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Thermally Activated Internal Conversion with 4-(Dimethylamino)benzonitrile, 4-(Methylamino)benzonitrile, and 4-Aminobenzonitrile in Alkane Solvents. No Correlation with Intramolecular Charge Transfer[†]

Sergey I. Druzhinin, Attila Demeter,[‡] Victor A. Galievsky, Toshitada Yoshihara,[§] and Klaas A. Zachariasse*

Max-Planck-Institut für biophysikalische Chemie, Spektroskopie und Photochemische Kinetik,
37070 Göttingen, Germany

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With 4-(dimethylamino)benzonitrile (DMABN), 4-(methylamino)benzonitrile (MABN), and 4-aminobenzonitrile (ABN) in an alkane solvent such as *n*-hexadecane, the fluorescence decay time τ and quantum yield Φ_f strongly decrease with increasing temperature. For DMABN in *n*-hexadecane, τ decreases from 3.43 ns at 25 °C to 0.163 ns at 284 °C, with a simultaneous drop in Φ_f from 0.14 to 0.006. Similar results are obtained for MABN and ABN. By measuring τ, Φ_f, and the intersystem crossing (ISC) yield Φ_{ISC} of the three aminobenzonitriles as a function of temperature in 2-methylpentane and *n*-hexadecane, covering a range from −151 to 284 °C, the rate constants for internal conversion (IC), ISC, and fluorescence are determined, together with their activation energies and preexponential factors. It is so established that DMABN, MABN, and ABN undergo efficient thermally activated IC. Upon increasing the temperature for DMABN in *n*-hexadecane from 18 to 287 °C, the IC yield Φ_{IC} increases from 0.04 to 0.95. This goes at the expense of ISC and fluorescence, with a decrease from 0.81 to 0.04 for the yield Φ_{ISC} and from 0.15 to 0.005 for the fluorescence quantum yield Φ_f between these two temperatures. With MABN and ABN, likewise with ISC as the main decay channel at room temperature, IC becomes the dominating deactivation pathway of the first excited singlet state S_1 at temperatures above 125 °C. The IC activation energies E_{IC} have similar values for the three aminobenzonitriles in the alkanes: 31.3 kJ/mol (DMABN), 34.3 kJ/mol (MABN), and 34.8 kJ/mol (ABN), with preexponential factors of around 5×10^{12} s^{-1}. The ISC activation energies E_{ISC} are considerably smaller, 3.9 kJ/mol (DMABN) and 5.6 kJ/mol (MABN and ABN), with relatively small preexponential factors of around 3×10^{8} s^{-1}, values in accord with the spin forbidden character of ISC. The different height of the barriers E_{IC} and E_{ISC} makes their separate determination at the high and low parts of the available temperature range possible. Contrary to what has previously been postulated for 1-aminonaphthalenes, the similarity of the barrier heights E_{IC} of DMABN, MABN, and ABN shows that the IC reaction of these molecules in alkane solvents is not governed by the energy gap $\Delta E(S_1,S_2)$ between the two lowest excited singlet states, which gap substantially increases in the series DMABN, MABN, ABN. Because intramolecular charge transfer (ICT) does not take place with any of these three aminobenzonitriles in alkane solvents, the thermally activated IC process reported here is mechanistically not related to ICT. The IC decay channel obviously should be taken into account in discussions of excited-state processes of DMABN and its derivatives at higher excitation energies.

Introduction

Internal conversion (IC) in the series of aromatic hydrocarbons from benzene to hexacene is governed by the energy gap law.[1−3] In cyclohexane at 25 °C, the IC rate constant k_{IC} increases from 8×10^2 s^{-1} (benzene) to 6.3×10^8 s^{-1} (hexacene), with a decrease of the energy $E(S_1)$ of the first excited singlet state from 37 080 to 14 500 cm^{-1}.[4−7] For anthracene, with $E(S_1) = 26\,580$ cm^{-1}, the IC yield Φ_{IC} under these conditions is still practically zero ($\Phi_{IC} = 1.6 \times 10^{-3}$), as calculated from k_{IC} (3.5×10^5 s^{-1}) and the fluorescence lifetime τ (4.7 ns) by using the expression $\Phi_{IC} = k_{IC}\,\tau$.[4] Not before an energy gap between S_1 and S_0 of 20 950 cm^{-1} (tetracene) is reached, an appreciable yield Φ_{IC} is observed, rapidly increasing as $E(S_1)$ becomes smaller: 0.083 (tetracene, 20 950 cm^{-1}), 0.75 (pentacene, 17 000 cm^{-1}), and 0.95 (hexacene, 14 500 cm^{-1}).[4−7] In accordance with these results, a value for Φ_{IC} of 0.66 is observed with pentacene ($E(S_1) = 17\,088$ cm^{-1}) in a Shpol'skii matrix of linear alkanes such as tetradecane at 4.2 K.[8]

In contrast to the polyacenes benzene, naphthalene, and anthracene, efficient thermally activated IC was found to take place with some of their amino-substituted derivatives,[9−15] which molecules still have relatively large S_1 energies. Examples are 3,5-dimethyl-4-(methylamino)benzonitrile (MHD),[9] 1-(dimethylamino)naphthalene (1DMAN),[10−14] and 9-cyano-10-(dimethylamino)anthracene (CDAN),[15] with energy gaps between the equilibrated S_1 state and its Franck−Condon ground state in

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* To whom correspondence should be addressed. Fax: +49-551-201-1501. E-mail: kzachar@gwdg.de.

[‡] On leave from the Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences. P. O. Box 17, 1525 Budapest, Hungary.

[§] Present address: National Institute of Advanced Industrial Science and Technology (AIST), Photoreaction Control Research Center, Higashi 1-1-1, Tsukuba, Ibaragi, 305-8565 Japan.

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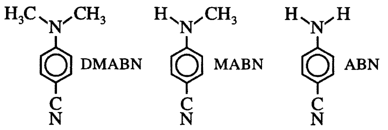
alkane solvents of 30 140, 25 840, and 20 660 cm^{-1}, respectively.[16] For these aromatic amines in alkanes at 25 °C, having larger or similar S_1/S_0 energy gaps than tetracene, the following values were observed for Φ_{IC}: 0.96 (MHD),[9] 0.97 (1DMAN),[10,11] and 0.95 (CDAN).[15] The IC process was found to be temperature dependent, with activation energies E_{IC} in *n*-hexane of 11.8 kJ/mol for MHD[9] and 18.2 kJ/mol for 1DMAN.[10,11]

In MHD, 1DMAN, as well as CDAN in the S_0 ground state, the amino group is twisted relative to the plane of the aromatic moiety, whereas the molecules relax to a more planar configuration in the equilibrated S_1 state (antitwist).[9−15] Based on this finding, it has been proposed that the occurrence of internal conversion is governed by the change in the twist angle of the amino group upon excitation from S_0 to S_1, as well as by the energy gap $\Delta E(S_1,S_2)$ between the two lowest excited singlet states.[15−19] It was assumed that the reaction proceeds via a conical intersection of the shifted S_1 and S_0 potential energy surfaces.[13,14] As support for this hypothesis, it could be shown that the IC efficiency in a series of 1DMAN derivatives increases with increasing amino twist angle in S_0.[12−14]

It therefore came as a surprise that efficient IC also takes place in anilines with effectively planar (not twisted) ground states, such as the F-substituted aminobenzonitriles 2-fluoro-4-(1-azetidinyl)benzonitrile (P4CF2) and 3-fluoro-4-(1-azetidinyl)benzonitrile (P4CF3) in alkane solvents at room temperature.[17] With their likewise planar parent compound 4-(1-azetidinyl)benzonitrile (P4C) in *n*-hexadecane, a similar IC channel opens up when increasing the temperature, reaching a yield Φ_{IC} of 0.95 at 284 °C.[17]

These results prompted us to investigate whether also 4-(dimethylamino)benzonitrile (DMABN) undergoes thermally activated IC. It has already been reported that for DMABN in *n*-hexane at 25 °C, the sum of the fluorescence quantum yield Φ_f and the yield of intersystem crossing Φ_{ISC} is close to unity,[20] showing that internal conversion is not an important deactivation pathway of its S_1 state in this solvent at room temperature. The experiments with DMABN are carried out in a number of alkane solvents, in which appreciable intramolecular charge transfer (ICT) does not take place.[18−24] For comparison, similar experiments were done with 4-(methylamino)benzonitrile (MABN) and 4-aminobenzonitrile (ABN), for which ICT has not been observed under any condition of solvent polarity or temperature.[21,25,26] In accordance with this observation of a single fluorescence band originating from a locally excited (LE) state, the fluorescence decays of the three 4-aminobenzonitriles are single exponential in alkane solvents.[3,10] As $\Delta E(S_1,S_2)$ increases in the series DMABN, MABN, and ABN in alkane solvents,[26] the influence of this S_1/S_2 energy gap on the IC process can also be studied.



