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ARTICLES

Formation and Anomalous Behavior of Aminonaphthalene−Cinnamonitrile Exciplexes

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The solvent dependence of the electronic spectra of several 1-aminonaphthalenes and 2-aminonaphthalenes in the absence and presence of two styrene derivatives, cinnamonitrile and 1-phenylpropene, has been investigated. The absorption maxima of the aminonaphthalenes are dependent upon both the polarity and hydrogen-bond donor and acceptor properties of the solvent and display both red and blue solvent shifts. The fluorescence maxima are more sensitive to solvent polarity than are the absorption maxima and display red shifts in both non-hydroxylic and hydroxylic solvents. The excited state dipole moments of the 1-aminonaphthalenes are larger than those of the 2-aminonaphthalenes. Quenching of the aminonaphthalene fluorescence by cinnamonitrile occurs with diffusion-controlled rates in all solvents, in accord with the occurrence of exergonic electron transfer. Exciplex fluorescence is observed only for the tertiary aminonaphthalenes in nonpolar solvents. The exciplex fluorescence displays anomalous temperature dependence in hexane solution, an increase in temperature resulting in blue-shifted exciplex fluorescence and an increase in the exciplex decay time. Quenching of the aminonaphthalene fluorescence by 1-phenylpropene is slower than diffusion-controlled and is not accompanied by exciplex fluorescence.

Aromatic amines are strong electron donors that have been widely employed in investigations of exciplex formation and photoinduced electron transfer.[1−5] In most such studies, ground state *N*,*N*-dialkylanilines have been used to quench relatively nonpolar singlet acceptors. Since the exciplex or contact ion pair formed in such reactions is more polar than the locally excited singlet state, solvent polarity has a pronounced effect on exciplex formation and behavior. Increasing solvent polarity has little effect on the fluorescence of the locally excited singlet but causes a red shift in the exciplex emission and a decrease in the exciplex fluorescence intensity and lifetime due increased rates of nonradiative decay or ionic dissociation. The formation of fluorescent exciplexes has been observed for *N*,*N*-dialkylanilines but not for primary or secondary anilines.[2] The absence of exciplex fluorescence from exciplexes formed by secondary and tertiary anilines has been attributed to proton transfer processes and enhanced intersystem crossing.[2,5]

Quenching of singlet aromatic amines by ground state acceptors can also result in electron transfer.[6−11] In comparison to the quenching of singlet acceptors by aromatic amines, quenching of singlet aromatic amines by ground state acceptors has received limited attention. Beens and Weller[1a] noted the failure of dimethylaniline and benzene to form an exciplex and suggested that it might be a consequence of limited orbital overlap. Intermolecular exciplex formation upon quenching of 2-dimethylaminonaphthalene by dimethylphthalates in nonpolar solvents was observed by Kaneta and Kiozumi.[6] Fluorescence

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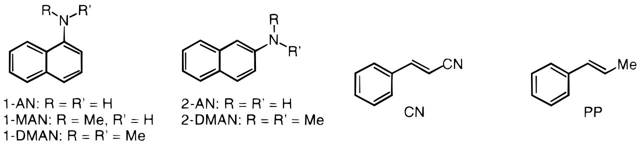
CHART 1



quenching of aromatic amines by chlorobenzenes,[7] chloromethanes,[8] and benzonitrile[9] has also been reported; however, exciplex formation was not observed in these reactions. Intramolecular exciplex formation between singlet dimethylaniline and alkene or styrene acceptors has been observed by Hansen and co-workers[10] and in this laboratory.[11]

We report here the results of our investigation of the quenching of several aminonaphthalenes (Chart 1) by the styrene derivatives cinnamonitrile (CN) and 1-phenylpropene (PP) in a number of solvents differing in both polarity and hydrogen-bonding strength. The effects of both N-alkylation and the position of the amine substituents on the behavior of 1- and 2-aminonaphthalenes have been investigated. The electronic spectra of the aminonaphthalenes have been extensively studied, providing essential information concerning their excited state structure and photophysical behavior.[12−19] Styrene derivatives have been previously employed as both electron donors and acceptors in a wide variety of exciplex-forming reactions, including our studies of intra- and intermolecular exciplex formation with tertiary amines.[20−22] Exciplex fluorescence is observed upon quenching of the tertiary aminonaphthalenes, but not the primary or secondary aminonaphthalenes, by CN but not by PP. The exciplex formed between 2-dimethylaminonaphthalenes and CN in hexane solution displays unprecedented temperature-dependent behavior.

Experimental Section

General Methods. UV absorption spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer. Steady state fluorescence spectra were obtained on a Spex Fluoromax spectrometer. Singlet energies were calculated from the crossing point of emission and excitation spectra. All samples of solutions for measurements of UV absorption, fluorescence, and fluorescence decay were degassed by bubbling with dry N_2 for a minimum of 15 min. The concentrations of aminonaphthalenes were in the range from 10^{-4} to 10^{-5} M, resulting in an absorbance of 0.2−0.3 at the wavelength used for fluorescence excitation. The concentration range of the quenchers CN and PP used in Stern−Volmer quenching studies were sufficient to provide >50% quenching of the aminonaphthalene fluorescence intensity. Higher CN concentrations were used in studies of exciplex fluorescence. The quenchers have negligible absorption for wavelengths >320 nm.[23] Quinine sulfate in 1.0 N H_2SO_4 was used as a reference standard for the measurement of fluorescence quantum yields ($\Phi_f = 0.546$ at 25 °C).[24] Fluorescence quantum yields were measured by comparing the integrated area under the fluorescence curve for aminonaphthalenes and the standard at equal absorbance at the same excitation wavelength.

