Solvent-Dependent Behavior of Phenanthrene-Amine Intramolecular Exciplexes

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Received: July 14, 1994[®]

The solvent dependence of the photophysical and photochemical behavior of several ((N,N-dimethylamino)alkyl)phenanthrenes in which the amino group is attached to the phenanthrene at C₉ or C₁ via a short polymethylene chain has been investigated. Intramolecular exciplex fluorescence is observed in moderately polar solvents but not in nonpolar solvents. The solvent dependence of exciplex fluorescence is attributed to exergonic formation of solvated exciplexes with loose geometries in polar solvents and endergonic exciplex formation in nonpolar solvents. In the case of the (aminoethyl)phenanthrene exciplex fluorescence is observed in highly polar solvents, including dimethylformamide, dimethyl sulfoxide, and acetonitrile-water binary mixtures and in frozen polar glasses. In the case of the (aminomethyl)phenanthrene moderately efficient photodeamination to yield 9-methylphenanthrene and 1,2-di-9-phenanthrylethane is observed. The solvent and temperature dependence of the kinetics of exciplex formation and decay are discussed and compared to results for other intramolecular arene-amine exciplexes.

Introduction

Solvent polarity plays a crucial role in the formation and behavior of inter- and intramolecular exciplexes.¹⁻⁸ Exciplex fluorescence from strong intermolecular donor-acceptor systems is commonly observed to decrease in intensity with increasing solvent polarity, becoming difficult to detect in polar solvents such as acetonitrile.¹⁻⁴ Intramolecular exciplexes of similar donor-acceptor systems connected by short flexible polymethylene chains are often fluorescent even in polar solvents.⁵⁻⁷ Weller¹ initially suggested that the decrease in intermolecular exciplex fluorescence intensity and lifetime with increasing solvent polarity was a consequence of ionic dissociation to yield nonfluorescent radical ions in polar solvents. Whereas intramolecular exciplexes cannot undergo ionic dissociation, their molecular structure was proposed by Mataga and co-workers⁵ to be solvent dependent, compact folded geometries being favored in nonpolar solvents and looser geometries in polar solvents. These compact and loose geometries correspond to those of the contact and solvent-separated radical ion pairs formed in intermolecular electron-transfer reactions. Evidence for the folding of intramolecular ((N,Ndimethylamino)alkyl)arene exciplexes into specific, energyminimized conformations in nonpolar solvents has been provided by the investigations of De Schryver and Van der Auweraer.⁶ Additional evidence for a change in the structure of intramolecular exciplexes from compact in nonpolar solvents to loose in polar solvents has been provided by Verhoeven and co-workers.⁷ They find that structural change occurs over a narrowly defined region of solvent polarity and suggest that the solvent-separated species is best described as a chargeseparated state in order to distinguish it from an exciplex in which the donor and acceptor are in contact or strongly coupled. We have recently reported that the photochemical behavior of intramolecular ((N,N-dimethylamino)alkyl)styrene exciplexes is also strongly solvent dependent, proton transfer occurring in nonpolar but not in highly polar solvents.⁸ A change in geometry from compact to extended was proposed to account for the large decrease in the exciplex proton-transfer rate constant observed in moderately polar solvents.

Most investigations of intramolecular exciplex formation have involved strong donor-acceptor systems for which exciplex formation is exergonic and irreversible in nonpolar and polar solvents. In cases where exciplex formation is less favorable, exciplex formation may either be highly reversible or fail to occur in nonpolar solvents. Mataga and co-workers⁵ have found that the use of a moderately polar solvent such as diethyl ether permits the observation of exciplex fluorescence in some such cases. We report here the results of our investigation of intramolecular exciplex formation in an exceptionally weak donor-acceptor system: the ((N,N-dimethylamino)alkyl)phenanthrenes. Quenching of singlet phenanthrene by triethylamine is reported to occur with rate constants well below the rate of diffusion and no exciplex emission is observed in polar or nonpolar solvents.⁹ We find that the ((N,N-dimethylamino)alkyl)phenanthrenes 9P1, 9P2, 9P3, and 1P3 form fluorescent



exciplexes in moderately polar solvents such as ethyl acetate and tetrahydrofuran and in solvents as polar as dimethyl sulfoxide or 20% aqueous acetonitrile but not in nonpolar solvents. An unusual photodeamination reaction is observed in the case of **9P1**. A complex mixture of products is formed upon irradiation of **9P2** while **9P3** and **1P3** are moderately photostable. The chain-length, solvent, and temperature dependence of the formation and decay of these exciplexes serve to elucidate the unique features of their structure and reactivity.