In the present paper, the kinetics and thermodynamics of thermally activated IC as well as ISC with DMABN, MABN, and ABN in alkane solvents is reported. The analysis is based on decay times τ derived from single-exponential fluorescence decays measured over a wide temperature range (between −151 and +284 °C) in *n*-hexadecane, 2-methylpentane, *n*-hexane, and cyclopentane, together with fluorescence quantum yields Φ_f and ISC yields Φ_{ISC}, likewise measured as a function of temperature. Thermally activated IC may play a role in the recently reported subpicosecond reaction taking place from the S_2 to the S_1 state of DMABN in the gas phase at 130 °C, which reaction was suggested to proceed via an ICT state having an energy larger than that of S_1.[27]

Experimental Section

DMABN and ABN were obtained from Aldrich. MABN was synthesized as described previously.[25] For these three aminobenzonitriles used in the fluorescence and absorption measurements, HPLC was the last purification step. The DMABN employed in the $T-T$ absorption experiments was synthesized from 4-bromo-*N*,*N*-dimethylaniline (Aldrich) in a reaction with CuCN.[28] With sublimed DMABN (Aldrich), lower values were obtained for Φ_{ISC} at 22 °C, possibly because of the presence of a 4-(dimethylamino)benzaldehyde impurity, identified by NMR in the unpurified material. Solubility tests in a series of solvents show that in alkanes the solubility decreases in the order DMABN, MABN, and ABN.

The alkane solvents *n*-hexadecane (Merck), 2-methylpentane (Aldrich), and cyclopentane (Merck) were chromatographed over Al_2O_3 just prior to use, whereas *n*-hexane (Merck, Uvasol) was used as received. The solutions, with an optical density between 0.4 and 0.6 at the maximum of the first band in the absorption spectrum, were deaerated by bubbling with nitrogen for 15 min.

The fluorescence spectra were measured with quantum-corrected Spex Fluorolog 3-22 and Shimadzu RF-5000PC spectrofluorometers. The fluorescence quantum yields Φ_f, with an estimated reproducibility of 2%, were determined relative to a solution of quinine sulfate in 1.0 N H_2SO_4 ($\Phi_f = 0.546$ at 25 °C),[29] with equal optical density at the excitation wavelength. The difference in refractive index between the standard solution and the alkanes was neglected.[30,31] In the determination of the temperature dependence of Φ_f, the change in optical density with temperature and its nonlinear dependence on fluorescence intensity were taken into account by using absorption spectra measured over the relevant temperature range. The absolute accuracy of the present Φ_f values is limited by the fact that the molecule and standard are excited at slopes of their absorption spectra. Therefore, also relative fluorescence quantum yield measurements were carried out for DMABN, MABN, and ABN in the two solvents *n*-hexadecane and 2-methylpentane, likewise with equal optical density at the excitation wavelength.

The fluorescence decay times were determined with picosecond laser (excitation wavelength $\lambda_{exc} = 276$ nm) or nanosecond ($\lambda_{exc} = 296$ nm) flashlamp single-photon counting (SPC) setups. These setups and the analysis procedure of the fluorescence decays have been described previously.[25,32] The instrument response function of the laser system has a half-width of 19 ps.

The yields Φ_{ISC} of the intersystem crossing from the equilibrated S_1 state to the lowest triplet state T_1 of DMABN and MABN in *n*-hexadecane at 22 °C were measured by triplet−triplet ($T-T$) absorption, employing a method based on $T-T$ energy transfer with perylene as the acceptor.[33,34] *N*-Methyl-1,8-naphthalimide (18NMNI) was used as a reference substance, with $\Phi_{ISC} = 0.96$ in *n*-hexane at 25 °C.[17] The triplet yields at higher and lower temperatures were obtained from the room-temperature data by multiplication with the corresponding ratio of the $T-T$ absorption signal, measured at the maxima of the spectra of DMABN and MABN. This method was tested by determining Φ_{ISC} by way of the perylene energy transfer method at the highest and lowest as well as at an intermediate temperature, giving similar results. The triplet yield of the reference compound 18NMNI in *n*-hexadecane is practically temperature independent up to 220 °C, as deduced from its

TABLE 1: Fluorescence Quantum Yields Φ_f, Yields of Intersystem Crossing Φ_{ISC}, and Internal Conversion Φ_{IC}, Extinction Coefficients ϵ^{max} and $\epsilon^{max}(TT)$ at the Maxima $\tilde{\nu}^{max}$ of the Absorption (abs) and Triplet−Triplet (TT) Absorption (TT-abs) Spectra, Maxima of the Fluorescence Spectra $\tilde{\nu}^{max}$(flu), Energy $E(S_1)$, and Energy Gap $\Delta E(S_1,S_2)$ for DMABN, MABN, and ABN in Alkane Solvents at 25 °C

	solvent	DMABN	MABN	ABN
Φ_f	*n*-hexadecane	0.14	0.20	0.21
	2-methylpentane	0.13	0.20	0.21
	n-hexane	0.14	0.21	0.21
	cyclopentane	0.14		
Φ_{ISC}	*n*-hexadecane	0.70[a]	0.63[a]	
	n-hexane	0.76[b]		
Φ_{IC} ($= 1 - \Phi_f - \Phi_{ISC}$)	*n*-hexadecane	0.14	0.15	
	n-hexane	0.10		
ϵ^{max} [1000 M^{-1} cm^{-1}]	*n*-hexadecane	29.82	26.74	21.27
	2-methylpentane	30.17	27.58	23.72
$\epsilon^{max}(TT)$ [1000 M^{-1} cm^{-1}][c]	*n*-hexadecane	6.34	8.17	
$\tilde{\nu}^{max}$(TT-abs) [1000 cm^{-1}]	*n*-hexadecane	26.65	28.58	
$\tilde{\nu}^{max}$(abs) [1000 cm^{-1}]	*n*-hexadecane	35.45	36.65	38.05
	2-methylpentane	35.65	36.85	38.25
$\tilde{\nu}^{max}$(flu) [1000 cm^{-1}]	*n*-hexadecane	29.40	30.10	30.95
	2-methylpentane	29.50	30.20	31.05
$E(S_1)$ [1000 cm^{-1}][d]	*n*-hexadecane	31.65	32.30	33.30
	2-methylpentane	31.85	32.45	33.40
$\Delta E(S_1,S_2)$ [1000 cm^{-1}]	*n*-hexadecane	3.80	4.35	4.75
	2-methylpentane	3.80	4.40	4.85
	2-methylpentane	3.83[e]		

[a] At 23 °C. [b] See ref 38. [c] Extinction coefficient at the maximum $\tilde{\nu}^{max}$(TT-abs) of the triplet−triplet absorption spectrum, see Figure 3. [d] The energy of the crossing of the absorption and fluorescence spectra, see Figures 1 and 2. [e] Energy difference between first peak and main maximum in the absorption spectrum at −155 °C (Figure 1a).

transient absorption signal. However, direct formation of the perylene triplet becomes more important with increasing temperature. The correction of this effect, which can be neglected at room temperature, therefore, becomes essential at higher temperatures. The temperature dependence of the optical density of the solutions at the excitation wavelength (308 nm) was determined by measuring the absorption spectra as a function of temperature, to correct for the change in solvent density. The solutions used in the $T-T$ absorption experiments were degassed by employing the freeze−pump−thaw method (5 cycles). The molar extinction coefficients of the triplet state of DMABN and MABN in *n*-hexadecane, see Figure 3 and Table 1, were determined relative to that of benzophenone triplet (6600 M^{-1} cm^{-1} at 525 nm)[35] measured at the same optical density (around 0.7) in acetonitrile at 22 °C.

The parameters for the photophysical processes of the aminobenzonitriles were obtained by a global nonlinear least-squares method, with the sum of the weighted squares of the residuals $S = \sum_j\sum_i w_{ij}(\ln y_{ij} - \ln y_{ij}^{exp})^2$ as the target function. In the expression for S, w is a weighting factor and y is a response function (fluorescence lifetime, fluorescence quantum yield, and triplet yield). The index j refers to the response functions, the index i counts the experimental points for each response function, and the index exp indicates that the quantity is an experimental value. The factor w is proportional to the inverse of the estimated dispersion of the experimental data. By using logarithms, S no longer depends on the scaling of the response function.

Results and Discussion

Fluorescence Spectra of DMABN, MABN, and ABN. The fluorescence spectra of DMABN, MABN, and ABN in 2-methylpentane and *n*-hexadecane at 25 °C, see Figures 1 and 2, consist of a single LE emission band without any indication for the presence of an additional red-shifted charge-transfer band. Similar results are obtained in *n*-hexane, cyclopentane, and other alkane solvents. This absence of dual fluorescence for the three 4-aminobenzonitriles is found over a large temperature range, between −155 °C (2-methylpentane) and +284 °C (*n*-hexadecane). The fluorescence quantum yields Φ_f are listed in Table 1: 0.14 and 0.13 (DMABN), 0.20 (MABN), and 0.21 (ABN), at 25 °C in *n*-hexadecane and 2-methylpentane.