Fluorescence decays were measured on a Photon Technology International (PTI) Timemaster stroboscopic detection instrument with a gated hydrogen arc lamp using a scatter solution to obtain the lamp decay profile. Nonlinear least-squares fitting of the decay curves employed the Levenburg−Marquardt algorithm as described by James et al.[25] and implemented by the PTI software (version 1.2). Goodness of fit was determined by judging the χ^2 values (<1.3 in all cases), the residuals, and the Durbin−Watson parameter (>1.6 in all cases). Low-temperature fluorescence spectra and lifetimes were measured in a nitrogen-cooled Oxford Instruments DN 1704 optical cryostat connected to an ITC 4 temperature controller (±0.5 K). High-temperature studies were performed by using Tempette/TE−8A thermostat with direct measurements of temperature in the cuvettes.

Redox potentials were measured using a BAS CV27 potentiostat with Ag/AgI in DMSO as the reference electrode and platinum as the working and auxiliary electrodes and 0.1 M Et_4NBF_4 as the electrolyte. Ferrocene was used as an internal reference, and all potentials are reported relative to the ferrocene/ferrocenium half-wave potential, which is +0.1 V relative to the standard calomel electrode.[26]

Materials. All solvents were spectral grade or HPLC grade and used as received. 1-Aminonaphthalene, 2-aminonaphthalene, and 2-dimethylaminonaphthalene were recrystallized and further purified by vacuum sublimation. 1-Dimethylaminonaphthalene was distilled under reduced pressure. 1-Methylaminonaphthalene was liberated from its hydrochloride salt by base extraction. *trans*-Cinnamonitrile and 1-phenylpropene were used as received.

Results and Discussion

Electronic Absorption Spectra. The electronic absorption spectra of the 1- and 2-aminonaphthalenes (Chart 1) have attracted the attention of both experimentalists and theoreticians interested in the interaction of the electron-donating amino group with the π-electrons of the naphthalene nucleus.[12,13,19] The absorption spectra of 1- and 2-dimethylaminonaphthalene (1-DMAN and 2-DMAN) in several solvents are shown in Figure 1. The spectrum of 1-DMAN displays a single broad long-wavelength band with a maximum at 306 nm in hexane, whereas 2-DMAN displays two long-wavelength bands, a broad band at 350 nm, and a structured band with a maximum at 286 nm in hexane solution. This difference in appearance is attributed to a larger separation between the two lowest absorption bands (L_a and L_b) of 2-DMAN than is the case for 1-DMAN.[27]

The absorption maximum and extinction coefficient of the 1-aminonaphthalenes 1-AN, 1-MAN, and 2-DMAN (Chart 1) and several solvents are summarized in Table 1 and the corresponding data for the 2-aminonaphthalenes 2-AN and 2-DMAN in Table 2. This data is in good agreement with the literature. The absorption maxima in hexane solution shift to longer wavelength upon N-methylation for 1-MAN vs 1-AN and for 2-DMAN vs 2-AN, as is the case for methylation of aniline.[28] However, the absorption maximum of 1-DMAN is at shorter wavelength than those of either 1-AN or 1-MAN. This blue shift has been attributed to a larger twist angle for the C−NMe_2 bond (ca. 60°) than for either the C−NH_2 or C−NHMe bonds (ca. 20°).[18] The larger twist angle for C−NMe_2 is a consequence of nonbonded interaction with the H8 hydrogen atom. Since this interaction is not present in 2-substituted naphthalenes, the twist angles are presumably similar for 2-AN and 2-DMAN.

The absorption maxima of the aminonaphthalenes display relatively modest solvent-induced shifts (Tables 1 and 2). As noted by Mataga[12] in an early investigation of the effects of solvent on the electronic spectra of 1-AN and 2-AN, these shifts cannot be correlated with a single solvent parameter. Small red shifts are observed in the non-hydroxylic solvents diethyl ether, acetonitrile, and dimethyl sulfoxide (DMSO) vs hexane. The maximum red shifts are somewhat larger for 1-AN and 2-AN (20 and 14 nm, respectively in DMSO) than for their methylated

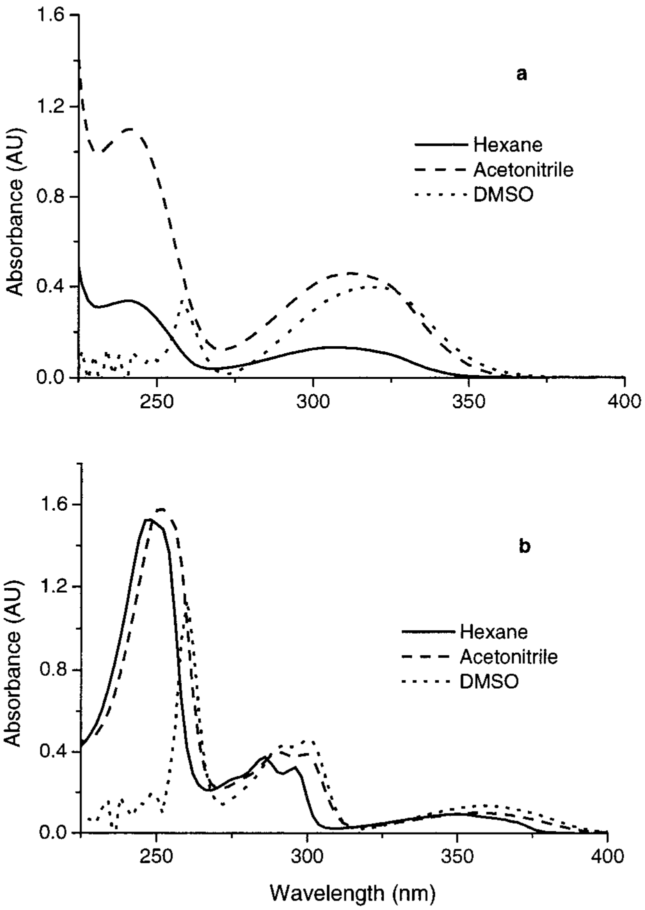


Figure 1. UV absorption spectra of (a) 1-dimethylaminonaphthalene in hexane (2.8×10^{-5} M), acetonitrile (9.3×10^{-5} M), and DMSO (8.9×10^{-5} M); (b) 2-dimethylaminonaphthalene in hexane (3.73×10^{-5} M), acetonitrile (5.8×10^{-5} M), and DMSO (5.88×10^{-5} M).