Results and Discussion

Solvent Dependence of Exciplex Emission. Quenching of singlet phenanthrene by triethylamine (TEA) has been investigated by Chen and co-workers.⁹ The fluorescence quenching rate constants reported for cyclohexane and acetonitrile solution $(k_q = 3.5 \times 10^6 \text{ and } 7.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$ are significantly slower than the rate constants for diffusion in these solvents. These observations are consistent with the calculated free energy for

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^{*} Abstract published in Advance ACS Abstracts, September 1, 1994.



Figure 1. Fluorescence spectra of **9P2** in diethyl ether (a), isobuty-ronitrile (b), and dimethyl sulfoxide (c) solution.

exciplex formation in nonpolar solvents (eq 1).^{1c} Using values

$$\Delta G_{\rm ex} = E_{\rm D}^{\rm ox} - E_{\rm A}^{\rm red} - E_{\rm S} + 0.38 \,\,{\rm V} \tag{1}$$

for the singlet energy of phenanthrene (3.59 eV), its reduction potential (-2.36 V in acetonitrile solution vs Ag/AgI), and the oxidation potential of TEA (1.01 V), exciplex formation is calculated to be endergonic by ca. 0.3 eV in hexane solution.⁹ The use of a more easily oxidized amine, diethylaniline ($E_{ox} =$ 0.80 V), in place of TEA results in more rapid quenching of singlet phenanthrene ($k_q = 1.0 \times 10^8$ and 1.9×10^{10} M⁻¹ s⁻¹ in hexane and acetonitrile solution) Exciplex emission is not observed for intermolecular quenching of phenanthrene by TEA or diethylaniline.^{9,10}

We have investigated the fluorescence spectra of the (aminoalkyl)phenanthrenes **9P1**, **9P2**, **9P3**, and **1P3** in a variety of solvents. Only emission from the locally excited phenanthrene is observed in hexane solution. Sugimoto et al.¹¹ have observed efficient quenching of the locally excited phenanthrene fluorescence and weak exciplex fluorescence from the ((aminomethyl)naphthyl)phenanthrenes 1 and 2 in benzene solution. The driving force for intramolecular electron transfer in these molecules has not been reported but is likely to be more favorable than that for the (aminoalkyl)phenanthrenes. In addition, the molecular conformation of 1 and 2 restricts the amine to lie above the phenanthrene plane.



Both locally excited and exciplex emission are observed for 9P1 in diethyl ether and more polar solvents and for 9P2, 9P3, and 1P3 in ethyl acetate and more polar solvents. The fluorescence spectra of 9P2 in deoxygenated ethyl ether, isobutyronitrile, and dimethyl sulfoxide are shown in Figure 1 and the emission maxima for exciplex fluorescence summarized in Table 1. The intensity of the locally excited fluorescence decreases with increasing solvent polarity but remains easily detectable even in the most polar solvents. The intensity of exciplex fluorescence increases with increasing solvent polarity, reaches a maximum in isobutyronitrile, and decreases in more polar solvents. Moderately intense exciplex emission is observed for 9P1 and 9P2 in dimethyl sulfoxide solution, whereas emission from 9P3 is very weak in this solvent. Exciplex emission in methanol and propylene carbonate solution is

solvent	€ ^a	f' ^b	9P 1 ^c	9 P2 ^c	9P3 ^c	1P3 ^c
hexane	1.89	0.093	d	d	d	d
diethyl ether	4.20	0.256	22.5	d	d	d
ethyl acetate	6.02	0.293	21.3	21.8	22.4	22.5
tetrahydrofuran	7.58	0.309	22.2	21.9	22.5	21.8
octanenitrile	13.9	0.347		21.5	22.2	
isobutyronitrile	20.4	0.372	21.4	21.1	21.8	21.0
propionitrile	27.2	0.383	20.2	20.7	21.3	
methanol	32.7	0.393	d	20.5	d	
acetonitrile	35.9	0.392	20.0	20.2	20.7	20.0
dimethylformamide	36.7	0.378	19.6	19.8	20.4	
dimethyl sulfoxide	46.5	0.374	19.2	19.1	20.0	
propylene carbonate	64.9	0.391		19.8		
acetonitrile-water 50:1				20.0		
acetonitrile-water 10:1				19.8		
acetonitrile-water 5:1				19.7		

^{*a*} Dielectric constants from ref 16. ^{*b*} See eq 2. ^{*c*} Emission frequency $cm^{-1} \times 10^{-3}$. ^{*d*} Exciplex emission not observed.

observed for **9P2** but not for **9P1** or **9P3**. Exciplex emission is also observed for **9P2** in aqueous acetonitrile containing up to 20% water by volume.

