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Photoproduct Formation with 4-Aminobenzonitriles in Acetonitrile and Its Effect on Photophysical Measurements

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Upon photoexcitation of 4-(dimethylamino)benzonitrile (DMABN) in the polar solvent acetonitrile (MeCN), a methyl group is subtracted from the dimethylamino substituent, producing 4-(methylamino)benzonitrile (MABN). The fluorescence of this photoproduct MABN occurs in the same spectral range as that of the locally excited (LE) state of DMABN. As DMABN undergoes efficient fluorescence quenching in MeCN, leading to a decrease of the LE fluorescence yield by a factor of 290 at 25 °C, whereas MABN is not quenched at all, even small amounts of this photoproduct strongly increase the apparent contribution of the LE emission to the total dual fluorescence spectrum of DMABN. As a further consequence of the photoproduct formation, the nanosecond decay time, τ_1, in the double-exponential LE fluorescence decay of DMABN in MeCN increases in relative intensity as compared to its picosecond counterpart, τ_2, as the fluorescence lifetime of MABN is similar to the τ_1 decay time of DMABN. The presence of the photoproduct MABN therefore can lead to a misinterpretation of the kinetic data derived from photostationary and time-resolved fluorescence experiments with DMABN in polar solvents. Photoproducts are also observed with 4-(*N*-pyrrolidinyl)aminobenzonitrile (P5C) and 4-(*N*-piperidinyl)aminobenzonitrile (P6C) in MeCN. In the case of P5C, 4-cyano-*N*-phenylpyrrole (PP4C) is the main product, whereas photolysis of P6C produces 4-aminobenzonitrile (ABN), among other photoproducts. This photodegradation, leading to the appearance of multiexponential decays, likewise has a negative influence on the ICT and LE fluorescence spectra and fluorescence decays of P6C and P5C, again impairing the validity of the kinetic analysis of these data. The isosbestic (absorption) and isoemission (fluorescence) points encountered in the spectra of DMABN and P6C during photoirradiation indicate that at least one photoproduct is formed.

Introduction

In contrast to the large number of studies on the photophysical and excited state properties of 4-(dimethylamino)benzonitrile (DMABN),[1−7] the possible formation of photoproducts with this molecule has received considerably less attention. This is somewhat surprising, as already in the first publications on the dual fluorescence of 4-(dialkylamino)benzonitriles the photodegradation of DMABN and 4-(diethylamino)benzonitrile (DEABN) in a polar solvent (not indicated, probably ethanol) was discussed.[1,2] It was concluded that the photoproduct of these aminobenzonitriles was formed by subtraction of a substituent, without further discussion of its identity. The fluorescence spectrum of the photolysis product was assumed to be similar to that of the locally excited (LE) state of DMABN and DEABN, without an emission from an intramolecular charge transfer (ICT) state, as the photoproducts caused a substantial decrease of the ICT-to-LE fluorescence quantum yield ratio, $\Phi'(\mathrm{ICT})/\Phi(\mathrm{LE})$.[1] Prolonged irradiation was found to have the same apparent effect on $\Phi'(\mathrm{ICT})/\Phi(\mathrm{LE})$ as cooling a fresh solution of DMABN at low temperatures.[1] This temperature effect, in the absence of photodegradation, mainly comes from the slowing down of the LE → ICT reaction upon lowering the temperature.[8]

With DMABN and several other derivatives of *N*,*N*-dimethyaniline (DMA) undergoing an excited state reaction with electron acceptor molecules such as 3-chloronitrobenzene, demethylation of the $N(\mathrm{Me})_2$ group takes place; that is, 4-(methylamino)benzonitrile (MABN) is generated in the case of DMABN.[10,11] For photoexcited DMABN solutions without additives, reports on the formation of MABN are not found in the literature, however. Oxidative *N*-demethylation of DMABN in the dark was observed in reactions mimicking the enzymatic action of cytochrome P-450.[12] DMABN in the electronic ground state is also demethylated[13] by mice and rats, with the cyano group remaining intact during the metabolism.

In all of these reactions, in the dark as well as after photoexcitation to the S_1 state, it is assumed that MABN is produced by the cleavage of a methyl group from the positively charged dimethylamino group, followed by hydrogen abstraction. The positive charge on the NMe_2 group of the DMA derivatives acting as electron donors (D) is thought to arise from an electron transfer reaction with an electron acceptor (A) molecule,[10−13] resulting in a charge transfer complex (A^-D^+) as the precursor. Different from the assumption discussed until now that MABN is formed upon photolysis of DMABN, it has recently been concluded that singlet excited DMABN in acetonitrile (MeCN) loses its cyano substituent and forms DMA.[14]

The generation of photoproducts can lead to serious problems in the analysis of time-resolved as well as photostationary data

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of dual (LE + ICT) fluorescent molecules such as DMABN. Especially in the case of polar aprotic (MeCN) or protic (methanol or ethanol) solvents, the LE emission is strongly quenched. For DMABN in MeCN at 25 °C, for example, an unquenched-to-quenched fluorescence quantum yield ratio, Φ_0(LE)/Φ(LE), of around 300 is observed for the LE emission.[9] This pronounced LE quenching is the cause of the large increase of the effective contribution of even minor amounts of fluorescent photoproducts to the overall fluorescence intensity in the spectral range of the LE emission band of DMABN. For this reason, unless special care is taken, the apparent ratio Φ'(ICT)/Φ(LE) (and similarly Φ_0(LE)/Φ(LE)) can be much smaller than the photophysically correct value. This would, for example, make one believe that the ICT → LE back reaction is much faster than it actually is. As a consequence, also the ICT (free) enthalpy differences $-\Delta G$ and $-\Delta H$ calculated from such experiments will appear to be much smaller than their true values. Similarly, the presence of a photoproduct will lead to a decrease of the relative amplitude of the short (picosecond) decay time in the double exponential LE fluorescence decay curves.[9,15,16] To clarify this situation and to establish the identity of the photoproduct of DMABN in MeCN, the present investigations were undertaken.

Experimental Section

DMABN was purchased from Aldrich and was used as received.[17] 4-(*N*-Pyrrolidinyl)aminobenzonitrile (P5C) and 4-(*N*-piperidinyl)aminobenzonitrile (P6C) were synthesized in a reaction between pyrrolidine (for P5C) or piperidine (for P6C) and 4-fluorobenzonitrile (Aldrich) in dimethyl sulfoxide (DMSO) at 90 °C, a procedure described in the literature.[18] Final purification of both compounds was carried out by high pressure liquid chromatography (HPLC). The solvents acetonitrile (MeCN), ethyl alcohol (EtOH), and *n*-hexane from Merck (Uvasol) were used as received.

DMABN Photolysis. A solution of 1 g of DMABN in 200 mL of MeCN in a cylindric quartz container (3.4 cm diameter, 20 cm length) was irradiated in a Rayonet RPR 100 photochemical reactor (16 lamps G8T5 (Philips), 254 nm) for 36 h under continuous nitrogen bubbling. The solvent was removed by using a rotary evaporator, and the solid material (800 mg) was chromatographed over Al_2O_3 with diethyl ether (Merck, Uvasol) as the eluent. The first analysis of the different fractions isolated from the photolysis mixture was performed by mass spectroscopy, leading to three fractions: fraction I (500 mg, the recovered starting material DMABN with a very small amount of the photoproduct MABN), the intermediate fraction II (164 mg, a mixture of DMABN and some MABN), and fraction III (102 mg, mainly the photoproduct MABN and a small amount of DMABN). The identity of the molecules (MABN and DMABN) in the fractions was established by ^{1}H NMR as well as by fluorescence and absorption spectra (see below).

P6C and P5C Photolysis. Similar photolysis experiments were carried out with P6C and P5C in MeCN. From a solution of 1 g of P6C in 200 mL of MeCN, after 135 h of irradiation, a fraction (II) of 16 mg (mainly 4-aminobenzonitrile (ABN)) was recovered after chromatography on silica (diethyl ether as the eluent), next to 537 mg of unchanged P6C (I) and 64 mg (III) of a complex reaction mixture (not analyzed). After an irradiation of 50 h, only P6C and ABN (smaller component) were detected by gas chromatography. The identity of ABN (around 65%) in fraction I, not showing a simple ^{1}H NMR spectrum, was established by ^{13}C NMR in a comparison with an authentic ABN sample.