TABLE 1: Absorption Maxima (λ_{max}^{abs}), Extinction Coefficients, Fluorescence Maxima (λ_{max}^{fl}), Stokes Shifts (Δv), Singlet Lifetime (τ), Fluorescence Quantum Yields (Φ_f) and Rate Constants (k_f) of 1-Aminonaphthalenes in Several Solvents

compd	solvent	λ_{max}^{abs}, nm	log ϵ_{max}	λ_{max}^{fl}, nm	$\Delta\nu$, cm^{-1}	τ, ns	$\Phi_f{}^b$	k_f, 10^7 s^{-1}
1-AN	hexane	318	3.83	373	4640	6.6	0.44	6.7
	Et_2O	328	3.86	397	5300	12.4	0.78	6.2
	MeCN	328	3.79	413	6280	16.7	0.86	5.1
	DMSO	338	3.88	425	6060	16.6		
	EtOH	322	3.74	423	7420	20.6		
	H_2O^a	312	3.60	455	10100	21.7	0.50	2.3
1-MAN	hexane	332	3.85	380	3800	7.4	0.58	7.8
	Et_2O	334	3.82	397	4750	11.7^b	0.82	7.0
	MeCN	334	3.82	416	5900	17.6	0.92	5.2
	DMSO	340	3.94	424	5830	14.6		
	EtOH	334	3.90	418	6020			
	H_2O	318	3.16	447	9080			
1-DMAN	hexane	306	3.68	379	6300	0.12^b	0.01	8.3
	Et_2O	308	3.61	396	7220	0.44^b	0.032	7.3
	MeCN	312	3.70	417	8070	4.5	0.21	4.7
	DMSO	318	3.65	425	7920	5.6		
	EtOH	306	3.65	413	8470			
	H_2O^a	296		452	11700	6.24	0.13^a	2.1

[a] Data from ref 14. [b] Data from ref 18b.

TABLE 2: Absorption Maxima (λ_{max}^{abs}), Extinction Coefficients, Fluorescence Maxima (λ_{max}^{fl}), Stokes Shifts (Δv), Singlet Lifetime (τ), Fluorescence Quantum Yields (Φ_f) and Rate Constants (k_f) of 2-Aminonaphthalenes in Several Solvents

compd	solvent	λ_{max}^{abs}, nm	log ϵ_{max}	λ_{max}^{fl}, nm	$\Delta\nu$, cm^{-1}	τ, ns	Φ_f	k_f, 10^7 s^{-1}
2-AN	hexane	338	3.35	372	2710	12.4	0.50	6.2
	Et_2O	344	3.38	387	3230	14.9		
	MeCN	344	3.33	395	3750	16.3	0.91	5.6
	DMSO	352	3.45	409	3960	17.4	0.98	5.6
	EtOH	340	3.31	401	4470	17.0		
	H_2O^a	336		414	5610			
2-DMAN	hexane	350	3.40	377, 394	2630	10.2	0.45	4.4
	Et_2O	352	3.41	394	3030			
	MeCN	354	3.24	412	3980	20.3	0.78	3.8
	DMSO	358	3.36	419	4070	19.5	0.89	4.6
	EtOH	352	3.02	406	3780			
	H_2O	336	3.29	426	6190			

[a] Data from ref 14.

derivatives. Blue shifts are observed in water and are larger for 1-DMAN and 2-DMAN (10 and 14 nm, respectively) than for their nonmethylated analogues. Red shifts of smaller magnitude are observed for several of the aminonaphthalenes in ethanol. Absorption maxima in DMSO−water and acetonitrile−water mixtures (data not shown) are intermediate between the values in the pure solvents.

Mataga[12] suggested that the absorption maxima of 1-AN and 2-AN might be sensitive to hydrogen-bonding interactions with the solvent in which the amine can serve as either a hydrogen bond donor or acceptor. The solvents diethyl ether, acetonitrile, and DMSO all can function as hydrogen bond acceptors but not donors. Their Taft solvatochromic β values are 0.47, 0.31, and 0.76 respectively, providing a measure of their relative hydrogen-bond acceptor ability.[29] The larger value for diethyl ether vs acetonitrile may account in part for their similar effect on the absorption maxima of the primary aminonaphthalenes, and the large β value for DMSO may account for its larger red shift. The smaller shifts observed for the tertiary aminonaphthalenes in these solvents are consistent with their inability to serve as hydrogen bond donors.

Water has a large Taft α value but a small Taft β (1.17 vs 0.18) indicating that it is a strong hydrogen bond donor, but weak acceptor.[29] The blue shifts observed in water have been attributed to hydrogen bonding with the aminonaphthalene serving as the acceptor.[12] The larger blue shifts observed for the tertiary vs secondary aminonaphthalenes are consistent with the higher energy of their lone pair electrons. Ethanol has similar Taft α and β values (0.83 vs 0.77) and thus can function as both a hydrogen bond donor and acceptor. The small shifts observed for ethanol solution are consistent with the near cancellation of hydrogen bond donor and acceptor and solvent polarity effects.

Fluorescence Spectra. The fluorescence spectra of the aminonaphthalenes have also received considerable attention.[14−18] The fluorescence spectra of 1-DMAN and 2-DMAN in several solvents are shown in Figure 2. The fluorescence of 2-AN and 2-DMAN is weakly structured in hexane solution but structureless in more polar solvents, whereas the fluorescence of the 1-aminonaphthalenes is structureless in all solvents. A single emission band is observed in all solvents. Unlike the corresponding naphthols, the aminonaphthalenes do not undergo singlet state proton transfer reactions.[30] N-methylation or dimethylation of 1-AN results in little or no change in the fluorescence maximum in a given solvent, whereas dimethylation of 2-AN results in red shifts of 5−17 nm (Tables 1, 2). The similar maxima for the three 1-aminonaphthalenes are attributed to similar planar structures for the fluorescent singlet states.[18] Evidently, the stability of the planar singlet excited state of 2-DMAN is sufficient to overcome, at least in part, the

