# Solvent-Dependent Radiationless Transitions of Excited 1-Aminonaphthalene Derivatives[†]

**K. Suzuki, H. Tanabe, S. Tobita,* and H. Shizuka***

*Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan*

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Photophysical parameters in the excited singlet states of a series of 1-aminonaphthalene derivatives in cyclohexane, 3-methylpentane, and acetonitrile have been determined by means of time-resolved and steady-state fluorometry and time-resolved thermal lensing technique with the aid of MO calculations to elucidate the mechanism of internal fluorescence quenching of 1-aminonaphthalenes observed in nonpolar media. It is revealed that (1) the radiationless processes in nonpolar solvents are mainly due to fast internal conversion (IC; $\Phi_{ic} = 0.97$, $k_{ic} = 8.1 \times 10^9$ s$^{-1}$ for *N*,*N*-dimethyl-1-aminonaphthalene (DMAN) in cyclohexane at 293 K), (2) the fast IC occurs predominantly in the compounds having a pretwisted and flexible amino group with respect to the naphthalene ring, and the rate remarkably depends on temperature (the activation energy for the temperature dependent IC process of DMAN in 3-methylpentane is 5.1 kcal mol$^{-1}$), indicating that the IC process is linked with an internal twisting motion of the amino group in nonpolar solvents, and (3) for the pretwisted compounds the rate of the $S_1 \rightarrow T_1$ intersystem crossing (ISC) is also enhanced both in nonpolar and polar solvents. On the basis of the rate parameters obtained, the IC and ISC mechanisms of 1-aminonaphthalenes are discussed together with the remarkable solvent effects on their relaxation processes.

## Introduction

Radiationless transitions in excited aromatic amines have recently attracted considerable interest in the context of understanding the internal fluorescence quenching of laser dyes (such as rhodamines and aminocoumarins)[1−8] and the formation of twisted intramolecular charge-transfer (TICT) state for *N*,*N*-dimethylaminobenzonitrile and related compounds.[9−12] It is well-known that the electronic character and photophysical properties of aromatic amino compounds are strongly affected by conformational changes in the corresponding amino group (e.g., twisting and inversion motions) upon excitation and also by solvent properties. In the formation of TICT or ICT state, special attention has been paid to the dynamic coupling between structural changes of the amino group and reorientations of polar solvent molecules around the solutes excited-state dipole moment.[13] It has been suggested that the radiationless transition of rhodamine, oxazine, and thiazine dyes is attributed to a process connected with the rotation of the dialkylamino groups, which becomes prominent as solvent polarity is increased. An explanation was given in terms of nonemissive TICT or biradicaloid charge-transfer (BCT) states acting as nonradiative funnels to the ground state.[1−4]

Phillips and co-workers made a detailed study of photophysics of 1-aminonaphthalene (AN) and *N*,*N*-dimethyl-1-aminonaphthalene (DMAN) in several solvents.[14] They found a fast radiationless process of excited DMAN recognized only in nonpolar media. The solvent-dependent radiationless process and Stokes shift in DMAN are of importance related to the use of substituted aminonaphthalene sulfonates as fluorescence probes in proteins and other macromolecules.[15−18] The characteristic change in fluorescence lifetime (or intensity) and the location of the fluorescence maxima of substituted aminonaphthalene sulfonates have permitted their use to determine “polar” and “nonpolar” sites in macromolecules. For DMAN, the fast radiationless process is observed only in nonpolar solvents and the rate decreases drastically with increasing solvent polarity.[14] The deactivation mechanism of DMAN is expected to be different from that of xanthene dyes and aminocoumarins, because in the latter compounds the radiationless processes are known to be prominent in polar solvents, which facilitate the formation of intramolecular charge transfer (ICT) states. Despite the importance of photophysical properties of 1-aminonaphthalenes, the mechanism of the internal fluorescence quenching of 1-aminonaphthalenes in nonpolar solvents, especially the roles of the amino group and solvent polarity to the nonradiative deactivation, has remained an open question.

We have recently studied relaxation processes of excited aromatic amines with particular interest in their nonradiative deactivation processes such as photoionization in aqueous solution[19] and an electron transfer process via the triplet exciplex between DMAN and benzophenone.[20] In the present work, the radiationless processes in the excited states of several 1-aminonaphthalene derivatives were studied by means of time-resolved and steady-state fluorometry and time-resolved thermal lensing (TRTL) techniques together with MO calculations to reveal the mechanism of the solvent-dependent radiationless transitions in 1-aminonaphthalenes. The sample molecules investigated are listed in Chart 1 along with abbreviations used.

## Experimental Section

**Materials.** 1-Aminonaphthalene (AN; Kanto, GR grade) was purified by vacuum sublimation. 2-Methyl-1-aminonaphthalene (2MAN; Tokyo Kasei), *N*-methyl-1-aminonaphthalene (MMAN; Tokyo Kasei), and *N*,*N*-dimethyl-1-aminonaphthalene (DMAN; Wako) were purified by distillation under reduced pressure. *N*,*N*-Diethyl-1-aminonaphthalene (DEAN) was synthesized by reduction[21] of *N*-acetyl-*N*-ethyl-1-aminonaphthalene, which was obtained by acetylation of *N*-ethyl-1-aminonaphthalene (Tokyo Kasei).[22] 1,2,3,4-Tetrahydro-7,8-benzoquinoline (THBQ) was produced by reduction of 7,8-benzoquinoline (Tokyo Kasei) by use of high-pressure $H_2$ gas (∼20 atm) in the presence of hydridochlorotris(triphenylphosphine)ruthenium(II) dichloride (Aldrich).[23] *N*-Methyl-1,2,3,4-tetrahydro-7,8-benzoquinoline (MTHBQ) was synthesized from THBQ and trimethylphosphine.[24] *N*-Methyl-2-methyl-1-aminonaphthalene (2MMMAN)

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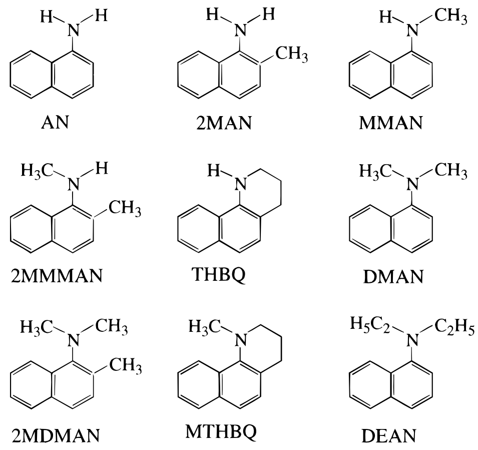
**CHART 1**



and *N*,*N*-dimethyl-2-methyl-1-aminonaphthalene (2MDMAN) were synthesized from 2MAN and trimethylphosphine. The products, THBQ, MTHBQ, 2MMMAN, and 2MDMAN, which were purified by column chromatography, were identified by NMR and mass spectra. Acetonitrile (MeCN; Kanto) was purified by distillation. Cyclohexane (CH; Aldrich, spectrophotometric grade) and polystyrene (PS; Aldrich, average MW ca. 280 000) were used without further purification. 3-Methylpentane (3MP; Wako GR grade) was dried with $CaCl_2$, refluxed over $LiAlH_4$, and then distilled.

