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Excited-State Dipole Moments of Dual Fluorescent 4-(Dialkylamino)benzonitriles. Influence of Alkyl Chain Length and Effective Solvent Polarity

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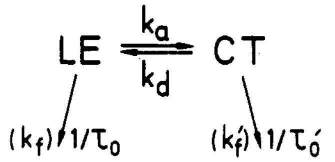
Singlet excited-state dipole moments of a number of aminobenzonitriles have been determined in cyclohexane, benzene, and 1,4-dioxane, using time-resolved microwave conductivity (TRMC) and fluorescence spectroscopy techniques. For the 4-(dialkylamino)benzonitriles (methyl, ethyl, propyl, and decyl) intramolecular charge transfer (ICT) occurs in the excited singlet state even in the nonpolar solvent cyclohexane. The overall dipole moment μ_S increases with the effective solvent polarity and with the length of the alkyl group, from 9.9 D in the case of 4-(dimethylamino)benzonitrile (DMABN) in cyclohexane to 17.2 D for 4-(didecylamino)benzonitrile (DDABN) in 1,4-dioxane. The individual dipole moments of the initially excited state (LE) and the charge transfer state (CT) were determined from the TRMC data using information on the [CT]/[LE] concentration ratio gained from time-correlated single-photon counting measurements in the picosecond time domain. A value of ca. 17 D was obtained for μ_S(CT) and of ca. 10 D for μ_S(LE). These values are to be compared with ground-state dipole moments, which have also been determined, of approximately 6.7 D. For 4-aminobenzonitrile (ABN), 4-(methylamino)benzonitrile (MABN), and 3-(diethylamino)benzonitrile (*m*-DEABN), none of which display evidence for ICT in the fluorescence measurements, μ_S values of 8.3, 9.5, and 10 D independent of solvent are found and are assigned to the LE state alone. Possible mechanisms for the increase in charge separation in the 4-(dialkylamino)benzonitrile series, rotational isomerization and rehybridization of the amino group, are discussed. From long-lived components of the TRMC transients, a triplet-state dipole moment μ_T of 12 D has been estimated for DMABN in both cyclohexane and *p*-dioxane, indicating that ICT does not occur in the triplet state. The singlet–triplet intersystem crossing efficiency Φ_{ISC} of the 4-aminobenzonitriles increases with the length of the *N*-alkyl substituent as well as with the effective solvent polarity.

Introduction

4-(Dimethylamino)benzonitrile (DMABN) and related compounds show dual fluorescence resulting from a reversible intramolecular charge-transfer (ICT) reaction. From the initially excited singlet state (LE), a species (CT) with a considerably larger dipole moment is produced.[1,2]

In Scheme I, k_a and k_d are the rate constants of the forward and backward charge-transfer reactions, respectively. τ_0 (LE) and τ'_0 (CT) are the fluorescence lifetimes. The radiative rate constants k_f (LE) and k'_f (CT) have also been indicated.

SCHEME I



Especially in the case of DMABN, the appearance of a dual fluorescence is well-documented for polar solvents as well as for media of intermediate effective polarity[3,4] such as 1,4-dioxane.[1,2] In benzene, a relatively unpolar ($\epsilon^{25} = 2.27$) but highly polarizable ($n^{25}_D = 1.49$) solvent,[5] a weak CT emission (shoulder) has been detected at room temperature.[1a] In the related solvent toluene, however, a strong dual fluorescence was found at lower temperatures.[6] For 4-(dialkylamino)benzonitriles in nonpolar alkanes, such as cyclohexane, excited-state charge transfer and dual fluorescence are generally considered to be absent.[1,2,7] Nevertheless, indications have been found that a CT reaction with DMABN might even occur in 3-methylpentane or in *n*-heptane.[8–10]

In the discussions concerning the molecular nature of the LE and CT states in systems such as DMABN, the values for the dipole moment of these two fluorescent species have been a point of considerable interest and debate, with a relatively large variation in the reported data.[1,2,11,12] In the original papers on dual fluorescence by Lippert et al.,[1a,b] the excited state dipole moments of DMABN and 4-(diethylamino)benzonitrile (DEABN) were determined by solvatochromic measurements, based on the difference in energy $\Delta\nu$ between the maxima of the LE or CT fluorescence bands and the corresponding absorption maxima, as a function of the polarity and polarizability of the solvent.[13] From these measurements, a value of 23 D was deduced in the case of DMABN for the dipole moment μ_S(CT) of the new anomalous emission, on the basis of a ground-state dipole moment μ_0 of 6.0 D.[1,14]

In this determination of μ_S(CT), it was assumed that the CT state can be populated directly by light absorption.[14] This assumption is a direct consequence of the interpretation initially given by Lippert,[1] that the new "anomalous" CT band is equivalent to the solvent-stabilized ^1L_a band of DMABN. It has, however, been shown[6] that the CT state is not accessible by direct excitation. Under these conditions, μ_S(CT) is determined by plotting the energy of the CT emission maximum $h\nu_c^{max}$ versus the solvent polarity parameter $f - {}^1/_2 f'$.[14] Using this procedure, which is also valid for exciplexes,[15] an excited-state dipole moment of 16.1 D has been obtained from the data of ref 1a.[16]

From the solvent dependence of the directly excited LE band of DMABN in ref 1a, the difference in dipole moments[14] $\Delta\mu = \mu_S(LE) - \mu_0$ is found to be close to zero. For DEABN even a slightly negative value is obtained for $\Delta\mu$. It would therefore appear that for these molecules the dipole moment of the LE state is close to or even slightly smaller than that of the ground state.

This somewhat surprising result could originate from the following difficulty encountered in these solvatochromic measurements. The lowest-energy absorption of DMABN and DEABN consists of two overlapping bands, as was already recognized by Lippert.[1] This makes the determination of the energy difference $\Delta\nu$ between the absorption and fluorescence maxima uncertain.

As a possible improvement on the Lippert–Mataga method,[13] a "simplified microstructural solvent interaction" model was applied to the solvatochromism of intramolecular charge-transfer systems.[17] Using this model, considerably lower values for the excited-state dipole moment μ_S(CT) (12.2 D for DMABN and 11.5 D for DEABN) were found than with the original method.[18,19]

Excited-state dipole moments have also been obtained by measuring the temperature dependence of the LE and CT

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TABLE I: Fluorescence Quantum Yield Ratios Φ′(CT)/Φ(LE), Fractional CT Concentrations *f*(CT), and Fluorescence Decay Times τ_S at 25 °C

	cyclohexane			benzene			1,4-dioxane		
substance[a]	Φ′/Φ	*f*(CT)[b]	τ_S[c] (ns)	Φ′/Φ	*f*(CT)[b]	τ_S[c] (ns)	Φ′/Φ	*f*(CT)[b]	τ_S[c] (ns)
ABN	0.0	0.0	5.3	0.0	0.0	4.0	0.0	0.0	3.3
MABN	0.0	0.0	4.0	0.0	0.0	3.6	0.0	0.0	3.2
DMABN	0.01	0.02	3.2	0.30	0.41	3.1	1.49	0.81	3.8
DEABN	0.16	0.26	2.6	2.48	0.85	2.8	8.52	0.96	3.6
DPrABN	0.28	0.38	2.6	3.75	0.90	2.9	10.4	0.97	3.6
DDABN	0.42	0.47	2.6	3.47	0.89	3.0	9.7	0.97	3.9
m-ABN	0.0	0.0	2.5	0.0	0.0	2.9	0.0	0.0	4.9
m-DEABN	0.0	0.0	4.3	0.0	0.0	12.1	0.0	0.0	14.3

[a] For abbreviations, see text. [b] Fractional CT concentration (eq 23). *f*(CT) is determined from Φ′/Φ, using the following values for the ratio k'_f/k_f (eq 21): 0.45 (cyclohexane), 0.43 (benzene), 0.35 (1,4-dioxane) (see Table III). For DDABN/cyclohexane, DDABN/benzene, and DMABN/1,4-dioxane, *f*(CT) is calculated from the [CT]/[LE] concentration ratios given in Table III. [c] Nanosecond fluorescence decay time. For the 4-(dialkylamino)benzonitriles DMABN, DEABN, DPrABN, and DDABN, this time represents the longest decay time τ_1 in a multiexponental fluorescence decay.[6,9] For the other compounds the value is that for the lifetime τ_0.

fluorescence maxima (thermochromic shift), a method similar in principle to solvatochromism.[20] Here, the variation in polarity (ϵ) and polarizability (n) is brought about by changing the temperature and not by using different solvents. From these measurements, Suppan reported the following values for DMABN: $\mu_S(\text{LE}) = 10$ D and $\mu_S(\text{CT}) = 19.5$ D in tetrahydrofuran and $\mu_S(\text{CT}) = 22$ D in 1-butanol.[20a,21]

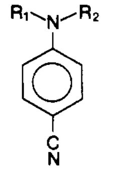
The first more direct measurements of the overall[22] singlet excited-state dipole moment of DMABN were carried out by Czekalla et al.,[23] employing the effect of external electric fields on fluorescence band positions and intensities. These electrochromic fluorescence experiments resulted in a dipole moment of 13 ± 2 D in 1,4-dioxane. Similarly, a value of 12.5 D was derived by Labhart from electrochromic absorption measurements.[24,25] Using the related integral electrooptical emission measurements, Baumann arrived at $\mu_S(\text{LE}) = 5.8$ D in cyclohexane and $\mu_S(\text{CT}) = 16.5$ D in 1,4-dioxane, the last value being an upper limit for the permanent dipole moment, when the specific influence of solvent polarizability[11] is neglected.[12]

More recently, excited-state dipole moments have been determined in nondipolar solvents by the time-resolved microwave conductivity (TRMC) technique.[19,26] A dipole moment of ca. 13 D has been reported using this technique for the excited singlet state of DMABN in benzene and 1,4-dioxane.[26c]

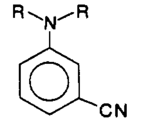
In the present paper the excited-state dipole moments measured by the TRMC technique for a series of 4-(dialkylamino)benzonitriles with different alkyl groups (methyl, ethyl, propyl, and decyl) are reported. Three solvents have been used of different effective polarity or solvating power as represented by their permittivities ϵ or $E_T(30)$ values: cyclohexane ($\epsilon^{25} = 2.02$), benzene ($\epsilon^{25} = 2.27$), and 1,4-dioxane ($\epsilon^{25} = 2.21$; $\epsilon_{\text{eff}} = 7$).[3,5] Using this series of solute/solvent systems, the separate dipole moments of the LE and CT states could be determined, by combining the TRMC data with results from steady-state and time-resolved fluorescence measurements. In addition, 4-aminobenzonitrile (ABN) and 4-(methylamino)benzonitrile (MABN) and also two meta-substituted aminobenzonitriles, 3-aminobenzonitrile (*m*-ABN) and 3-(diethylamino)benzonitrile (*m*-DEABN), all of which do not undergo intramolecular charge transfer (see below), were investigated for comparative purposes. Ground-state dipole moments and dipole relaxation times, which are necessary for the data analysis, have also been measured.