The formation of fluorescent intramolecular exciplexes in nonpolar solvents has been reported for a number of ((N,Ndimethylamino)alkyl)arenes in which the amine is connected to benzene,^{6a,f} naphthalene,^{6b,c} styrene,⁸ or stilbene^{8c} by a flexible ethyl or propyl linker. The emission maxima of these intermolecular exciplexes are at shorter wavelength than their intermolecular counterparts, possibly due to restrictions on exciplex geometry introduced by the linker. Several linked arene-amines have previously been reported to display exciplex emission in ethers and more polar solvents but not in nonpolar solvent. These include the (aminoalkyl)pyrenes 3 and 4,^{6d} the (anilinoalkyl)anthracenes 5 and 6 (7 is fluorescent in nonpolar solvents),^{5e} and the (anilinoalkyl)naphthalene 8.^{7c} Since exciplex emission is observed in nonpolar solvents from the intermolecular counterparts of each of these systems, the absence of exciplex fluorescence from these intramolecular systems may reflect both a relatively small driving force for exciplex formation (eq 1) and the energetic requirements for attaining a compactly folded geometry. In the case of the flexibly linked systems, these geometries are destabilized by eclipsing or gauche interactions^{6,12} while in the case of the semiflexible molecule 8, a boat conformation would be required.^{7c} Mataga^{5g} suggested



that the formation of fluorescent exciplexes from 5 to 6 in diethyl ether and more polar solvents was a consequence of electron transfer in loose, rather than compact, conformations. Similarly, Verhoeven et al.^{7c} attribute the emission observed from 8 in ethers and more polar solvents to a charge-separated state in which there is no contact between donor and acceptor.

Exciplex fluorescence is often observed in nonpolar solvents for heteroexcimers in which complete electron transfer is endergonic and stabilization results from exciton resonance.¹ The driving force for exciplex formation from the (aminoalkyl)phenanthrenes is actually more favorable than that for the (aminoalkyl)pyrenes ($E_s = 3.30$ eV and $E_{rdn} = 1.15$ V);^{6d} however, exciplex fluorescence is observed for 4 but not for **9P3** of **1P3** in diethyl ether solution. We have also observed



Figure 2. Exciplex emission frequency (ν_{ex}) as a function of solvent dielectric constant for 9P1 (+), 9P2 (\triangle), 9P3 (\bigcirc), and 1P3 (\square). Dashed and solid lines are least-squares fits to the data for 9P2 and 9P3, respectively.

that ((*N*,*N*-dimethylamino)alkyl)phenanthrenecarboxamides fail to form fluorescent exciplexes.¹³ The apparent reluctance of phenanthrene to form fluorescent heteroexcimers may be related to its inability to form a stable excimer, which has been attributed to ineffective exciton resonance in phenanthrene and other arenes with lowest ${}^{1}L_{b}$ singlet states.¹⁴

The intensity of intramolecular arene-amine exciplex emission is normally observed to decrease in polar solvents, becoming weak or absent in acetonitrile solution. To our knowledge, exciplex fluorescence has not previously been investigated in solvents with higher dielectric constants than that of acetonitrile or in acetonitrile-water binary solvent mixtures. The solvent dependence of the exciplex emission maxima, ν_{ex} , conventionally is correlated with the solvent polarity Δf (eq 2) where ν_{ex}° is the gas-phase emission maximum,

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)$$
 (2)

$$v_{\rm ex} = v_{\rm ex}^{\circ} - (2\mu^2/hc\varrho^3)\Delta f \tag{3}$$

h is Planck's constant, *c* is the velocity of light, *q* is the effective radius of the solvent cavity occupied by the molecule, ϵ is the solvent dielectric constnat, and *n* is its index of refraction. As previously noted by Okada et al.^{5e} and Verhoeven et al.^{7c} values of Δf converge to a limiting value <0.4 in highly polar solvents and thus eq 3 may not be appropriate for correlations of emission maxima with solvent polarity in solvents more polar than acetonitrile. The data in Table 1 indicate that this is indeed the case. Empirical solvent polarity scales such as $E_{\rm T}$ and Z which are based on solvatochromism were also found to correlate poorly with the exciplex fluorescence maxima in Table 1.¹⁶