**Methods.** The absorption and fluorescence spectra were measured with a UV/vis spectrophotometer (JASCO, Ubest-50) and a spectrofluorometer (Hitachi, F-4010), respectively. The fluorescence quantum yield ($\Phi_f$) was determined by using the value (0.47)[14] of AN in CH as standard.[25] The fluorescence lifetime ($\tau_f$) was obtained with a time-correlated single photon counting fluorometer (Edinburgh Analytical Instruments, FL900CDT). For the compounds with $\tau_f$ less than 1 ns, the lifetime was determined by using a picosecond laser system consisting of a $Nd^{3+}$-YAG laser (Continuum PY 61-10; 355 nm; FWHM, ~40 ps) and a streak scope (Hamamatsu C4334).

For the TRTL measurements, the third harmonics (355 nm) of a $Nd^{3+}$-YAG laser (Spectra Physics, GCR-130, pulse width 5 ns) was used as an excitation source. The excitation beam was focused into a 10-mm quartz cell by a 300-mm focal length lens. The laser beam radius ($R$) at the focal point was about 100 $\mu$m (half-width at 1/e of the signal maximum). The acoustic transit time, $\tau_a$ ($=R/V_a$), which determines the time resolution of TRTL measurements,[26-28] was estimated to be about 70 ns in CH or MeCN by using the velocity of sound ($V_a$) in each solvent. A He−Ne laser (NEC, GLG2026; 633 nm) focused coaxially with the excitation beam by a 30-mm focal length lens was used as a probe beam for the TRTL signals. The signals were detected by a photomultiplier tube (Hamamatsu, R928) after passing through a pinhole (Corion, 2401; 300-$\mu$m diameter) and a monochromator (JOBIN-YVON, H-20). The output signals were converted to the voltage with a digitizing oscilloscope (Tektronix, TDS-744; 500 MHz 2G samples/s) connected with a personal computer (NEC, PC-9821Ap). The absorbance of the sample solutions was adjusted to ca. 0.10 at 355 nm. The benzophenone/MeCN solution ($\Phi_{isc} = 1.0$)[29] was used to confirm optimized experimental conditions.

The nanosecond laser flash photolysis experiments were carried out by using the third harmonics of a $Nd^{3+}$-YAG laser. Details for the laser photolysis system were reported elsewhere.[19]

Molecular orbital calculations were performed by use of the PM3 method (MOPAC ver.6.01)[30] and ab initio MO method (Gaussian 94)[31] on an IBM RS/6000 workstation (Model 41T). The ground-state potential curves in 1-aminonaphthalenes were calculated as a function of the torsional angle between the amino group and the naphthalene moiety by using the semiempirical PM3 method. The geometries were optimized as a function of the dihedral angle, ($CH_3$ or H)−N−C(α)−C(*β*) of 1-aminonaphthalenes. All calculations were carried out with full optimization of geometrical variables (bond lengths, bond angles, and dihedral angles) using analytical gradients.

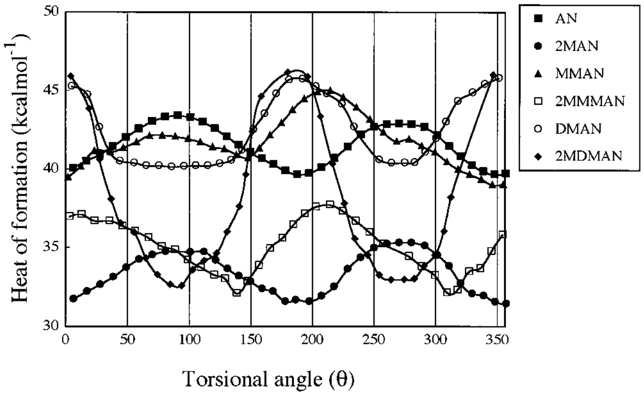
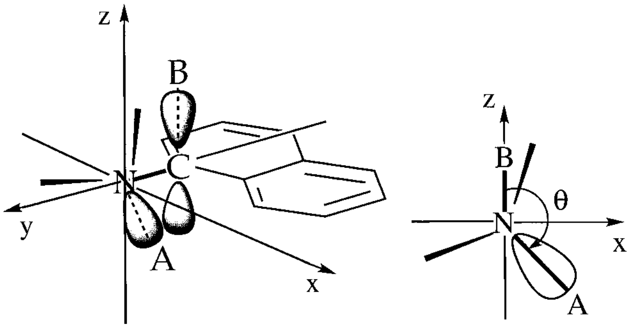


**Figure 1.** Calculated heats of formation as a function of the angle (*θ*) shown in Chart 2. The calculations were performed by the PM3 method.

**CHART 2: Naphthalene Ring Is in *xy* Plane**[a]



[a] The dihedral angle (A−N−C−B) shows the twist angle (*θ*) between the lone-pair lobe on the nitrogen atom and the carbon 2p*π*-orbital on the naphthalene ring plane.

## Results

**Ground-State Geometries and Electronic Spectra of 1-Aminonaphthalenes.** The optimized structures of the ground-state 1-aminonaphthalenes in Chart 1 were obtained by PM3 calculations. The calculated heats of formation of 1-aminonaphthalenes are plotted in Figure 1 as a function of the angle (*θ*) between the lone-pair lobe on nitrogen and the carbon 2p*π*-orbital on the naphthalene ring shown in Chart 2. Inspection of the potential energy curves in Figure 1 enables us to evaluate dominant structures in the ground state. AN and 2MAN give similar potential energy curves in shape. The energy minima for AN, 2MAN, and MMAN are located at $\theta \sim 0°$. In these compounds, the conformation of the amino lone-pair orbital is favorable for conjugation with the *π*-orbitals in the naphthalene ring, whereas in DMAN and 2MDMAN the optimized conformations of the amino group correspond to structures having a twisted lone-pair orbital with respect to the carbon 2p*π*-orbital in the naphthalene ring. In 2MDMAN, the methyl groups on the nitrogen atom are subject to electronic repulsion by the hydrogen atom at the periposition and also by the adjacent methyl group in the naphthalene ring. As a result, the rotational barrier of the amino group in 2MDMAN becomes the highest (~15 kcal mol$^{-1}$) among the compounds in Figure 1. The optimized geometries of MTHBQ also showed a pretwisted structure with the amino torsional angle of 60°.