Experimental Section

Solutes and Solvents. The following compounds were obtained commercially: 4-aminobenzonitrile (ABN) from Fluka; DMABN and *m*-ABN from Aldrich and DEABN from K&K. 4-(Methylamino)benzonitrile (MABN) and 4-(ethylamino)benzonitrile (EABN) were synthesized as described before.[6] The other *m*- and *p*-(dialkylamino)benzonitriles, 4-(di-*n*-propylamino)benzonitrile (DPrABN), 4-(di-*n*-decylamino)benzonitrile (DDABN), and 3-(diethylamino)benzonitrile (*m*-DEABN), were made by alkylation of the corresponding aminobenzonitrile with alkyl iodide in anhydrous methanol containing anhydrous sodium carbonate. After boiling the mixture for 12 h, the solvent was evaporated and the residue was heated (220 °C) at 15 Torr for 3.5 h. The resulting (dialkylamino)benzonitrile was extracted with diethyl ether and separated from the monoalkyl derivative by column chromatography. The following melting points were found: 33.4 °C (DDABN) and 52.8 °C (*m*-DEABN). The other newly synthesized substances were not crystalline. All compounds used in the fluorescence measurements were purified by HPLC. The solvents cyclohexane (Aldrich; Gold Label), benzene (Fluka; "for UV spectroscopy"), and 1,4-dioxane (Merck; Uvasol) were purified by chromatography. The solutions in the fluorescence experiments were degassed by employing the freeze–pump–thaw method. Solute concentrations were approximately 3×10^{-5} M (fluorescence). In the TRMC measurements, the optical density at the excitation wavelength of 308 nm was approximately 1.0 (ca. 1×10^{-4} M). These solutions were bubbled with dry CO_2 to remove oxygen and to quench any spurious TRMC transients which might result from mobile electrons formed in low yield photoionization events.



4 - AMINOBENZONITRILES



3 - AMINOBENZONITRILES

Fluorescence Experiments. The fluorescence spectra were measured using a quantum-corrected Perkin-Elmer MPF-44E spectrophotometer. Fluorescence quantum yields were determined using quinine sulfate in 1.0 N H_2SO_4 as a standard (Φ = 0.546 at 25 °C).[27] The nanosecond time-resolved single-photon counting (SPC) measurements listed in Table I were carried out with an apparatus described previously.[28] The decay times were determined at the maximum of the LE fluorescence band. The picosecond laser data were obtained employing a laser system consisting of an argon ion laser (Coherent, Innova 100-10), a dye laser (Coherent 702-1CD; Rhodamine 6G), and a frequency doubler (KDP, 296 nm).[6] The fluorescence and scatter records were detected with a Hamamatsu R2809U-07 MCP photomultiplier (-3300 V). The instrument response function has a width of 30–40 ps at the excitation wavelength. The analysis of the fluorescence decays was carried out using modulating functions, extended by global analysis.[29,30]

Ground-State Dipole Moments. The ground-state dipole moments μ_0 (see Table IV, below), used in the evaluation of the TRMC data, were determined in 1,4-dioxane at 25 °C from measurements of the dielectric constant, the refractive index, and the density of solutions at five or six solute mole fractions, extrapolated to zero solute concentration. This method is based on that of Hedestrand,[31] restricted to a single temperature. The 1,4-dioxane was dried over molecular sieves. The value $\mu_0 = 6.6$ D obtained for DMABN (see Table IV, below) is similar to the literature values.[32-34]

TRMC Technique. The TRMC technique used for the determination of the excited-state dipole moments, including the design of the microwave cell and circuitry, has been described in detail previously.[19] In brief, a solution of the molecule of interest was photoexcited by a 308-nm (XeCl) pulse of ca. 7-ns fwhm from a Lumonics Hyper EX-400 excimer laser. The pulse shape was determined with a subnanosecond time response photodiode, the output of which was digitalized with a Tektronix 7912 transient digitizer. The light intensity of the pulse was monitored regularly during the course of the measurements using a Scientech 365 power meter. The transient change in microwave conductivity of the solution was measured at the resonant frequency of the cell, approximately 10 GHz. The detection response time is controlled mainly by the quality of the microwave cavity and was 5–6 ns. The change in output of the microwave detector diode which was used to monitor the power reflected by the cavity was fed to the digitizer, and up to 64 traces from single pulses were averaged. In the present measurements, the cavity characteristics from which the sensitivity factor is determined were monitored immediately prior to the TRMC measurements. The change in the conductivity within the solution can be directly derived from the transient change in power reflected by the cell.[19]

A benzene solution of 4-(dimethylamino)-4′-nitrostilbene (DANS), with an optical density of ca. 1.0, was used as an internal actinometer. The TRMC transient for this solution was subjected to the same fitting procedure[19] as that used for the compounds of interest, but fixed fitting parameters based on prior measurements[35] were employed. The light intensity incident on the solution within the cell determined in this manner was approximately 7 mJ/cm^2 per pulse. It was reproducible within a few percent from pulse to pulse and remained reasonably constant during the course of the measurements.

The concentrations of the singlet and triplet states present at a given time after laser excitation were calculated by numerical integration of the differential rate equations for these states. This method, including convolution over the laser pulse and the known time response of the microwave cavity together with averaging over the concentration distribution within the cavity, has been described elsewhere.[19]

TRMC Data Analysis. The property of primary interest in TRMC measurements is the high-frequency conductivity $\sigma(\omega)$, which is related to the dielectric loss by $\epsilon'' = \sigma(\omega)/\omega\epsilon_0$, where ϵ_0 is the vacuum permittivity and ω is the radian microwave frequency ($\omega = 2\pi f$ with f being the frequency in hertz). The conductivity resulting from a small concentration of a dipolar solute in a nonpolar solvent is related to the solute concentration N and its dipole moment μ (eq 1).[36]

$$\sigma(\omega) = (\epsilon' + 2)^2\mu^2 N F(\omega\tau_D)/27k_BT\tau_D \tag{1}$$

In eq 1, ϵ' is the relative dielectric constant of the medium, τ_D is the dipole relaxation time, k_B is the Boltzmann constant, and T is the absolute temperature. $F(\omega\tau_D)$[37] is the Debye dispersion term, which, for solutes with a single dipole relaxation time,[38] is given by

$$F(\omega\tau_D) = (\omega\tau_D)^2/[1 + (\omega\tau_D)^2] \tag{2}$$

The conductivity $\sigma(\omega)_0$ in the ground state can be written in the form of eq 3, where e is the elementary charge and M is the previously defined[19] rotational charge mobility. The parameter M_0, for molecules in the ground state, is given by eq 4. M_0 can

$$\sigma(\omega)_0 = eN_0M_0 \tag{3}$$

$$M_0 = (\epsilon' + 2)^2\mu_0^2F(\omega\tau_D)/27ek_BT\tau_D \tag{4}$$

be determined by measuring the increase in conductivity $\sigma(\omega)_0$ with increasing solute concentration N_0 (eqs 3 and 4), in the absence of laser excitation. The values of M_0 which have been measured for the present solute/solvent combinations are given in Table IV. Knowing M_0 and μ_0, the dipole relaxation time can be calculated using eqs 2 and 4. The values of τ_D determined in this way are also listed in Table IV.

When a solute is photoexcited, a change in the microwave conductivity of the solution $\Delta\sigma(\omega)_*$ will occur if an excited state (or other photoproduct) is formed with a dipole moment different from that of the ground-state molecule. This change in $\sigma(\omega)$ is given by eq 5, where N_* is the (transient) concentration and M_*,

$$\Delta\sigma(\omega)_* = eN_*(M_* - M_0) - eN_*\Delta M_* \tag{5}$$

the rotational charge mobility of the photoexcitation product, is given by an expression similar to eq 4 with a dipole moment μ_*.

When dipolar singlet and triplet states are formed, as in the present case, one obtains

$$\Delta\sigma(\omega)_* = e\{N_S\Delta M_S + N_T\Delta M_T\} \tag{6}$$

The difference in the rotational charge mobility of a solute in the singlet (ΔM_S) or triplet (ΔM_T) excited state and in the ground state is given by

$$\Delta M_* = M_* - M_0 = (\epsilon' + 2)^2({\mu_*}^2 - {\mu_0}^2)F(\omega\tau_D)/27ek_BT\tau_D \tag{7}$$

assuming the rotational relaxation time τ_D to be the same for the two states. Therefore, from eqs 4 and 7

$$\Delta M_*/M_0 = ({\mu_*}^2 - {\mu_0}^2)/{\mu_0}^2 \tag{8}$$

This leads, on rearrangement, to an expression for μ_*, valid for both μ_S and μ_T, the dipole moments of the excited singlet and triplet states.

$$\mu_* = \mu_0(\Delta M_*/M_0 + 1)^{0.5} \tag{9}$$

In conclusion, if the value of μ_0 is known, μ_* can be calculated from ΔM_* and M_0 via eq 9.