Of the many solvent polarity parameters considered, the best linear correlation with the v_{ex} data in Table 1 was obtained using the solvent dielectric constant (Figure 2). A monotonic decrease in v_{ex} with increasing ϵ was observed in all nonhydroxylic solvents except for **9P2** in the highly viscous solvent propylene carbonate. Values of v_{ex} in acetonitrile-water solvent decrease in nonlinear fashion with increasing water content. The decreasing change in v_{ex} with increasing water content is similar to that observed for the absorption maxima of the diphenyl betaine solvatochromatic probe $(E_{\rm T})$.^{17a} The nonlinearity of the $E_{\rm T}$ plot was interpreted in terms of disruption of the acetonitrile liquid structure by small amounts (<20%) of water followed by a transition to a stable acetonitrile—water (3:2) microphase. Alcohols are known to quench arene—amine exciplex fluorescence and to cause smaller shifts in $\nu_{\rm ex}$ than would be expected on the basis of their dielectric constants.^{17b}

The data for 1P3 and 9P3 in Figure 2 are observed to lie on roughly parallel lines. The lower energy of the 1P3 vs 9P3 exciplex emission is consistent with the lower reduction potential for 1-methylphenanthrene vs 9-methylphenanthrene (-2.15 V and -2.21 V, respectively, in acetonitrile solution). The difference in reduction potentials (0.06 V) is similar to the difference in exciplex emission maxima in isobutyronitrile solution (0.07 V). A similar positional dependence of the emission maxima for 1- vs 2-(aminoalkyl)naphthalenes was observed by Swinnen et al.^{6b} The exciplex emission maxima of 9P2 and 9P1 also lie at lower energy than those for 9P3. Since a propyl linker permits better overlap than an ethyl linker, the emission maxima of the folded exciplexes formed from (aminopropyl)arene exciplexes are usually at lower energy than those of (aminoethyl)arene exciplexes in nonpolar solvents.^{5,6,8} The observation of lower energy exciplex maxima for 9P2 vs 9P3 thus provides additional evidence for loose geometries for the (aminoalkyl)phenanthrene exciplexes in moderately and highly polar solvents.

Temperature Dependence of Exciplex Emission. We have investigated the temperature dependence of the fluorescence spectra of the (aminoalkyl)phenanthrenes in isobutyronitrile solution and frozen glasses. The choice of solvent was based on the high intensity of exciplex fluorescence at room temperature (Figure 1). Below the melting point of isobutyronitrile (ca. 200 K) only the fluorescence of the locally excited phenanthrene can be observed for 1P3 and 9P3. Broad exciplex emission, weaker than that of the locally excited state, is observed for 9P1 and 9P2 in an isobutyronitrile glass. Okada and Mataga^{5c} attributed the observation of exciplex emission observed from the linked anthracene-aniline 7 in a cyclohexane glass to excitation of loosely folded ground-state conformers which may be favored by π stacking. The absence of exciplex emission from 1P3 or 9P3 in the glassy state indicates that there is no significant population of ground-state folded conformers in which the amine lone pair is near the phenanthrene π orbitals. In contrast, significant ground-state populations of conformations in which the amine lone pair is near phenanthrene are expected for 9P1 and 9P2.

Above the melting point of isobutyronitrile weak exciplex emission is observed for 9P1, 9P2, and 9P3; however, exciplex emission is not detected below 220 K for 1P3. The exciplex fluorescence maxima continuously shift to higher energy with increasing temperature. Maxima at 223 and 293 K are at 500 and 476 nm for 1P3, 491 and 472 nm for 9P2, and 485 and 462 nm for 9P3. This shift is similar to that previously reported for (aminoalkyl)pyrene exciplex emission in ethyl acetate solution and attributed to a decrease in the solvent dielectric constant with increasing temperature.^{6d} Increasing temperature results in an increase in the relative intensity of exciplex vs locally excited fluorescence. Stevens-Ban¹⁸ plots of the ratio of exciplex: locally excited fluorescence intensities $(\ln(I_{ex}/I_{le}))$ determined at the emission maxima vs T^{-1} are shown in Figure 3. Values of I_{ex}/I_{le} for **9P3** and **9P2** display maxima between 250 and 260 K and decrease at higher temperatures, while the value for 1P3 is still increasing at room temperature. The appearance of the data in Figure 3 is similar to that previously reported for (aminoalkyl)pyrenes.^{6d} The increase in I_{ex}/I_{le} with



Figure 3. Temperature dependence of $\ln(I_{ex}/I_{le})$ for 9P2 (\triangle), 9P3 (\bigcirc), and 1P3 (\square) in isobutyronitrile solution.

increasing temperature is attributed to activated but largely irreversible exciplex formation at low temperatures. The decrease in the value of I_{ex}/I_{le} observed at high temperatures for **9P3** and **9P2** indicates that the exciplex and locally excited state are in equilibrium at higher temperatures in isobutyronitrile solution. This interpretation is supported by fluorescence decay measurements (vide infra). At room temperature exciplex formation apparently is less reversible for **1P3** than for **9P3** or **9P2** in accord with the greater stability of the **1P3** exciplex (Figure 2).