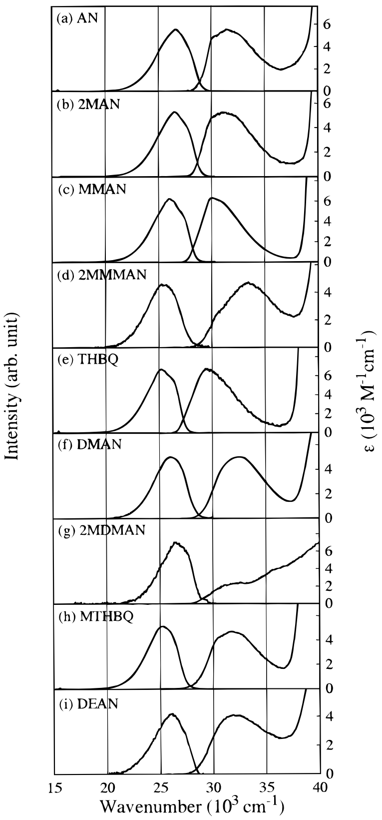


**Figure 2.** Absorption and fluorescence spectra of 1-aminonaphthalenes in CH at 293 K.

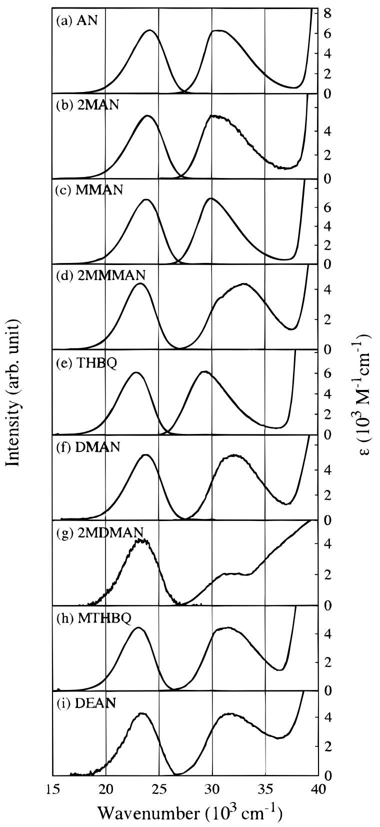


**Figure 3.** Absorption and fluorescence spectra of 1-aminonaphthalenes in MeCN at 293 K.

Figure 2 shows the absorption and fluorescence spectra of 1-aminonaphthalenes in CH at 293 K. The first absorption band of AN consists of two electronic transitions: modified $^1L_b \leftarrow {}^1A$ (shoulder at ~30 000 cm$^{-1}$) and $^1L_a \leftarrow {}^1A$ (the first absorption maximum at ~31 500 cm$^{-1}$) transitions.[32] In MMAN, a slight red shift in the $^1L_a$ band is seen, which can be attributed to the mesomeric effect (-E effect) of the methyl group. In 2MMMAN, the *N*-methylamino group is twisted against the naphthalene ring plane by steric effects of the peri-hydrogen atom and the 2-methyl group, resulting in a blue shift of the $^1L_a$ band.[33,34] The -E effect of dialkyl substituents in DMAN and DEAN is found to compensate for the blue shift caused by their twisted structures. The blue shifts observed in the absorption bands of *N,N*-dialkylamino compounds imply that in these two compounds the amino group is twisted to the naphthalene ring plane owing to repulsion between the alkyl substituents on the nitrogen atom and the peri-hydrogen atom on the naphthalene ring. This is consistent with the results of MO calculations (see Figure 1). The first absorption maxima of THBQ and MTHBQ are shifted slightly to longer wavelengths compared to corresponding flexible analogues, MMAN and DMAN, suggesting that the amino moieties of THBQ and MTHBQ have more planar conformations to the naphthalene ring plane. The absorption spectrum of 2MDMAN is significantly different from those of other 1-aminonaphthalenes. Since the amino group in 2MDMAN has an almost perpendicular structure, this spectral change would be caused by a large blue shift of the $^1L_a$ band. The fluorescence spectra of 1-aminonaphthalenes in Figure 2 exhibit no clear change in spectral shape; however, the peak wavelengths are different from each other, depending on the substituents.

Figure 3 shows the absorption and fluorescence spectra of 1-aminonaphthalenes in MeCN at 293 K. It can be seen that the location and shape of the absorption spectra are scarcely affected by changing the solvent from nonpolar CH to polar MeCN. In contrast, the fluorescence maxima of all the compounds in MeCN remarkably shift to red compared to those in CH (Figure 2), resulting in larger Stokes shifts in polar solvent, MeCN (Table 1). A similar large Stokes shift is also seen for MTHBQ in which the internal motion of the amino moiety is restricted by the methylene ring. Phillips and coworkers[14] suggested that the red shifts in the fluorescence maxima of 1-aminonaphthalenes in polar solvents result from two relaxation mechanisms: (a) an intramolecular reorganization of the amino group and (b) a bulk relaxation of the solvent dipoles about the solutes excited-state dipole moment. The large Stokes shift observed for MTHBQ suggests that the solvent reorientation (mechanism (b)) plays a dominant role for the remarkable red shifts in the fluorescence spectra. In addition, it is considered that in the pretwisted compounds like DMAN and DEAN the conformational change of the amino group (mechanism (a)) also contributes to the large Stokes shift as will be discussed later.

**Photophysical Properties of 1-Aminonaphthalenes at 293 K.** The fluorescence lifetime ($\tau_f$) and fluorescence quantum yield ($\Phi_f$) of 1-aminonaphthalenes are listed in Table 1. The values of $\tau_f$ and $\Phi_f$ are found to be significantly affected by alkylation of the amino group, a methyl substitution at the 2-position in the naphthalene ring, and also solvent polarity. In both solvents (MeCN and CH), DMAN, 2MMMAN, 2MDMAN, and DEAN give smaller $\tau_f$ values than those of other compounds. In particular, dramatic decreases in $\tau_f$ can be recognized for 2MMMAN (0.37 ns), DMAN (0.12 ns), 2MDMAN (0.36 ns), and DEAN (0.35 ns) by use of nonpolar solvent (CH), and the $\Phi_f$ values of these compounds become considerably small in CH, 0.012, 0.011, 0.024, and 0.030, respectively. For 2MDMAN, $\tau_f$ and $\Phi_f$ values are found to be small even in polar solvent, 2.2 ns and 0.016, respectively. It should be noted here that such a remarkable decrease in $\tau_f$ and $\Phi_f$ in CH is not seen for THBQ and MTHBQ having a structurally restricted amino group, indicating that the presence of a flexible alkylamino group with a pretwisted structure in the ground state plays