Results and Discussion

Fluorescence Spectra and Intramolecular Charge Transfer. Information on the occurrence of a CT reaction in the aminobenzonitriles can be obtained from an inspection of their fluorescence spectra. When a CT reaction takes place, a new ("anomalous") emission band appears, red-shifted with respect to the LE emission.[1,2] This process often leads to a reduction in the overall fluorescence quantum yield of the system, which can be used as additional evidence for ICT.

The fluorescence spectra of the 4-(dialkylamino)benzonitriles DMABN, DEABN, DPrABN, and DDABN in the solvents cyclohexane, benzene, and 1,4-dioxane at 25 °C are presented in Figure 1. All spectra exhibit a red-shifted band (CT), next to the emission from the LE state (Table I). In the case of cyclohexane, the CT band is apparent as a broadening of the emission spectrum without a distinct maximum as observed for the other solvents. The dotted spectra in Figure 1 are those for MABN, which shows no evidence of CT formation. Further photostationary and time-resolved fluorescence measurements of these systems will be presented separately.[39]

It can be seen from the spectra in Figure 1, and also from the CT/LE fluorescence quantum yield ratio $\Phi'(\mathrm{CT})/\Phi(\mathrm{LE})$ in Table I, that the relative intensity of the CT band increases in the order cyclohexane, benzene, 1,4-dioxane. This effect is due to the increase in the effective solvation and hence stabilization of the CT state exerted by the solvent, as expressed, for example, by the solvent polarity parameter $f - {}^1/{}_2f'$ or alternatively $E_T(30)$.[3,14,40,41] The increasing effective polarity in the present solvent series is apparent as a decrease in the energy maximum $h\nu_c^{\max}$ of the CT band, from 26 000 cm^{-1} for DEABN/cyclohexane to 23 200 cm^{-1} for DDABN/1,4-dioxane (Table II).[3]

Furthermore, somewhat unexpectedly, the CT/LE fluorescence intensity ratio of the 4-(dialkylamino)benzonitriles also strongly increases in each of the three solvents with increasing length of the alkyl substituents, from DMABN to DDABN (Figure 1). This is even the case in cyclohexane, for which, as mentioned above, clear evidence for intramolecular charge transfer in 4-(dialkylamino)benzonitriles has not previously been reported.

In contrast, there is no evidence for a CT reaction for ABN and MABN, as well as for *m*-ABN and *m*-DEABN, in any of the three solvents, i.e., $\Phi'/\Phi = 0.0$ (Table I).[6,9] This follows from the fluorescence spectra as well as from time-resolved (picosecond) SPC measurements as a function of temperature.[39] The fluorescence spectra of these molecules (see dotted spectra in

TABLE II: Fluorescence Quantum Yields Φ(LE) and Φ'(CT) and Emission Maxima $h\nu_c^{max}$ of CT State for Aminobenzonitriles

	cyclohexane			benzene			1,4-dioxane		
substance[a]	Φ(LE)	Φ'(CT)	$h\nu_c^{max}$ [b]	Φ(LE)	Φ'(CT)	$h\nu_c^{max}$ [b]	Φ(LE)	Φ'(CT)	$h\nu_c^{max}$ [b]
ABN	0.15	0.0		0.15	0.0		0.13	0.0	
MABN	0.16	0.0		0.18	0.0		0.15	0.0	
EABN	0.17	0.0							
DMABN	0.122	0.001	(26)[c]	0.081	0.024	24	0.022	0.033	22.7
DEABN	0.076	0.012	26	0.013	0.032	24.2	0.007	0.059	22.9
DPrABN	0.073	0.020	26.2	0.011	0.042	24.3	0.005	0.047	23.2
DDABN	0.062	0.026	26.2	0.014	0.049	24.3	0.005	0.052	23.2
m-ABN	0.10	0.0		0.12	0.0		0.18	0.0	
m-DEABN	0.12	0.0		0.31	0.0		0.35	0.0	

[a] For abbreviations, see text. [b] In 1000 cm^{-1}. [c] Accuracy limited by the small value of Φ'/Φ.

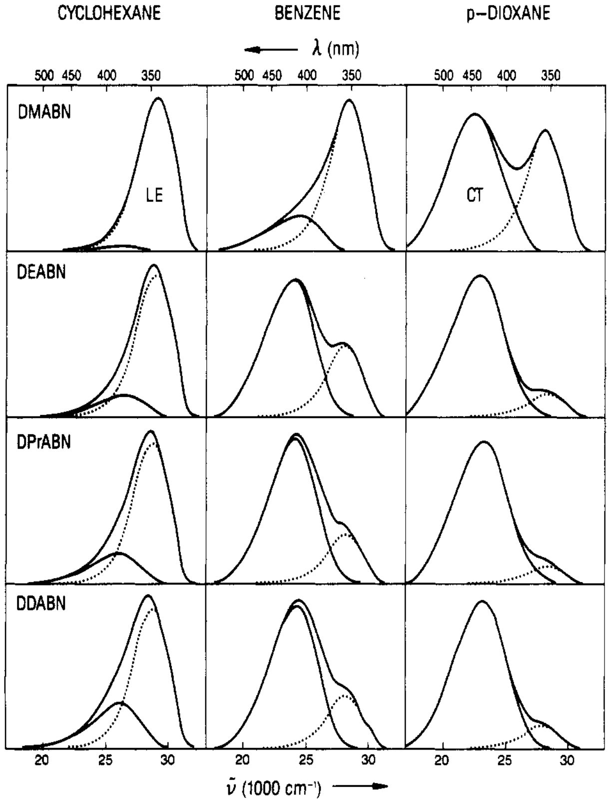


Figure 1. Fluorescence spectra of the 4-(dialkylamino)benzonitriles DMABN (methyl), DEABN (ethyl), DPrABN (*n*-propyl), and DDABN (*n*-decyl) at 25 °C in cyclohexane, benzene, and 1,4-dioxane. The two emission bands CT and LE (see text (Scheme I)) were separated by taking the fluorescence spectrum of 4-(methylamino)benzonitrile (MABN) to be representative of the LE state alone.

Figure 1) are similar in shape to those of unsubstituted anilines such as *N,N*-dimethylaniline.[42] In addition, the fluorescence quantum yields of ABN, MABN, EABN, *m*-ABN, and *m*-DEABN, contrary to those of the 4-(dialkylamino)benzonitriles, do not give any indication that a quenching process has set in (Table II). This conclusion is supported by the observation that even in strongly polar solvents such as acetonitrile or methanol a CT emission does not occur for ABN, MABN, *m*-ABN, or *m*-DEABN, down to temperatures close to the melting point of the solvent.[39] This means that only the LE state is formed upon excitation in the case of ABN and the other three compounds; i.e., the excited-state dipole moment determined by TRMC (see below) or otherwise is that of the pure LE state.

Equilibrium Conditions for LE and CT States. In the measurements of the excited-state dipole moments by the time-resolved microwave conductivity (TRMC) technique, the resulting overall dipole moment is composed of contributions from all dipolar species present in solution.[22] In addition to the singlet-state species LE and CT (Scheme I), molecules in the triplet state have to be taken into account (see eq 6). Their contribution can be separated from that of the singlet states due to the much longer lifetime of the triplet species. This will be treated in a later section (see Figure 4).

If the equilibrium between the two species LE and CT in the excited singlet state is established on a time scale considerably shorter than the several nanoseconds time response of the TRMC detection system, but longer than the 15-ps radian revolution time of the microwaves, then the equilibrium concentrations of LE and CT may be taken to contribute independently to the overall microwave conductivity.

In this section, the time scale on which the equilibrium between the LE and CT states of the (dialkylamino)benzonitriles is established at room temperature (25 °C) will be discussed. This will be investigated in detail for DMABN in 1,4-dioxane. Similar conditions are found to prevail for DMABN in toluene and diethyl ether as well as for DDABN in cyclohexane, benzene, and toluene,[6,9,39] and by analogy also for the other 4-(dialkylamino)benzonitriles studied here.

The equilibrium between LE and CT is established when the concentration ratio [CT]/[LE], see eqs 10 and 11, has become independent of time, i.e., when both excited-state species decay with the same decay time.[43]

For the time dependence of [LE] and [CT] the following equations hold

$$[\mathrm{LE}](t) = A_{11}e^{-t/\tau_1} + A_{12}e^{-t/\tau_2} \tag{10}$$

$$[\mathrm{CT}](t) = A_{21}e^{-t/\tau_1} - A_{22}e^{-t/\tau_2} \tag{11}$$

with the decay times τ_i (i = 1,2) and the amplitudes A_{ij} given in eqs 10 and 11.

$$1/\tau_{1,2} = \tfrac{1}{2}\{(X + Y) \mp [(X - Y)^2 + 4k_a k_d]^{1/2}\} \tag{12}$$

with

$$X = k_a + 1/\tau_0 \tag{13}$$

$$Y = k_d + 1/\tau_0 \tag{14}$$

$$A_{11} = (1/\tau_2 - X)[\mathrm{LE}]_0/(1/\tau_2 - 1/\tau_1) \tag{15}$$

$$A_{12} = (X - 1/\tau_1)[\mathrm{LE}]_0/(1/\tau_2 - 1/\tau_1) \tag{16}$$

$$A_{21} = -A_{22} = k_a[\mathrm{LE}]_0/(1/\tau_2 - 1/\tau_1) \tag{17}$$

$[\mathrm{LE}]_0$ in eqs 15–17 is the concentration of LE at the moment of excitation (t = 0). An expression for $[\mathrm{CT}](t)/[\mathrm{LE}](t)$ can now be derived from eqs 12–17:

$$\frac{[\mathrm{CT}](t)}{[\mathrm{LE}](t)} = \frac{k_a(e^{-t/\tau_1} - e^{-t/\tau_2})}{(1/\tau_2 - X)e^{-t/\tau_1} + (X - 1/\tau_1)e^{-t/\tau_2}} \tag{18}$$

At long times ($t \rightarrow \infty$), as $\tau_1 > \tau_2$ (eq 12):

$$[\mathrm{CT}]/[\mathrm{LE}] = k_a/(1/\tau_2 - X) \tag{19}$$

For DMABN in 1,4-dioxane at 25 °C, the values for τ_1, τ_2, k_a, and X (eq 18) have been determined from the LE and CT fluorescence decays in a global analysis (Figure 2). These fluorescence decays $i(t)$ are directly related to the concentrations (eqs 10 and 11): $i_{\mathrm{LE}}(t) = k_f[\mathrm{LE}](t)$ and $i_{\mathrm{CT}}(t) = k'_f[\mathrm{CT}](t)$.