Kinetics of Exciplex Formation and Decay. The fluorescence decay constants of the (aminoalkyl)phenanthrenes determined at the emission maxima of the locally excited and exciplex states (368 and 460 nm, respectively) in several solvents are reported in Table 2. In hexane solution no exciplex fluorescence is observed and the decay of the locally excited fluorescence can be fit to a single exponential. The decay times for 9P2, 9P3, and 1P3 are all slightly longer than those for 9-methyl- and 1-methylphenanthrene in hexane solution (48.7 and 54.6 ns, respectively) while that for 9P1 is somewhat shorter. This suggests that no exciplex formation occurs in hexane solution except in the case of 9P1, for which highly reversible exciplex formation may occur. The steady-state concentration of the 9P1 exciplex in hexane solution may be too low to permit observation of exciplex fluorescence. In tetrahydrofuran solution both locally excited and exciplex fluorescence are observed and both decay with the same singleexponential decay constant. This suggests that reversion of the exciplex to the locally excited singlet state is the predominant pathway for exciplex decay but that the steady-state exciplex concentration is sufficiently high to permit observation of exciplex fluorescence. The long-lived locally excited singlet in effect serves as a reservoir for repopulation of a weakly bound intramolecular exciplex. This would not be possible for an intermolecular exciplex, in accord with the absence of exciplex fluorescence from phenanthrene-TEA in moderately polar solvents.

More complex fluorescence decay kinetics are observed for **9P2**, **9P3**, and **1P3** in isobutyronitrile and acetonitrile solution. The emission from the locally excited state (368 nm) displays dual-exponential decay in both solvents, the long-lived component making the major contribution to the total emission in

isobutyronitrile and the short-lived component in acetonitrile. Both components are shorter lived than 9-methyl- and 1methylphenanthrene in acetonitrile solution (48.7 and 52.4 ns. respectively). On the basis of analogy to related intramolecular exciplexes, it seems likely that the short-lived and long-lived components of the locally excited emission can be attributed to the prompt emission from unquenched locally excited phenanthrene and delayed emission resulting from slow reversion of the exciplex to the locally excited state. However, we have not undertaken the detailed kinetic analysis necessary for the interpretation of complex fluorescence decays.¹⁹ The exciplex emission (460 nm) displays a single decaying component whose decay time is similar to that of the long-lived component of the locally excited emission. In some cases a rising component whose rise time is the same as the decay time of the short-lived component of locally excited fluorescence is observed.

Rate constants for exciplex decay $(k_d = \tau_{ex}^{-1})$ can be determined in polar solvents in which the exciplex and locally excited emission display different decay constants. This data is reported in Table 3. Values of k_d are observed to increase with increasing solvent polarity as observed by Van der Auweraer et al.^{6f} for ((N,N-dimethylamino)alkyl)benzene exciplexes and by Mataga et al.^{5h} for the (anilinoalkyl)anthracenes 5-7. Exciplex decay can occur via intersystem crossing to the locally excited arene triplet or via nonradiative decay to the singlet ground state. Since the exciplex fluorescence energies (Table 1) are lower than that of phenanthrene triplet (21 600 cm^{-1}) we assume that exciplex intersystem crossing to yield the locally excited phenanthrene triplet does not compete effectively with nonradiative decay. Nonradiative decay via return electron transfer is highly exergonic and hence in the Marcus inverted region. Thus the increase in k_d is consistent with the decrease in exciplex energy with increasing solvent polarity.

A larger value of k_d is observed for **9P1** than for the other (aminoalkyl)phenanthrenes in acetonitrile solution. This may be related to the observation of moderately efficient photolysis of **9P1** but not the other (aminoalkyl)phenanthrenes. Okada et al.^{5f} have reported that (aminomethyl)pyrene exciplexes undergo abnormally rapid intersystem crossing in nonpolar solvents to form the locally excited arene triplet, resulting in very short singlet exciplex lifetimes. Rapid intersystem crossing and nonradiative decay are no doubt responsible for the absence of exciplex fluorescence from other ((*N*,*N*-dimethylamino)methyl)arenes.⁸ However, Mataga et al.^{5h} have reported that the value of k_d for (anilinoalkyl)anthracenes **5**–**7** and (anilinoalkyl)pyrenes in acetonitrile solution increases with increasing chain length. Thus the effects of chain length appear to be dependent upon the choice of donor-acceptor system and the solvent polarity.