In the case of P5C, 1 g of this substance in 200 mL of MeCN was irradiated for 150 h. After chromatography of the photolyzed material (0.9 g, on silica with 1/1 cyclohexane/toluene as the eluent), three fractions were obtained: (I) 66 mg of 4-cyano-*N*-phenylpyrrole (PP4C), (II) 158 mg of a mixture of PP4C and P5C, and (III) 266 mg of P5C. A gas chromatogram of the solution directly after photolysis showed the presence of two main substances: PP4C and P5C (major component). A small amount of ABN could also be detected. The identity of PP4CN in fraction I was established by ^{1}H NMR and mass spectrometry as well as by fluorescence and absorption spectra (see below).

Controlled Photodecomposition. In the photodecomposition experiments, the solutions (N_2 bubbled) were irradiated with the excitation light of the Fluoromax 3 spectrofluorometer (slit width 10 nm): 277 nm for DMABN in MeCN and EtOH and 285 nm for P6C in MeCN. The incident light intensity (4.5×10^{15} photons/s at 277 nm and 4.7×10^{15} photons/s at 285 nm) was measured by employing a Coherent FieldMaster power meter with an LM-2UV head, having a flat spectral absorption profile. For the calculation of the decomposition quantum yields during the irradiation experiments on the Fluoromax 3 spectrofluorometer, fluorescence spectra were measured with a much lower excitation intensity at 277 and 285 nm (1.0×10^{14} photons/s, slit width 1.5 nm) than that used for the photolysis.

The ^{1}H and ^{13}C NMR spectra were measured with a Varian Unity-300 or Gemini-300 (^{1}H) spectrometer. The fluorescence spectra were measured with quantum-corrected ISA-SPEX Fluorolog 3-22 or Fluoromax 3 (modified)[19] spectrofluorometers. The absorption spectra were run on a Cary 500 spectrometer. The fluorescence decay times were obtained with a picosecond laser system (excitation wavelength 276 nm) consisting of a mode-locked titanium−sapphire laser (Coherent, MIRA 900F) pumped by an argon ion laser (Coherent, Innova 415) or with a setup consisting of an argon ion laser (Coherent Innova Sabre R-TSM-10 with APE modelocker), a dye laser (Coherent 701-1CD; rhodamine 6G), and a frequency doubler (BBO, 298 nm). These laser systems and the analysis procedure of the fluorescence decays have been described previously.[6,17] The instrument response function of the laser SPC systems has a full width at half-maximum of 19 ps (MIRA) or 26 ps (dye laser).[6,17,20]

Results and Discussion

Photoproduct MABN from Photolysis of DMABN in MeCN. The photoproduct in fraction III obtained after the photolysis of DMABN in MeCN (see the Experimental Section) could be identified as MABN. This identification is based on the ^{1}H NMR spectrum in $CDCl_3$ (7.24 ppm), with the following results: ^{1}H NMR (300 MHz, in ppm): 2.81 (s, $N-CH_3$), 4.40 (s, broad, NH), 6.51 (d, H3, $J = 8.8$ Hz), 7.36 (d, H2, $J = 8.8$ Hz).[6,21] The same ^{1}H NMR spectrum was obtained with an authentic sample of MABN. This identification is supported by the observation that, upon adding pure MABN to the CD_3Cl solution of fraction III, the NMR signals attributed to MABN did increase in intensity, without a change in the chemical shifts. By way of an analysis of the integrated areas for the $N-CH_3$ signal in the ^{1}H NMR spectra, it was established that fraction III mainly consists of MABN, with 17 mol % DMABN. By a similar analysis, it was found that the intermediate fraction II contains 7 mol % MABN, next to the major component DMABN. Evidence for other photodegradation products, such as *N*,*N*-dimethylaniline (DMA) reported as the photoproduct in the literature,[14] could not be obtained from the NMR spectra of the solid material obtained after the photoirradiation. A

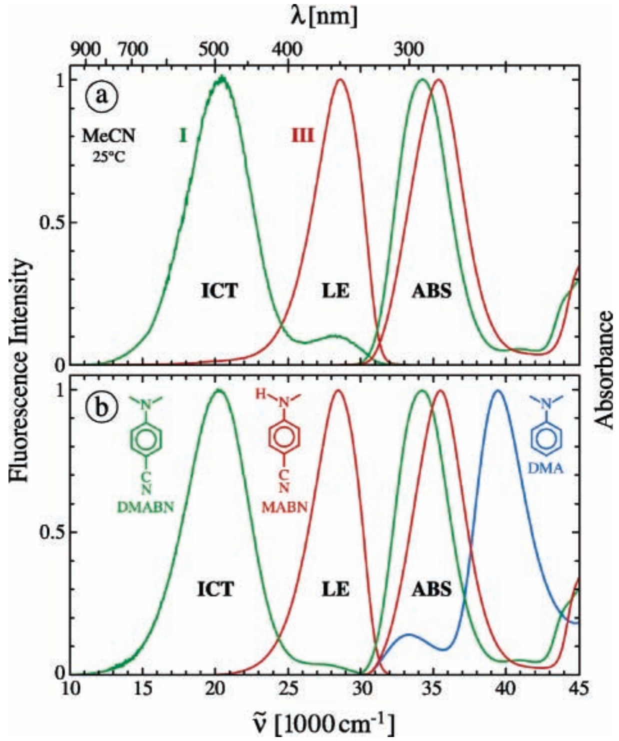


Figure 1. Normalized fluorescence (LE and ICT) and absorption (ABS) spectra in acetonitrile (MeCN) at 25 °C. In part a, the spectra for two of the fractions obtained after photolysis (Rayonet PRP100) at 254 nm of a concentrated solution (1 g in 200 mL) of 4-(dimethylamino)-benzonitrile (DMABN) are depicted. Red, fraction III mainly consisting of the photoproduct 4-(methylamino)benzonitrile (MABN); green, fraction I with DMABN (see text). In part b, spectra of pure solutions of DMABN (green), MABN (red), and *N*,*N*-dimethylaniline (DMA) (blue) are presented. The fluorescence spectra consist of emissions from an intramolecular charge transfer (ICT) state (DMABN) and from a locally excited (LE) state (DMABN, MABN, and DMA). In part b, the fluorescence spectrum of DMA is not shown, as it practically completely overlaps with that of MABN; see Supporting Information Figure 1S.

GC/MS analysis of the reaction solution just after the photolysis likewise only revealed the presence of MABN and DMABN, as also found from the absorption spectrum of the photolysis solution (see Figure 1). It is therefore concluded that MABN is the major photoproduct formed upon excitation at 254 nm of DMABN in MeCN at room temperature.

The same conclusion comes from inspection of the fluorescence and absorption spectra of fractions I and III; see Figure 1a. The absorption spectrum of fraction III (MABN with 17% DMABN) is red-shifted as compared with that of MABN due to the presence of DMABN. The fluorescence spectrum of this fraction, however, shows only a weak additional fluorescence around 20 000 cm^{-1} due to the contribution of the ICT fluorescence of DMABN (Figure 1). This small influence of 17% DMABN is caused by the strong fluorescence quenching of DMABN in MeCN, due to efficient intramolecular charge transfer (ICT), with an unquenched-to-quenched LE fluorescence quantum yield ratio, Φ_0(LE)/Φ(LE), of 290 at 25 °C.[9] The photoproduct MABN, in contrast to DMABN, does not undergo an ICT reaction, so that the LE emission of DMABN in the overall photostationary fluorescence spectrum of fraction III is reduced by just this factor Φ_0(LE)/Φ(LE). It is of interest to note here that the fluorescence spectrum of DMA in MeCN is practically identical to that of MABN (see Supporting Information Figure 1S), making the detection of DMA in the fluorescence spectra of the photoirradiation fractions difficult. The absorption spectrum of DMA, however, is clearly different from the spectra of MABN and DMABN, with the main band peaking at 39 430 cm^{-1} and a weaker band peaking around 33 300 cm^{-1}. A search for DMA (at levels of around 1%) can hence not be carried out on the basis of its fluorescence spectrum but must rely on the absorption spectrum and the NMR data, as discussed in the first part of this section. The fluorescence spectrum of fraction I (recovered DMABN with some MABN) has an ICT/LE fluorescence quantum yield ratio, Φ'(ICT)/Φ(LE), of 13. The presence of MABN in this fraction has reduced the ratio Φ'(ICT)/Φ(LE) as compared with the value of 39.5 for pure DMABN in MeCN.[9]

Irradiation of concentrated solutions (3.4×10^{-2} M) of 1 g of DMABN in 200 mL of ethanol as well as in 200 mL of methanol, under the same experimental conditions as those used for the irradiation of DMABN described above, did not result in any appreciable photoproduct formation. See below (Figure 3b) for the behavior of diluted solutions.