Using these data, the ratio [CT]/[LE] can be obtained as a function of time (eq 18). This time dependence is depicted in

TABLE III: Ratio of CT-to-LE Radiative Rates k'_f/k_f (Scheme I) and Data Derived from Fluorescence Decays for (Dialkylamino)benzonitriles at 25 °C

solvent	solute[a]	τ_1 (ns)	τ_2 (ps)	A[b]	τ_0[c] (ns)	k_a[d] (10^9 s^{-1})	k_d[d] (10^9 s^{-1})	$1/\tau'_0$[d] (10^9 s^{-1})	[CT]/[LE][e]	Φ'/Φ[f]	k'_f/k_f
cyclohexane	DDABN	2.60	35	0.90	4.4	13.5	14.7	0.56	0.9	0.4[g]	0.45
benzene	DDABN	2.99	31	8.82	3.6	28.8	3.3	0.34	7.9	3.47	0.43
1,4-dioxane	DMABN	3.88	25	4.37	3.9	32.3	7.4	0.26	4.2	1.49	0.35
toluene[h]	DMABN					16.8	27.8	0.40	0.60	0.25[g]	0.42
toluene[h]	DDABN					28.6	3.2	0.35	8.06	3.31	0.41
diethyl ether[h]	DMABN					26.0	24.0	0.47	1.06	0.44	0.41

[a] DDABN: 4-(didecylamino)benzonitrile. DMABN: 4-(dimethylamino)benzonitrile. [b] $A = A_{12}/A_{11}$ (eqs 6 and 7). [c] Lifetime of 4-(methylamino)benzonitrile (MABN) in *n*-heptane (used for cyclohexane), in toluene (for benzene) and in diethyl ether (for 1,4-dioxane). A variation of 10% in τ_0 does not affect the value of [CT]/[LE]. [d] See Scheme I in text. [e] See eq 20. With the 4-(dialkylamino)benzonitriles, [CT]/[LE] $\simeq A$.[46] [f] From Table I. [g] The accuracy of Φ'/Φ is limited by the relatively small spectral separation between the CT and LE fluorescence bands (cyclohexane) and by the low value of Φ'/Φ (toluene). The separation between the CT and LE bands is smaller in cyclohexane than in the solvents benzene and 1,4-dioxane due to the larger effective polarity of the latter solvents (see ref 3 and text). [h] Rate parameters k_a, k_d, and $1/\tau'_0$, extrapolated from lower temperatures[6,9] (see text).

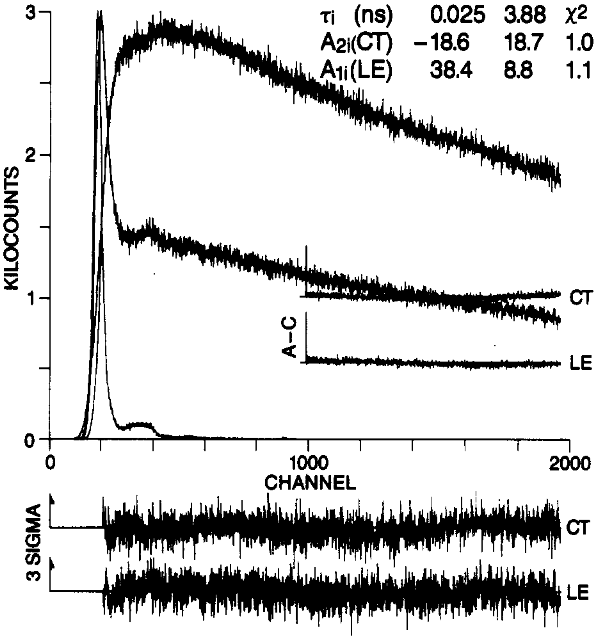


Figure 2. Initially excited (LE, at 328 nm) and charge-transfer (CT, at 480 nm) fluorescence response functions of 4-(dimethylamino)benzonitrile (DMABN) in 1,4-dioxane at 25 °C (see Figure 1). The LE and CT decays are analyzed simultaneously (global analysis). The decays were obtained using picosecond laser excitation (295 nm) in 1800 effective channels with 1.242 ps/channel. The decay times (τ_1, τ_2) and their preexponential factors A_{1i} (LE) and A_{2i} (CT) are given (see eqs 10 and 11). The time τ_2 is listed first. The weighted deviations, expressed in σ (expected deviations), the autocorrelation functions A–C, and the values for χ^2 are also indicated.

Figure 3. It is seen that 160 ps after excitation, [CT]/[LE] has reached 99% of its long-time ($t = \infty$) value. In the case of DMABN, with $\tau_2 \ll \tau_1$ (Figure 2 and ref 9), this long-time value is equal to the expression for [CT]/[LE] valid under photostationary conditions (eq 20).[44] A similar time dependence of

$$[\mathrm{CT}]/[\mathrm{LE}] = k_a/(k_d + 1/\tau'_0) \tag{20}$$

[CT]/[LE] is found for DMABN in toluene at 25 °C (99% of the long-time limit is reached at 100 ps), using values for τ_1, τ_2, k_a, and X (eq 18) extrapolated[45] from data determined between −50 and −94 °C,[6] and likewise for the other 4-(dialkylamino)benzonitriles in the three solvents employed here.

Concentration Ratio of CT and LE. In the analysis of the TRMC measurements to be presented below, the equilibrium concentration ratio [CT]/[LE] is needed to separate the contributions of the CT and LE states (Scheme I) to the overall dipole moment. This concentration ratio can either be evaluated directly (eq 20) from the rate constants k_a and k_d and the CT lifetime τ'_0, calculated from the time-resolved data, or from the fluorescence quantum yield ratio $\Phi'(\mathrm{CT})/\Phi(\mathrm{LE})$ when k'_f/k_f, the ratio of the radiative rates for the CT and LE emissions, is known (eq 21).

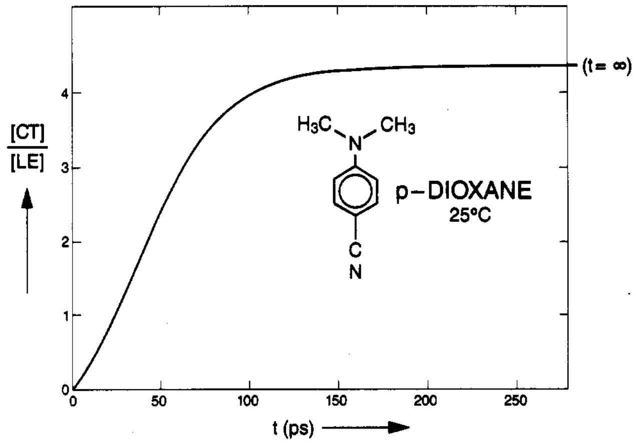


Figure 3. Time dependence of the concentration ratio [CT]/[LE] for 4-(dimethylamino)benzonitrile (DMABN) in 1,4-dioxane at 25 °C. The ratio [CT]/[LE] was determined from the fluorescence decays depicted in Figure 2, using eq 18 (see text).

$$\frac{\Phi'(\mathrm{CT})}{\Phi(\mathrm{LE})} = \frac{k'_f}{k_f}\frac{[\mathrm{CT}]}{[\mathrm{LE}]} = \frac{k'_f}{k_f}\frac{k_a}{(k_d + 1/\tau'_0)} \tag{21}$$

[CT]/[LE] from Fluorescence Decays. The concentration ratio [CT]/[LE] was obtained directly from the fluorescence decays of DMABN in 1,4-dioxane at 25 °C (Figure 2). The decay times τ_1 = 3.88 ns and τ_2 = 25 ps and their amplitude ratio (eqs 15 and 16) $A = A_{12}/A_{11}$ = 4.37 were determined by global analysis of the two decays $i_{LE}(t)$ and $i_{CT}(t)$, measured at wavelengths where either only the LE (328 nm) or the CT (480 nm) state emits. From these data one calculates[6,43] $k_a = 32.3 \times 10^9$ s^{-1}, $k_d = 7.4 \times 10^9$ s^{-1}, and $1/\tau'_0 = 0.26 \times 10^9$ s^{-1}, resulting (eq 20) in a value of 4.2 for [CT]/[LE] (see Table III).