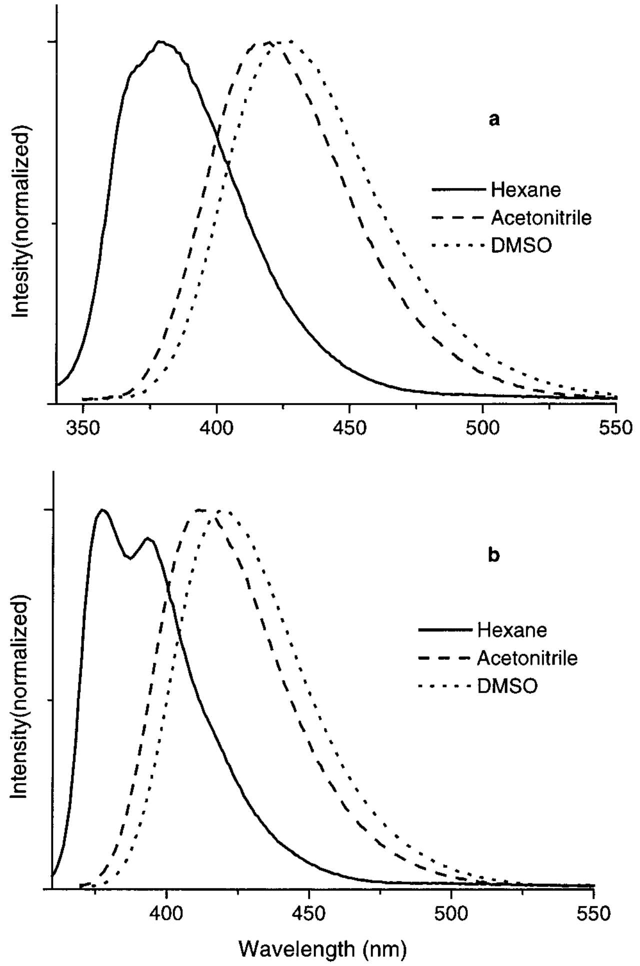


Figure 2. Fluorescence spectra of (a) 1-dimethylaminonaphthalene and (b) 2-dimethylaminonaphthalene in several solvents.

nonbonded interaction of the dimethylamino group with H8.

An increase in solvent polarity results in a red shift of the fluorescence of the aminonaphthalenes in hydroxylic as well as nonhydroxylic solvents. Substantial broadening of the fluorescence band is observed in water. The Stokes shifts increase with increasing solvent polarity as a consequence of the larger solvatochromic shifts for fluorescence vs absorption spectra. The change in dipole moment between the excited state vs ground state ($\Delta\mu = \mu_e - \mu_g$) can be calculated from a plot of the fluorescence maxima in nonhydroxylic solvents vs the solvent polarity parameter $f - f'$ using eqs 1 and 2

$$\upsilon_{fl} = C[\mu_e(\mu_e - \mu_g)/\rho^3](f - f') + \text{const} \qquad (1)$$

$$f - f' = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1) \qquad (2)$$

where C is a constant and ρ is the Onsager radius, which is assumed to be similar to the value calculated by Rückert et al. for 1-AN.[18b] Experimental values of μ_g from the literature[31] are reported in Table 3 along with the calculated values of Rückert et al.[18b] for the 1-aminonaphthalenes and our results for the 2-aminonaphthalenes. The value of μ_g increases with methylation for 1-MAN vs 1-AN and for 2-DMAN vs 2-AN. However, the value for 1-DMAN is smaller than that of either 1-AN or 1-MAN. The small value of μ_g for 1-DMAN has been attributed to the nonplanarity of the dimethylamine group. The larger values of μ_e vs μ_g are indicative of the contributions of charge transfer configurations to the lowest singlet states. N-methylation has little effect on the values of μ_e, in accord with the proposal of similar excited state structures for the three 1-aminonaphthalenes. The values of μ_e for the 1-aminonaphthalenes are larger than those for the 2-aminonaphthalenes. This is consistent with the short-axis polarization of the lowest singlet state of both 1- and 2-aminonaphthalenes.[19]

TABLE 3: Oxidation Potentials (E_{Ox}) and Ground State (μ_g) and Excited State(μ_e) Dipole Moments of the Aminonaphthalenes

compound	E_{ox}, V[a]	μ_g, D	μ_e, D
1-AN	0.33 (0.34)	1.55[b]	7.2[b]
1-MAN	0.40 (0.47)	1.75[b]	7.4[b]
1-DMAN	0.55 (0.54)	1.05[b]	7.1[b]
2-AN	0.41 (0.41)	1.71[c]	4.4
2-DMAN	0.46 (0.38)	1.90[c]	4.6

[a] Oxidation potentials vs ferrocene/ferrocenium in acetonitrile or DMSO (values in parentheses). [b] Data from ref 18b. [c] Data from ref 31.

The singlet lifetimes and fluorescence quantum yields for the aminonaphthalenes in several solvents are reported in Tables 1 and 2. Moderately long lifetimes (>5 ns) and large quantum yields (>0.4) are observed except in the case of 1-DMAN in nonpolar solvents. The anomalously short fluorescence lifetime of 1-DMAN was initially reported by Meech et al.[14] and subsequently investigated by Suzuki et al.[17] and by Zachariasse and co-workers.[18] The latter workers attributed the short lifetime to an activated internal conversion resulting from vibronic coupling of S_1 and S_2. Increasing solvent polarity increases the small S_1-S_2 energy gap, resulting in a decrease in the rate constant for internal conversion.