The exciplex decay constant for 9P3 in isobutyronitrile solution decreases with decreasing temperature from 31.3 ns at 293 K to 19.9 ns at 224 K while the decay constant for 9P2 is essentially temperature independent (ca. 12 ns) over this temperature range. Exciplex lifetimes would be expected to increase with a decrease in temperature as a consequence of activated nonradiative decay or reversion to the locally excited state. However, decreasing temperature in a polar solvent is accompanied by an increase in the solvent polarity and a redshift in the exciplex fluorescence maximum. Decreased energy should result in an increase in the rate constant for exciplex nonradiative decay. Evidently the change in solvent polarity is more important for 9P3 while decreasing temperature and increasing solvent polarity are effectively counterbalanced for 9P2. A temperature dependence similar to that for 9P3 was

solvent	9P1-le	9P1-ex	9P2-le	9 P2 -ex	9 P3- le	9P3 -ex	1P3-le	1P3-ex
hexane	43.8		48.8		49.1		53.3	
tetrahydrofuran	40.8^{b}	3.4	31.7	31.2	46.8	46.0	45.0	45.3
isobutyronitrile			0.79 ^c	12.0	$0.47^{c,d}$	31.3	1.34 ^c	20.8
methanol			10.0	f				
acetonitrile	0.4	1.1^{d}	0.62^{c}	7.2	0.51°	5.3	1.14^{c}	3.1°
dimethylformamide			0.56 ^c	2.5°				
dimethyl sulfoxide			0.39	1.0				

 TABLE 2:
 Fluorescence Decay Times^a

^a Decay times in nanoseconds determined by single-photon counting in deoxygenated solutions at 368 nm (le) and 460 nm (ex). ^b Short-lived component with decay time similar to that for exciplex emission also detected. ^c Long-lived component with decay time similar to that for exciplex emission also detected. ^d Component with longer lifetime than exciplex also detected. ^e Rising component with lifetime similar to that of locally excited state also detected. ^f Multicomponent decay.

TABLE 3: R	ate Constants	for Excip	olex Decay
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	$10^{-9}k_{\rm d}$				
solvent	9 P 1	9P2	9P3	1P3	
isobutyronitrile		0.08	0.03	0.05	
dimethylformamide	2.5	0.13	0.19	0.32	
dimethyl sulfoxide		1.0			

reported for the exciplex decay times of ((N,N-dimethylamino)-propyl)pyrene in diethyl ether and ethyl acetate solution.^{6c}

The observation of intramolecular exciplex fluorescence in highly polar solvents such as dimethyl sulfoxide requires that the exciplex lifetime be sufficiently long to permit fluorescence to compete with nonradiative decay. In cases for which the exciplex lifetime is determined mainly by the rate constant for return electron transfer, the observation of exciplex fluorescence in highly polar solvents may be limited by the magnitude of the energy gap, and hence the rate constant, for return electron transfer. Exciplex fluorescence for other arene-amine intramolecular exciplexes has been observed in acetonitrile solution with maxima at lower energy and shorter exciplex lifetimes than are observed for 9P2 and 9P3 in dimethyl sulfoxide solution (Tables 1 and 2).⁵⁻⁷ For example, the value of k_d for (anilinoethyl)anthracene 6 in acetonitrile solution $(1.0 \times 10^9 \text{ s}^{-1})$ is the same as that for **9P2** in dimethyl sulfoxide solution. Thus it may be possible to extend the investigation of intramolecular exciplex fluorescence to solvents even more polar than dimethyl sulfoxide. This is not likely to be the case for intermolecular exciplexes which would be expected to undergo rapid ionic dissociation in such highly polar solvents. The P/TEA exciplex is nonfluorescent in all solvents.9

Exciplex Chemistry. Irradiation of 9P1 results in clean conversion to a mixture of 9-methylphenanthrene and 1,2-di-9-phenanthrylethane in a ca. 1.2:1 ratio. Quantum yields for conversion of 9P1 to 9-methylphenanthrene are solvent dependent, decreasing from 3.4×10^{-2} in hexane to 9×10^{-3} in tetrahydrofuran and 3×10^{-3} in acetonitrile. The products observed upon irradiation of 9P1 are presumably formed via C-N homolysis followed by hydrogen abstraction or combination of the phenanthrenemethyl radical (Scheme 1). Since exciplex formation is reversible, photolysis may occur via either the locally excited singlet state or the exciplex. Photolysis of C-N bonds in benzylamines has previously been observed for several N-benzyladanine derivatives^{20a} and for some ((N,N-N))dimethylamino)methyl)styrenes.^{20b} However, it has not been reported for several (aminomethyl)arenes which are known to undergo intramolecular electron transfer. The scope and mechanism of this reaction are under continuing investigation.