In cyclohexane and benzene at 25 °C, the ratio [CT]/[LE] could not be obtained with sufficient precision from time-resolved measurements with DMABN, due to the fact that the ratio Φ'/Φ, and consequently [CT]/[LE] (eq 20), is relatively small in these solvents (see Figure 1 and Table I). This leads to a small value for the amplitude ratio $A = A_{12}/A_{11}$, as $A \simeq$ [CT]/[LE],[46] which limits the accuracy of the determination of the shortest decay time τ_2 next to τ_1. The measurements in cyclohexane and benzene can, however, be carried out with DDABN, which has larger values for Φ'/Φ than DMABN (Figure 1 and Table I). With DDABN in cyclohexane at 25 °C, a ratio [CT]/[LE] = 0.9 results, whereas in benzene a value of 8.0 is found, see Table III, using (eq 20) the data for k_a, k_d, and $1/\tau'_0$ listed there.[39,46]

[CT]/[LE] from Fluorescence Quantum Yields. Influence of k'_f/k_f. With the [CT]/[LE] data presented in the previous section, the ratio of radiative rates k'_f/k_f can be determined (eq 21) from the fluorescence quantum yield ratio Φ'/Φ. From [CT]/[LE] = 4.2 for DMABN in 1,4-dioxane and Φ'/Φ = 1.49 (Table I), k'_f/k_f

TABLE IV: Dipole Moments of Overall Excited Singlet State μ_S and CT State μ_S(CT) from Time-Resolved Microwave Conductivity (TRMC) Measurements at Room Temperature

solvent	solute[a]	M_0^{meas}[b] (10^{-9})	τ_D[c] (ps)	M_0^{calc}[d] (10^{-9})	ΔM_S[e] (10^{-9})	μ_S/μ_0[f,g]	μ_0[g] (D)	μ_S[h] (D)	μ_S(CT)[i] (D)
cyclohexane	ABN	8.48	47	7.62	4.12	1.21	(6.6)	8.0	
	MABN	7.41	56	7.46	7.37	1.41	(6.6)	9.3	
	DMABN	7.54	55	7.26	9.51	1.50	(6.6)	9.9	(17)[j]
	DEABN	5.75	77	5.80	13.2	1.82	(6.7)	12.2	17.5
	DPrABN			4.08	12.5	2.01	(6.7)	13.5	18.1
	DDABN			2.23	9.3	2.27	(6.7)	15.2	19.6
	m-ABN	5.98	42	5.98	*k*	*k*	(5.3)	7–10[k]	
	m-DEABN	4.57	64	5.17	11.9	1.89	(5.5)	10.4	
benzene	ABN	9.68	46		6.4	1.29	(6.6)	8.5	
	MABN	9.49	47		8.8	1.39	(6.6)	9.2	
	DMABN	9.26	49		22.6	1.85	(6.6)	12.2	15.1
	DEABN	7.52	65		28.5	2.19	6.7[l]	14.7	15.4
	DPrABN	5.35	95		23.6	2.33	(6.7)	15.6	16.1
	DDABN	2.94	175		12.2	2.27	(6.7)	15.2	15.7
	m-ABN	7.42	36		*k*	*k*	(5.3)	7–10[k]	
	m-DEABN	6.58	47		11.3	1.65	(5.5)	9.1	
1,4-dioxane	ABN			4.84	2.8	1.26	6.6	8.3	
	MABN			4.73	5.9	1.50	6.6	9.9	
	DMABN	4.57	102	4.57	19.1	2.29	6.6	15.1	16.1
	DEABN			3.59	19.4	2.55	6.7	17.1	17.3
	DPrABN			2.48	13.7	2.57	(6.7)[m]	17.2	17.4
	DDABN			1.34	7.5	2.57	6.7	17.2	17.4
	m-ABN			3.92	*k*	*k*	5.3	7–10[k]	
	m-DEABN			3.28	8.1	1.87	5.5	10.3	

[a] For abbreviations, see text. [b] Measured rotational charge mobility in the ground state (m^2/Vs). [c] Rotational relaxation time in the ground state, calculated from M_0 and μ_0 (eq 3) (see ref 19). [d] Calculated rotational charge mobility in the ground state (m^2/Vs) (see text). [e] The change in rotational charge mobility on excited singlet formation (eq 7). [f] Calculated (eq 9) from ΔM_S and M_0. [g] Ground-state dipole moment μ_0 determined in 1,4-dioxane at 25 °C (see Experimental Section). The dioxane data were also used for cyclohexane and benzene (values in parentheses). [h] For error limits see ref 50. [i] Calculated using eq 26 from μ_S and the fractional CT concentration f(CT) (eq 23) with μ_S(LE) = 9.7 D (see text). [j] Using this value for μ_S(CT), μ_S(LE) = 9.7 D is obtained from μ_S (eq 25) (see text). [k] Due to large triplet component in TRMC curve (see text) only lower and upper limits of 7 and 10 D could be estimated for *m*-ABN. [l] For DEABN in benzene at 25 °C a value of 6.68 D has been reported.[34] [m] Value interpolated from the data for DEABN and DDABN.

= 0.35 results. Similarly, k'_f/k_f = 0.45 for DDABN in cyclohexane and k'_f/k_f = 0.43 for DDABN in benzene, calculated from the data for Φ'/Φ and [CT]/[LE] given in Tables I and III. These values for k'_f/k_f in the different solvents will be used to obtain [CT]/[LE] for all 4-(dialkylamino)benzonitriles.

The accuracy of the ratio [CT]/[LE] derived from the quantum yield ratios Φ'/Φ using eq 21 obviously depends on the reliability of the value for k'_f/k_f, which suffers from the inherent inaccuracies of the fluorescence quantum yields (Φ'/Φ) as well as of the SPC measurements ($k_a/(k_d + 1/\tau'_0)$). The impact of k'_f/k_f, however, decreases with increasing [CT]/[LE] ratio, i.e., it decreases for the 4-(dialkylamino)benzonitriles in the series cyclohexane, benzene, 1,4-dioxane. For DMABN in 1,4-dioxane, as an example, a variation of 25% in k'_f/k_f (0.4 ± 0.1) results in 5% uncertainty in the fractional CT concentration, which only leads to a variation of 0.2 D in the dipole moment μ_S(CT) determined from the TRMC data (see below).[47]

Values for k'_f/k_f by Extrapolation from Lower Temperatures. The ratio k'_f/k_f cannot be determined with adequate precision for systems with only a relatively small extent of ICT, such as DMABN in cyclohexane or toluene[6] at room temperature. This is because the accuracy of k'_f/k_f is determined by Φ'/Φ and A (eq 21). For systems with small values for A at room temperature, sufficiently accurate fluorescence decay parameters can be obtained by extrapolation from lower temperatures. This is the case, as for DMABN and related molecules, A and τ_2 increase with decreasing temperature,[6,9] leading to a larger contribution, $A_2\tau_2/\sum_i A_i\tau_i$, of the shortest decay time τ_2 to the total decay.

For DMABN in toluene and diethyl ether, SPC measurements have been carried out over a range of temperatures down to the melting point of the solvents, resulting in linear Arrhenius plots for k_a and k_d.[6,9] Such a procedure is not possible in benzene, cyclohexane, or 1,4-dioxane, the solvents of interest here, because of their relatively high melting points.[5] For the determination of k'_f/k_f for DMABN in toluene at 25 °C, using eq 21, the values for k_a, k_d, and $1/\tau'_0$ are obtained by extrapolation from the temperature range (−50 to −94 °C) where these rate constants were determined from the double-exponential LE and CT fluorescence decays.[6] A similar procedure was followed with DDABN in toluene.[9] Using these data together with those for Φ'/Φ, a value for k'_f/k_f of 0.42 (DMABN) and 0.41 (DDABN) results (eq 21) (see Table III). Note that the value for Φ'/Φ of DDABN is relatively large (3.31), which increases the accuracy of k'_f/k_f. For DMABN in diethyl ether at 25 °C a value k'_f/k_f = 0.41 is similarly obtained by extrapolation from a set of decay parameters measured as a function of temperature[9] (see Table III). These data for k'_f/k_f give additional support to the values derived directly at room temperature, which were reported in the previous section.

TRMC Measurements. The overall excited-state dipole moments of the present aminobenzonitriles in the singlet and triplet excited state, μ_S and μ_T, were obtained from time-resolved microwave conductivity experiments after laser excitation, combined with steady-state measurements of the dipole properties of the electronic ground state. The dipole moments of the two singlet excited states (Scheme I) involved in the intramolecular charge transfer with the 4-(dialkylamino)benzonitriles, μ_S(LE) and μ_S(CT), could then be determined from μ_S, employing the concentration ratio [CT]/[LE] derived from the picosecond laser experiments described earlier. In addition, the rotational relaxation times of the solutes τ_D could be evaluated from the rotational charge mobility in the ground-state M_0, using the ground-state dipole moments μ_0.

Rotational Charge Mobility M_0. For all the aminobenzonitriles studied here the value of M_0 (eq 4) was determined in benzene. This was also done for several compounds in cyclohexane as well as for DMABN in 1,4-dioxane (see Table IV). The corresponding rotational relaxation times τ_D in benzene were then calculated by employing eq 3, assuming a single relaxation time and using the ground-state dipole moments μ_0 listed in Table IV.

In cyclohexane and 1,4-dioxane, values of M_0 for all of the solutes were calculated from those determined in benzene, by multiplying τ_D by a constant factor and resubstituting these numbers in eq 3. The multiplication factor was chosen to give the best overall fit to the measured M_0 values in cyclohexane or 1,4-dioxane.[48,49] These calculated data are listed in Table IV. In