The fluorescence rate constants ($k_f = \Phi_f\tau^{-1}$) for the three 1-aminonaphthalenes in hexane solution are similar (Table 1), in accord with the proposal of similar singlet state structures.[18] The value of k_f for 2-AN is similar to that of the 1-aminonaphthalenes; however, the value for 2-DMAN is somewhat smaller. The fluorescence rate constants decrease modestly with increasing solvent polarity in non-hydroxylic solvents. Thus, the increase in lifetime with increasing solvent polarity results mainly from a decrease in the nonradiative rate constants, internal conversion in the case of 1-DMAN, and intersystem crossing in the case of the other aminonaphthalenes.[18b] A large decrease in the k_f for 1-AN and 1-DMAN is observed in water, resulting in a decrease in the fluorescence quantum yield compared to the values observed in acetonitrile. The large Stokes shift, fluorescence band broadening, and small value of k_f observed in water indicate that hydrogen bonding can influence the electronic structure of singlet excited state as well as the ground state.

The electrochemical oxidation of the aminonaphthalenes has been investigated both in acetonitrile and DMSO solution by means of cyclic voltametry. The peak potentials for irreversible oxidation are reported in Table 3. The values are observed to increase with increasing alkylation (except for the 2-aminonaphthalenes in DMSO for which a small decrease is observed). This trend is opposite that for alkylation of aniline, which results in a decrease in oxidation potential in the series $PhNH_2$, PhNHMe, $PhNMe_2$ (E_{ox} = 1.28, 1.03, 0.79, respectively).[4b] Analysis of the photoelectron spectra of the aminonaphthalenes indicates that the first ionization process involves a naphthalene-like delocalized π-orbital which has some mixing with the nitrogen lone pair orbital.[32] The increase in oxidation potentials with alkylation thus may reflect decreasing mixing as the twisting about the $C-NR_2$ bond increases.

Fluorescence Quenching by Styrene Derivatives. The fluorescence intensity and lifetime of the aminonaphthalenes

TABLE 4: Stern-Volmer Constants, Singlet Quenching Rate Constants, Singlet Energies, and Free Energies for Electron Transfer Quenching of the Aminonaphthalenes by Cinnamonitrile in Different Solvents

compound	solvent	K_{SV}, M^{-1}	k_q, 10^{10} M^{-1} s^{-1}	E_S, eV[a]	$-\Delta G$, eV[b]
1-AN	hexane	262	4.0	3.61	0.61
	Et_2O	409	3.3	3.46	0.57
	MeCN	408	2.4	3.41	0.63
	DMSO	100	0.60	3.28	0.53
	EtOH	190	0.92	3.37	0.58
1-MAN	hexane	227	3.0	3.51	0.44
	MeCN	346	2.0	3.33	0.48
	DMSO	100	0.70	3.27	0.39
1-DMAN	hexane	3.8	3.1	3.60	0.38
	MeCN	88	2.0	3.43	0.43
	DMSO	28	0.50	3.43	0.48
2-AN	hexane	529	4.3	3.50	0.42
	Et_2O	397	2.7	3.58	0.41
	MeCN	360	2.2	3.37	0.51
	DMSO	107	0.61	3.25	0.43
	EtOH	191	1.1	3.33	0.46
2-DMAN	hexane	348	3.4	3.35	0.22
	MeCN	387	2.0	3.20	0.29
	DMSO	128	0.66	3.17	0.38

[a] Singlet energy from crossing point of fluorescence excitation and emission spectra. [b] Free energy change calculated from eq 5.

TABLE 5: Stern−Volmer Constants, Singlet Quenching Rate Constants, Singlet Energies, and Free Energies for Electron Transfer Quenching of the Aminonaphthalenes by 1-Phenylpropene in Different Solvents

compd	solvent	K_{SV}, M^{-1}	k_q, 10^9 M^{-1} s^{-1}	$-\Delta G$, eV[a]
1-AN	hexane	23	3.5	0.26
	MeCN	13	0.76	0.28
1-MAN	hexane	7.8	1.0	0.09
	MeCN	11	0.65	0.13
1-DMAN	hexane	2.3	19	0.03
	MeCN	7.2	1.8	0.08
2-AN	hexane	18	3.0	0.07
	MeCN	9.9	1.2	0.16
2-DMAN	hexane	0.59	0.054	−0.13
	MeCN	0.45	0.023	−0.06

[a] Free energy change calculated from eq 5.

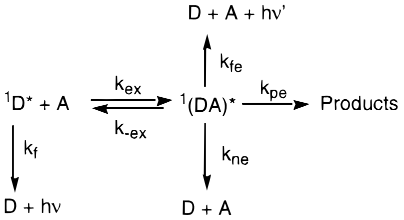
are quenched by added cinnamonitrile (CN) or 1-phenylpropene (PP). The added quencher causes no change in the appearance of the aminonaphthalene absorption or emission spectrum. Exciplex fluorescence is observed only for quenching of the tertiary aminonaphthalenes 1-DMAN and 2-DMAN by CN in nonpolar solvents (vide infra). Linear Stern−Volmer plots (eq 3) for quenching of the fluorescence intensity provide values of the quenching constants K_{SV} reported in Tables 4 and 5. Quenching of the fluorescence lifetimes was also determined at one or more quencher concentrations for each combination of aminonaphthalene, quencher, and solvent and provided values of K_{SV} indistinguishable from to those obtained by intensity quenching. Thus, fluorescence quenching occurs exclusively via a dynamic mechanism as opposed to a static mechanism for which intensity quenching would be more efficient than lifetime quenching.[22]

$$I_0/I = \tau_0/\tau = 1 + K_{SV}[Q] \tag{3}$$

The generalized mechanism for exciplex formation and decay is given in Scheme 1, where *D** is the singlet aminonaphthalene and *A* is the quencher. According to this scheme, the quenching rate constant ($k_q = K_{SV}\tau_0^{-1}$) is described by eq 4

$$k_q = k_{ex}[k_{de}/(k_{de} + k_{-ex})] \tag{4}$$

SCHEME 1



where $k_{de} = k_{fe} + k_{pe} + k_{ne}$. The resulting values of k_q are reported in Tables 4 and 5. The values of k_q for quenching of all of the aminonaphthalenes by CN are close to the rates of diffusion calculated from the solvent viscosity at 20 °C.[33] Thus, the fastest rates are observed in the least viscous solvents (hexane and diethyl ether) and the slowest rates in the most viscous solvents (DMSO and ethanol) or in a DMSO−water mixture (data not shown), which has a higher viscosity than either pure solvent. The observation of diffusion-controlled quenching requires that exciplex formation be irreversible ($k_{de} \gg k_{-ex}$) and hence the observed quenching rate constant is determined only by the rate of exciplex formation ($k_q = k_{ex}$).