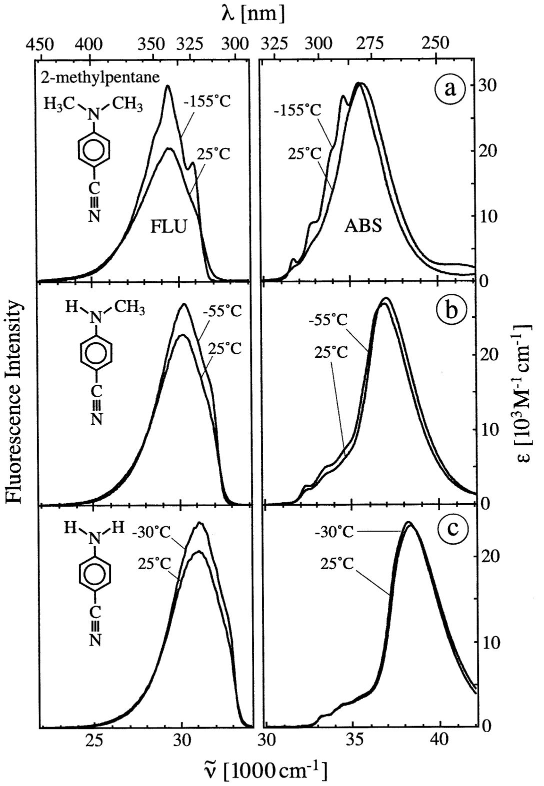


Figure 1. Fluorescence and absorption spectra in 2-methylpentane at different temperatures of (a) 4-(dimethylamino)benzonitrile (DMABN), (b) 4-(methylamino)benzonitrile (MABN), and (c) 4-aminobenzonitrile (ABN). The fluorescence consists of an emission from a locally excited (LE) state.

The fluorescence quantum yield of DMABN in 2-methylpentane increases by a factor of 1.2 upon lowering the temperature from +25 to −155 °C (Figure 1a). A similar observation is made for MABN and ABN (Figure 1, parts b and c), see Table 1. Especially, the fluorescence spectrum of DMABN in 2-methylpentane develops a vibrational structure at lower temperatures, as is shown by the spectrum at −155 °C (Figure 1a). For MABN, solubility problems limit the lowest accessible temperature for MABN in 2-methylpentane to −55 °C and to −30 °C for ABN. Below these temperatures, the fluorescence (and absorption) spectra start to become reminiscent of those for dimers of DMABN.[36]

The fluorescence intensity of DMABN, MABN, as well as ABN in *n*-hexadecane strongly decreases, however, upon increasing the temperature. This can be seen from Figure 2, where the fluorescence spectra at 25 and 284 °C are depicted. Over this temperature range, the fluorescence quantum yields Φ_f decrease by a factor of around 25, see Table 3 below, reaching the following values at 284 °C: 0.006 (DMABN), 0.01 (MABN), and 0.009 (ABN).

Absorption Spectra of DMABN, MABN, and ABN. The absorption spectra and extinction coefficients of DMABN, MABN, and ABN in 2-methylpentane and *n*-hexadecane were

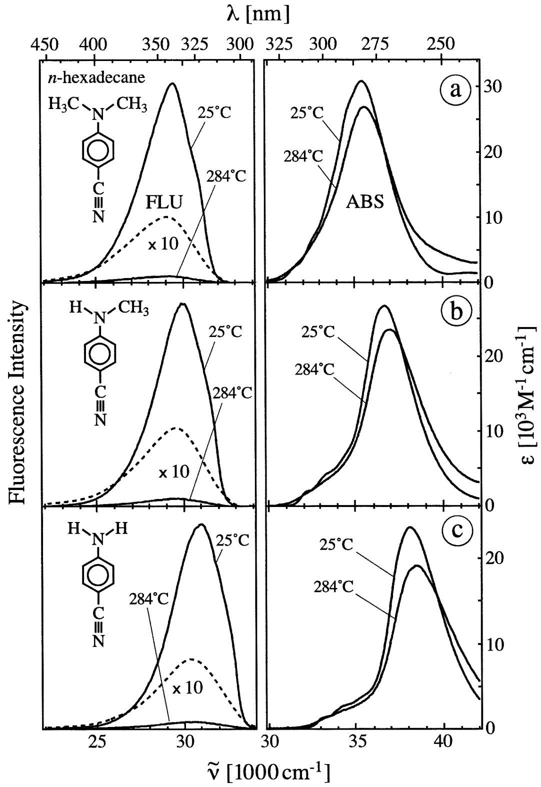


Figure 2. Fluorescence and absorption spectra in *n*-hexadecane at 25 and 284 °C of (a) 4-(dimethylamino)benzonitrile (DMABN), (b) 4-(methylamino)benzonitrile (MABN), and (c) 4-aminobenzonitrile (ABN). The fluorescence consists of an emission from a locally excited (LE) state.

determined as a function of temperature, see Figures 1 and 2. These spectra are required for the correction of the fluorescence quantum yield data for the temperature dependence of the optical density. The energy difference $\Delta E(S_1,S_2)$ between the two lowest excited singlet states in the series ABN, MABN, and DMABN is seen to become smaller by substituting methyls in the amino group, as discussed previously.[26] This phenomenon has been connected with the absence of dual fluorescence in the two latter molecules.[21,26,37] Especially, the absorption spectra in 2-methylpentane show a clearly developed vibrational structure at the lower temperatures, which also becomes evident in the fluorescence spectrum of DMABN (Figure 1c).

Yields of Intersystem Crossing, Fluorescence, and Internal Conversion at Room Temperature. To establish the nature of the nonradiative decay processes in the present aminobenzonitriles, intersystem crossing yields Φ_{ISC} were determined in *n*-hexadecane at 23 °C by the triplet−triplet energy transfer method, giving the following results: 0.70 (DMABN)[20,38] and 0.63 (MABN), see Table 1. The $T-T$ absorption spectra of DMABN and MABN in *n*-hexadecane are depicted in Figure 3. The triplet yield obtained for DMABN is similar to that obtained in *n*-hexane by triplet energy transfer to anthracene (0.80),[39] as well as to that determined by optoacoustic experiments, with values 0.73 (*n*-heptane)[40] and 0.63 (*n*-hexadecane).[41] For the fluorescence quantum yields in *n*-hexadecane at 25 °C, the following values were determined, already mentioned in the previous section: 0.14 (DMABN)[42] and 0.20 (MABN), see Table 1. As there is no evidence that the fluorescence quantum yields at this temperature are reduced by photochemical reactions, the internal conversion yields can be calculated by using the expression $\Phi_{\mathrm{IC}} = 1 - \Phi_{\mathrm{f}} - \Phi_{\mathrm{ISC}}$, giving in *n*-hexadecane the values 0.14 for DMABN and 0.15 for MABN (Table 1).[43] It follows from these experimental data that at room temperature IC is only a minor deactivation pathway for the S_1 state of the two aminobenzonitriles, whereas ISC is the main decay channel in the alkane solvents.

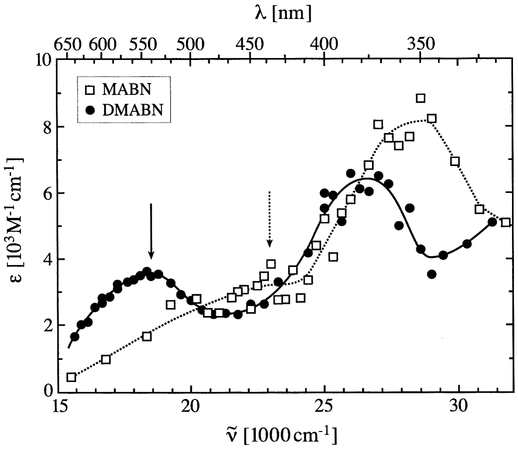


Figure 3. Triplet−triplet absorption spectra of 4-(dimethylamino)benzonitrile (DMABN) and 4-(methylamino)benzonitrile (MABN) in *n*-hexadecane at 22 °C. The arrows indicate the spectral position used for the analyzing light in the experiments to determine the yield of intersystem crossing Φ_{ISC}.

Fluorescence Decay Times and Rate Constants for Internal Conversion, Intersystem Crossing, and Fluorescence in 2-Methylpentane and *n*-Hexadecane at 25 °C. The fluorescence decays of DMABN, MABN, and ABN in *n*-hexadecane at 25 °C are shown in Figure 4. The decays are single exponential, supporting the conclusion reached from the fluorescence spectra (Figure 1) that dual fluorescence does not occur with these molecules in the alkane solvents investigated here. The decay times τ of DMABN (3.43 ns), MABN (4.22 ns), and ABN (5.32 ns), see Table 2, are all in the nanosecond range, indicating that fast deactivation processes do not occur in the LE state. From these decay times and the yields of fluorescence, intersystem crossing, and internal conversion for DMABN and MABN discussed in the previous section (Table 1), preliminary values for the rate constants of these deactivation processes can be calculated by using the relationship $k_i = \Phi_i/\tau$ (i = f, IC, ISC), see Table 2 and eqs 1−4. The rate constant for internal conversion k_{IC} in *n*-hexadecane at 25 °C, 4×10^7 s^{-1} for DMABN and MABN, has similar values as the radiative rate constant $k_{\mathrm{f}} = 4.1 \times 10^7$ s^{-1} (DMABN) and 4.7×10^7 s^{-1} (MABN). The main process clearly is ISC, with rate constants k_{ISC} of 2.1×10^8 s^{-1} (DMABN) and 1.5×10^8 s^{-1} (MABN), see Table 2. These rate constants are to be compared with the final data obtained by fitting the entire data set for τ, Φ_{f}, and Φ_{ISC} measured here as a function of temperature, as will be described in a later section

$$1/\tau = k_{\mathrm{f}} + k_{\mathrm{IC}} + k_{\mathrm{ISC}} \tag{1}$$

$$k_{\mathrm{f}} = k_{\mathrm{f}}(0)n^2 \tag{2}$$

$$k_{\mathrm{IC}} = k_{\mathrm{IC}}^0 \exp(-E_{\mathrm{IC}}/RT) \tag{3}$$

$$k_{\mathrm{ISC}} = k_{\mathrm{ISC}}(0) + k_{\mathrm{ISC}}^0 \exp(-E_{\mathrm{ISC}}/RT) \tag{4}$$