Photoproduct ABN from Photolysis of P6C in MeCN. The small fraction II of the photolysis material obtained with P6C contains around 65% ABN, as estimated from a comparison of its ^{13}C NMR spectrum and that of a pure ABN sample; see the Experimental Section. Fluorescence and absorption spectra identical to those of ABN were obtained after separation of fraction II into its components by HPLC. Although only a small amount of ABN is produced by the photolysis, a large impact on the fluorescence spectrum and decays nevertheless occurs, because of the strong quenching of the P6C fluorescence in MeCN, similar to the situation with DMABN discussed in the previous section. In MeCN at 25 °C, Φ(LE) = 0.0015 for P6C, as compared with 0.000 76 for DMABN.[9] With P5C in MeCN, the fluorescence quenching is somewhat smaller (Φ(LE) = 0.0021), leading to a similar influence of photoproducts as in the case of DMABN and P6C; see below.[15,16]

Photoproduct PP4C from Photolysis of P5C in MeCN. The ^{1}H NMR spectrum of fraction I of the photolysis material of P5C in MeCN (see Experimetal Section), containing only one compound, is identical to that of a sample of pure PP4C: (300 MHz, CDCl$_3$, in ppm) 6.413 (m, H9), 7.144 (m, H8), 7.49 (m, H2), 7.73 (m, H3). This identification is fully supported by a comparison of the fluorescence and absorption spectra of fraction I and PP4C in *n*-hexane and MeCN (Figure 2).[22] Fraction III consists of pure, not photolyzed, P5C.

Fluorescence and Absorption Spectra of DMABN in MeCN. In Figure 3a, the development of the fluorescence spectrum of a dilute (1.3×10^{-5} M) solution of DMABN in MeCN at 25 °C with increasing duration of the irradiation at 285 nm is shown. The fluorescence intensity of the band with a maximum around 28 650 cm^{-1} increases, with a simultaneous decrease in intensity of the ICT emission band ($\tilde{\nu}^{\max}$(ICT) = 20 310 cm^{-1}). Simultaneously, corresponding changes in the absorption spectra occur; see Figure 3a. As discussed in the previous section, the apparent increase of the LE fluorescence intensity and decrease of the ICT emission is caused by the formation of the photoproduct MABN, with a band maximum $\tilde{\nu}^{\max}$ (LE) at 28 670 cm^{-1}, not very strongly shifted to larger wavenumbers as compared to that (27 700 cm^{-1}) of the LE band of DMABN; see Figure 1b. This relatively small difference in $\tilde{\nu}^{\max}$ (LE) does not prevent the appearance of an isoemission as well as an isosbestic point[23−31] at 23 170 and 36 000 cm^{-1}, respectively (Figure 3a). The observation of such points has been considered to be an indication of the presence of only two emitting excited states (LE and ICT).[3] This will be discussed in the next section.

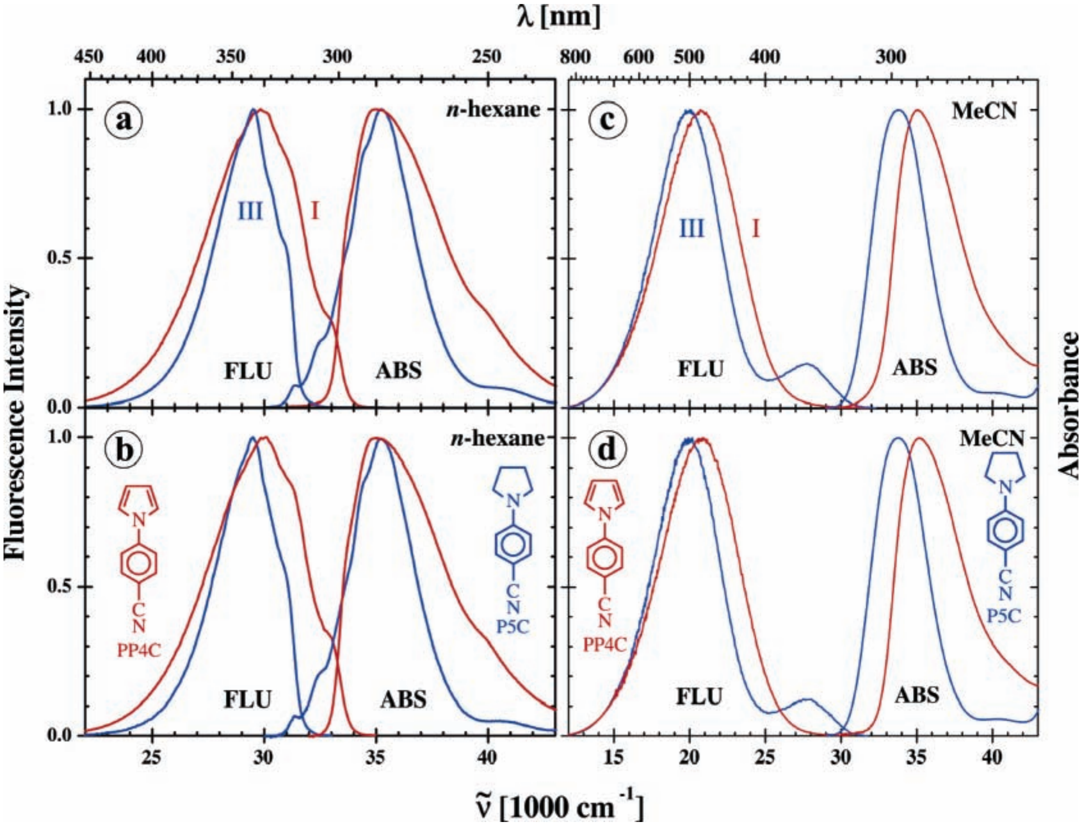


Figure 2. Normalized fluorescence (FLU) and absorption (ABS) spectra of fractions I and III obtained after photolysis of 4-(*N*-pyrrolidinyl)-aminobenzonitrile (P5C) (at 254 nm, see text) in a comparison with those of 4-cyano-*N*-phenylpyrrole (PP4C), in *n*-hexane and acetonitrile (MeCN) at 25 °C. The red spectra of fraction I in parts a and c are identical to those of PP4C in parts b and d, whereas the spectra (blue) of fraction III are the same as those of P5C.

A similar irradiation experiment (Figure 3b) carried out with a diluted solution (3×10^{-5} M) of DMABN in ethanol, same concentration as that for DMABN in MeCN, resulted in practically identical spectral changes with irradiation time. It is quite surprising, in this connection, that irradiation of a concentrated solution (3.4×10^{-2} M) of DMABN in ethanol did not produce appreciable amounts of a photoproduct, as mentioned above.

For P6C (Figure 3c) in MeCN at 25 °C, a similar influence of irradiation time on the LE and ICT fluorescence bands and on the absorption spectrum is observed, likewise with isoemission and isosbestic points.[23−31] Also, for P6C, a photoproduct fluorescence is observed in the spectral region of the LE emission, accompanied by a decrease in intensity of the ICT fluorescence band.

Photophysical Significance of Isosbestic and Isoemission Points. For the three sets of absorption spectra in Figure 3, an isosbestic (or isoabsorption) point[24−26] is observed. In general, this signifies that at the wavelength λ(isb) of this point a linear relation exists between the extinction coefficients of the reactant (DMABN or P6C) and all (photo)products, with the sum of the optical densities remaining constant (eq 1).[30] The observation of such an isosbestic point does not necessarily mean, however, that only two molecular species are involved in the reaction under investigation, contrary to what can be found in the literature.[3,31]

For a reaction with the stoichiometric coefficients σ_i

$$A_1 \rightarrow \sum_{i=2}^{n} \sigma_i A_i \tag{1}$$

the optical density at wavelength λ is

$$D(\lambda) = \sum_{i=1}^{n} \epsilon_i(\lambda) C_i \tag{2}$$

where the concentration $C_i = [A_i]$, with extinction coefficient ϵ_i.