The Stern−Volmer constants for quenching of the aminonaphthalenes by PP are smaller than those for quenching by CN and are dependent upon both the aminonaphthalene structure and solvent polarity (Table 5). The calculated value of k_q for quenching of 1-DMAN in hexane is close to the rate constant for diffusion, but smaller values of k_q are observed for the other aminonaphthalenes. Values of $k_q < k_{diff}$ are indicative of reversible exciplex formation ($k_{-ex} > k_{de}$). Rate constants of quenching in the polar solvent acetonitrile are slower than in hexane, except in the case of 1-MAN for which similar values are observed in the two solvents. No exciplex emission is observed upon quenching of the aminonaphthalenes by PP, as is usually the case when exciplex formation is reversible.

The free energy for electron transfer quenching of the aminonaphthalenes can be calculated using Weller's equation (eq 5)[34]

$$\Delta G_{et} = E_{ox} - E_{red} - E_s + C \tag{5}$$

where E_S is the aminonaphthalene singlet energy, obtained from the crossing point of the normalized absorption and fluorescence spectra (Table 4), E_{ox} is the amine half-wave oxidation potential measured in acetonitrile or DMSO solution (Table 3), E_{red} is the half-wave reduction potential of CN (−2.29 V and −2.25 V vs ferrocene/ferrrocenium in acetonitrile and DMSO, respectively) or PP (−2.54 V vs ferrocene/ferrrocenium in acetonitrile[35]), and C is an empirical solvent constant.[36] The calculated values of ΔG_{et} for quenching by CN are exergonic by >0.2 eV in all solvents, in accord with the observation of diffusion-controlled quenching (Table 4). In contrast, the values of ΔG_{et} for quenching by PP in hexane range from moderately endergonic for 2-DMAN to exergonic for 1-AN (Table 5). Values of k_q for quenching by PP generally decrease as the calculated value of ΔG_{et} becomes more positive. The failure to observe a linear correlation of log k_q with ΔG_{et} may reflect structure-specific exciplex stability.

Free energies for electron transfer quenching of nonpolar aromatic hydrocarbon singlet states become more exergonic with increasing solvent polarity (eq 5) and thus quenching rate constants for endergonic quenching are expected to increase. This is not the case for quenching of the aminonaphthalenes by PP which is slower in acetonitrile than in hexane solution (Table 5). This seeming anomaly is due, at least in part, to the solvent-dependent singlet energy of the polar aminonaphthalenes (Table 4). The decrease in singlet energy with increasing solvent polarity nearly compensates for the decrease in the solvent constant *C*, resulting in only a modest change in the calculated value of ΔG_{et} (Table 4). Another contributing factor might be an increase in the solvent reorganization energy, similar to that observed in highly polar solvents for intramolecular electron transfer in rigidly linked donor–acceptor systems.[5,37,38]

There have been several previous investigations of the quenching of aminonaphthalenes by electron acceptors. Kaneta and Koizumi[6] observed that fluorescence quenching of 2-DMAN by dimethyl *m*-phthalate occurs with a rate constant of ca. 1×10^{10} M^{-1} s^{-1} in cyclohexane solution and is accompanied by weak exciplex fluorescence in nonpolar solvents. Slower quenching was observed with weaker benzoate acceptors. Schaffner and Fischer[9] recently reported a rate constant of 7×10^9 M^{-1} s^{-1} for quenching of 1-DMAN by benzonitrile ($E_{red} = -2.35$ V vs SCE) in acetonitrile solution. Avila et al.[7] investigated the quenching of 1-AN, 1-DMAN, and 2-AN by chlorobenzenes in methanol solution. Rate constants $\sim 3 \times 10^9$ M^{-1} s^{-1} were observed for trichlorobenzenes ($E_{red} \sim -2.0$ V vs SCE) and slower rate constants for dichlorbenzenes which have higher reduction potentials. Dogra and co-workers[8] studied the quenching of 1-AN, 2AN, and several additional aromatic amines by chloromethanes. Rate constants near the rate of diffusion were observed for quenching by carbon tetrachloride ($E_{red} = -0.78$ V vs SCE), but much slower rates were observed for quenching by chloroform ($E_{red} = -1.67$ V vs SCE), even though quenching should be highly exergonic. The observation of diffusion-controlled quenching and fluorescent exciplex formation for the aromatic acceptors CN and dimethyl *m*-phthalate[6] suggests that π-type aromatic acceptors are more effective quenchers of the aminonaphthalenes than are chlorocarbons of substantially lower oxidation potential.

Exciplex Fluorescence. Exciplex fluorescence is observed to accompany quenching of the fluorescence of 1-DMAN and 2-DMAN by CN in nonpolar solvents. The total emission spectra in hexane solution shown in Figure 3 have normalized locally excited (LE) intensities in order to enhance the relatively weak exciplex emission. Higher concentrations of quencher are needed to observe quenching of 1-DMAN vs 2-DMAN due to the difference in their singlet decay times (Tables 1 and 2). This results in some competitive absorption by CN at the excitation wavelength and an apparent blue shift in the LE fluorescence spectrum. Single-exponential exciplex fluorescence decays are observed with decay times longer than that of the LE fluorescence, indicative of irreversible exciplex fluorescence.

The exciplex fluorescence intensities (Figure 3) and lifetimes decrease at high CN concentrations, presumably due to quenching of the exciplex by a second CN molecule. We have previously found that in cases of irreversible exciplex formation, the dependence of the exciplex lifetime, τ_{ex}, on quencher concentration is given by eq 6.[22]

$$\tau_{ex}^{-1} = k_{qex}[\mathrm{CN}] + k_{dex} \tag{6}$$

The plot of the 1-DMAN/CN exciplex decay time vs CN concentration shown in Figure 4 provides a rate constant for exciplex quenching, $k_{qex} = 2.4 \times 10^9$ M^{-1} s^{-1}. This value is similar to that for quenching of 1-cyanophenanthrene–triethylamine exciplexes by a second molecule of amine.[39] The long exciplex lifetimes and large rate constants for exciplex quenching are responsible for the relatively weak exciplex fluorescence observed in hexane solution (Figure 3).