The temperature dependence of the radiative rate constant k_{f} is calculated from that of the refractive index n by using the expression $k_{\mathrm{f}} = k_{\mathrm{f}}(0)n^2$ [17,44,45] in which $k_{\mathrm{f}}(0)$ does not depend on temperature (eq 2). Arrhenius expressions are used for k_{IC}

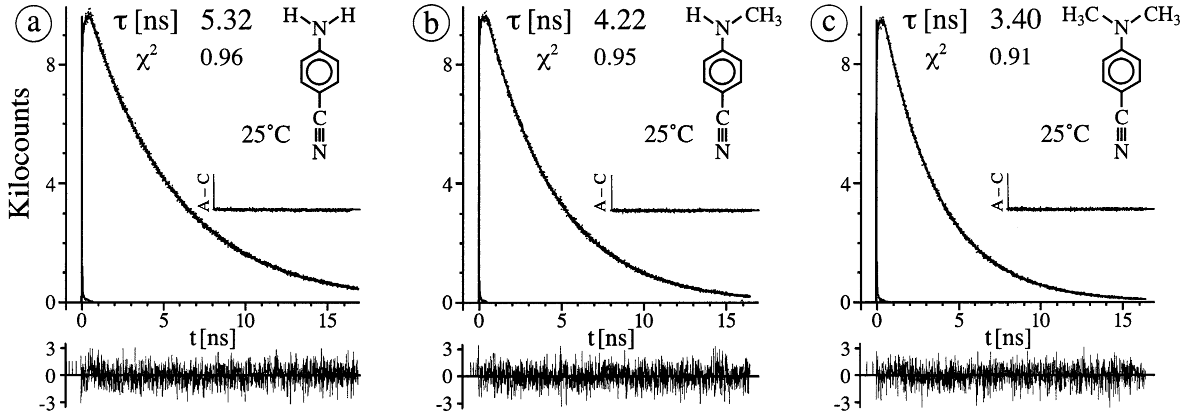


Figure 4. Single-exponential fluorescence decays with decay time τ of (a) 4-aminobenzonitrile (ABN), (b) 4-(methylamino)benzonitrile (MABN), and (c) 4-(dimethylamino)benzonitrile (DMABN) in *n*-hexadecane at 25 °C. The weighted deviations, the autocorrelation functions A−C, and the values for χ^2 are also indicated. Excitation wavelength: 276 nm. Resolution: 10.38 ps/channel, with a time window of 1700 effective channels.

TABLE 2: Fluorescence Decay Times τ and Rate Constants for Fluorescence k_f, Intersystem Crossing k_{ISC}, and Internal Conversion k_{IC} of DMABN, MABN, and ABN in Alkane Solvents at 25 °C Calculated from τ, Φ_f, Φ_{ISC}, and Φ_{IC} (Table 1) via $k_i = \Phi_i/\tau$, See Text and Eq 1

	solvent	DMABN	MABN	ABN
τ [ns]	*n*-hexadecane	3.43	4.22	5.32
	2-methylpentane	3.42	4.37	5.65
	n-hexane	3.45	4.96	
	cyclopentane	3.26		
k_f [10^7 s^{-1}][a]	*n*-hexadecane	4.1	4.7	3.9
	2-methylpentane	3.9	4.5	3.8
	n-hexane	4.0	4.1	
	cyclopentane	4.2		
k_{IC} [10^7 s^{-1}][b]	*n*-hexadecane	4.2	3.6	
	n-hexane	3.0		
k_{ISC} [10^7 s^{-1}][c]	*n*-hexadecane	21	15	
	n-hexane	22		

[a] $k_f = \Phi_f/\tau$. [b] $k_{IC} = \Phi_{IC}/\tau$. [c] $k_{ISC} = \Phi_{ISC}/\tau$.

TABLE 3: Experimental Data for the Fluorescence Decay Times τ, the Fluorescence Quantum Yields Φ_f, and the Intersystem Crossing Yields Φ_{ISC} of DMABN, MABN, and ABN in Alkane Solvents, Indicating the Temperature Range (Lowest and Highest Temperatures) Investigated

	solvent	T [°C]	τ [ns]	Φ_f	Φ_{ISC}
DMABN	*n*-hexadecane	20	3.47	0.14[a]	0.70[b]
		284	0.163	0.0060	0.093[c]
	2-methylpentane	−151	4.12	0.16[d]	
		61	2.96		
	cyclopentane	−90	3.92		
		45	3.00		
	n-hexane	−70	4.00		
		69	2.82		
MABN	*n*-hexadecane	21	4.28	0.20[e]	0.63[b]
		284	0.230	0.0096	0.23[f]
	2-methylpentane	−105	5.32	0.22[g]	
		60	3.95		
	n-hexane	19	4.28		
		−91	5.24		
ABN	*n*-hexadecane	21	5.35	0.21[a]	
		284	0.288	0.0088	
	2-methylpentane	−100	6.96	0.24[h]	
		60	5.10	0.20	

[a] At 25 °C (Table 1). [b] At 23 °C. [c] At 227 °C. [d] At −51 °C. [e] At 22 °C. [f] At 172 °C. [g] At −55 °C. [h] At −30 °C.

and k_{ISC} (see eqs 3 and 4), with a temperature independent rate constant $k_{ISC}(0)$ in the latter case (eq 4).

Temperature Dependence of Fluorescence Decay Times of DMABN, MABN, and ABN. The fluorescence decays of DMABN, MABN, and ABN were measured as a function of temperature in *n*-hexadecane and 2-methylpentane, to cover a large temperature range (−151 to +284 °C). With DMABN in these solvents, the decays are single exponential at all temperatures measured. Examples are shown for the solvent *n*-hexadecane at 25 (Figure 4) and 284 °C (Figure 5). In the case of MABN and ABN, however, likewise having single exponential decays in *n*-hexadecane at all temperatures investigated here, the fluorescence decays in 2-methylpentane start to become double exponential upon cooling below −105 and −100 °C (Table 3), respectively, presumably because of solubility problems, such as the formation of aggregates and microcrystals as discussed above for the fluorescence and absorption spectra. In alkane solvents, secondary and primary aromatic amines generally are less soluble than tertiary amines, as also found here for the series DMABN, MABN, and ABN (see Experimental Section).

From the decay times τ (eq 1), combined with data for Φ_f and Φ_{ISC}, the IC and ISC Arrhenius parameters as well as $k_{ISC}(0)$ and $k_f(0)$ can be determined by a fitting procedure based on eq 1. This is possible when IC and ISC dominate the deactivation process of S_1 in different temperature ranges as a consequence of sufficiently different activation energies E_{IC} and E_{ISC}. In less favorable cases, E_{ISC} (or E_{IC}) may be fixed, as discussed in ref 17.

Φ_f and Φ_{ISC} as a Function of Temperature. The fluorescence quantum yields Φ_f of the three aminobenzonitriles DMABN, MABN, and ABN, measured as a function of temperature in 2-methylpentane and *n*-hexadecane, are presented in Figure 6. It is seen that Φ_f decreases with increasing temperature, reaching for the three molecules in *n*-hexadecane at 284 °C a relatively small value of between 0.005 and 0.01.

The temperature dependence of the intersystem crossing yield Φ_{ISC} for DMABN and MABN in *n*-hexadecane is shown in Figure 7. The ratio of $\Phi_{ISC}/\Phi_{ISC}(25\ °C)$ of the ISC yield relative to that at 25 °C strongly decreases with increasing temperature, reaching at 175 °C a value of 0.20 for DMABN and 0.36 for MABN. This shows that a thermally activated quenching process is competing with ISC.

The Φ_f and Φ_{ISC} data presented here will be used in the fitting procedure for the fluorescence decay times τ of DMABN and MABN measured as a function of temperature, as will be treated in the following sections. In the case of ABN, only Φ_f will be used for this purpose.