It follows (eq 3) from eq 1 for $i = 2, 3, \ldots, n$ that

$$\frac{\partial C_i}{\partial C_1} = -1/\sigma_i \tag{3}$$

Hence, eq 4 holds at the isosbestic point, where the optical density is per definition independent of the composition of the solution.

$$\frac{\partial D(\lambda)}{\partial C_1} = \sum_{i=1}^{n} \epsilon_i(\lambda) \frac{\partial C_i}{\partial C_1} = 0 \tag{4}$$

From eqs 3 and 4, the following condition for the existence of an isosbestic point is then obtained:

$$\epsilon_1(\lambda) = \sum_{i=2}^{n} \epsilon_i(\lambda)/\sigma_i \tag{5}$$

When in the present case of DMABN only one photoproduct (MABN) would be formed ($\sigma_2 = 1$, eq 1), the isosbestic point will occur at the wavelength λ(isb) where the extinction coefficient of MABN is equal to that of DMABN. When more than one photoproduct is produced, an isosbestic point may still exist at a different wavelength, with a more complex relationship between the extinction coefficients of the reactant and the product molecules (eq 5).[32]

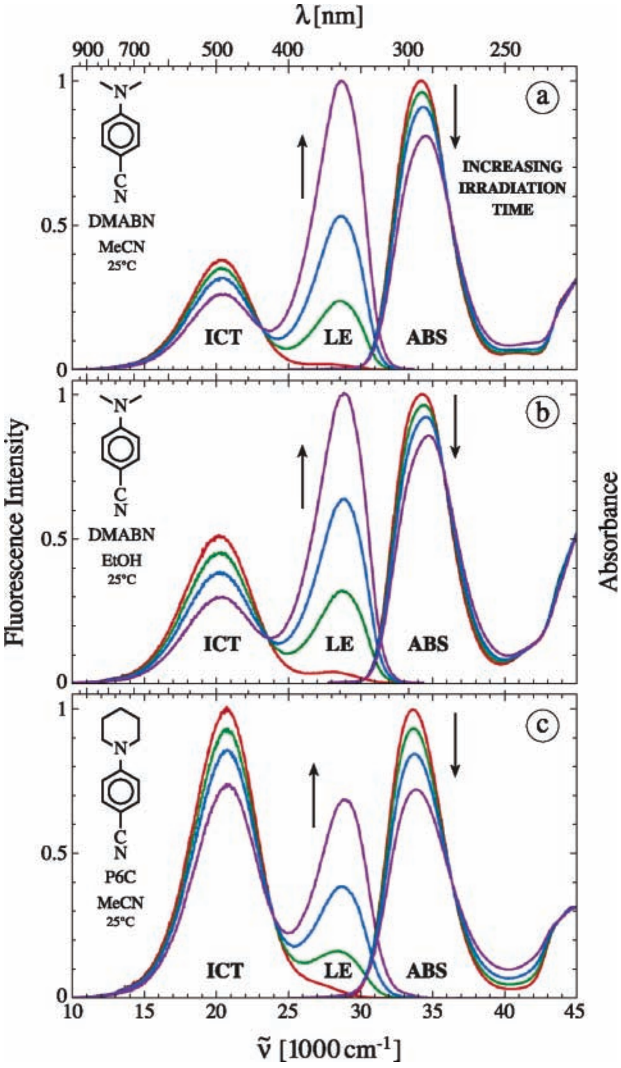


Figure 3. Fluorescence (dual emission: LE and ICT) and absorption spectra at 25 °C, in arbitrary units, of (a) 4-(dimethylamino)benzonitrile (DMABN) in acetonitrile (MeCN), (b) DMABN in ethanol (EtOH), and (c) 4-(*N*-piperidinyl)aminobenzonitrile (P6C) in MeCN, showing the change in the spectra with increasing duration of controlled photoexcitation at 285 nm (Fluoromax 3), red to violet, caused by photoproduct formation. In the case of DMABN, the photoproduct is 4-(methylamino)benzonitrile (MABN). Note the isoemission and isosbestic points at 23 170 and 36 000 $\mathrm{cm^{-1}}$ in part a, 23 560 and 35 680 $\mathrm{cm^{-1}}$ in part b, and 24 000 and 36 350 $\mathrm{cm^{-1}}$ in part c; see text. The spectra of the fresh solutions are in red. The arrows indicate the effect of increasing irradiation time. Irradiation time in hours (with the optical density at the absorption maximum at time zero in parentheses) (a) DMABN/MeCN: 0 (0.856), 0.35, 0.80, 1.58; (b) DMABN/EtOH: 0 (0.804), 0.35, 0.81, 1.61; (c) P6C/MeCN: 0 (0.873), 0.78, 1.76, 3.04. The red absorption spectra are normalized to the fluorescence band with the largest intensity and hence do not indicate relative photochemical stabilities of the systems in the figure.

In addition to the isosbestic points in the absorption spectra, isoemission points are observed in the fluorescence spectra of Figure 3, for all three systems undergoing photodegradation. The presence of an isoemission point, at which the fluorescence intensity remains constant during photolysis, likewise does not mean that only two excited species are present, as is sometimes concluded.[23b,c,33] This clearly follows, for example, from the fact that the photoproduct formation with DMABN in MeCN and EtOH as well as with P6C in MeCN involves at least three excited state species: the LE and ICT state of the starting material and also the photoproduct in the singlet excited state.

TABLE 1: Extinction Coefficients, $\epsilon^{\max}$, Frequencies of the Isosbestic, $\tilde{\nu}^{\max}$(isb), and Isoemission, $\tilde{\nu}^{\max}$(iem), Points and the Photodecomposition Quantum Yield, Φ(pd), for DMABN and P6C at 25 °C

reactant	solvent	$\epsilon^{\max}$	$\tilde{\nu}^{\max}$(isb) (1000 $\mathrm{cm^{-1}}$)	$\tilde{\nu}^{\max}$(iem) (1000 $\mathrm{cm^{-1}}$)	Φ(pd)
DMABN	MeCN[a]	27 190	36.00	23.17	0.0018
DMABN	EtOH[b]	26 970	35.68	23.56	0.0023
P6C	MeCN[a]	24 190	36.35	24.00	0.00061

[a] Acetonitrile. [b] Ethanol.

The condition for the appearance of an isoemission point at the wavelength λ(iem) during the present photolysis experiments with the dual fluorescence molecule DMABN is given by eq 6, valid for excitation in the isosbestic point; see the Appendix.

$$\Phi(LE)F_{\mathrm{LE}} + \Phi'(\mathrm{ICT})F_{\mathrm{ICT}} = \Phi(P)F_{\mathrm{P}} \tag{6}$$

In this equation, F ($\int F(\lambda)\,\mathrm{d}\lambda = 1$) is the normalized fluorescence intensity of LE, ICT, and P at λ(iem). According to eq 6, the requirement for the appearance of an isoemission point is that the sum of the LE and ICT fluorescence quantum yields, each multiplied by their corresponding factors F_{LE} and F_{ICT}, is equal to the product $\Phi(P)F_{\mathrm{P}}$. In other words, the isoemission point appears as the crossing point of the fluorescence quantum yield spectrum of the aminobenzonitrile (LE and ICT) and that of the photoproduct.

In a solution of a substance undergoing photodegradation, such as DMABN in MeCN, the composition of the solution continuously changes. Whereas the photolysis starts with a solution only containing DMABN, the concentration of the photoproduct MABN increases with the duration of the photolysis, with a corresponding decrease of that of DMABN. Although MABN is formed from DMABN after its excitation to the singlet excited state, there is no longer a kinetic photophysical connection between the two molecules when they are both excited from their S_0 states and produce the overall fluorescence spectrum of the solution: DMABN (LE + ICT) and MABN (LE).

Photodecomposition Yields for DMABN in MeCN and EtOH and for P6C in MeCN. A quantitative study was made to determine the photodecomposition yields, Φ(pd), at 25 °C for DMABN in MeCN and EtOH as well as for P6C in MeCN. The absorption and fluorescence spectra of these systems as a function of irradiation dose are shown in Figure 3. The solutions were irradiated in the spectral range of the isosbestic points (Table 1).