**TABLE 1: Absorption ($\lambda_{max}^{abs}$) and Fluorescence ($\lambda_{max}^{fluo}$) Peaks, Stokes Shift ($\Delta\bar{\nu}$), Fluorescence Lifetime ($\tau_f$), Quantum Yields of Fluorescence ($\Phi_f$), ISC ($\Phi_{isc}$), and IC ($\Phi_{ic}$) of 1-Aminonaphthalenes in MeCN and CH at 293 K**

| compound | solvent | $\lambda_{max}^{abs}$, nm | $\lambda_{max}^{fluo}$, nm | $\Delta\bar{\nu}$,[b] $10^3$ cm$^{-1}$ | $\tau_f$, (ns) | $\Phi_f$ | $\Phi_{isc}$ | $\Phi_{ic}$ |
|---|---|---|---|---|---|---|---|---|
| AN | MeCN | 322 (6200)[a] | 414 | 6.90 | 17.3 | 0.70 | 0.12 | 0.18 |
| | CH | 318 (5500) | 376 | 4.85 | 6.2 | 0.47 | 0.22 | 0.31 |
| 2MAN | MeCN | 334 (5200) | 417 | 5.96 | 21.3 | 0.75 | 0.070 | 0.18 |
| | CH | 315 (5100) | 375 | 5.08 | 8.2 | 0.61 | 0.17 | 0.22 |
| MMAN | MeCN | 333 (7000) | 418 | 6.11 | 17.0 | 0.53 | 0.10 | 0.37 |
| | CH | 331 (6300) | 383 | 4.10 | 6.0 | 0.36 | 0.24 | 0.40 |
| 2MMMAN | MeCN | 303 (4600) | 430 | 9.75 | 7.9[c] | 0.23 | 0.058 | 0.72 |
| | CH | 299 (4700) | 394 | 8.06 | 0.37 | 0.012 | 0.037 | 0.95 |
| THBQ | MeCN | 340 (6000) | 438 | 6.58 | 22.8 | 0.66 | 0.070 | 0.27 |
| | CH | 340 (6700) | 396 | 4.16 | 10.9 | 0.69 | 0.089 | 0.23 |
| DMAN | MeCN | 312 (5200) | 419 | 8.18 | 4.3 | 0.17 | 0.32 | 0.51 |
| | CH | 308 (5000) | 384 | 6.43 | 0.12 | 0.011 | 0.020 | 0.97 |
| 2MDMAN | MeCN | 311 (2000) | 430 | 8.90 | 2.2 | 0.016 | 0.80 | 0.18 |
| | CH | 308 (2400) | 376 | 5.87 | 0.36 | 0.024 | 0.046 | 0.93 |
| MTHBQ | MeCN | 318 (4500) | 433 | 8.35 | 15.6 | 0.56 | 0.15 | 0.29 |
| | CH | 314 (4700) | 400 | 6.85 | 5.3 | 0.36 | 0.29 | 0.35 |
| DEAN | MeCN | 317 (4200) | 425 | 8.02 | 4.0 | 0.094 | 0.63 | 0.28 |
| | CH | 313 (4200) | 384 | 5.91 | 0.35 | 0.030 | 0.070 | 0.90 |

[a] In parenthesis the molar absorption coefficient, $\epsilon$ (M$^{-1}$ cm$^{-1}$) at $\lambda_{max}^{abs}$ is shown. [b] Calculated from the energy difference between the first absorption and fluorescence band peaks. [c] Since the fluorescence decay curve of 2MMMAN in MeCN consisted of double-exponential components with lifetimes of $\tau_1 = 2.53$ ns ($A_1 = 0.083$) and $\tau_2 = 15.3$ ns ($A_2 = 0.061$), the mean lifetime calculated by $\langle\tau\rangle = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$ is shown.

an important role in the radiationless deactivation processes of excited 2MMMAN, DMAN, 2MDMAN, and DEAN in CH.

In order to clarify the contribution of intersystem crossing (ISC) and internal conversion (IC) to the fast nonradiative processes in 2MMMAN, DMAN, 2MDMAN, and DEAN in nonpolar solvent, TRTL measurements were carried out. The quantum yield of ISC ($\Phi_{isc}$) can be determined from the following equation by measurements of the ratio of the slow and total TRTL signal intensities ($U_{slow}/U_{total}$):[26,35,36]

$$\frac{U_{Slow}}{U_{Total}} = \frac{\Phi_{isc}E_T}{E_{ex} - \Phi_f\langle E_S\rangle} \qquad (1)$$

where $E_{ex}$ and $E_T$ are the excitation energy and the 0−0 transition energy of the lowest triplet state ($T_1$), respectively, and $\langle E_S\rangle$ is the average energy dissipated by fluorescence from the $S_1$ state:

$$\langle E_s\rangle = \frac{\int \bar{\nu} I_f(\bar{\nu})\,d\bar{\nu}}{\int I_f(\bar{\nu})\,d\bar{\nu}} \qquad (2)$$

where $I_f(\bar{\nu})$ is the spectral distribution of fluorescence in wavenumber ($\bar{\nu}$). It was confirmed that the effect of $T_n \leftarrow T_1$ absorption on the TRTL signals at the wavelength (633 nm) of the probe beam could be neglected by measuring the $T_n \leftarrow T_1$ absorption spectra of the sample compounds and by performing the TRTL measurements at a different probe wavelength (685 nm of a diode laser). The TRTL signals of DMAN, 2MDMAN, and MTHBQ in MeCN and CH are shown in Figure 4. The time evolution of the TRTL signal of DMAN in MeCN (Figure 4a) consists of prompt and slow rise components. The former arises from the heat released by nonradiative deactivation processes from the lowest excited singlet state ($S_1$) and the latter corresponds to the slow thermal release from the lowest triplet state ($T_1$). In nonpolar solvent (CH), the slow rise component almost disappears (Figure 4b), indicating clearly a drastic decrease in the triplet formation yield. Figures 4c and 4d show the TRTL signals of 2MDMAN in MeCN and CH, respectively. In polar MeCN, a large contribution of the slow rise component can be seen, nevertheless, in nonpolar CH, the TRTL signal scarcely involves the slow rise component. Interestingly, such a remarkable solvent dependence of the TRTL signal is not recognized for MTHBQ as seen from Figure 4e,f; i.e., the $T_1$ state of MTHBQ is formed to a similar extent both in polar and nonpolar solvents. The values of $\Phi_{isc}$ of 1-aminonaphthalenes determined by means of the TRTL method are summarized in Table 1. Since the contribution of photochemical reactions to the relaxation processes of excited 1-aminonaphthalenes was negligible, the quantum yield of IC ($\Phi_{ic}$) can be estimated from the following equation:

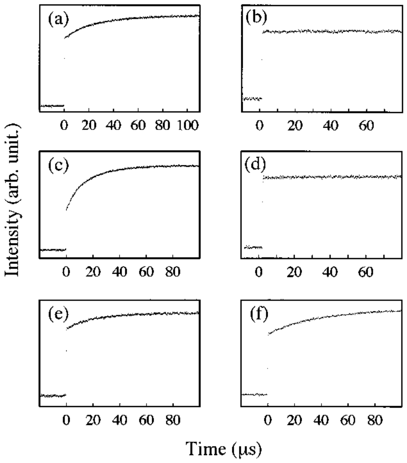


**Figure 4.** Time evolution of the TRTL signal of (a) DMAN in MeCN, (b) DMAN in CH, (c) 2MDMAN in MeCN, (d) 2MDMAN in CH, (e) MTHBQ in MeCN, and (f) MTHBQ in CH at 293 K.

$$\Phi_f + \Phi_{isc} + \Phi_{ic} = 1 \qquad (3)$$

The $\Phi_{ic}$ values calculated are also listed in Table 1. It is apparent from Table 1 that the efficient nonradiative deactivation processes observed for 2MMMAN, DMAN, 2MDMAN, and DEAN in nonpolar CH are mainly due to the $S_1 \rightarrow S_0$ internal conversion.

The rate constants for fluorescence ($k_f$), ISC ($k_{isc}$), and IC ($k_{ic}$) were calculated by use of the $\tau_f$ values and the corresponding quantum yields in Table 1 as

$$k_f = \Phi_f\tau_f^{-1} \qquad k_{isc} = \Phi_{isc}\tau_f^{-1} \qquad k_{ic} = \Phi_{ic}\tau_f^{-1} \qquad (4)$$

The results are listed in Table 2. The most notable feature in Table 2 is that the $k_{ic}$ values of 2MMMAN, DMAN, 2MDMAN, and DEAN show a drastic increase by changing the solvent from polar MeCN to nonpolar CH. All these compounds have

**TABLE 2: Rate Constants of Fluorescence ($k_f$), ISC ($k_{isc}$), and IC ($k_{ic}$), $\langle\bar{\nu}_f^{-3}\rangle_{av}^{-1}$, and $|M_{1u}|$ of 1-Aminonaphthalenes in MeCN and CH at 293 K**

| compound | solvent | $k_f$, $10^7$ s$^{-1}$ | $\langle\bar{\nu}^{-3}\rangle_{av}^{-1}$, $10^{13}$ cm$^{-3}$ | $\lvert M_{1u}\rvert$,[a] D | $k_{isc}$, $10^7$ s$^{-1}$ | $k_{ic}$, $10^7$ s$^{-1}$ |
|---|---|---|---|---|---|---|
| AN | MeCN | 4.0 | 1.290 | 0.202 | 0.7 | 1.0 |
| | CH | 7.2 | 1.748 | 0.213 | 3.4 | 4.8 |
| 2MAN | MeCN | 3.5 | 1.267 | 0.190 | 0.3 | 0.9 |
| | CH | 7.5 | 1.470 | 0.218 | 2.1 | 2.6 |
| MMAN | MeCN | 3.1 | 1.244 | 0.181 | 0.6 | 2.2 |
| | CH | 6.0 | 1.647 | 0.200 | 4.0 | 6.7 |
| 2MMMAN | MeCN | 2.9 | 1.154 | 0.182 | 0.7 | 9.1 |
| | CH | 3.2 | 1.540 | 0.151 | 10 | 260 |
| THBQ | MeCN | 2.9 | 1.107 | 0.185 | 0.3 | 1.2 |
| | CH | 6.3 | 1.508 | 0.214 | 0.8 | 2.9 |
| DMAN | MeCN | 4.0 | 1.247 | 0.205 | 7.4 | 12 |
| | CH | 9.2 | 1.643 | 0.248 | 17 | 810 |
| 2MDMAN | MeCN | 0.7 | 1.140 | 0.090 | 36 | 8.2 |
| | CH | 6.7 | 1.764 | 0.204 | 13 | 260 |
| MTHBQ | MeCN | 3.6 | 1.129 | 0.205 | 1.0 | 1.9 |
| | CH | 6.8 | 1.490 | 0.224 | 5.5 | 6.6 |
| DEAN | MeCN | 2.4 | 0.839 | 0.194 | 16 | 7.0 |
| | CH | 8.6 | 1.823 | 0.228 | 20 | 260 |

[a] The transition moment, $|M_{1u}|$, was estimated experimentally from $k_f$ and $\langle\bar{\nu}_f^{-3}\rangle_{av}^{-1}$ on the basis of eqs 6 and 7. For details, see text.

pretwisted structures, and a similar solvent effect is not seen in rigidized analogues, THBQ and MTHBQ. These facts suggest that the fast IC in the pretwisted compounds is induced by internal twisting motions of the amino group in the excited singlet state in nonpolar solvents.

**Temperature and Polymer Matrix Effects on the Photophysical Properties of DMAN and MTHBQ.** In order to reveal the dynamical effect of the amino group on the relaxation processes of excited 1-aminonaphthalenes, the photophysical quantities ($\tau_f$, $\Phi_f$, and $\Phi_{isc}$) for two typical compounds (DMAN and MTHBQ) were measured in 3MP at various temperatures between 77 and 295 K. In the $\Phi_f$ measurements, the temperature dependence was corrected for the refractive index of the solvent by using the fluorescence signal of 9,10-diphenylanthracene in 3MP as an external standard.[37] The values of $\Phi_{isc}$ were obtained by measuring the initial absorbance of $T_n \leftarrow T_1$ absorption. Since the spectral shapes of the $T_n \leftarrow T_1$ absorption of DMAN and MTHBQ were not affected appreciably by temperature change, we assumed that the molar absorption coefficients of their $T_n \leftarrow T_1$ absorption at the monitoring wavelength (530 nm) were constant over the temperature range investigated. The temperature dependences of the photophysical parameters of DMAN and MTHBQ in 3MP are shown in Figures 5 and 6, respectively. It is evident from Figure 5 that a drastic decrease in $\tau_f$ with increasing temperature for pretwisted DMAN is mainly due to a large increase in $k_{ic}$. The temperature dependence of $k_{ic}$ can be written as

$$k_{ic} = k_{ic}^{\circ} + k_{ic}' \exp\left(-\frac{\Delta E_{ic}}{RT}\right) \qquad (5)$$

where $k_{ic}^{\circ}$ (=1.9 (± 0.1) × $10^8$ s$^{-1}$) is independent of $T$, and the temperature-dependent component of $k_{ic}$ is described by an Arrhenius term consisting of the frequency factor ($k_{ic}'$) and activation energy ($\Delta E_{ic}$). By plotting $\ln(k_{ic} - k_{ic}^{\circ})$ vs $T^{-1}$, $\Delta E_{ic}$ and $k_{ic}'$ were obtained to be 5.1 kcal mol$^{-1}$ and 5 × $10^{13}$ s$^{-1}$, respectively. In contrast to the results of DMAN, $k_{ic}$ of MTHBQ with a structurally restricted amino group in 3MP is not so affected by the temperature change, indicating that the temperature-dependent IC process of DMAN is related to the internal twisting motion of the dimethylamino group.