IC and ISC Arrhenius Parameters from Temperature Dependence of Fluorescence Decay Times. Fitting Methodology. With P4C, P4CF2, and P4CF3 in *n*-hexane,[17] as well as

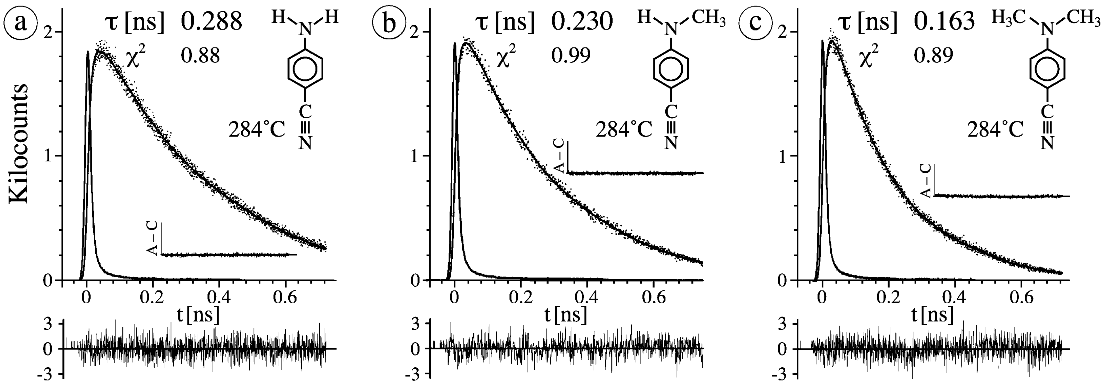


Figure 5. Single-exponential fluorescence decay curves with decay time τ of (a) 4-aminobenzonitrile (ABN), (b) 4-(methylamino)benzonitrile (MABN), and (c) 4-(dimethylamino)benzonitrile (DMABN) in *n*-hexadecane at 284 °C. The weighted deviations, the autocorrelation functions A−C, and the values for χ^2 are also indicated. Excitation wavelength: 276 nm. Resolution: 0.50 ps/channel (DMABN and ABN) and 0.99 ps/channel (MABN), with a time window of 1600 effective channels.

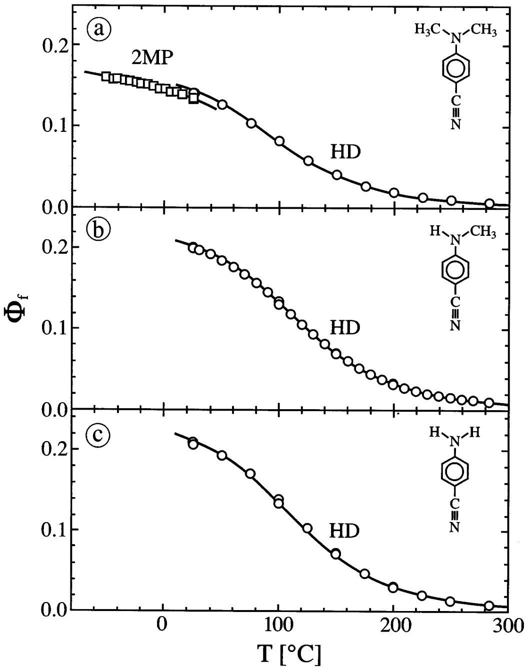


Figure 6. Fluorescence quantum yields Φ_f as a function of temperature for (a) 4-(dimethylamino)benzonitrile (DMABN) in 2-methylpentane (2MP) and *n*-hexadecane (HD), (b) 4-(methylamino)benzonitrile (MABN) in *n*-hexadecane, and (c) 4-aminobenzonitrile (ABN) in *n*-hexadecane.

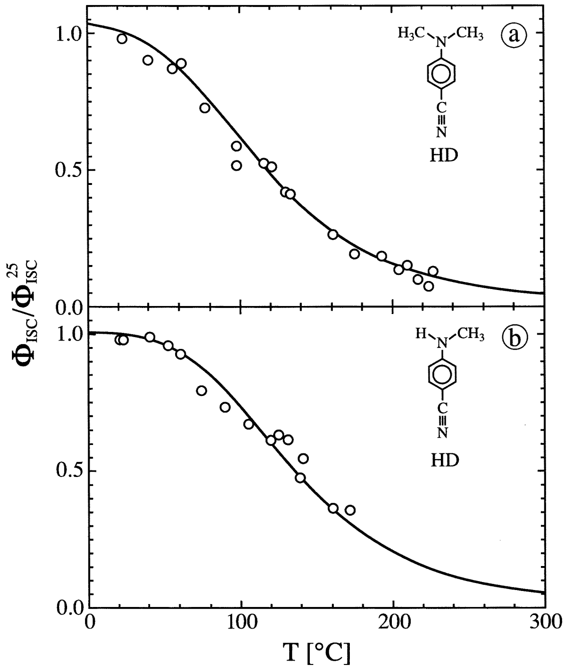


Figure 7. Temperature dependence of the intersystem crossing yield Φ_{ISC} relative to that at 25 °C for (a) 4-(dimethylamino)benzonitrile (DMABN) and (b) 4-(methylamino)benzonitrile (MABN) in *n*-hexadecane (HD).

with 1DMAN in isopentane and *n*-hexane,[13] the IC and ISC activation energies E_{IC} and E_{ISC} with their corresponding preexponential factors k_{IC}^0 and k_{ISC}^0 have been determined from the fluorescence decay times τ measured as a function of temperature. This has been done by fitting the τ data (when available) with an equation in which the rate constants k_{IC} and k_{ISC} are given in Arrhenius form.[13,14] With the present molecules DMABN, MABN, and ABN a similar fitting procedure is followed. The possibility to determine at the same time E_{IC} as well as E_{ISC} by this method obviously depends on the difference in magnitude between these activation energies and the experimentally accessible temperature range.

DMABN. Fluorescence Decay Times as a Function of Temperature. To investigate the kinetics of the IC and ISC deactivation processes in DMABN, its fluorescence decays were measured as a function of temperature in *n*-hexadecane and 2-methylpentane, as well as in *n*-hexane and cyclopentane, see Figure 8. The fluorescence decay time τ of DMABN in *n*-hexadecane substantially decreases from 3.47 ns at 20 °C to 0.160 ns at 284 °C (Table 3 and Figures 4, 5, and 8). For DMABN in 2-methylpentane, only a relatively small decrease in τ occurs with increasing temperature over the accessible temperature range, from 4.12 ns at −151 °C to 2.96 ns at 61 °C, see Figure 8. This data set was fitted by using eq 1, together with the fluorescence quantum yields Φ_f measured as a function of temperature in *n*-hexadecane and 2-methylpentane (Figure 6a) and the ISC yields Φ_{ISC} determined in *n*-hexadecane between 23 and 227 °C (Figure 7a). Three fitting procedures were used, which will be described in the following section.

Fitting Procedures for DMABN. First, the decay times τ, the yields Φ_f, and the ratio of the ISC yields Φ_{ISC}/Φ_{ISC} (25 °C) measured for DMABN in *n*-hexadecane up to high temperatures (Table 3) were fitted with eq 1, as these data have a pronounced temperature dependence in this solvent (Figures 4−8). The results are collected in Table 4, showing that the IC process has a relatively large activation energy E_{IC} of 30.9 kJ/mol with $k_{IC}^0 = 4.7 \times 10^{12}$ s^{-1}. It appears that an optimal fit is

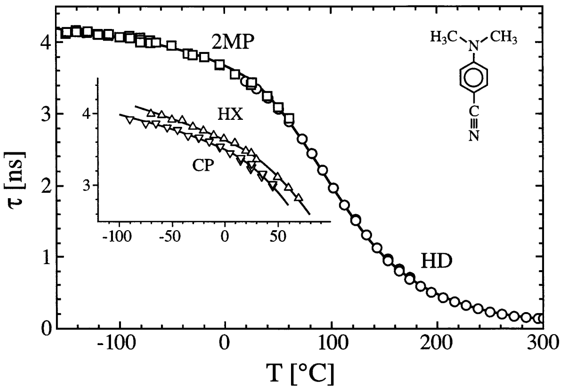


Figure 8. Plots of the fluorescence decay times τ of 4-(dimethylamino)-benzonitrile (DMABN) in 2-methylpentane (2MP), *n*-hexadecane (HD), *n*-hexane (HX), and cyclopentane (CP) as a function of temperature. The lines through the data points represent the fitting procedure described in the text (eq 1).

obtained without thermally activated ISC: $k_{ISC}(0) = 2.3 \times 10^8$ s^{-1}.

As the next step, the data for the decay times τ of DMABN measured as a function of temperature in 2-methylpentane, *n*-hexane, and cyclopentane down to the melting point of the solvents were analyzed together with the results for the fluorescence quantum yields Φ_f determined over a range of temperatures in 2-methylpentane and at 25 °C in *n*-hexane and cyclopentane (Figures 6 and 8 and Tables 1 and 3). From these data, the results presented in Table 5 were obtained. In the fitting procedure over this low-temperature range, the activation energies E_{IC} and E_{ISC} were required to be the same for the three solvents. The following data were found, now with a temperature dependent as well as a nonactivated ISC decay channel: $E_{IC} =$ 30 kJ/mol, k^0_{IC} between 1.9 and 2.5 $\times$ 10^{12} s^{-1}, $E_{ISC} = 6.7$ kJ/mol, k^0_{ISC} around 7 $\times$ 10^8 s^{-1}, and $k_{ISC}(0) = 2.0 \times 10^8$ s^{-1}.