The kinetics of the photodecomposition reaction, with excitation in the isosbestic point, can be described by the following differential equation (eq 7).

$$-V\frac{\mathrm{d}C}{\mathrm{d}t} = \Phi(\mathrm{pd})I_{\mathrm{a}}\frac{C}{C_0} \tag{7}$$

where C_0 and C are the concentrations of the parent substance at time zero and t, I_{a} is the intensity of the absorbed light, and V is the solution volume. After integration of eq 7 with the initial condition $C(0) = C_0$, eq 8 is obtained, showing that ln(C) linearly depends on the reduced absorbed radiation dose, $I_{\mathrm{a}}t/VC_0$.

$$\ln\left(\frac{C}{C_0}\right) = -\Phi(\mathrm{pd})\frac{I_{\mathrm{a}}}{VC_0}t \tag{8}$$

The quantum yield, Φ(pd), is then determined as follows. A solution of DMABN in MeCN (0.13 μmol in 4.25 mL, N_2

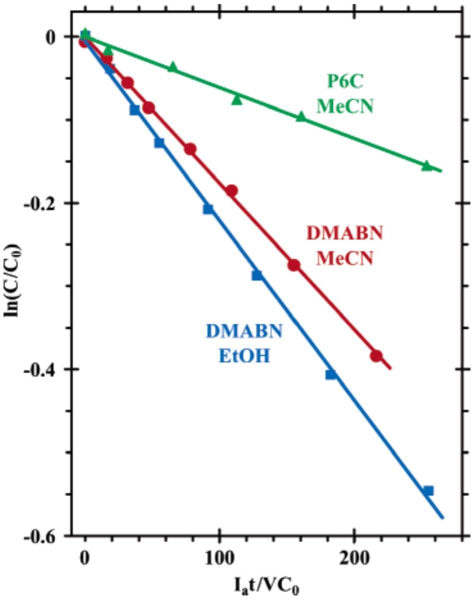


Figure 4. Plot of ln(C/C_0) versus I_at/VC_0 (see eq 8 and text) for P6C in acetonitrile (MeCN) (0.14 μmol), DMABN in MeCN (0.13 μmol), and DMABN in ethanol (EtOH) (0.12 μmol) at 25 °C. The plot shows the dependence of the concentration, C, of the reactant as a function of the accumulated dose of absorbed light, I_at. Irradiation at 285 nm (incident light intensity 4.7 × 10^{15} photons/s) for P6C and at 277 nm (incident light intensity 4.5 × 10^{15} photons/s) for DMABN, close to the isosbestic points (Figure 3 and Table 1). The volume, V, of the solutions is ~4 mL. The straight line is calculated by employing eq 8. The absolute value of its slope is equal to the photodecomposition yield, Φ(pd).

bubbled) was irradiated with 277 nm light. The decomposition of DMABN during the photolysis was determined from the decrease in fluorescence intensity at the maximum of its ICT emission band, where a spectral overlap with the fluorescence spectrum of the photoproduct (MABN) can be neglected; see Figure 1b. Similar photolysis experiments were carried out with DMABN in EtOH and with P6C in MeCN. The decrease in concentration, C, of these molecules as a function of the reduced absorbed radiation, I_at/VC_0, is shown in Figure 4.

It is seen that the experimental data for all three systems are satisfactorily described by eq 8. From the slope of the plots of ln(C/C_0) versus I_at/VC_0 in Figure 4, the quantum yield of photoproduct formation, Φ(pd), can hence be determined. The quantum yields, Φ(pd), and the isosbestic and isoemission points are listed in Table 1. The photodecomposition quantum yield, Φ(pd), increases in the order P6C/MeCN, DMABN/MeCN, and DMABN/EtOH. It follows from these data that P6C in MeCN has a larger photostability than DMABN in MeCN and EtOH. This difference may be caused by the fact that P6C has a heterocyclic amino substituent, preventing the release of an alkyl residue after the initial cleavage of the *N*-alkyl bond, or by increasing the recombination probability of the primary photocleavage product by an "intramolecular" cage effect. DMABN in MeCN is found to be 3 times less photostable than P6C in this solvent. At the present low concentrations (see above), the photostability of DMABN decreases by 30% when going from the aprotic solvent MeCN to the protic solvent EtOH.

Influence of Photoproduct Formation on the Picosecond LE Fluorescence Decays of DMABN in MeCN. As already mentioned in the Introduction, the LE fluorescence decay of DMABN in MeCN is strongly influenced by the formation of the photoproduct MABN;[9,15,16] see Figure 5. In Figure 5a, the double-exponential LE fluorescence decay i_f(LE) is that of a

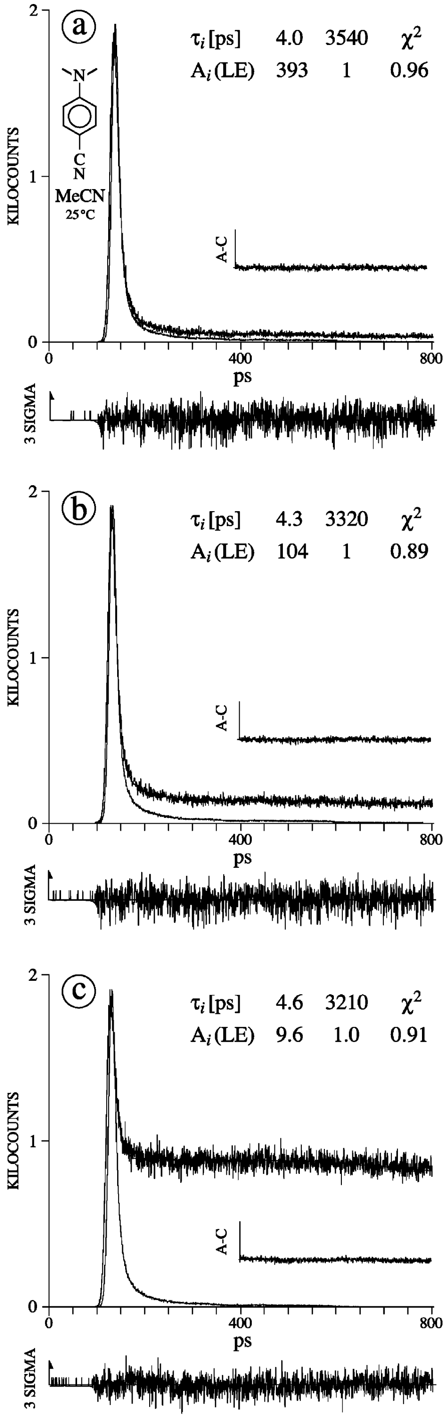


Figure 5. LE fluorescence decay curves of DMABN in acetonitrile (MeCN) at 25 °C, with decay times τ_2 and τ_1 and the corresponding amplitudes A_{1i}(LE) and A_{2i}(ICT); see eqs 9 and 10. The shortest decay time is listed first. The weighted deviations sigma, the autocorrelation functions A−C, and the values for χ^2 are also indicated. The decays are presented for solutions with increasing duration of laser excitation time from part a to part c. In part a, practically no photoproduct is present, whereas the amount of the photoproduct MABN increases from part a to part c; see Table 2. In parts a and b, double-exponential fits are adequate (Scheme 1 and eqs 9 and 10). In part c, a double-exponential fit is shown, although a fit with three exponentials (see Table 2 and ref 9) is of better quality (smaller χ^2). Note the increase of the contribution from the longest decay time as the photoproduct formation proceeds. The kinetic analysis of the decay parameters is presented in Table 2, showing the influence of increasing amounts of MABN on the ICT rate constants. Excitation wavelength, 276 nm; emission wavelength, 350 nm; see Figure 1. Time resolution, 0.496 ps/channel in 2000 channels (1600 shown).