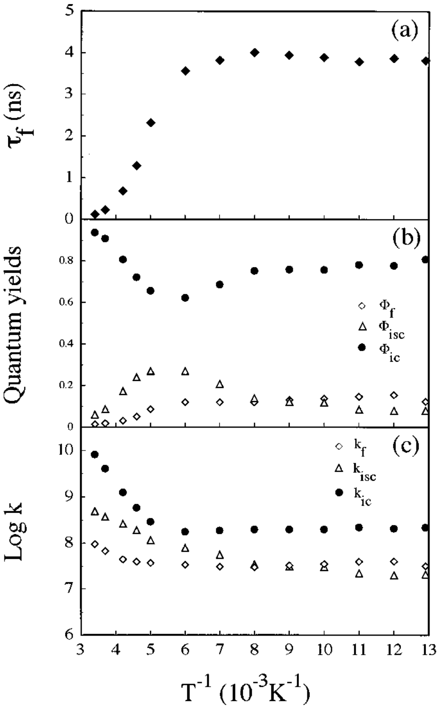


**Figure 5.** Temperature dependence of the fluorescence lifetime (a), the quantum yields (b), and the rate constants (c) for relaxation processes of excited DMAN in 3MP.

In order to reveal polymer matrix effects on the nonradiative rates, we measured fluorescence lifetimes of DMAN and DEAN in polystyrene at 293 K. The fluorescence lifetimes obtained by 320- and 350-nm excitation of DMAN were $\tau_1$ = 3.1 ns (58%) and $\tau_2$ = 6.9 ns (42%) and $\tau_1$ = 4.2 ns (68%) and $\tau_2$ = 8.1 ns (32%), respectively. The fluorescence decay profiles of DEAN in polystyrene also consisted of two exponential decay components as $\tau_1$ = 3.2 ns (33%) and $\tau_2$ = 8.5 ns (67%) upon 370-nm excitation. The fluorescence and its excitation spectra of DMAN changed slightly depending on the excitation and monitoring wavelengths. Thus, a possible reason for the biexponential decay might come from the presence of different amino group conformers in polystyrene. The fact that the mean fluorescence lifetimes of DMAN and DEAN in polystyrene increased significantly compared to those in CH suggests that the fast internal conversion process in pretwisted compounds in nonpolar fluid solvents is related to the internal twisting motion of the amino group.

## Discussion

**(1) Electronic Structure of the Fluorescent State of Pretwisted 1-Aminonaphthalenes.** Ab initio MO calculations

**TABLE 3: Calculated Properties of the Ground State and the Low-Lying Excited Singlet States at Franck−Condon (FC) and Equilibrium (EQ) Nuclear Configurations of DMAN**[a]

| | electronic character | | relative energy, eV | | oscillator strength | | dipole moment, D | |
|---|---|---|---|---|---|---|---|---|
| state | STO-3G | 3-21G | STO-3G | 3-21G | STO-3G | 3-21G | STO-3G | 3-21G |
| FC state | | | | | | | | |
| $S_0$ | | | | | | | 1.005 | 1.087 |
| $S_1$ | $^1L_b$ | $^1L_a$ | 0 | 0 | 0.014 | 0.149 | 0.846 | 1.427 |
| $S_2$ | $^1L_a$ | $^1L_b$ | 0.06 | 0.14 | 0.173 | 0.002 | 1.504 | 1.153 |
| $S_3$ | ICT | ICT | 1.16 | 1.44 | 0.017 | 0.054 | 6.402 | 5.478 |
| EQ state | | | | | | | | |
| $S_1$ | $^1L_a$ | $^1L_a$ | | | 0.419 | 0.307 | 2.916 | 3.042 |

[a] For the calculations of FC states, the ground-state geometry optimized by 3-21G basis sets was used.

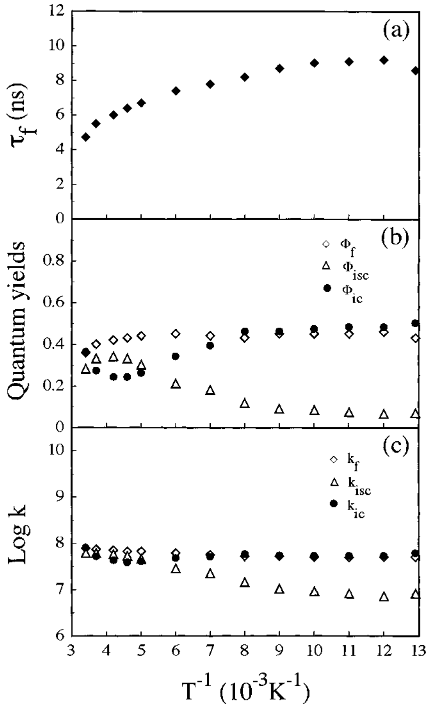


**Figure 6.** Temperature dependence of the fluorescence lifetime (a), the quantum yields (b), and the rate constants (c) for relaxation processes of excited MTHBQ in 3MP.

were performed on the ground and excited singlet states of DMAN by using STO-3G and 3-21G basis sets[31] in order to clarify the electronic structures of the low-lying excited singlet states. The geometry of the ground DMAN optimized by the ab initio calculations with 3-21G basis sets corresponded to the amino conformation at $\theta = 68°$. This twist angle of the lone-pair orbital of the amino group is consistent with that obtained by the semiempirical PM3 calculations (Figure 1).[30] The optimized $S_1$ state geometry of DMAN was calculated at the CIS/STO-3G or CIS/3-21G level, which gave the equilibrium conformation corresponding to $\theta = 42°$ (STO-3G) and 44° (3-21G), showing that the conformation of the amino group relaxed from an almost perpendicular to a more planar structure in the excited singlet state. Calculated properties of low-lying excited singlet states (electronic character, relative energy, oscillator strength, and dipole moment) of DMAN are shown in Table 3 for both Franck−Condon and equilibrium excited states. The $S_1$ and $S_2$ states are located very close in energy in the Franck−Condon excited states, although the relative energies of $^1L_b$ and $^1L_a$ states are reversed for STO-3G and 3-21G basis sets. The $S_3$ state lying 1.0−1.5 eV above the $S_1$ state has intramolecular charge transfer (ICT) character. Judging from the small oscillator strength (0.017 (STO-3G) and 0.054 (3-21G)), the electronic transition from the ground state to the $S_3$ state is found to be forbidden. In the excited equilibrium conformation, the $^1L_a$ state becomes the lowest excited singlet state. The calculated dipole moments of the $S_1(^1L_a)$ state (2.916 D (STO-3G) and 3.042 D (3-21G)) for the equilibrium excited state of DMAN are close to that (2.9−3.9 D) estimated experimentally by Meech *et al.*[14] from Stokes shifts of the fluorescence spectra in various solvents. The decrease in $pK_a$ values of DMAN upon excitation ($pK_a(S_0) = 4.6$, $pK_a(S_1) = 2.5$)[38] supports the above-mentioned charge-transfer character from the dimethylamino group to the naphthalene ring in the emitting state.