In the final fitting procedure, the data for the low and high-temperature ranges in the four solvents (Table 3) were combined. Also in this case, the restriction was made that the activation energies E_{IC} and E_{ISC} had to be the same for the four solvents. In addition, $k_{ISC}(0)$ was required to be the same in *n*-hexadecane and 2-methylpentane. The results are presented in Table 6: $E_{IC} = 31.3$ kJ/mol with k^0_{IC} between 5.1 and 5.6 $\times$ 10^{12} s^{-1}, $E_{ISC} =$ 3.9 kJ/mol with k^0_{ISC} between 2.0 and 3.1 $\times$ 10^8 s^{-1} and $k_{ISC}(0)$ around 1.9 $\times$ 10^8 s^{-1}. For the temperature independent factor $k_f(0)$ of the fluorescence channel (eq 2), values around 2 $\times$ 10^7 s^{-1} were found. The line through the data points for τ in Figure 8, and similarly that for Φ_f (Figure 6a) and Φ_{ISC} (Figure 7a), shows the good quality of the fit. Further discussions of the IC, ISC, and fluorescence decay channels of DMABN will be based on the data listed in Table 6.

Temperature Dependence of Φ_{IC}, Φ_{ISC} and Φ_f for DMABN. By using the data for the Arrhenius parameters of k_{IC} and k_{ISC} as well as for $k_{ISC}(0)$ and $k_f(0)$ (see eqs 1−4) obtained in the previous section, the temperature dependence of the yields Φ_{IC}, Φ_{ISC}, and Φ_f for DMABN in *n*-hexadecane and 2-methylpentane can be calculated by employing the expression $\Phi_i = k_i\tau$ ($i = f$, IC, ISC), see Figure 9 and Table 7. It is seen from these data that in *n*-hexadecane Φ_{IC} sharply increases from 0.043 at 18 °C to 0.95 at 287 °C, whereas Φ_{ISC} strongly decreases from 0.81 to 0.043 between these two temperatures. Also Φ_f decreases from 0.148 to 0.005 over this temperature interval. For DMABN in 2-methylpentane, the IC yield rises from 0.061 at 25 °C to 0.204 at 62 °C, with a corresponding decrease in Φ_{ISC} from 0.80 to 0.69.

TABLE 4: Activation Energies E_i and Preexponential Factors k^0_i of the Internal Conversion (IC) and Intersystem Crossing (ISC) Radiationless Decay Channels and the Temperature-Independent ISC Rate Constant $k_{ISC}(0)$ and Factor $k_f(0)$ of the Radiative Rate Constant k_f (eqs 1−4) for DMABN, MABN, and ABN in *n*-Hexadecane

	E_{IC} [kJ/mol]	k^0_{IC} [10^{12} s^{-1}]	E_{ISC} [kJ/mol]	k^0_{ISC} [10^9 s^{-1}]	$k_{ISC}(0)$ [10^9 s^{-1}]	$k_f(0)$ [10^7 s^{-1}]
DMABN	30.9	4.7	*a*	*a*	0.23	2.1
MABN	34.2	6.6	0.8	0.3	*b*	2.3
ABN	34.7	6.3	1.1	0.2	*b*	2.0

[a] Optimal fit is obtained without the thermally activated ISC channel, see text and eq 4. [b] Optimal fit is obtained without $k_{ISC}(0)$, see text and eq 4.

It clearly follows from these results that IC dominates in the high-temperature range of *n*-hexadecane (Table 4) and that ISC is the most important decay channel at the lower temperatures in 2-methylpentane, *n*-hexane, and cyclopentane (Table 5). This is the reason that both E_{IC} and E_{ISC} are accessible by fitting the τ, Φ_f, and Φ_{ISC} data, see the previous section and Table 7.

MABN. Fluorescence Decay Times as a Function of Temperature. The decay times τ of MABN measured as a function of temperature in the three solvents *n*-hexadecane, 2-methylpentane, and *n*-hexane are plotted in Figure 10, showing a decrease of τ with increasing temperature, similar to that observed with DMABN (Figure 8). In *n*-hexadecane, τ gradually decreases from 4.28 ns at 21 °C to 0.230 ns at 284 °C (see Figures 4 and 5), whereas in 2-methylpentane the decay time is not so strongly temperature dependent, becoming longer upon cooling from 3.95 ns at 60 °C to 5.32 ns at −105 °C (Table 3). The value for the decay time of MABN in *n*-hexane of 3.77 ns at 69 °C shows that effective deactivation processes do not yet operate at this temperature.

The data set consisting of τ (eq 1) and Φ_f of MABN in the three solvents measured over a considerable temperature range (Figure 6b) and the available ISC yields relative to Φ_{ISC} at 25 °C in *n*-hexadecane (Figure 7b) was fitted following the same procedures that were used with DMABN as described in the previous sections (Tables 4−6). During the fitting of the data over the range down to low temperatures in 2-methylpentane and *n*-hexane (τ and Φ_f), the activation energies E_{IC} and E_{ISC} were again required to be the same (Table 5), whereas in the fitting of the complete data set (see above and Table 6) also k^0_{IC}, k^0_{ISC}, and $k_{ISC}(0)$ were forced to be equal for 2-methylpentane and *n*-hexane. The lines through the three sets of data points for τ in Figure 10 as well as that for Φ_f in *n*-hexadecane (Figure 6b), both based on the final fitting procedure (Table 6), show that fits of good quality are obtained. The following parameters are determined (Table 6): $E_{IC} = 34.3$ kJ/mol with k^0_{IC} between 3.2 and 6.7 $\times$ 10^{12} s^{-1}, $E_{ISC} = 5.6$ kJ/mol with k^0_{ISC} between 2.1 and 5.1 $\times$ 10^8 s^{-1} and $k_{ISC}(0)$ between 1.3 and 1.6 $\times$ 10^8 s^{-1}. For $k_f(0)$, values ranging from 2.3 to 2.6 $\times$ 10^7 s^{-1} were found.

Temperature Dependence of Φ_{IC}, Φ_{ISC} and Φ_f for MABN. From the Arrhenius parameters for IC and ISC, $k_{ISC}(0)$, and $k_f(0)$ of MABN discussed above (Table 6), the three yields Φ_{IC}, Φ_{ISC}, and Φ_f in *n*-hexadecane and 2-methylpentane can be calculated (eqs 1−4), see Figure 11 and Table 7. It follows from Figure 11 that Φ_{IC} in *n*-hexadecane rises sharply with increasing temperature, from 0.020 at 18 °C to 0.942 at 287 °C. This increase in Φ_{IC} leads to a decrease of Φ_{ISC} as well as of Φ_f when the temperature becomes higher, from 0.775 to 0.050 (Φ_{ISC}) and from 0.205 to 0.009 (Φ_f) between 18 and 287 °C.

TABLE 5: Activation Energies E_i and Preexponential Factors k_i^0 of the Internal Conversion (IC) and Intersystem Crossing (ISC) Radiationless Decay Channels and the Temperature-Independent ISC Rate Constant $k_{ISC}(0)$ and Factor $k_f(0)$ of the Radiative Rate Constant k_f (eqs 1−4) for DMABN, MABN, and ABN in Alkane Solvents Measured down to Low Temperatures (see Table 3)[a]

	solvent	E_{IC} [kJ/mol]	k_{IC}^0 [10^{12} s^{-1}]	E_{ISC} [kJ/mol]	k_{ISC}^0 [10^9 s^{-1}]	$k_{ISC}(0)$ [10^9 s^{-1}]	$k_f(0)$ [10^7 s^{-1}]
DMABN	2-methylpentane	30	2.0	6.7	0.66	0.20	2.1
	cyclopentane	30	2.5	6.7	0.73	0.20	2.0
	n-hexane	30	1.9	6.7	0.70	0.20	2.0
MABN	2-methylpentane	34	3.6	5.5	0.49	0.13	2.4
	n-hexane	34	2.4	5.5	0.53	0.13	2.6
ABN	2-methylpentane	26	0.20	5.3	0.36	0.09	2.0

[a] E_{ISC} and E_{IC} are required to be the same in the fitting procedure for each molecule, see text.

TABLE 6: Activation Energies E_i and Preexponential Factors k_i^0 of the Internal Conversion (IC) and Intersystem Crossing (ISC) Radiationless Decay Channels and the Temperature-Independent ISC Rate Constant $k_{ISC}(0)$ and Factor $k_f(0)$ of the Radiative Rate Constant k_f (eqs 1−4) for DMABN, MABN, and ABN in the Complete Set of Alkane Solvents Investigated[a]

	solvent	E_{IC} [kJ/mol]	k_{IC}^0 [10^{12} s^{-1}]	E_{ISC} [kJ/mol]	k_{ISC}^0 [10^9 s^{-1}]	$k_{ISC}(0)$ [10^9 s^{-1}]	$k_f(0)$ [10^7 s^{-1}]
DMABN	*n*-hexadecane	31.3	5.1	3.90	0.20	0.19	2.0
	2-methylpentane	31.3	5.4	3.90	0.20	0.19	2.1
	cyclopentane	31.3	5.6	3.90	0.29	0.19	2.0
	n-hexane	31.3	3.9	3.90	0.31	0.18	2.0
MABN	*n*-hexadecane	34.3	6.7	5.56	0.21	0.16	2.3
	2-methylpentane	34.3	3.2	5.56	0.51	0.13	2.4
	n-hexane	34.3	3.2	5.56	0.51	0.13	2.6
ABN	*n*-hexadecane	34.8	6.4	5.56	0.25	0.12	2.0
	2-methylpentane	34.8	3.5	5.56	0.41	0.09	2.0

[a] E_{ISC} and E_{IC} are required to be the same in the fitting procedure for each molecule. For MABN k_{IC}^0, k_{ISC}^0, and $k_{ISC}(0)$ are restricted to be equal in 2-methylpentane and *n*-hexane, whereas $k_{ISC}(0)$ is required to be the same in 2-methylpentane and *n*-hexadecane, see text.

