} of 1-(dimethylamino)naphthalene (1DMAN) in three solvents of different polarity at 25°C

	ε_r^{20} [a]	Φ	τ (ns)	k_f ($\times 10^7$ s^{-1})	k_{IC} ($\times 10^7$ s^{-1})	E_{IC} (kJ mol^{-1})
n-pentane	1.84	0.01	0.106	9.1	960	18.6
diethyl ether	4.3	0.03	0.440	7.3	200	27.4
acetonitrile	37.5	0.21	4.40	4.7	12	30.3

[a] Static dielectric constant at 20 °C. Data from Ref. [34].

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[2] See footnote 1.

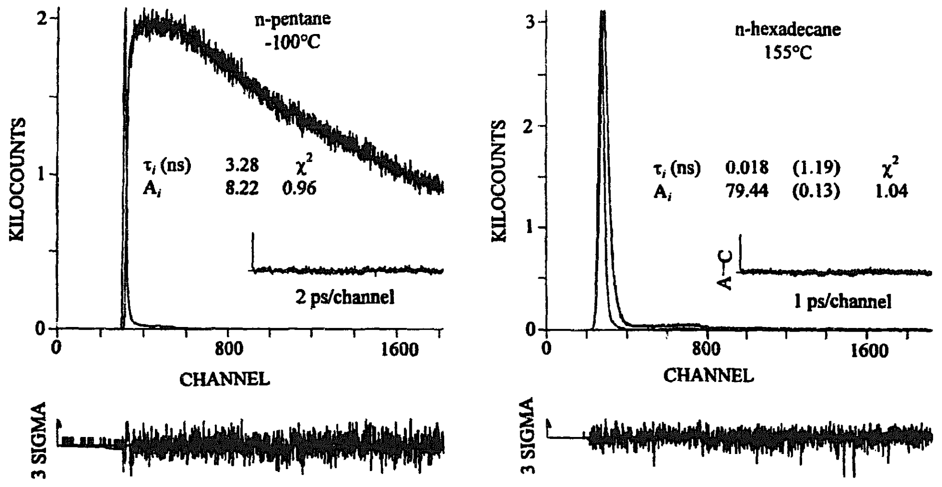

Fig. 9. Fluorescence response functions of 1-(dimethylamino)naphthalene (1DMAN) in (left) *n*-pentane at −100 °C and (right) *n*-hexadecane at 155 °C. The decay time in parentheses (left) is attributed to an impurity. See the caption of Fig. 4.

Table 3
Fluorescence quantum yield Φ and fluorescence lifetime τ of four aminohaphthalenes in *n*-hexane at 25 °C

	1DMAN [a]	1AN [b]	1MAN [c]	2DMAN [d]
τ (ns)	0.120	6.65	7.80	10.5
Φ	0.010	0.44	0.47	–

[a] 1-(dimethylamino)naphthalene.
[b] 1-aminonaphthalene.
[c] 1-(methylamino)naphthalene.
[d] 2-(dimethylamino)naphthalene.

data indicate that a solvent polarity dependent radiationless process takes place in 1DMAN. Somewhat surprisingly, such a process does not occur with 1-aminonaphthalene (1AN), 1-(methylamino)naphthalene (1MAN) and 2-(dimethylamino)naphthalene (2DMAN), see Table 3 for data in *n*-hexane at 25 °C. The solvent polarity dependent radiationless process operating in 1DMAN was first described by Phillips, as part of an investigation of its excited state properties and their significance for the widely used aminonaphthalene sulphonate solvent polarity probes [35].

The fluorescence decay time τ of 1DMAN in alkane solvents strongly depends on temperature, increasing in isopentane from 106 ps at 25 °C to 3.94 ns at −150 °C. A similar temperature dependence can be seen in Fig. 9. By combining measurements of the fluorescence quantum yield Φ, the lifetimes τ and the T–T absorption intensity of 1DMAN in a variety of alkanes as a function of temperature, it could be established that an efficient thermally activated internal conversion (IC) process occurs with 1DMAN [36]. The activation energy E_{IC} of the internal conversion rate constant k_{IC} increases with solvent polarity from 18.6 kJ mol^{-1} in *n*-pentane to 30.3 kJ mol^{-1} in acetonitrile (Table 2), showing that internal conversion still operates in polar solvents, although with a strongly reduced efficiency.