The electronic transition moment $|M_{1u}|$ of the fluorescent state for 1-aminonaphthalenes can also be deduced from the experimentally obtained $k_f$ values as shown in Table 2. To compare the $k_f$ values in different solvents, a number of corrections are required. The most important correction is needed for the spectral red shift given by $\langle \bar{\nu}_f^{-3} \rangle_{av}^{-1}$ and the refractive index ($n$) of the solvent used. According to the theoretical treatment by Strickler and Berg,[39] the radiative rate constant $k_f$ for a transition from a higher electronic state (u) to a lower electronic state (1) is given by

$$k_f = \frac{64\pi^4 n^3}{3h} \langle \bar{\nu}_f^{-3} \rangle_{av}^{-1} |M_{1u}|^2 \tag{6}$$

where

$$\langle \bar{\nu}_f^{-3} \rangle_{av}^{-1} = \frac{\int I(\bar{\nu})\, d\bar{\nu}}{\int \bar{\nu}^{-3} I(\bar{\nu})\, d\bar{\nu}} \tag{7}$$

and $|M_{1u}|$ is given by

$$|M_{1u}| = \langle \Psi_u | \sum e\mathbf{r} | \Psi_1 \rangle \tag{8}$$

The estimated values of $\langle \bar{\nu}_f^{-3} \rangle_{av}^{-1}$ and $|M_{1u}|$ calculated by use of eq 6 for 1-aminonaphthalenes in MeCN and CH are shown in Table 2. It can be recognized that $|M_{1u}|$ tends to decrease in polar MeCN except for 2MMMAN. As there is not so remarkable change in their absorption intensity (see Figures 2 and 3), we may conclude that electronic character of the fluorescent state of 1-aminonaphthalenes in polar solvents is different from that in nonpolar ones. Since the first absorption bands ($^1L_b \leftarrow {}^1A$ and $^1L_a \leftarrow {}^1A$) of 1-aminonaphthalenes lie close in energy, the electronic wave function of the fluorescent state $\Psi_f$ can be expressed as a linear combination of the wave functions of the $^1L_b$ and $^1L_a$ states,[15,18]

$$\Psi_f = a\Psi(^1L_b) + b\Psi(^1L_a) \tag{9}$$

where $a$ and $b$ are the corresponding coefficients ($a^2 + b^2 = 1$). According to MO descriptions taking configuration interactions into account, $\Psi_f$ may be represented by[14]

$$\Psi_f = \sum_i a_i \Psi_i(\mathrm{LE}) + \sum_j b_j \Psi_j(\mathrm{CT}) \tag{10}$$

where $\Psi_i$(LE) and $\Psi_j$(CT) denote various electronic states of locally excited (LE) and charge transfer (CT) configurations, respectively. The remarkable stabilization by solvent relaxation in polar MeCN suggests the large dipole moment in the emitting state,[14] and thus substantial CT character should be involved in the fluorescent state in polar solvents.[34] The fact that the $|M_{1u}|$ value decreased with an increase of solvent polarity excludes a simple level inversion model, since the oscillator strength of the $^1L_a$ state is calculated to be significantly larger than that of the $^1L_b$ state (see Table 3). The decrease of $|M_{1u}|$ in polar solvent would suggest that CT character in the emitting state of 1-aminonaphthalenes partly comes from the mixing with the $S_3$ (ICT) state. For 2MDMAN, the $|M_{1u}|$ value (0.090) in MeCN is significantly smaller than that (0.204) in CH, showing that the fluorescent state of 2MDMAN in polar media has different character from that of other 1-aminonaphthalenes.

**(2) The Mechanism for the Fast IC Process of Pretwisted 1-Aminonaphthalenes in Nonpolar Solvents.** The experimental facts observed on the fast IC of 1-aminonaphthalenes can be summarized as follows: (1) the fast IC is seen only for pretwisted compounds in nonpolar solvents, (2) in polar solvents the IC rate dramatically decreases depending on solvent polarity, and (3) temperature and polymer matrix effects on the IC rate and also the absence of fast IC process in MTHBQ show that the internal twisting motion of the amino group plays an important role for the fast IC. Such a fast IC process is not observed for *N,N*-dimethyl-2-aminonaphthalene, where the $S_1$-($^1L_b$) and $S_2$($^1L_a$) energy gap is relatively large both in nonpolar and polar solvents.[31] Hence, one can expect that the mechanism of the fast IC of 1-aminonaphthalenes is related to the proximity of the $S_1$($^1L_b$) and $S_2$($^1L_a$) states.[40] The results of MO calculations showed that in the excited singlet state the lone-pair orbital of the amino group of pretwisted 1-aminonaphthalenes changes the conformation from an almost perpendicular structure to one more parallel to carbon 2p$\pi$-orbitals of the naphthalene ring. This conformational change of the amino group would promote vibronic coupling between close-lying $S_1$ and $S_2$ states, resulting in an increase in the Franck–Condon factor for the $S_1 \rightarrow S_0$ IC process. The temperature dependence of $k_{ic}$ showed the presence of an energy barrier (5.1 kcal mol$^{-1}$) for the IC process. This may correspond to the energy required for the twisting motion of the amino group. The temperature dependence of $k_{ic}$ for DMAN in Figure 5 shows the presence of an inherent IC process with a significantly smaller temperature dependence. Such an almost temperature-independent IC process is also seen for MTHBQ (Figure 6). The fast IC process of pretwisted 1-aminonaphthalenes is not observed in polar MeCN. This fact can be explained by an increase of the energy gap between $S_1$ and $S_2$ states in polar solvent, because intramolecular CT states ($^1L_a$ and ICT states) are more stabilized compared to the $^1L_b$ state by solvent reorientation.