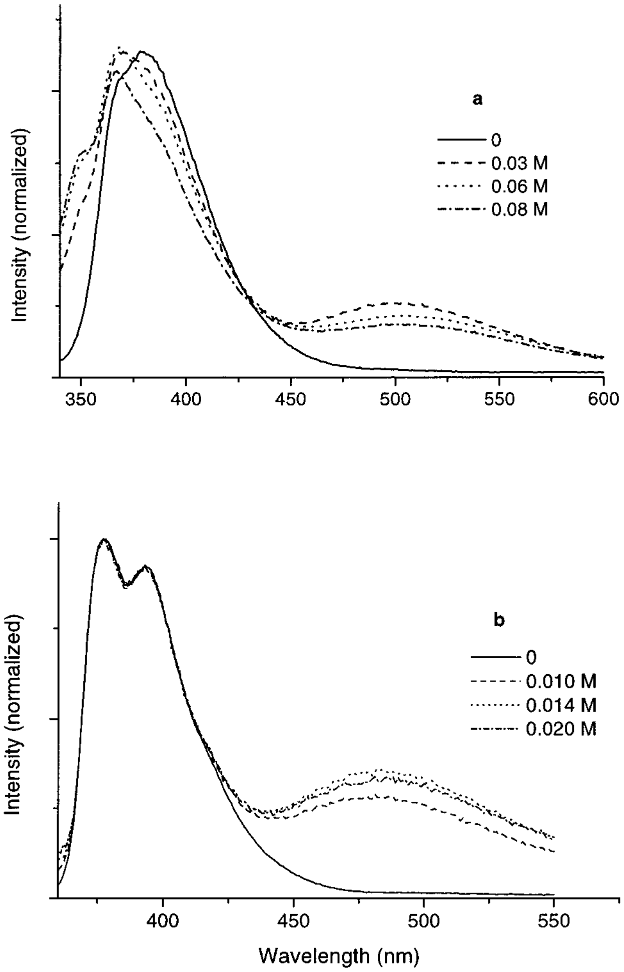


Figure 3. Normalized fluorescence spectra of (a) 1-dimethylaminonaphthalene (2.8×10^{-5} M)/cinnamonitrile and (b) 2-dimethylaminonaphthalene (3.73×10^{-5} M)/cinnamonitrile with increasing concentration of *trans*-cinnamonitrile in hexane.

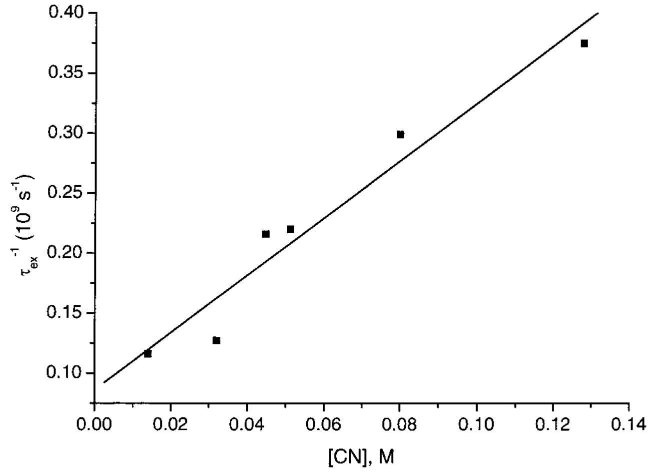


Figure 4. Plot of the exciplex decay constant vs *trans*-cinnamonitrile concentration for 1-dimethylaminonaphthalene (2.8×10^{-5} M)/cinnamonitrile in hexane.

Increasing solvent polarity results in a red shift of the exciplex fluorescence and a decrease in intensity. The emission maximum for 2-DMAN/CN shifts from 472 nm in hexane to 496 nm in dibutyl ether, a frequency shift of ca. 1030 cm^{-1}. This shift is is similar to that of the exciplex formed upon quenching of *N*,*N*-dimethylphenanthrene-9-carboxamide by *N*,*N*-dimethylaniline.[5] The 2-DMAN/CN exciplex emission is too broad and weak to