8.2. *Internal conversion and level interaction between S_1 and S_2*

With the four aminonaphthalenes 1AN, 1MAN, 1DMAN and 2DMAN the magnitude of the energy gap $\Delta E(S_1,S_2)$ is relatively small [37]. This energy gap has the smallest value for 1DMAN. Even a state reversal from $S_1(^1L_b)$, $S_2(^1L_a)$, the level ordering present in the other three aminonaphthalenes, to $S_1(^1L_a)$, $S_2(^1L_b)$ has been discussed in the literature [37–39]. As a further difference, the dimethylamino group of 1DMAN in its electronic ground state is strongly twisted with respect to the naphthalene plane [40]. In the S_1 state the molecule is considered to be planar, based on the analysis of the influence of the *N*-methyl substituents on the absorption and fluorescence spectra of the three 1-aminoaminonapthalenes [37,39] and the planarity of 1AN in the S_1 state [38]. A ground state twist of the amino group is not present with 1AN, 1MAN or 2DMAN [40]. The question now arises, whether the proximity of S_1 and S_2 is responsible for the fast internal conversion process in 1DMAN. Further, it is of interest to investigate whether the antitwist movement of 1DMAN upon excitation from S_0 (twisted) to S_1 (planar) plays a role in the radiationless process.

In the NH_2-derivative 1MAN, according to the MO calculations of Suzuki [41], the S_1 state has predominantly ^1L_b character with an important admixture of ^1L_a and several CT states, whereas the S_2 state has a similar composition but is mainly of ^1L_a character. When we assume that the state reversal mentioned above has already taken place for 1DMAN in *n*-pentane, the more polar composite ^1L_a state has a lower energy than the composite ^1L_b state. When this is the case, the $\Delta E(S_1,S_2)$ energy gap will increase with increasing solvent polarity. This would explain the observed polarity dependent increase of E_{IC} (Table 2). It is assumed that the activation energy E_{IC} of the internal conversion is related to the energy gap $\Delta E(S_1,S_2)$. The mechanistic details of the fast internal conversion operating in 1DMAN are under further investigation.

8.3. Photophysical similarities between 1DMAN and DMABN

It is of interest to point out that for 1DMAN as well as for DMABN a level interaction between the S_1 and S_2 states, made possible by a sufficiently small energy gap $\Delta E(S_1, S_2)$, is invoked in the explanation of their specific photophysical reactions treated here: internal conversion in the case of 1DMAN and dual fluorescence for DMABN. The new photophysical reactions disappear when in derivatives of both molecules the proximity of the S_1 and S_2 levels no longer exists. Examples of such derivatives are 1MAN for the aminonaphthalenes and MABN for the aminobenzonitriles, as discussed above.

9. Conclusion

On the basis of the double exponential LE and CT fluorescence decays of DMABN in various solvents, it is concluded that its dual fluorescence originates from a reversible ICT reaction in the singlet excited state. A polar solvent is not necessary for this reaction, as dual fluorescence has been observed with several 4-(dialkylamino)benzonitriles in nonpolar alkane solvents. From measurements of time-resolved fluorescence data as a function of temperature it appears that the largest contribution to the substantial red shift of the CT emission comes from the repulsion energy $\Delta E_{rep}(CT)$ of the Franck–Condon ground state reached during the CT emission. Changes in the solvent reorganisation around the emerging dipole and especially changes in the molecular configuration such bond lengths and bond angles occurring as a consequence of the increase in charge separation during the ICT reaction are assumed to contribute to the magnitude of $\Delta E_{rep}(CT)$.

Evidence is presented that dual fluorescence is observed with 4-aminobenzonitriles when two requirements are fulfilled: (a) a sufficiently small energy gap $\Delta E(S_1,S_2)$, leading to vibronic interaction between the two lowest singlet excited state S_1 and S_2, and (b) the possibility to change the configuration of the amino nitrogen from pyramidal towards planar within the time range set by the LE fluorescence lifetime of several nanoseconds. With M4D, for which the lowest excited state is of (^1L_a, CT) character, contrary to the $S_1(^1L_b)$ state of DMABN, dual fluorescence is in fact observed. As with DMABN, the energy gap $\Delta E(S_1,S_2)$ of M4D is relatively small.

From the observation that in the series P3C to P8C, having a three- to eight-membered heterocyclic amino group, the ICT efficiency strongly decreases with decreasing size of the amino ring, it is concluded that the configurational change of the amino nitrogen from pyramidal to planar is an important ICT reaction coordinate. This attributed to the increase in the ICT activation energy E_a when the amino ring becomes smaller. In accordance with this hypothesis, no dual fluorescence but only an LE emission is observed with P3C, having a three-membered aziridinyl ring.