TABLE 2: Effect of the Presence of the Photoproduct MABN on the LE Fluorescence Decay Parameters and Apparent and Optimal Rate Constants for the ICT Reaction of DMABN in MeCN at 25 °C (See Scheme 1 and eqs 9−13)

	τ_2 (ps)	τ_1 (ns)	A	τ_0[a] (ns)	k_a (10^{11} s^{-1})	k_d (10^9 s^{-1})	τ'_0(ICT) (ns)	k_a/k_d	ΔG (kJ/mol)
DMABN[b] (ref 9)	4.0[c]	3.80[c]	516[c]	3.41	2.5	0.48	3.80[d]	516	−15.5
DMABN[e] (Figure 5a)	4.0[c]	3.54[c]	393[c]	3.41	2.5	0.63[f]	3.54[d,f]	393[f]	−14.8[f]
DMABN[g] (Figure 5b)	4.3[c]	3.32[c]	104[c]	3.41	2.3[f]	2.2[f]	3.32[d,f]	104[f]	−11.5[f]
DMABN[h] (Figure 5c)	4.6[c]	3.21[c]	9.6[c]	3.41	2.0[f]	20.5[f]	3.19[f]	9.6[f]	−5.6[f]
	3.6[i]	3.21[i]	12.1[i]	3.41	2.6[f]	21.2[f]	3.20[f]	12.1[f]	−6.2[f]

[a] Fluorescence lifetime of the model compound MABN in MeCN at 25 °C. [b] Optimized values obtained from a simultaneous analysis of photostationary and time-resolved data (ref 9). [c] From double-exponential LE fluorescence decay. [d] Equal to τ_1, due to large value of A. [e] Best experimental conditions obtained for LE decay; see text. [f] Value affected by the presence of the photoproduct MABN. [g] Solution of DMABN after laser excitation, containing MABN as photoproduct; see text. [h] Solution of DMABN after prolonged laser excitation and photoproduct formation; see text. [i] From triple-exponential LE fluorescence decay curve; see text.

fresh solution of DMABN in MeCN at 25 °C, containing only a minor (but nonzero) amount of MABN, the lowest amount we were able to achieve.[9] The amplitude ratio, A, of the shortest decay time, τ_2 (4.0 ps),[9,34,35] relative to that of the longest nanosecond time, τ_1 (eqs 9 and 10), equals 393; see Table 2.[9] This value for A is still somewhat smaller, due to the presence of MABN, than our optimal result (516) obtained from a simultaneous analysis of photostationary and time-resolved data for DMABN in MeCN over a large temperature range (−45 to 75 °C) reported separately.[9]

From Figure 5b, showing an LE decay after longer laser irradiation than in the case of Figure 3a, it is seen that the amplitude ratio, A, has decreased substantially, from 393 to 104. This decrease is again caused by the fluorescence of MABN with a lifetime of 3.41 ns under the same experimental conditions,[9] a time close to the τ_1 decay time (3.54 ns) of DMABN in Figure 5a. A similar influence of photochemical product formation on the fluorescence decay parameters of DMABN in MeCN ($\tau_2 = 6$ ps, $\tau_1 = 3.12$ ns, and $A = 10$)[15,16] was found previously.[15,16,36,37] For the short decay time, τ_2, of DMABN in MeCN, a value of 6 ps has also been reported in the literature.[38−40]

The interference of MABN photoproduct formation leads to an apparent (incorrect) increase of the ICT → LE rate constant, k_d, from 0.5 to 2.2 × 10^9 s^{-1} (Table 2).[9] The effect on the forward ICT rate constant, k_a, is much less severe than that for k_d: an apparent decrease from 2.4 to 2.3 × 10^{11} s^{-1} (eqs 11 and 12, see Table 2).

Upon prolonged laser excitation, a further decrease of the ratio A takes place, to 9.6, as seen from the double-exponential fit of the decay curve in Figure 5c. From the slightly better fit with three exponentials, $A = 12.1$ is found (Table 2). The decay parameters of the decay curve in Figure 5c lead to a considerable apparent increase of k_d (from 0.6 to 20 × 10^9 s^{-1}), whereas k_a undergoes an apparent decrease from 2.4 to 2.0 × 10^{11} s^{-1}, when the results of the double-exponential fit of Figure 5c are employed. Similar data obtained from a triple-exponential fit are also listed in Table 2. The increasing generation of the photoproduct thus causes a strong apparent increase in k_d (factor of 40) and a smaller decrease in k_a (factor of 1.2), with both effects resulting in a substantial reduction of the apparent value for $-\Delta G$: from 15.5 to around 6 kJ/mol; see Table 2.[9]

$$i_f(\mathrm{LE}) = A_{11}\exp(-t/\tau_1) + A_{12}\exp(-t/\tau_2) \qquad (9)$$

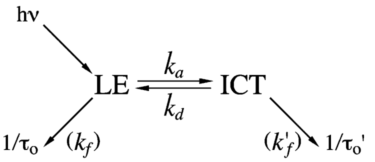
$$A = A_{12}/A_{11} \qquad (10)$$

$$k_a = (1/\tau_1 + A/\tau_2)/(1 + A) - 1/\tau_0 \qquad (11)$$

$$k_d = \{(1/\tau_2 - 1/\tau_1)^2 - (2k_a + 2/\tau_0 - 1/\tau_1 - 1/\tau_2)^2\}/4k_a \qquad (12)$$

$$1/\tau'_0(\mathrm{ICT}) = 1/\tau_1 + 1/\tau_2 - k_a - k_d - 1/\tau_0 \qquad (13)$$

SCHEME 1



In eqs 9−13 and Scheme 1, k_a and k_d are the rate constants of the forward and backward ICT reaction, τ_0(LE) and τ'_0(ICT) are the fluorescence lifetimes, and k_f(LE) and k'_f(ICT) are the radiative rate constants.

Influence on the LE Fluorescence Decay of a DMABN Solution by Adding MABN. The LE fluorescence decay of a solution of DMABN in MeCN to which a small amount of MABN (around 7 mol %) is added is shown in Figure 6. From a comparison with the LE decay in Figure 5a, it is seen that the addition of MABN leads to a substantial decrease of the amplitude ratio, A (eq 10), from 393 to 10.3. The decrease of the ratio A found here is similar to that observed for a photolyzed DMABN solution in MeCN (Figure 5c) in which MABN is the photoproduct.

Picosecond LE Fluorescence Decays of P6C and P5C in MeCN and Photoproduct Formation. The influence of laser excitation on the LE fluorescence decays of P6C in MeCN at 25 °C is shown in Figure 7. The decay in Figure 7a can be fitted with two exponentials, 1.7 ps and 3.19 ns, with an amplitude ratio, A, of 377. For the decay in part b of the solution after prolonged laser excitation, a double-exponential approach no longer leads to an acceptable fit. Three exponentials are needed in this case (c), which reveals that photoproduct formation (see Figure 3b) leads to the appearance of an additional middle decay time of several hundred (283) picoseconds. A similar result is obtained with P5C in MeCN (Figure 8), for which an additional time of 68 ps appears in the LE fluorescence decay after extended photoexcitation. After prolonged laser excitation of solutions of P6C and P5C in MeCN, the fluorescence intensity of the band in the spectral range of the LE emission increases relative to that of the ICT fluorescence; see Supporting Information Figure 2S. This change is attributed to the photoproduct ABN.

From the decay parameters of P6C and P5C, in accordance with Scheme 1, the kinetic parameters of the ICT reaction were again calculated by employing eqs 11−13 (Table 3). It follows from these data that the presence of a photoproduct causes an apparent decrease of k_a and a strong increase of k_d, resulting in a much too low value for $-\Delta G$, similar to what was presented above for DMABN (Table 2). From the LE fluorescence decays of fresh solutions of P6C (Figure 7a) and P5C (Figure 8a) in MeCN at 25 °C, it follows that the LE → ICT rate constant, k_a, is considerably larger for P6C (5.9 × 10^{11} s^{-1}) than for P5C (0.6 × 10^{11} s^{-1}), in accordance with previous treatments.[15,16]

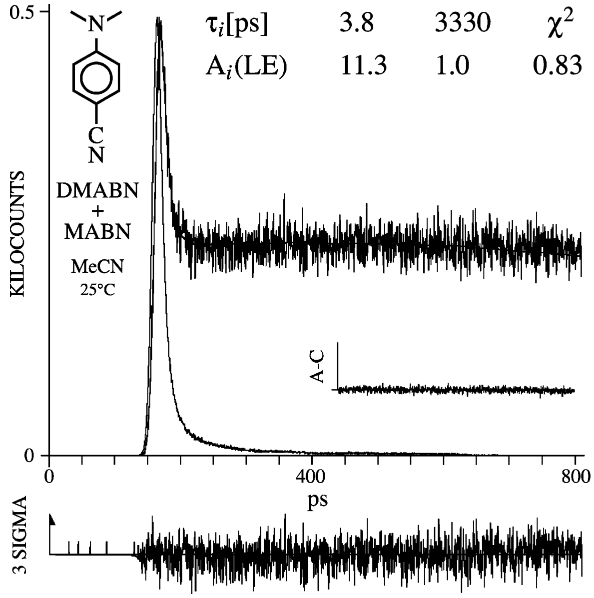


Figure 6. LE fluorescence decay curve of DMABN with added MABN (around 7 mol %) in acetonitrile (MeCN) at 25 °C. The addition of MABN leads to a decrease of the amplitude ratio, A, from 393 (Figure 5a) to 11.3. The intensity ratio of the LE and ICT bands, $I'(\text{ICT})/I(\text{LE})$, in the fluorescence spectrum of this DMABN/MABN mixture is somewhat larger (1.3) than that in the green spectrum of the irradiated DMABN solution in Figure 3a. See caption of Figure 5.