Irradiation of **9P2** results in the formation of a complex mixture of products which was not analyzed. The decomposition of **9P2** is less efficient than that of **9P1**. Both **9P3** and **1P3** are photochemically unreactive, as are the ((aminomethyl)-

SCHEME 1



naphthyl)phenanthrenes 1 and 2.¹² None of the ((*N*,*N*-dimethylamino)alkyl)phenanthrenes undergo efficient exciplex proton transfer, a process which we have recently investigated for several (aminoalkyl)styrenes.⁸ Since proton transfer was found to occur from folded conformations of intramolecular exciplexes in nonpolar solvents, it is not surprising that the (aminoalkyl)phenanthrenes fail to undergo exciplex proton transfer. Efficient intramolecular phenanthrene—amine N—H addition is observed upon direct irradiation of secondary ((*N*-phenylamino)alkyl)phenanthrenes²¹ but not ((*N*-methylamino)alkyl)phenanthrenes.^{22a} Intramolecular quenching of phenanthrene fluorescence is observed in the former but not in the latter compounds. Intramolecular phenanthrene—amine N—H addition is also observed upon electron-transfer-sensitized irradiation of primary (aminoalkyl)phenanthrenes.^{22b}

Concluding Remarks. The formation of fluorescent intramolecular exciplexes has made tertiary (aminoalkyl)arenes attractive subjects for photophysical and photochemical investigations.⁵⁻⁸ Exciplex formation and behavior are found to be dependent upon the choice of arene acceptor, amine donor, the length of the connecting polymethylene chain, and solvent polarity. Thus while analogy can often be drawn between the behavior of various arene-amine systems, each system appears to have unique characteristics. As a group, the (aminoalkyl)phenanthrenes have in common their failure to form stable exciplexes in nonpolar solvents and the formation of fluorescent exciplexes with loosely folded geometries in moderate and highly polar solvents. This has permitted the initial observations of exciplex fluorescence in solvents as polar as dimethyl sulfoxide and 20% aqueous acetonitrile. The photochemical reactivity of the (aminoalkyl)phenanthrenes increases with decreasing polymethylene chain length. Only in the case of the (aminomethyl)phenanthrene is a moderately efficient photochemical reaction observed: an unusual C-N cleavage reaction.

Experimental Section

General Methods. NMR spectra were recorded in CDCl₃ solutions using a Gemini 300 Varian spectrometer with TMS as an internal standard. High-resolution mass spectra were determined on a Hewlett-Packard 5985 GC/VG70-250SE MS apparatus with an ionizing voltage of 70 V. Ultraviolet absorption spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer. Melting points were measured on a Fisher-Johns apparatus and are uncorrected. Steady-state fluorescence spectra were obtained on a Spex Fluoromax

spectrometer. Fluorescence decay times were measured on a PTI-LS1 single-photon counter (time resolution ca. 0.2 ns) using a gated arc lamp as the excitation source. Data was analyzed by deconvolution and least squares fitting. Solutions for fluorescence studies (ca. $1 \times 10-4$ M) were purged thoroughly with nitrogen. Fluorescence lifetime decays and spectra taken under nitrogen were found to be identical to those of the samples subjected to several freeze-pump-thaw cycles. Reduction potentials were measured on a BAS CV27 voltammeter in dimethyl sulfoxide using 0.1 M Et₄NBF₄ as the electrolyte and ferrocene as a reference. Ag/AgI was used as a reference electrode with glassy carbon as a working electrode. A platinum wire 1.6 mm in diameter provided the auxiliary electrode. The half-wave potential of ferrocene is 0.668 ± 0.002 V under these conditions. Temperature studies were carried out in an Oxford Instrument DN1704 variable-temperature liquid nitrogen cryostat equipped with an ITC4 temperature controller. High-temperature studies were performed in a heated stainless steel cell with a single sapphire window capable of withstanding high pressures. Preparative-scale irradiations were carried out under nitrogen in Pyrex test tubes using a Rayonet reactor fitted with RPR 3000 lamps. Quantum yield measurements were carried out in the Rayonet reactor using trans-stilbene as the actinometer.²³ Irradiated solutions were analyzed by a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a $10 \times 0.53 \text{ mm}^2$ fused silica column coated with poly(methyldisiloxane).