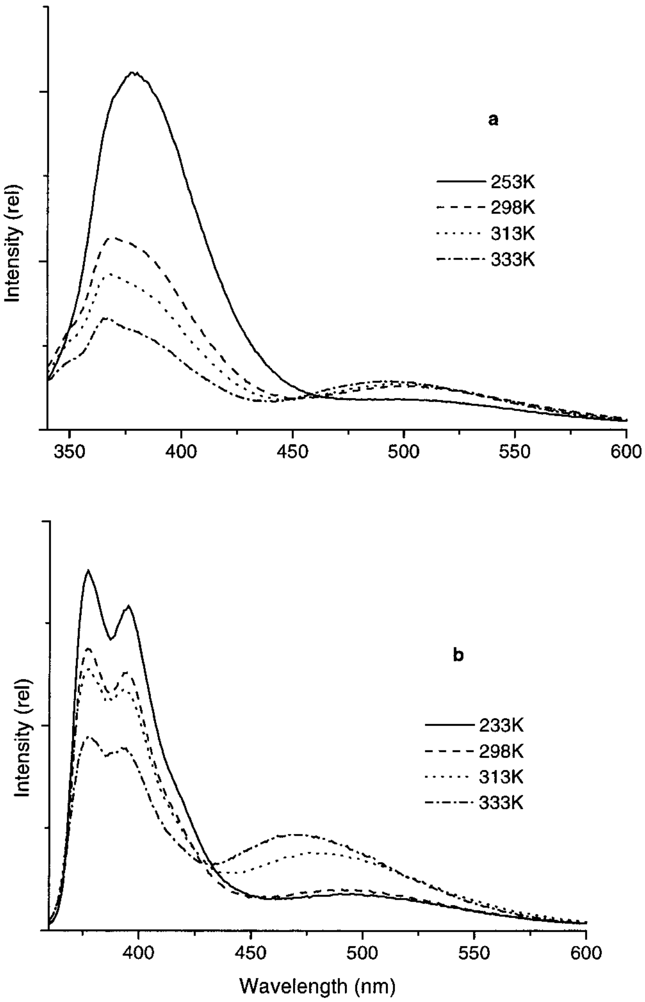


Figure 5. Temperature-dependent fluorescence spectra of (a) 1-dimethylaminonaphthalene (2.8×10^{-5} M)/cinnamonitrile (0.03 M) and (b) 2-dimethylaminonaphthalene (3.73×10^{-5} M)/cinnamonitrile (0.014 M) in hexane.

TABLE 6: Temperature Dependence of the Locally Excited and Exciplex Fluorescence from 2-DMAN/CN in Hexane Solution

T, K	λ_{ex}. nm	I_{ex}/I_{le}	τ_{le}, ns	τ_{ex}, ns
233	490	0.10	3.2	11.3
253	487	0.15	2.6	13.5
273	487	0.20	2.0	15.9
393	475	0.31	1.8	20.0
313	475	0.39	1.8	24.1
323	472	0.44	1.9	26.0

be resolved in diethyl ether and more polar solvents. This solvent dependence is characteristic of exciplexes with a high degree of charge transfer character.[40]

The emission spectra of 1-DMAN/CN and 2-DMAN/CN obtained at several temperatures in hexane solution are shown in Figure 5. In both cases an increase in the ratio of exciplex/LE fluorescence intensity (I_{ex}/I_{le}) is observed as expected for diffusion-controlled exciplex formation.[41] Values of I_{ex}/I_{le} and LE and exciplex decay times for the 2-DMAN/CN exciplex are reported in Table 6. The slope of a linear plot of $\ln(I_{ex}/I_{le})$ vs T^{-1} provides an activation energy for exciplex formation, E_a = 2.5 kcal/mol, similar to the value for viscous flow in alkane solvents.[42,43] There is no sign of curvature in this plot at high temperatures, indicating that exciplex dissociation does not occur over this temperature range.

Most remarkable is the effect of temperature upon the 2-DMAN/CN exciplex fluorescence maximum and lifetime in hexane solution (Table 6). Increasing the temperature from 233 to 323 K results in a blue shift in the exciplex fluorescence maximum from 490 to 472 nm, accompanied by an increase in exciplex lifetime from 11.3 to 26.0 ns. Blue-shifted exciplex emission has been observed with increasing temperature in moderately polar solvents for several inter- and intramolecular exciplexes.[44] These shifts are attributed to a decrease in the solvent dielectric constant with increasing temperature; however, the hexane dielectric constant should not change appreciably with temperature. In fact, Knibbe et al.[1c] observed no temperature dependence of the emission maximum of the 1,2-benzanthracene−diethylaniline exciplex in methylcyclohexane solution.

A change in exciplex geometry appears to be the most likely source of the temperature dependence of the exciplex emission maximum and lifetime. Intermolecular exciplexes are believed to have very shallow potential energy surfaces, changes in the overlap and plane-to-plane separation having only a small effect on the free energy.[45] The studies of intramolecular exciplexes with semiflexible linkers by Verhoeven and co-workers[43,46] have established that an increase in the D−A separation leads to a decrease in the emission maximum. The exciplexes formed between two polar molecules such as 2-DMAN and CN might be more sensitive to such changes than the more conventional arene−aniline exciplexes. Rückert et al.[18b] observed that the ratio k_f/n^2 for 1-AN increases with increasing temperature in hexane and acetonitrile solution and suggested the CT character of the lowest singlet might increase with increasing temperature. This change might also result in a temperature-dependent change in exciplex geometry.

No exciplex fluorescence is observed for quenching of the primary amines 1-AN and 2-AN or the secondary amine 1-MAN by CN. The observation of exciplex fluorescence from tertiary but not secondary or primary amines is analogous to previous studies in which ground state amines were used as quenchers of singlet aromatic hydrocarbons.[2,22,47] Okada et al.[2] reported that bimolecular quenching of singlet pyrene by *N*-methylaniline results in the formation of a nonfluorescent exciplex which decays via intersystem crossing and N−H proton transfer, a chemical decay pathway not available to the exciplexes of tertiary amines. Preliminary studies of the photochemical reactions of the aminonaphthalenes with PP indicate that primary and secondary amines undergo N−H addition to the styrene double bond in nonpolar solvents, but that tertiary amines are not photochemical reactive.[48] This behavior is similar to that of the intramolecular *N*-(styrylalkyl)aniline exciplexes which we have recently investigated.[11]

Concluding Remarks. The interactions of the excited singlet states of the aminonaphthalenes with ground state styrene electron acceptors are in many respects similar to those of singlet styrenes with ground state aminoalkanes.[21,22] Exciplex formation is observed for tertiary amines, but not for primary or secondary amines. Competing nonradiative decay pathways (N−H hydrogen transfer and intersystem crossing) are presumably responsible for the absence of fluorescence from the exciplexes formed by primary or secondary aminoarenes or aminoalkanes. Exciplex fluorescence is also observed only in cases where exciplex formation is irreversible, as judged by diffusion-controlled quenching rate constants. The exciplexes formed by the aminonaphthalenes with cinnamonitrile are more sensitive to solvent polarity than are their aminoalkane counterparts, exciplex fluorescence being detected only in nonpolar solvents. This may reflect the polar nature of the singlet state as well as the exciplex.

Without precedent is the temperature dependence of the exciplexes formed between the tertiary aminonaphthalenes and cinnamonitrile in hexane solution. Increasing temperature results in both a blue shift of the exciplex and an increase in exciplex fluorescence lifetime. These changes are attributed to a change in the exciplex structure.

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