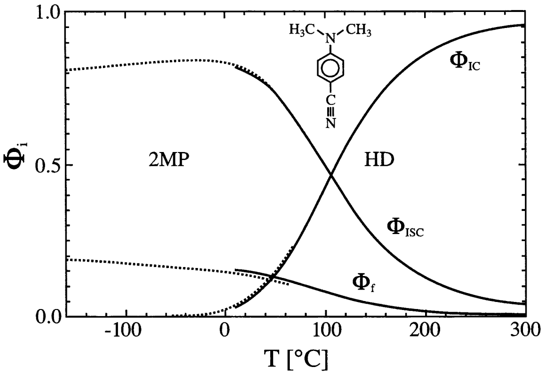


Figure 9. Temperature dependence of the internal conversion yield Φ_{IC}, the intersystem crossing yield Φ_{ISC}, and the fluorescence quantum yield Φ_f of 4-(dimethylamino)benzonitrile (DMABN) in 2-methylpentane (2MP) and *n*-hexadecane (HD). See text.

Because of the relatively large difference in magnitude between E_{IC} and E_{ISC} (34.3 against 5.6 kJ/mol, see Table 6), ISC predominates in 2-methylpentane at all temperatures (Figure 11), IC becoming somewhat more important upon increasing the temperature, with the yields $\Phi_{IC} = 0.056$ and $\Phi_{ISC} = 0.77$ at 62 °C. Under these conditions, the IC and the ISC parameters can both be determined by fitting the data in the high-temperature region (*n*-hexadecane) together with that in the low temperature (*n*-hexane and cyclopentane) range, similar to what is discussed for DMABN in previous sections.

ABN. Fluorescence Decay Times in *n*-Hexadecane and 2-Methylpentane as a Function of Temperature. The temperature dependence of the fluorescence decay times τ of ABN in *n*-hexadecane and 2-methylpentane is shown in Figure 12. In the case of ABN in *n*-hexadecane, an appreciable decrease of τ with increasing temperature is again observed, from 5.35 ns at 21 °C to 0.273 ns at 284 °C (Table 3). With ABN in 2-methylpentane, the temperature dependence of τ is relatively small, only decreasing from 6.96 ns at −100 °C to 5.10 ns at 60 °C (Figure 12 and Table 3).

This set of decay times, together with the data for Φ_f over this temperature range in *n*-hexadecane and at 25 °C in 2-methylpentane (Figure 6c), was fitted by using eq 1 in the procedures employed in previous sections for DMABN and MABN (Tables 4−6). The following results were obtained (Table 6): $E_{IC} = 34.8$ kJ/mol with k_{IC}^0 between 3.5 and 6.4 × 10^{12} s^{-1}, $E_{ISC} = 5.6$ kJ/mol with k_{ISC}^0 between 2.5 and 4.1 × 10^8 s^{-1}. For $k_{ISC}(0)$, the values 1.2 × 10^8 s^{-1} (*n*-hexadecane) and 0.9 × 10^8 s^{-1} were found and $k_f(0) = 2.0 \times 10^7$ s^{-1} was determined in both solvents.

Temperature Dependence of Φ_{IC}, Φ_{ISC} and Φ_f for ABN. From the IC and ISC Arrhenius parameters, $k_{ISC}(0)$, and $k_f(0)$ derived in the previous section, the three yields Φ_{IC}, Φ_{ISC}, and Φ_f can be calculated (eqs 1−4), see Figure 13 and Table 7. It follows from this figure that in *n*-hexadecane Φ_{IC} rises sharply with increasing temperature, from 0.019 at 18 °C to 0.941 at 287 °C. This increase in Φ_{IC} leads to a strong decrease of Φ_{ISC} as well as of Φ_f when the temperature becomes higher, from 0.77 to 0.050 (Φ_{ISC}) and from 0.22 to 0.009 (Φ_f) between 18 and 287 °C. For ABN in 2-methylpentane, it is found that IC is negligible at temperatures below 0 °C (Table 7 and Figure 13).

Similar IC Activation Energies E_{IC} of DMABN, MABN, and ABN. For DMABN, MABN, and ABN in the alkane solvents investigated here, similar values are obtained for the Arrhenius parameters E_{IC} of the IC process, 31.3, 34.3, and 34.8 kJ/mol, respectively, with preexponential factors k_{IC}^0 around 5 × 10^{12} s^{-1}, see Table 6. For the molecularly related aminobenzonitrile P4C in *n*-hexadecane, a comparable IC barrier height of 38.1 kJ/mol has been found, but with a larger value for k_{IC}^0 (19 × 10^{12} s^{-1}), possibly reflecting the strongly pyramidal amino nitrogen of P4C.[17] The large IC barrier for the three aminobenzonitriles DMABN, MABN, and ABN in alkane solvents explains that IC in these molecules only becomes an important decay channel above room temperature. As a consequence of the fact that the IC activation energies E_{IC} of these molecules are considerably larger than those of ISC, see

TABLE 7: Calculated Radiative Rate Constants k_f, Rate Constants for Internal Conversion k_{IC} and Intersystem Crossing k_{ISC}, Fluorescence Decay Times τ, Fluorescence Quantum Yields Φ_f, Yields of Internal Conversion Φ_{IC}, and Intersystem Crossing Φ_{ISC} of DMABN, MABN, and ABN in Alkane Solvents at the Melting and Boiling Points of the Solvents as well as at 25 °C[a]

	solvent	T [°C]	k_f [10^7 s^{-1}]	k_{IC} [10^7 s^{-1}]	k_{ISC} [10^7 s^{-1}]	τ [ns]	Φ_f	Φ_{IC}	Φ_{ISC}
DMABN	*n*-hexadecane	18	4.22	1.24	23.1	3.50	0.148	0.0434	0.809
		25	4.20	1.68	23.2	3.43	0.144	0.0577	0.798
		287	3.49	615	27.8	0.155	0.00540	0.952	0.0430
	2-methylpentane	−154	4.46	<0.001	19.4	4.19	0.187	<0.001	0.813
		25	3.87	1.77	23.2	3.47	0.134	0.0614	0.804
		62	3.74	7.12	24.0	2.87	0.107	0.204	0.688
	cyclopentane	−94	4.42	<0.001	20.8	3.97	0.176	<0.001	0.824
		25	4.00	1.86	24.7	3.27	0.131	0.0609	0.808
		49	3.91	4.77	25.5	2.93	0.115	0.140	0.746
	n-hexane	−95	4.08	<0.001	20.0	4.16	0.170	<0.001	0.830
		25	3.70	1.27	24.2	3.43	0.127	0.0436	0.829
		69	3.56	6.44	25.6	2.81	0.0999	0.181	0.719
MABN	*n*-hexadecane	18	4.82	0.473	18.2	4.25	0.205	0.0201	0.775
		25	4.80	0.659	18.3	4.20	0.202	0.0277	0.770
		287	3.99	426	22.4	0.221	0.00882	0.942	0.0496
	2-methylpentane	−154	5.24	<0.001	12.9	5.52	0.289	<0.001	0.711
		25	4.54	0.310	18.1	4.35	0.198	0.0135	0.789
		62	4.39	1.43	19.7	3.93	0.172	0.0560	0.772
	n-hexane	−95	5.46	<0.001	13.9	5.17	0.282	<0.001	0.718
		25	4.95	0.310	18.1	4.28	0.212	0.0132	0.775
		69	4.76	1.83	19.9	3.77	0.179	0.0691	0.752
ABN	*n*-hexadecane	18	4.02	0.362	14.2	5.37	0.216	0.0194	0.765
		25	4.00	0.507	14.4	5.29	0.212	0.0268	0.761
		287	3.33	362	19.2	0.260	0.00865	0.941	0.0500
	2-methylpentane	−154	4.36	<0.001	9.40	7.27	0.317	<0.001	0.683
		25	3.78	0.280	13.6	5.66	0.214	0.0158	0.770
		62	3.66	1.32	14.8	5.05	0.184	0.0666	0.749

[a] The data are calculated by using the parameters (eqs 2−4) from Table 6.