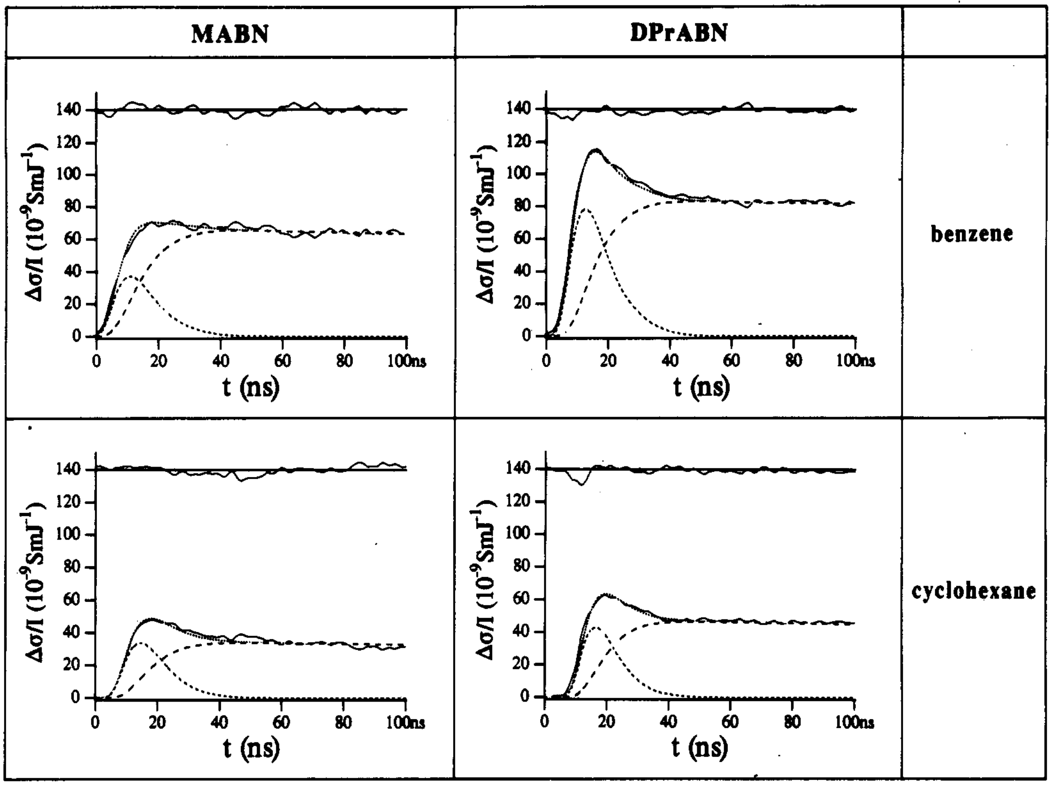


Figure 4. Time-resolved microwave conductivity (TRMC) transients observed on flash photolysis of solutions of 4-(methylamino)benzonitrile (MABN) and 4-(di-*n*-propylamino)benzonitrile (DPrABN) in cyclohexane and benzene. The dotted lines are fits to the experimental data calculated as described in the text. The dashed lines show the individual contributions from the excited singlet and triplet states. The transients have been corrected for small differences in the intensity I (J/m^2) of the laser flash.

the subsequent data analysis, experimental values of M_0 were used where available and calculated ones otherwise.

TRMC Transient Signals and Fitting Procedure. In Figure 4 are shown traces of the change in the microwave conductivity on flash photolysis of solutions of MABN and DPrABN in benzene and cyclohexane. These TRMC transients are similar in general form to those found for the other solute/solvent combinations. They display an initial "fast" component that decays within nanoseconds to tens of nanoseconds after the pulse, to be followed by a "slow" component which decays over a much longer time scale of microseconds. The two components are assigned to the excited singlet and triplet states of the solute, respectively, both of which must have dipole moments larger than that of the ground state in order to give positive TRMC signals.

As mentioned in the Experimental Section, the absolute magnitude of the transient conductivity change can be described by eq 6 in terms of the concentrations and rotational charge mobilities of the excited singlet and triplet species. In the analysis of the TRMC data a kinetic scheme was used in which only a single singlet excited state, S, and a triplet state, T, are formed on photoexcitation of the ground-state molecule, G.[19] The rate constants k_{SG}, k_{ST}, and k_{TG} describe the transitions between these states. The lifetime of the excited singlet state is then given by $\tau_S = 1/(k_{SG} + k_{ST})$, and the intersystem crossing efficiency by $\Phi_{ISC} = \tau_S k_{ST}$.

The general form of the TRMC transient is determined by the temporal behavior of the concentrations of the intermediates. These are calculated by numerical integration of the differential rate equations for [S] and [T] according to the above scheme, using the measured pulse shape and including convolution with the response time of the microwave cavity.[19] Using this procedure, a time resolution of a few nanoseconds can be attained. This was however insufficient to accurately determine the lifetimes of the excited singlet states from the TRMC transients alone, particularly in the presence of the relatively large triplet components. The values of τ_S used in the fitting procedure were therefore taken from the nanosecond fluorescence decay time measurements (Table I). The lifetimes of the triplet-state transients, $\tau_T = 1/k_{TG}$, were a microsecond or longer and were not always accurately measured. The fits to the heights of the singlet- and triplet-state levels, which were carried out on data within the first 100 ns, were insensitive to the value taken for k_{TG}.

With τ_S known from the fluorescence measurements, the parameters which are varied in order to obtain a quantitative fit to the conductivity transients are ΔM_S, ΔM_T, and Φ_{ISC}. The last two parameters are very close to being inversely related to each other in the fitting procedure, and since Φ_{ISC} is usually not known, the actual parameter used to quantitatively fit the triplet component to the data is the product $\Delta M_T \Phi_{ISC}$. Examples of fits to the TRMC transients are plotted in Figure 4. The individual singlet and triplet components are also shown. The values of ΔM_S and $\Delta M_T \Phi_{ISC}$ necessary to fit all of the solute/solvent combinations studied are listed in Tables IV and V.

Overall Singlet-State Dipole Moments. A qualitative impression of changes in the dipolar character of molecules in the excited singlet state can often be obtained from the raw TRMC data. This is the case for the traces shown in Figure 4, which were all taken under similar conditions of solute optical density and pulse intensity. In going from MABN to DPrABN, the singlet-state lifetime τ_S decreases substantially for both benzene (from 3.6 to 2.9 ns) and cyclohexane (from 4.0 to 2.6 ns) (Table I). In addition, the rotational relaxation time of DPrABN is close to a factor of 2 longer than that of MABN (Table IV). Both of these changes would have caused a decrease in the magnitude of the TRMC signal from the singlet state if its dipole moment had remained the same. The observation that the singlet component actually increases with increasing length of the *N*-alkyl substituents, as shown by the transients in Figure 4, is therefore a direct indication, even without quantitative data analysis, that the dipole moment of the singlet state must have increased significantly in going from MABN to DPrABN in both benzene and cyclohexane.

The values of the singlet-state dipole moments of the aminobenzonitriles in the three solvents have been derived using eq 9 from the measured values of M_0, ΔM_S, and μ_0. The data for μ_S are listed in Table IV.[50] It follows from these data that μ_S for the 4-(dialkylamino)benzonitriles becomes larger with increasing

TABLE V: Triplet-State Dipole Moments μ_T, Derived from the Fitting Parameter $\Delta M_T\ \Phi_{ISC}$ from the Long-Lived TRMC Transients and the Intersystem Crossing Efficiency Φ_{ISC}

	cyclohexane			benzene		1,4-dioxane		
solute[a]	$\Delta M_T\Phi_{ISC}$[b] (10^{-9} m^2/(V s))	Φ_{ISC}[c]	μ_T[d](D)	$\Delta M_T\Phi_{ISC}$[b] (10^{-9} m^2/(V s))	Φ_{ISC}[c]	$\Delta M_T\Phi_{ISC}$[b] (10^{-9} m^2/(V s))	μ_{ISC}[c]	μ_T[d] (D)
ABN	0.62	0.03		3.31	0.15	2.63	0.24	
MABN	1.73	0.10		3.20	0.15	2.69	0.25	
DMABN	3.08	0.18[e]	11.9	5.66	0.27	4.20	0.40[e]	12.0
DEABN	2.90	0.22		4.80	0.28	3.29	0.40	
DPrABN	2.32	0.25		4.28	0.35	2.28	0.40	
DDABN	1.48	0.29		2.08	0.31	1.38	0.45	
m-ABN	4.88	0.35		8.59	0.50	3.77	0.42	
m-DEABN	6.37	0.61		5.74	0.38	3.39	0.45	

[a] For abbreviations, see text. [b] The product $\Delta MT\Phi_{ISC}$ was determined from TRMC measurements (see text). ΔM_T is the change in rotational charge mobility on triplet-state formation (eq 7). [c] Φ_{ISC} was calculated from the measured parameters $\Delta M_T\Phi_{ISC}$ and M_0 (Table IV), using a constant value of 2.3 for the ratio $\Delta M_T/M_0$, as determined for DMABN in 1,4-dioxane and cyclohexane employing the measured values for Φ_{ISC} given in the table.[51] This is equivalent (eq 9) to assuming a constant dipole moment μ_T of 12.0 D for the *p*-aminobenzonitriles and of 10 D for the meta-substituted derivatives (see text). [d] μ_T was calculated employing eq 28, with the data for M_0 and μ_0 taken from Table IV. [e] Experimental value, see ref 51.

alkyl chain length of the dialkylamino group in each of the three solvents and also increases with effective solvent polarity, reaching a maximum value of 17.2 D for DDABN in 1,4-dioxane.

For ABN and MABN the dipole moments are seen to be close to the average values of 8.3 and 9.5 D for the three solvents, showing no trend to increase with increasing effective solvent polarity. This is in agreement with the findings of the fluorescence measurements that intramolecular charge transfer does not occur in the singlet excited states of these compounds. The dipole moments observed can therefore be assigned to the LE state alone.

For DMABN the situation is clearly different with μ_S increasing dramatically from cyclohexane, 9.9 D, to benzene, 12.2 D, and further to 1,4-dioxane, 15.1 D. In addition, while the value for DMABN in cyclohexane is what might have been expected for the LE state on the basis of the results for ABN and MABN (Table IV), the μ_S values for benzene and 1,4-dioxane are substantially larger. These results are in agreement with the fluorescence spectra in Figure 1, which show that for DMABN a second emission band, attributed to the occurrence of ICT, is hardly discernible for cyclohexane, visible as a shoulder for benzene, and becomes the dominant feature for 1,4-dioxane.

In a previous publication[26c] by two of the present authors (S.A.J. and J.M.W.), values of μ_S = 13.1 and 13.0 D were reported for DMABN in benzene and 1,4-dioxane, respectively, also using the TRMC technique. The present dipole moment of 12.2 D for benzene is smaller and that of 15.0 D for 1,4-dioxane is considerably larger than the previous results. The smaller value of μ_S for benzene in the present work mainly results from the use of a longer fluorescence lifetime, τ_S = 3.1 ns (Table I), rather than the 2.6 ns employed previously. The value of 3.1 ns is favored because of the better time resolution of the SPC apparatus used here. In the case of 1,4-dioxane, the calculation of μ_S in the previous publication was based on a value for M_0 of 0.65×10^{-8} m^2/(V s). For the purpose of the present work we have remeasured M_0 for DMABN in the three solvents studied here, using improved microwave equipment and fitting procedures and have found a much lower value of $M_0 = 0.46 \times 10^{-8}$ m^2/(V s). If this value of M_0 is used together with the previously reported $\Delta M_S = 1.92 \times 10^{-8}$ m^2/(V s), a dipole moment of μ_S = 15.0 D is found, which agrees with the present determination.