Fluorescence spectra of DMABN in diethyl ether and of DDABN in *n*-heptane at room temperature were studied as a function of pressure to address the question of the viscosity dependence of their ICT reactions. The fluorescence quantum yield ratio $\Phi'(CT)/\Phi(LE)$ of DDABN in *n*-hexane remains practically constant when increasing the pressure to 6000 bar. With DMABN in diethyl ether, however, such a pressure increase leads to a 3 times larger $\Phi'(CT)/\Phi(LE)$ ratio. In view of the negligible pressure dependence found for DDABN in *n*-hexane, the higher ICT efficiency observed for DMABN is attributed to the polarity increase of diethyl ether under pressure. It is therefore concluded that the dual fluorescence and ICT reaction in the 4-aminobenzonitriles is practically not influenced by solvent viscosity. This means that it is not likely that a large amplitude motion takes place during the ICT reaction of DMABN or DDABN from the ground state to the final equilibrated CT state, in accordance with our PICT model of a planar CT configuration.

With the rigidized but slightly flexible molecule NMC7, in which the amino nitrogen is connected to the phenyl moiety as part of a seven-membered ring, dual fluorescence with a predominant CT component is observed in acetonitrile. With the more rigid derivatives NMC5 and NMC6 only an LE emission is found. These results show that a perpendicular configuration of the CT state, leading to a complete electronic decoupling of the amino group from the benzonitrile moiety, is not a necessary requirement for the appearance of dual fluorescence in these systems.

The aminonaphthalene 1DMAN undergoes a fast thermally activated internal conversion in alkane solvents. The activation energy E_{IC} of this process increases with solvent polarity, from 19 kJ mol^{-1} in *n*-pentane to 30 kJ mol^{-1} in acetonitrile. It is suggested that a vibronic interaction between the two lowest excited states S_1 and S_2 induces the internal conversion. The increase of E_{IC} with solvent polarity is attributed to a similar polarity dependent enlargement of the energy gap $\Delta E(S_1,S_2)$. Attention is drawn to the similar dependence on $\Delta E(S_1,S_2)$ of the internal conversion in 1DMAN and the ICT reaction in DMABN.

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References

[1] Z.R. Grabowski, K. Rotkiewcz, A. Siemiarczuk, D.J. Cowley, W. Baumann, Nouv. J. Chim. 3 (1979) 443.

[2] W. Rettig, Angew. Chem., Int. Ed. Engl. 25 (1986) 971.

[3] E. Lippert, W. Rettig, V. Bonačić-Koutecký, F. Heisel, J.A. Miehé, Adv. Chem. Phys. 68 (1987) 1.

[4] J. Dobkowski, Z.R. Grabowski, J. Jasny, Z. Zieliński, Acta Phys. Polon. A 88 (1995) 455.

[5] U. Leinhos, W. Kühnle, K.A. Zachariasse, J. Phys. Chem. 95 (1991) 2013.

[6] Th. von der Haar, A. Hebecker, Yu. Il'ichev, Y.-B. Jiang, W. Kühnle, K.A. Zachariasse, Rec. Trav. Chim. Pays-Bas 114 (1995) 430.

[7] K.A. Zachariasse, M. Grobys, Th. von der Haar, A. Hebecker, Yu.V. Il'ichev, Y.-B. Jiang, O. Morawski, W. Kühnle, J. Photochem. Photobiol A: Chem. 102 (1996) 59.

[8] W. Schuddeboom, S.A. Jonker, J.M. Warman, U. Leinhos, W. Kühnle, K.A. Zachariasse, J. Phys. Chem. 96 (1992) 10809.

[9] W. Rettig, G. Wermuth, E. Lippert, Ber. Bunsenges. Phys. Chem. 83 (1979) 692.

[10] M.C.C. de Lange, D. Thorn Leeson, K.A.B. van Kuijk, A.H. Huizer, C.A.G.O. Varma, Chem. Phys. 177 (1993) 243.

[11] A. Kummer, W. Kühnle, K.A. Zachariasse, unpublished results.

[12] E. Lippert, W. Lüder, F. Moll, H. Nagele, H. Boos, H. Prigge, I. Siebold-Blankenstein, Angew. Chem. 73 (1961) 695.

[13] K. Rotkiewicz, K.H. Grellmann, Z.R. Grabowski, Chem. Phys. Lett. 21 (1973) 212.

[14] A. Siemiarczuk, Z.R. Grabowski, A. Krówczyński, M. Asher, M. Ottolenghi, Chem. Phys. Lett. 51 (1977) 315.

[15] (a) O.S. Khalil, R. Hofeldt, S.P. McGlynn, Chem. Phys. Lett. 35 (1975) 172. (b) E.M. Kosower, H. Dodiuk, J. Am. Chem. Soc. 98 (1976) 924. (c) R.J. Visser, C.A.G.O. Varma, J. Chem. Soc., Faraday Trans. 2 76 (1980) 453. (d) C. Cazeau-Dubroca, S. Ait Lyazidi, P. Cambou, A. Peirigua, Ph. Cazeau, M. Pesquer, J. Phys. Chem. 93 (1989) 2347.