The observed ΔG value for P6C (-14.7 kJ/mol) is larger than that for P5C (-12.8 kJ/mol).

The data presented here clearly show that for P6C as well as P5C the ICT reaction in the aprotic solvent MeCN at room temperature can be correctly described by Scheme 1, as also was found to be the case for DMABN in MeCN as discussed in the previous sections.[9] In other words, there is no experimental evidence for the operation of a barrierless ICT mechanism, leading to multiexponential fluorescence decays, as reported in the literature.[3,41,42]

The multiexponential fluorescence decays observed in protic solvents such as EtOH, besides being due to the presence of photoproducts, are also caused by an overlap of the time ranges of ICT and solvent relaxation.

Conclusion

Upon photoexcitation of DMABN in MeCN, MABN is produced. This photoproduct leads to a large increase of the apparent LE fluorescence in the ICT + LE dual fluorescence spectrum of DMABN in this solvent, due to the spectral similarity of the LE fluorescence spectra of MABN and DMABN. This presence of MABN strongly affects the fluorescence quantum yield ratios $\Phi'(\text{ICT})/\Phi(\text{LE})$ and $\Phi_0(\text{LE})/\Phi(\text{LE})$, both becoming considerably smaller than the photophysically correct values. The MABN photoproduct likewise interferes with the LE fluorescence decays of DMABN in MeCN, influencing the τ_2/τ_1 amplitude ratio, A, in the double-exponential decays. This causes a substantial increase of the apparent value of the ICT → LE rate constant, k_d. Both factors result in a decrease of the apparent value for $-\Delta G$ of the ICT reaction. After extended photoirradiation, a third middle decay time starts to appear in the fluorescence decays.

The negative influence of photoproduct generation on the investigation of the ICT kinetics is not restricted to DMABN. Upon irradiation of P6C in MeCN, ABN could be indentified

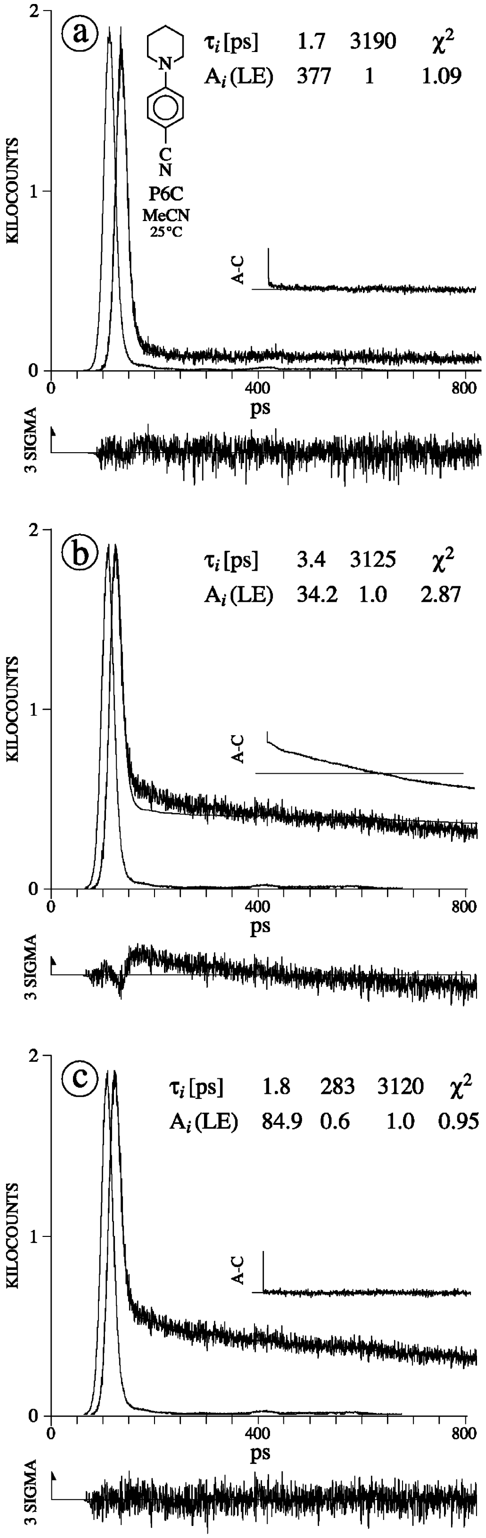


Figure 7. LE fluorescence decay curves of 4-(N-piperidinyl)aminobenzonitrile (P6C) in acetonitrile (MeCN) at 25 °C, showing the effect of laser excitation. The fresh solution in part a is practically free from photoproduct, whereas this product is strongly present in parts b and c, decay curves of a solution after prolonged laser excitation; see Figure 3b. A fit with two exponentials is adequate for the decay curve in part a (eqs 9 and 10), whereas for the decay in parts b and c three exponentials are needed, as is clear from the double-exponential fit of this solution in part b. Note the larger contribution from the longest decay time in parts b and c, showing the effect of photoproduct formation. Excitation wavelength, 298 nm; emission wavelength, 355 nm; see Figure 3b for P6C. Time resolution, 0.513 ps/channel in 2000 channels (1600 shown). See caption of Figure 5.

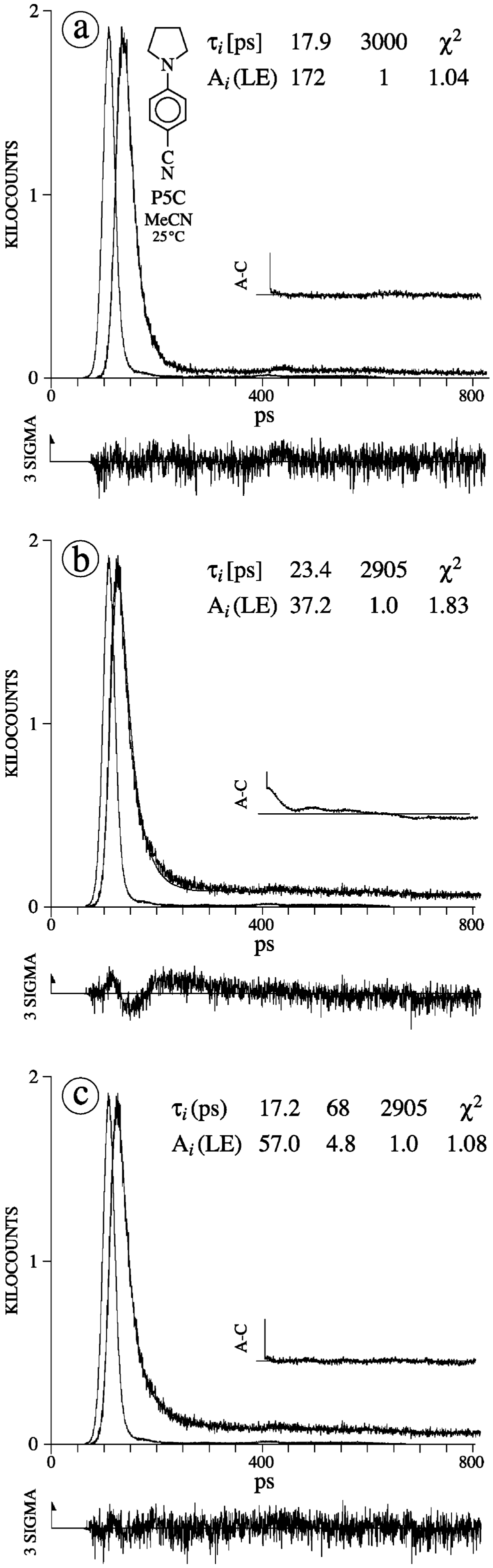


Figure 8. LE fluorescence decay curves of 4-(*N*-pyrrolidinyl)-aminobenzonitrile (P5C) in acetonitrile (MeCN) at 25 °C, showing the effect of laser excitation. In the fresh solution in part a, practically no photoproduct is present, whereas this product is strongly present in parts b and c, decay curves of a solution after prolonged laser excitation; see Figure 7. A fit with two exponentials is adequate for the decay curve in part a (eqs 9 and 10), whereas for the decay curves in parts b and c three exponentials are needed, as is clear from the double-exponential fit of this solution in part b. Note the larger contribution from the longest decay time in parts b and c, showing photoproduct formation. Excitation wavelength, 298 nm; emission wavelength, 350 nm; see Figure 7. Time resolution, 0.513 ps/channel in 2000 channels (1600 shown). See caption of Figure 5.