The further increase in μ_S with increasing length of the *N*-alkyl substituents found for the 4-(dialkylamino)benzonitriles also parallels the observation of the increasing importance of the CT emission bands in their fluorescence spectra. Of particular interest is that this trend is apparent for the compounds with the longer alkyl groups even in the case of the nonpolar solvent cyclohexane. The occurrence of a specific solvent interaction with the LE state would therefore appear to be an unnecessary prerequisite for the formation of the highly polar charge-transfer state.

In the case of *m*-ABN the large triplet component in the TRMC transients made it impossible to obtain an accurate evaluation of the contribution due to the singlet state. Only lower and upper limits for μ_S of 7 and 10 D could therefore be estimated for this compound (Table IV). While the triplet transients for *m*-DEABN were also large, the substantially longer singlet fluorescence lifetimes (Table I) allowed a reasonably accurate estimate of μ_S to be made. The values found are within the range of 9–10 D and show no clear dependence on solvent polarity, in contrast with the results for DEABN. This is in agreement with the conclusion from the fluorescence measurements that only one excited singlet state (LE) is formed in the meta-substituted molecules.

Individual LE- and CT-State Dipole Moments. It was shown in a previous section that, for the 4-(dialkylamino)benzonitriles treated here, the equilibrium between the singlet excited states LE and CT is established at room temperature within the duration of the laser excitation used in the present TRMC experiments. Therefore, the equilibrium concentrations [LE] and [CT] may be taken to contribute independently to the overall TRMC signal observed. Under these conditions, the change in rotational charge mobility (eq 7) is given by

$$\Delta M_S = (1 - f(\mathrm{CT}))\ \Delta M_S(\mathrm{LE}) + f(\mathrm{CT})\ \Delta M_S(\mathrm{CT}) \quad (22)$$

with f(CT) being the fractional CT concentration

$$f(\mathrm{CT}) = [\mathrm{CT}]/([\mathrm{CT}] + [\mathrm{LE}]) \quad (23)$$

On substituting for the ΔM values, using eq 9, one obtains

$$\mu_S^2 = (1 - f(\mathrm{CT}))(\mu_S(\mathrm{LE}))^2 + f(\mathrm{CT})\ (\mu_S(\mathrm{CT}))^2 \quad (24)$$

This gives by rearrangement an expression for the dipole moment μ_S(LE)

$$\mu_S(\mathrm{LE}) = \{[\mu_S^2 - f(\mathrm{CT})\ (\mu_S(\mathrm{CT}))^2]/(1 - f(\mathrm{CT}))\}^{0.5} \quad (25)$$

Similarly, for μ_S(CT)[50]

$$\mu_S(\mathrm{CT}) = \{[\mu_S^2 - (1 - f(\mathrm{CT}))(\mu_S(\mathrm{LE}))^2]/f(\mathrm{CT})\}^{0.5} \quad (26)$$

In order to determine the dipole moments of the two excited-state species LE and CT separately, it follows from eqs 25 and 26 that, besides their concentration ratio [CT]/[LE], (f(CT), eq 23), also the excited-state dipole moment of one of these species, μ_S(LE) or μ_S(CT), must be known.

Singlet-State Dipole Moments as a Function of f(CT). In terms of the fractional concentration f(CT) (eq 23) of the CT state at equilibrium, eq 24 can be rearranged to give

$$\mu_S^2 = \mu_S(\mathrm{LE})^2 + f(\mathrm{CT})[(\mu_S(\mathrm{CT}))^2 - (\mu_S(\mathrm{LE}))^2] \quad (27)$$

If the assumption is made that μ_S(LE) and μ_S(CT) are constant parameters, then a plot of μ_S^2 against f(CT) should be linear and give as intercepts $(\mu_S(\mathrm{LE}))^2$ for f(CT) = 0 and $(\mu_S(\mathrm{CT}))^2$ for f(CT) = 1. Such a plot is shown in Figure 5, taking the values for μ_S from Table IV. f(CT) was determined from the data for Φ'/Φ (Table I) and k'_f/k_f (Table III), employing eqs 21 and 23. While the data show considerable scatter, the general trend expected on the basis of eq 27 is seen to be obeyed. The intercept values of the straight line drawn through the data points in Figure

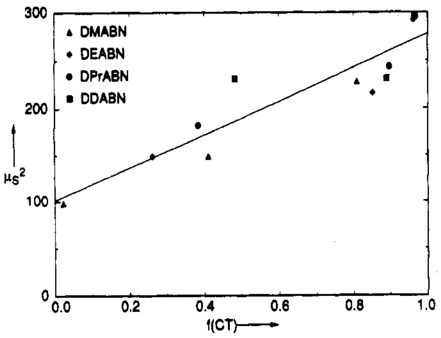


Figure 5. Plot of the square of the excited singlet-state dipole moment μ_S^2 (Table IV) of the 4-(dialkylamino)benzonitriles DMABN, DEABN, DPrABN, and DDABN, in cyclohexane, benzene and 1,4-dioxane, against the concentration factor f(CT) (see eq 23 and text). From the intercepts f(CT) = 0 and f(CT) = 1 of the linear least-squares fit of the data points, the dipole moments μ_S(LE) = 10.1 D and μ_S(CT) = 16.7 D are determined (eq 27).

5 lead to the individual dipole moments μ_S(LE) = 10.1 D and μ_S(CT) = 16.7 D.

Singlet-State Dipole Moments μ_S(LE) and μ_S(CT). The overall singlet excited-state dipole moments of ABN and MABN obtained by TRMC are those of the LE state, μ_S(LE), as these molecules do not undergo a charge-transfer reaction, as discussed above (Table I). It is seen from the data in Table IV that μ_S(LE) has an average value of 8.3 D for ABN and 9.5 D for MABN. Apparently, the introduction of one methyl substituent in the amino group increases the dipole moment by more than 1 D. This increase in dipole moment is continued upon further methylation of the amino group, as can be concluded from the overall dipole moment μ_S = 9.9 D for DMABN in cyclohexane (Table IV). As practically no ICT occurs in this solute/solvent system (see Figure 1 and Table I), the dipole moment of the LE state of DMABN can be considered to have an upper limit of 9.9 D. If the fractional CT concentration f(CT) (eq 23), determined from Φ'/Φ and k'_f/k_f (Tables I and III), is taken into account, a dipole moment μ_S(LE) of 9.7 D can be obtained using eq 25 (see Table IV).

The value of 9.7 D for μ_S(LE), derived from DMABN, is also taken to be valid for the other 4-(dialkylamino)benzonitriles, independent of the length of the alkyl groups. With this fixed dipole moment and the data for f(CT), determined from photostationary and time-resolved fluorescence measurements (Table I), the dipole moments μ_S(CT) were determined using eqs 25 and 26. The results are listed in Table IV. A value of 17 ± 1 D results for μ_S(CT), when the data for the three solvents (cyclohexane, benzene, and 1,4-dioxane) are combined. It should be noted that the accuracy of the dipole moment evaluation increases from cyclohexane to 1,4-dioxane as well as from DMABN to DDABN. This is due to the increase in the [CT]/[LE] ratio with solvent polarity and length of the *N*-alkyl substituents, which diminishes the influence of the exact value of this ratio on that of the dipole moment μ_S(CT).[47]

When the ratio [CT]/[LE] increases, μ_S approaches μ_S(CT) (see eq 26). As the concentration ratio [CT]/[LE] is relatively large for the 4-(dialkylamino)benzonitriles in 1,4-dioxane and increases from DMABN to DDABN (Table IV), the overall dipole moment μ_S = 17.2 D determined for DDABN is therefore only slightly smaller than the dipole moment calculated for the pure CT state: μ_S(CT) = 17.4 D (Table IV). In such a case, the number used for μ_S(LE) has hardly any influence on the final outcome for μ_S(CT).

The value for μ_S(CT) of 17 D derived here compares well with literature data discussed in the Introduction, in particular with those obtained from solvatochromic measurements using the data treatment of ref 16, as well as from electrooptical emission measurements.[12]

Triplet-State Dipole Moments. From the fitting procedure of the long-lived triplet component in the transient microwave decay of the aminobenzonitriles, as described above,[19] the product $\Delta M_T\Phi_{ISC}$ is derived. The results are presented in Table V. From these data, the triplet-state dipole moments μ_T can be evaluated, using eq 28. This expression is analogous to eq 9, written in terms

$$\mu_T = \mu_0[1 + (\Delta M_T\Phi_{ISC})/(\Phi_{ISC}M_0)]^{0.5} \qquad (28)$$

of the fitting parameter $\Delta M_T\Phi_{ISC}$. The values for M_0 and μ_0, appearing in eq 28, can be found in Table IV. Values for the intersystem crossing efficiency, which are necessary to determine ΔM_T and ultimately μ_T, have only been published for DMABN in cyclohexane (Φ_{ISC} = 0.18) and 1,4-dioxane (Φ_{ISC} = 0.40).[26a,51] Using these values, triplet-state dipole moments of 11.9 and 12.0 D are determined for DMABN in cyclohexane and 1,4-dioxane, respectively. This independence of μ_T on the effective solvent polarity contrasts with the change in the singlet-state dipole moments μ_S from 9.9 to 15.1 D for DMABN in the same solvents. It is therefore concluded that DMABN does not undergo intramolecular charge transfer in the triplet state. This conclusion is in accord with observations in the literature,[2b] which also indicates that ICT for diaminobenzonitriles and related compounds is limited to the singlet excited state.

The values of Φ_{ISC} for the other solute/solvent combinations of the para-substituted aminobenzonitriles, listed in Table V, have been derived from the parameter $\Delta M_T\Phi_{ISC}$ (eqs 9 and 28) using as a constant dipole moment μ_T = 12.0 D, adopted from DMABN/1,4-dioxane (Table V). These data show a definite tendency for the intersystem crossing efficiency to increase substantially with the length of the *N*-alkyl groups. Φ_{ISC} also increases with solvent polarity.