**(3) The Mechanism of the ISC Process of Pretwisted 1-Aminonaphthalenes.** It is noteworthy in Table 2 that the rate constants of ISC in pretwisted compounds in CH are significantly greater than those of other compounds. The enhancement of $k_{isc}$ of the pretwisted compounds in CH can be explained by vibronic coupling between close-lying $S_1$ and $S_2$ states in a similar manner as the enhancement of IC.

Table 2 also shows that $k_{isc}$ of 2MDMAN is significantly large both in polar MeCN and nonpolar CH. A possible explanation for the remarkably large $k_{isc}$ of 2MDMAN is given in terms of pseudo-nonbonding character of the lone-pair electrons of the amino substituent.[41–43] According to the theoretical treatment by Henry and Siebrand,[44] the matrix element for the ISC from the pure-spin adiabatic Born–Oppenheimer state ($^1\Psi_{S1}$) to triplet states which is mixed by the spin–orbit operator $H_{so}$ and the nuclear kinetic energy operator $T(Q)$ with other pure-spin product states lying outside the $S_1$ energy region can be written as

$$\langle S_1|H_{so} + T(Q)|T_1\rangle = \langle ^1\Psi_{S1}|H_{so}|^3\Psi_{T1}\rangle + \sum_i \frac{\langle ^1\Psi_{S1}|T(Q)|^1\Psi_i\rangle\langle ^1\Psi_i|H_{so}|^3\Psi_{T1}\rangle}{E_i - E_{T1}} + \sum_j \frac{\langle ^1\Psi_{S1}|H_{so}|^3\Psi_j\rangle\langle ^3\Psi_j|T(Q)|^3\Psi_{T1}\rangle}{E_j - E_{T1}} \quad (11)$$

Here, the first term corresponds to the direct spin–orbit coupling mechanism for ISC. This term is known to become a dominant ISC mechanism when $\pi,\sigma^*$ or n,$\pi^*$ states coupled with $\pi,\pi^*$ states. The latter efficient ISC mechanism [ISC, $^1(\pi,\pi^*) \rightarrow {^3}(n,\pi^*)$ and $^1(n,\pi^*) \rightarrow {^3}(\pi,\pi^*)$] is well-known as the El-Sayed rule.[45,46] The second and third terms in eq 11 represent the spin–orbit coupling through vibronic interactions. Since electronic character of the $S_1$ state of 2MDMAN is characterized, at least in part, by the charge-transfer transition of one of the lone-pair electrons on the nitrogen atom to $\pi^*$-orbitals (designated as $l \rightarrow a_\pi$ by Kasha),[42] the major contributors to the first term in eq 11 can be reduced to matrix elements involving the lone-pair orbital ($\phi_n$) and the carbon 2p$\pi$-orbitals ($\phi_{2p\pi}$) of the naphthalene ring as follows:

$$\langle \phi_{2p\pi}|H_{so}|\phi_n\rangle \sin\theta \quad (12)$$

where $\theta$ is the angle between the *l*- and $\pi$-directions. Although the matrix element in eq 12 is of two-center nature, it may be expected to be larger than that of the three-center terms which are responsible for spin–orbit mixing of the $\pi,\pi^*$ states of simple planar aromatics. If the *l*-orbital is not parallel to the $\pi$-direction, i.e., the amino group is twisted to the naphthalene ring as in the case of 2MDMAN, eq 12 and thus the first term in eq 11 can become relatively large.

As shown in Figures 5c and 6c, the $k_{isc}$ values for DMAN and MTHBQ are found to decrease with a decrease of temperature, although the $k_{ic}$ values become constant at $T <$ ca. 170 K. Temperature-dependent ISC can be seen even for MTHBQ having a structurally restricted amino group. These results suggest the presence of an ISC process through higher triplet states which can couple efficiently with a thermally activated $S_1$ vibrational state.

Solvent-dependent radiationless processes have also been reported for typical laser dyes such as rhodamines and aminocoumarins, where the internal fluorescence quenching is thought to be caused by the TICT or biradicaloid state formation in polar environments.[1–8] In 2MDMAN, it can be considered that there exists a quenching mechanism due to ISC via an ICT state in polar media. Differences between internal quenching mechanisms of the dye molecules mentioned above and that of 2MDMAN may lie in their amino conformations in the ground state. In 2MDMAN, the amino group is already twisted and sterically restricted with respect to torsional motions, which is in contrast with a more planar and flexible amino group of the dye molecules. As a result, it is conceivable that the ICT state arising from ($l,\pi^*$)-transition in 2MDMAN accelerates the rate of ISC and causes fluorescence quenching. For other pretwisted 1-aminonaphthalenes, the remarkable solvent dependence of the internal fluorescence quenching through IC can be ascribed to the vibronic coupling between close-lying $S_1$ and $S_2$ states connected with the twising motion of the amino group. Very recently, Rückert *et al.* had reported similar results on the relaxation processes of 1-aminonaphthalenes.[47]

## Concluding Remarks

The relaxation processes of the excited singlet state of a series of 1-aminonaphthalenes were investigated by means of time-resolved and steady-state fluorometry and TRTL technique to reveal the mechanism of internal fluorescence quenching of 1-aminonaphthalenes in nonpolar media. The following concluding remarks can be drawn from this work:

(1) The results of TRTL measurements clearly showed that the fast nonradiative processes observed for 1-aminonaphthalenes are mainly due to internal conversion (IC).

(2) The fast IC process was prominent in the compounds with a flexible and pretwisted amino group. The IC rate of DMAN decreased remarkably with decreasing temperature, and for DMAN and DEAN in polystyrene significant increases in the fluorescence lifetime were observed. On the other hand, for MTHBQ having a structurally restricted amino group, the fast IC was not observed both in CH and MeCN, and the IC rate was independent of temperature. These facts suggested that the fast IC process of pretwisted 1-aminonaphthalenes is linked with the internal twisting motion of the amino group.

(3) For pretwisted 1-aminonaphthalenes, the rate of ISC was also found to increase compared with that of more planar 1-aminonaphthalenes in both nonpolar and polar solvents. With the aid of the results of MO calculations, it was concluded that the fast IC and ISC in the excited pretwisted 1-aminonaphthalenes were caused by vibronic coupling between close-lying $S_1$ and $S_2$ states promoted by the internal twisting motion of the amino group.

(4) The photophysical properties of excited 2MDMAN having an almost perpendicular structure of the amino group were distinct from those of the other compounds. The marked increase in the $S_1 \rightarrow T_1$ ISC rate was observed for 2MDMAN even in polar MeCN. The fast ISC of 2MDMAN in MeCN could be explained by ICT character of the emitting state, which involves transitions from the pseudo-nonbonding orbital of the twisted dimethylamino group to $\pi^*$-orbitals in the naphthalene ring.

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