as the photoproduct. Similarly, PP4C was found in a photolyzed solution of P5C in MeCN. Besides these substances, photolysis of P6C as well as P5C resulted in further photoproducts. The ^{1}H NMR spectra of the chromatography fractions containing these photodegradation products present a complex pattern. In accordance with this finding of complex photoproduct formation, the picosecond fluorescence decays of the MeCN solutions of P6C and also of P5C after photolysis show multiexponential picosecond fluorescence decays. With P6C and P5C in MeCN, an additional decay time in the 100 ps range appears next to the decay times τ_2 (picoseconds) and τ_1 (nanoseconds) of the initially double-exponential LE fluorescence decay of fresh solutions. It is hence concluded that multiexponential LE and ICT fluorescence decays of P6C and P5C in MeCN are caused by photoproducts and can not be considered as an indication that the two-state model (LE and ICT) is not adequate for the ICT mechanism of aminobenzonitriles in aprotic solvents. P6C is more photostable than DMABN, with a photodecomposition quantum yield in MeCN of 0.000 61 as compared with DMABN in MeCN (0.0018) and in EtOH (0.0023). The isosbestic (absorption) and isoemission (fluorescence) points encountered in the spectra of DMABN, P6C, and P5C during photoirradiation indicate that at least one photoproduct is formed.

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Appendix

LE and ICT with One Photoproduct. For the photolysis of a dual fluorescence molecule such as DMABN involving one photoproduct P, with three excited states (LE, ICT, and P*) in the reaction scheme, the total fluorescence intensity, *I*, at wavelength λ_f will depend on the excitation wavelength, λ_{exc}, and on the fraction $x = C/C_0$ (eq 8) of the unreacted starting material S, that is, on the ratio of the concentration at a certain time as compared to that at the start of the photolysis. The intensity, *I*, can then be expressed by eq A1.

$$I = I_{LE} + I_{ICT} + I_P \tag{A1}$$

In general, the fluorescence intensity, *I*, at the wavelength λ_f (eq A2) is the product of the absorbed light intensity, *W*, the normalized fluorescence intensity, $F(\lambda_f)$ (with $\int F(\lambda)\,d\lambda = 1$), and the fluorescence quantum yield, Φ.

$$I = W_S(\Phi(LE)F_{LE} + \Phi'(ICT)F_{ICT}) + W_P\Phi(P)F_P \tag{A2}$$

For the light absorption intensity, W_S, of the starting material S (fraction *x*, with extinction coefficient ϵ_S) and that, W_P, of the photoproduct P (fraction $1 - x$, with extinction coefficient ϵ_P), one has, with the total light absorption intensity

TABLE 3: Effect of Prolonged Photoexcitation of Dilute Solutions in Acetonitrile (MeCN) at 25 °C of 4-(*N*-Piperidinyl)aminobenzonitrile (P6C) and 4-(*N*-Pyrrolidinyl)aminobenzonitrile (P5C) on the LE Fluorescence Decay Parameters and Apparent and Optimal/Real Rate Constants for the ICT Reaction (See Scheme 1 and eqs 9−13)[a]

	τ_2 (ps)	τ_1 (ns)	A	$\tau_0{}^b$ (ns)	k_a (10^{11} s^{-1})	k_d (10^9 s^{-1})	τ'_0(ICT) (ns)	k_a/k_d	ΔG (kJ/mol)
P6C (Figure 7a)	1.7[c]	3.19[c]	377[c,d]	3.41	5.86	1.56	3.19[e]	377	−14.7
P6C (Figure 7b)	3.4[c]	3.13[c]	34[c]	3.41	2.85	8.39	3.12	34	−8.7
P6C (Figure 7c)	1.8[f]	3.13[f]	85[f,g]	3.41	5.49	6.46	3.13[e]	85	−11.0
P5C (Figure 8a)	17.9[c]	3.00[c]	172[c]	3.41	0.55	0.32	3.00[e]	172	−12.8
P5C (Figure 8b)	23.4[c]	2.91[c]	37[c]	3.41	0.41	1.11	2.90[e]	37	−9.0
P5C (Figure 8c)	17.2[f]	2.91[f]	57[f,g]	3.41	0.57	1.00	2.90	57	−10.0

[a] All kinetic data are affected to some extent by photoproduct formation, the influence becoming more serious with increasing irradiation time; see text. [b] Fluorescence lifetime of the model compound MABN in MeCN at 25 °C. [c] From double-exponential LE fluorescence decay. [d] Best experimental conditions obtained for LE decay; see text. [e] Equal to τ_1, due to the large value of *A*. [f] From triple-exponential LE fluorescence decay. [g] Amplitude ratio of the shortest and the longest decay time.

$$W = W_S + W_P$$

$$W_S = Wx\epsilon_S/(\epsilon_S x + \epsilon_P(1 - x)) \qquad (A3)$$

$$W_P = W(1 - x)\epsilon_P/(\epsilon_S x + \epsilon_P(1 - x)) \qquad (A4)$$

It the follows from eqs A2−A4 that

$$I(x) = W\frac{\epsilon_S x(F_{LE}\Phi(LE) + F_{ICT}\Phi'(ICT)) + \epsilon_P(1 - x)F_P\Phi(P)}{\epsilon_S x + \epsilon_P(1 - x)} \qquad (A5)$$

On the basis of eq A5, the conditions for the appearance of an isoemeission point can now be formulated.

Conditions for the Appearance of an Isoemission Point. An isoemission point appears during a photolysis experiment (increasing x) when at a certain wavelength, λ(iem), the fluorescence intensity, I (eq A5), does not depend on the progression of the photodegradation, that is, when $\partial I(x)/\partial x = 0$. This independence of I on x will be treated here for two conditions of W: (a) W does not depend on x (constant W) and (b) W is proportional to the optical density, D.

(a) When W is constant, the requirement $\partial I(x)/\partial x = 0$ defining the isoemission point leads from eq A5 to eq A6.

$$\Phi(LE)F_{LE} + \Phi'(ICT)F_{ICT} = \Phi(P)F_P \qquad (A6)$$

(b) When $W \sim D = (\epsilon_S x + \epsilon_P(1 - x))C_0$, the requirement $\partial I(x)/\partial x = 0$ for eq A5 leads to eq A7.

$$\epsilon_S(\Phi(LE)F_{LE} + \Phi'(ICT)F_{ICT}) = \epsilon_P\Phi(P)F_P \qquad (A7)$$

For excitation in the isosbestic point ($\epsilon_S = \epsilon_P$, see eq 5), eq A6 becomes valid.

Isoemission Points. The necessary condition for the appearance of an isoemission point during photolysis with excitation in the isosbestic point of a dual fluorescent molecule such as DMABN and its photoproduct (MABN) hence is (eq A6) that at λ(iem) the sum of $\Phi(LE)F_{LE}$ and $\Phi'(ICT)F_{ICT}$ is equal to $\Phi(P)F_P$. This means that the isoemission point occurs at the crossing of the fluorescence quantum yield spectra of DMABN and the photoproduct. The product $\Phi F(\lambda)$ defines these spectra, as $\int\Phi F(\lambda)\,d\lambda = \Phi$. When excitation is not carried out at the isosbestic point, a different expression containing the extinction coefficients ϵ_S and ϵ_P holds (eq A7) and the isoemission point will shift to a different wavelength. Note that the product ΦF for an fluorescence spectrum is formally equivalent to the extinction coefficient in an absorption spectrum (eq 5).

Supporting Information Available: Fluorescence and absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) From the expression for $\Phi'(ICT)/\Phi(LE) = k'_f/k_f\{k_a/(k_d + 1/\tau'_0)\}$, see Scheme 1, it follows that the ratio $\Phi'(ICT)/\Phi(LE)$ only will become smaller upon cooling in the temperature range where $k_d \ll 1/\tau'_0$. Under this condition, which prevails for DMABN in MeCN below −5 °C (ref 9), $\Phi'(ICT)/\Phi(LE)$ is mainly governed by the forward ICT rate constant, k_a, as the ICT → LE rate constant, k_d, is already relatively small in the case of DMABN in MeCN at 25 °C (data in Table 2) and decreases more strongly upon cooling than does k_d, due to the larger value of its activation energy E_d as compared to E_a ($E_a - E_d = \Delta H$); see refs 1−7 and 9.

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