Dipole Moment and Amino Group Conformation. The observation of a dipole moment μ_S(CT) = 17 D for the 4-(dialkylamino)benzonitriles in this paper confirms that substantial additional intramolecular charge separation takes place subsequent to excitation to the LE state for which μ_S(LE) $\simeq$ 9.7 D. An increase in the net positive charge on the amino group could result from conformational changes involving (a) rotational isomerization around the amino–phenyl bond (TICT model)[2] and (b) a change from planar (sp^2) to pyramidal (sp^3) hybridization of the amino nitrogen. In the TICT ("twisted internal charge transfer") model, the CT state of DMABN and related molecules is postulated to be a rotational isomer of a planar LE state, with the amino group in a plane perpendicular to that of the phenyl ring.[2] This bond rotation is supposed to lead to localization of unit positive charge on the nitrogen atom of the amino group. The negative charge is thought to be delocalized as in the radical anion of benzonitrile.[52] Such a complete decoupling of the amino group from the benzonitrile subunit in the aminobenzonitriles has also been described as the "principle of minimum overlap".[53,54]

The dipole moment of such a hypothetical, decoupled species (A^-–D^+) can be calculated by vector summation of the point charge dipole moments using the charge distribution of the benzonitrile radical anion. This charge distribution can be derived from the spin densities of the anion taken from ESR measurements and by scaling with the coefficients of the lowest antibonding molecular orbital of benzonitrile.[52,55] It should be noted that only approximately one-seventh of the total negative charge of the benzonitrile anion resides on the cyano group.

From this procedure a dipole moment of 15.9 D results, taking as bond distances those obtained from an X-ray analysis of DMABN.[56,57] A charge distribution as expected for a quinoidal resonance structure of DMABN would lead to a much larger dipole moment, of between 30 and 33 D,[1a,b] depending on the values taken for the bond lengths. Note that such a CT structure, with a double bond between the amino nitrogen and the phenyl ring, would be expected to be planar.

Even without rotational isomerization, pyramidalization of the amino nitrogen can in principle also decouple the nitrogen lone pair from the π electrons of the phenyl ring. This would also lead to an increase in the localization of the positive charge on the amino group and, hence, to a larger value of the dipole moment of the CT state in donor/acceptor substituted phenyl compounds such as DMABN.

Our observation that the extent of intramolecular charge transfer, i.e., [CT]/[LE], increases from DMABN to DDABN indicates that in the singlet excited state the amino nitrogen in the 4-(dialkylamino)benzonitriles becomes more pyramidal with increasing alkyl chain length. This conclusion is supported by photoelectron spectroscopy measurements,[58] which show that the amino nitrogen is less strongly coupled to the phenyl ring in DEABN than in DMABN. Gleiter and Rettig assumed that the amino group of ground-state DEABN is already twisted with respect to the plane of the phenyl ring, whereas DMABN was supposed to be planar. An alternative interpretation is that the differences found between DEABN and DMABN arise from an increase in the sp^3 character of the amino nitrogen.[9]

In addition to conformational changes involving the amino group, molecular deformation similar to the loss of 6-fold symmetry of the phenyl ring, which occurs on radical anion formation of benzene, could possibly take place for the present compounds and lead to an increase of the charge separation in the CT state of the 4-(dialkylamino)benzonitriles.[52b,59] This Jahn–Teller distortion[60,61] causes an asymmetry in the local charge densities, which could result in an increase in the solvation energy of the deformed radical anion.

Conclusion

With the 4-(dialkylamino)benzonitriles DMABN, DEABN, DPrABN, and DDABN, the presence of an additional red-shifted CT emission in the fluorescence spectrum indicates that intramolecular charge transfer occurs at room temperature in 1,4-dioxane, benzene and, unexpectedly, also in the nonpolar solvent cyclohexane. ICT does not take place with the aminobenzonitriles ABN, MABN, *m*-ABN, and *m*-DEABN, for which no additional fluorescence band was observed. The fluorescence quantum yield ratio $\Phi'(\mathrm{CT})/\Phi(\mathrm{LE})$ of the 4-(dialkylamino)benzonitriles (Table I) becomes larger with increasing effective solvent polarity in the series cyclohexane, benzene, and 1,4-dioxane, as well as with increasing chain length of the alkyl groups on the amino nitrogen (methyl to decyl).

The dipole moments in the singlet excited states of the series of aminobenzonitriles were determined at room temperature by using the TRMC technique. With the 4-(dialkylamino)benzonitriles the value for the overall dipole moment in the singlet state μ_S, and hence the extent of ICT, increases with increasing length of the alkyl groups, as well as with increasing effective solvent polarity in the series cyclohexane, benzene, 1,4-dioxane, in accord with the fluorescence measurements. The largest overall dipole moment $\mu_S = 17.2$ D is reached for DDABN in 1,4-dioxane, in which system the CT state is the predominant species. This value must therefore be almost equal to that for the dipole moment of the CT-state $\mu_S(\mathrm{CT})$ alone.

The individual dipole moments of the two excited singlet states of the 4-(dialkylamino)benzonitriles $\mu_S(\mathrm{LE})$ and $\mu_S(\mathrm{CT})$ could be determined separately by combining the TRMC data with the values for the equilibrium concentration ratio [CT]/[LE] evaluated from time-resolved SPC fluorescence measurements in the picosecond time domain. As a general result for the 4-(dialkylamino)benzonitriles it is concluded that the dipole moment of these compounds increases upon light absorption, from 6.6 D in the ground state to ca. 10 D for the LE state. From this LE state an intramolecular charge transfer takes place under further charge separation, to a CT state with a dipole moment of approximately 17 D. The triplet-state dipole moments μ_T determined for DMABN in cyclohexane and 1,4-dioxane are the same, independent of effective solvent polarity, with a value close to 12 D. This shows that ICT does not occur in the triplet state of these molecules.

The intersystem crossing efficiency Φ_{ISC} of the *p*-aminobenzonitriles is found to increase with the length of the *N*-alkyl substituents as well as with solvent polarity.

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Registry No. ABN, 873-74-5; MABN, 4714-62-9; DMABN, 1197-19-9; DEABN, 2873-90-7; DPrABN, 96795-43-6; DDABN, 144436-23-7; *m*-ABN, 2237-30-1; *m*-DEABN, 144436-24-8.

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(44) From Scheme I: $d[CT]/dt = k_a[LE] - (k_d + 1/\tau'_0)[CT]$. Hence, under photostationary conditions ($d[CT]/dt = 0$): $[CT]/[LE] = k_a/(k_d + 1/\tau'_0)$. With $1/\tau_1 + 1/\tau_2 = (k_a + 1/\tau_0) + (k_d + 1/\tau'_0) = X + Y$ (eqs 12–14) and $1/\tau_2 \gg 1/\tau_1$, the following relation results: $(1/\tau_2 - X) = (k_d + 1/\tau'_0)$, showing that eq 19 becomes equal to eq 20.

(45) For DMABN in toluene at 25 °C the following values are obtained (see Scheme I and eqs 12–20):[6] τ_1 = 3.01 ns; τ_2 = 21.6 ps; $k_a = 1.68 \times 10^{10}$ s^{-1}; $X = k_a + 1/\tau_0 = 1.71 \times 10^{10}$ s^{-1} with τ_0 = 3.7 ns (model compound MABN[6]).

(46) With DMABN and the other 4-(dialkylamino)benzonitriles at 25 °C, the conditions $k_a, k_d \gg 1/\tau_0, 1/\tau'_0$ and $\tau_1 \gg \tau_2$ hold.[6,9] Hence, $[CT]/[LE] \simeq A$, as $[CT]/[LE] \simeq k_a/k_d$ (eq 20) and, similarly, (eqs 15 and 16) $A = A_{12}/A_{11} = (X - 1/\tau_1)/(1/\tau_2 - X) \simeq k_a/(k_a + k_d - k_a) = k_a/k_d$. This follows from (eqs 12–14) $1/\tau_1 + 1/\tau_2 = k_a + k_d + 1/\tau_0 + 1/\tau'_0$, which reduces under the prevailing conditions to $1/\tau_2 \simeq k_a + k_d$.

(47) With $\Phi'/\Phi = 1.49$ for DMABN/1,4-dioxane (Table I) and $k'_f/k_f = 0.4 \pm 0.1$, a fractional CT concentration $[CT]/([CT] + [LE])$ of 0.79 ± 0.04 results, using eqs 21 and 23. This leads to a variation of 0.2 D in the dipole moment μ_S(CT), calculated from the TRMC data for the overall dipole moment μ_S = 15.1 D and μ_S(LE) = 9.7 D (Table IV), employing eqs 23 and 26.

(48) To a first approximation, the multiplication factor would be expected to be close to the ratio of the solvent viscosities, $\eta(\text{benzene})^{25} = 0.603$ cP,[49a] $\eta(\text{cyclohexane})^{25} = 0.898$ cP,[49a] and $\eta(\text{1,4-dioxane})^{25} = 1.196$ cP.[49b] This expectation is fulfilled for 1,4-dioxane, where the factor of 2.09 required to obtain an adequate fit of the measured TRMC trace for DMABN is close to the ratio 1.98 for the viscosities of 1,4-dioxane and benzene. For cyclohexane the factor of 1.17 used to obtain the best data fits is considerably smaller than the cyclohexane/benzene viscosity ratio of 1.49, which may indicate that the molecules have a larger rotational freedom in cyclohexane than would be expected on the basis of the bulk viscosity.

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(50) The absolute values of ΔM_S determined for a given solute/solvent combination have been found to differ by up to 10% over a long period of time. The error limits for the dipole moments μ_S in Table IV correspond to this magnitude of error in ΔM_S. As a typical example, $\mu_S = 17.2 \pm 0.7$ D for DDABN/1,4-dioxane.

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