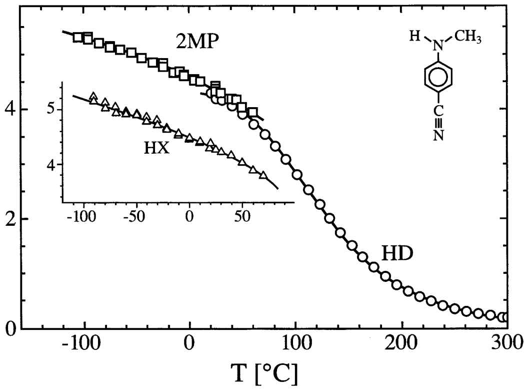


Figure 10. Plots of the fluorescence decay times τ of 4-(methylamino)-benzonitrile (MABN) in 2-methylpentane (2MP), *n*-hexadecane (HD), and *n*-hexane (HX) as a function of temperature. The lines through the data points represent the fitting procedure described in the text (eq 1).

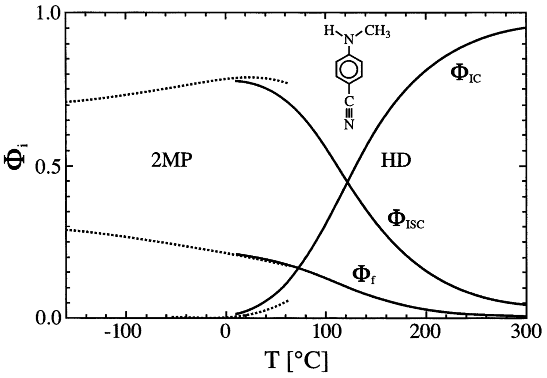


Figure 11. Temperature dependence of the internal conversion yield Φ_{IC}, the intersystem crossing yield Φ_{ISC}, and the fluorescence quantum yield Φ_f of 4-(methylamino)benzonitrile (MABN) in 2-methylpentane (2MP) and *n*-hexadecane (HD). See text.

Table 6, IC becomes the dominant deactivation process for S_1 at higher temperatures, as shown in Figures 9, 11 and 13 (Table 7).

No Correlation of IC with the Energy Gap $\Delta E(S_1,S_2)$. As has been reported previously, the magnitude of the energy gap $\Delta E(S_1,S_2)$ decreases with increasing methyl substitution in the series ABN, MABN, and DMABN.[26] An indication of the value of this gap is given by the difference in energy between the lowest peak of the structured S_1 absorption band and the maximum of the main broad second absorption band, see Figures 1 and 2 and Table 1.[26] From the values for E_{IC} in Table 6, it is clear that no correlation exists between the IC activation energy and $\Delta E(S_1,S_2)$. As ICT is not an important deactivation channel for the three aminobenzonitriles in the alkane solvents studied here, only LE fluorescence being observed, there also is no evidence for a correlation between IC and ICT processes in these molecules.

Mechanism of Internal Conversion. The occurrence of efficient temperature-dependent internal conversion from S_1 to S_0 taking place in the molecules DMABN, MABN, and ABN in alkane solvents could indicate that the energy gap $\Delta E(S_0,S_1)$ between these states can become considerably smaller than the energy $E(S_1)$ of the S_1 state reached by absorption from the equilibrated ground state. Under these conditions, fast IC can take place, as described by the energy gap law.[1−3] The presence of the activation energies E_{IC} would then mean that a thermally activated structural change in S_1 brings the aminobenzonitriles in a configuration which is energetically strongly unfavorable in the ground state and hence leads to a smaller $S_1{-}S_0$ energy gap.

As seen from the absorption spectra (Figures 1 and 2 and Table 1), the energy gap $\Delta E(S_1,S_2)$ becomes smaller in the series ABN, MABN, DMABN, whereas the parameters E_{IC} and k^0_{IC} have similar values for the three molecules. This means that the magnitude of $\Delta E(S_1,S_2)$ does not exert a significant influence

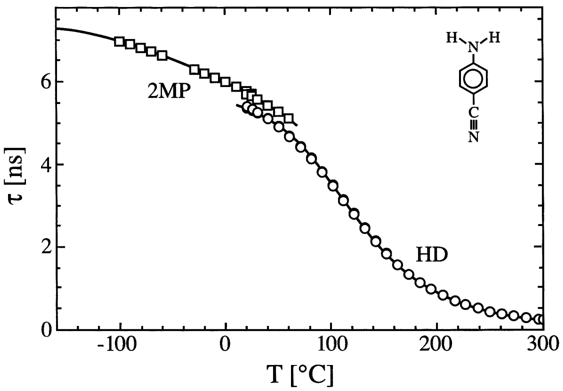


Figure 12. Plots of the fluorescence decay times τ of 4-aminobenzonitrile (ABN) in 2-methylpentane (2MP) and *n*-hexadecane (HD) as a function of temperature. The lines through the data points represent the fitting procedure described in the text (eq 1).

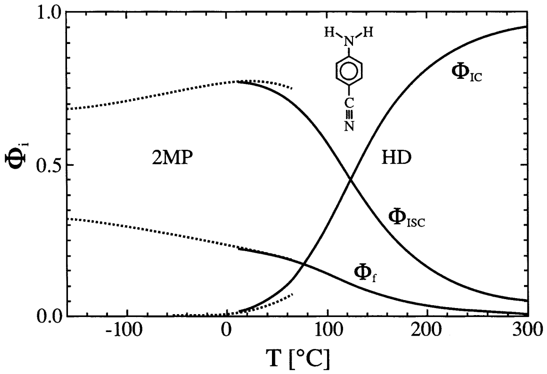


Figure 13. Temperature dependence of the internal conversion yield Φ_{IC}, the intersystem crossing yield Φ_{ISC}, and the fluorescence quantum yield Φ_f of 4-aminobenzonitrile (ABN) in 2-methylpentane (2MP) and *n*-hexadecane (HD). See text.

on the IC process in the aminobenzonitriles, different from what has been concluded for 1-aminonaphthalenes[9,11−15] as well as for the ICT reaction in aminobenzonitriles.[20−23,26,37a] For DMABN in the gas phase at 130 °C, the involvement of a conical intersection in a deactivation process originating from the S_2 state has recently been postulated.[27]

Conclusion

The fluorescence spectra of the three 4-aminobenzonitriles DMABN, MABN, and ABN in alkane solvents such as *n*-hexadecane and 2-methylpentane consist of a single emission band from an LE state. There is no indication for ICT and dual emission in the spectra and the fluorescence decays are accordingly single exponential over the entire temperature range investigated. With these aminobenzonitriles in *n*-hexadecane, the fluorescence quantum yield Φ_f and the fluorescence decay time τ strongly decrease upon increasing the temperature above room temperature. For DMABN, as an example, Φ_f decreases from 0.14 at 25 °C to 0.006 at 284 °C, whereas τ sharply drops from 3.47 ns to 163 ps over this temperature range.

By measuring τ, Φ_f, and the intersystem crossing yield Φ_{ISC} as a function of temperature in the alkane solvents (from -151 to $+284$ °C), the rate constants for internal conversion (IC), ISC, and fluorescence could be determined, as well as their activation energies (E_{IC}, E_{ISC}) and preexponential factors (k^0_{IC}, k^0_{ISC}) and also $k_{ISC}(0)$. Although IC is of minor importance for DMABN, MABN, and ABN in the alkanes at room temperature, IC replaces ISC as the dominant S_1 decay channel in *n*-hexadecane at temperatures higher than 125 °C, a consequence of its large IC activation energy E_{IC}: 31.3 kJ/mol (DMABN), 34.3 kJ/mol (MABN), and 34.8 kJ/mol (ABN), as compared to the ISC barriers of 3.9 (DMABN) and 5.6 kJ/mol (MABN and ABN). This increase in IC efficiency goes at the expense of ISC and fluorescence. The preexponential factors k^0_{ISC} for DMABN, MABN, and ABN, around 3×10^8 s^{-1}, are more than 3 orders of magnitude smaller than their IC counterparts k^0_{IC} (around 5×10^{12} s^{-1}), which supports the spin-forbidden character of the decay channel identified as ISC.

The occurrence of efficient thermally activated IC in the molecules DMABN, MABN, and ABN with planar (not twisted) amino groups was unexpected, because IC in 1-aminonaphthalenes, 4-(methylamino)benzonitrile, and 9-(dimethylamino)-10-cyano-anthracene was shown to be governed by the difference in the amino twist angle in the ground state and in S_1. In addition, especially in the case of the 1-aminonaphthalenes, the influence of the energy gap $\Delta E(S_1,S_2)$ between the two lowest excited singlet states S_1 and S_2 on the IC efficiency was discussed. The similarity of the barrier height E_{IC} (as well as the preexponential factor k^0_{IC}) for the temperature-dependent IC process in DMABN, MABN, and ABN shows, however, that the Arrhenius parameters and efficiency of this reaction do not depend on the energy gap $\Delta E(S_1,S_2)$, which increases from DMABN to ABN. It is also argued that the IC process in these molecules is not correlated with ICT, for which a dependence on $\Delta E(S_1,S_2)$ has also been documented.

A detailed mechanism explaining the thermally activated IC process reported here for DMABN, MABN, and ABN is presently not available. It may be argued that the measured activation energies E_{IC} are the barriers that have to be overcome to bring the aminobenzonitriles into an S_1 configuration which is energetically strongly unfavorable in the ground state. In this manner, the energy gap between S_1 and S_0 would be reduced, opening up an IC deactivation channel. A similar reasoning has also been presented in the case of the structurally related aminobenzonitriles P4C, P4CF2, and P4CF3.

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