[16] M. Hashimoto, H. Hamaguchi, J. Phys. Chem. 99 (1995) 7875.

[17] K.A. Zachariasse, Th. von der Haar, U. Leinhos, W. Kühnle, J. Inf. Rec. Mats. 21 (1994) 501.

[18] Th. von der Haar, A. Hebecker, Yu. Il'ichev, W. Kühnle, K.A. Zachariasse, in: Fast Elementary Processes in Chemical and Biological Systems, Lille, France, 1995, AIP Conf. Proc. 364 (1996) 295.

[19] K.A. Zachariasse, M. Grobys, Th. von der Haar, A. Hebecker, Yu.V. Il'ichev, W. Kühnle, O. Morawski, J. Inf. Recording 22 (1996) 553.

[20] (a) J. Hicks, M. Vandersall, Z. Barbarogic, K.B. Eisenthal, Chem. Phys. Lett. 116 (1985) 18. (b) J. Hicks, M. Vandersall, E. Sitzmann, K.B. Eisenthal, Chem. Phys. Lett. 135 (1987) 413.

[21] Z.R. Grabowski, J. Dobkowski, Pure Appl. Chem. 55 (1983) 245.

[22] A. Hebecker, Ph.D. Thesis, University Göttingen, 1995.

[23] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 991.

[24] (a) G. Striker, in: M. Bouchy (ed.), Deconvolution and Reconvolution of Analytical Signals, University Press, Nancy, 1982, p. 329. (b) K.A. Zachariasse, G. Duveneck, W. Kühnle, P. Reynders, G. Striker, Chem. Phys. Lett. 133 (1987) 390.

[25] D. Schwarzer, Habilitationsschrift, University Göttingen.

[26] U. Leinhos, Ph.D. Thesis, University Göttingen, 1991.

[27] (a) N. Gee, K. Shinsaka, J.-P. Dodelet, G.R. Freeman, J. Chem. Thermodynamics 18 (1986) 221. (b) D. Beysens, P. Calmettes, J. Chem. Phys. 66 (1977) 766.

[28] K.A. Zachariasse, Th. von der Haar, A. Hebecker, U. Leinhos, W. Kühnle, Pure Appl. Chem. 65 (1993) 1745.

[29] J. Herbich, K. Rotkiewicz, J. Waluk, B. Andresen, E.W. Thulstrup, Chem. Phys. 138 (1989) 105.

[30] M. Oki, Applications of Dynamic NMR Spectroscopy to Organic Chemistry, VCH, Weinheim, 1985.

[31] (a) K. Schäfer (ed.), Landolt-Börnstein, Zahlenwerte und Funktionen, Vol. 6, Bd. II/5a, Springer, Berlin, 1969. (b) D.W. Brazier, G.R. Freeman, Can. J. Chem. 47 (1969) 893. (c) M.G. Gonikberg, Chemical Equilibria and Reaction Rates at High Pressures, 2nd ed. (Engl. translation of Izdatel'stvo Akademii Nauk SSSR, Moscow, 1960).

[32] W. Schuddeboom, R. Piet, J. Warman, M. Grobys, K.A. Zachariasse, in preparation.

[33] G. Köhler, K. Rechthaler, K. Rotkiewicz, W. Rettig, Chem. Phys. 207 (1996) 85.

[34] O. Madelung (ed.), Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series Vol. IV/6, Springer, Berlin, 1991.

[35] S.R. Meech, D.V. O'Connor, D. Phillips and A.G. Lee, J. Chem. Soc. Faraday Trans. 2 79 (1983). 1563

[36] I. Rückert, O. Morawski, K.A. Zachariasse, in preparation/ unpublished results.

[37] (a) N. Mataga, Bull. Chem. Soc. Jpn. 36 (1963) 654. (b) N. Mataga, T. Kubota, Molecular Interactions and Electronic Spectra, Dekker, New York, 1970.

[38] G. Berden, W.L. Meerts, D.F. Plusquellic, I. Fujita, D.W. Pratt, J. Chem. Phys. 104 (1996) 3935.

[39] S. Suzuki, T. Fujii, A. Imai, H. Akahori, J. Phys. Chem. 81 (1977) 1592.

[40] (a) L. Ernst, Z. Naturforsch. 30b (1975) 794. (b) H.S. Freeman, W.N. Hsu, J.F. Esancy, M.K. Esancy, Dyes and Pigments 9 (1988) 672.

[41] S. Suzuki, T. Fujii, H. Baba, J. Mol. Spectrosc. 47 (1973) 243.