Materials. Hexane, ethyl acetate, tetrahydrofuran, acetonitrile, methanol, *N*,*N*-dimethylformamide, and dimethyl sulfoxide (Aldrich, spectrograde) were used as received. Diethyl ether (Fisher) was used as received. Isobutyronitrile and propionitrile (Aldrich) were distilled under nitrogen over calcium hydride prior to use. Heptyl cyanide and propylene carbonate (Aldrich) were used as received.

1-Methylphenanthrene: o-Tolualdehyde and benzyltriphenylphosphonium chloride (Aldrich) were combined via a Wittig reaction. Purification of the product via silica gel by column chromatography (eluent: 20% CHCl₃, 80% hexane) provided a mixture of *cis*- and *trans-o*-methylstilbene in 70% yield. 1-Methylphenanthrene was prepared following the procedure of Wood and Mallory.²⁴ Silica gel chromatography followed by recrystallization from methanol afforded a crystalline solid in 60-70% yield: mp 117 °C (lit.²⁴ 117.6-119.6 °C).

9-Methylphenanthrene: 9-(Hydroxymethyl)phenanthrene was prepared from 9-bromophenanthrene (Aldrich) by the method of Bachmann²⁵ and purified via flash chromatography (gradient elution starting with 50% hexane, 50% CHCl₃) to give a 45% yield. The alcohol was converted to the chloride via reaction with thionyl chloride. The crude chloride was dissolved in anhydrous diethyl ether and added dropwise to a stirring solution of LiAlH₄ (1 equiv) in diethyl ether under nitrogen at room temperature. After addition of the halide was complete, the solution was gently refluxed for 24 h. Cold water was added to quench any unreacted LiAlH₄. After evaporation of the organic phase under reduced pressure, a solid residue remained. Recrystallization several times in MeOH gave pure 9-methylphenanthrene in 52% yield: mp 89 °C (lit.²⁶ 92–92.5 °C).

9-((*N*,*N*-Dimethylamino)methyl)phenanthrene (9P1): The primary amine was prepared from 9-phenanthrenecarbonitrile (Aldrich) in 98% yield following the procedure of Corina and Platt²⁷ (¹H NMR: δ 8.70 (m, 2H); 8.12 (m, 1 H); 7.89 (m, 1 H); 7.75–7.57 (m, 5 H); 4.39 (s, 2 H); 1.64 (bs, 2 H)). Reductive alkylation using the method of Borch and Hasssid²⁸ for reactive amines gave the tertiary amine. The product was purified by preparative thick-layer chromatography (eluent: 6% MeOH, 94% CHCl₃) to give a colorless crystalline solid in 50% yield: mp 115–116 °C (lit.²⁹ mp 116 °C); ¹H NMR δ 8.68–8.76 (m, 2H); 8.37 (m, 1H); 7.90 (d, 1H); 7.60–7.70 (m, 5H); 3.89 (s, 2H); 2.38 (s, 6H).

9-((N,N-Dimethylamino)ethyl)phenanthrene (9P2): 9-(2-Chloroethyl)phenanthrene was prepared from 9-bromophenanthrene in 63% overall yield using the method of Bergmann and Blum-Bergmann.³⁰ The chloride was converted to 9-(2-aminoethyl)phenanthrene in 50% yield via a Gabriel synthesis. The ¹H NMR spectrum of the amine was similar to that previously reported.²² Reductive alkylation²⁸ gave the tertiary amine which was purified via acid/base extractions followed by preparative thick-layer chromatography (eluent: MeOH, 0.5% ammonium hydroxide) to give a colorless crystalline solid in 50% yield: mp 59-60 °C;^{31 1}H NMR δ 8.65-8.77 (m, 2H); 8.13 (m, 1H); 7.84 (d, 1H); 7.58-7.68 (m, 5H); 3.32 (t, 2H); 2.73 (t, 2H); 2.41 (s, 6H). ¹³C NMR (decoupled) δ 134.66, 131.86, 131.21, 130.73, 129.72, 128.08, 126.84, 126.79, 126.69, 126.25, 126.11, 124.35, 123.32, 122.48, 60.42, 45.65, 32.04. HRMS 249.1517 (calcd) and 249.1530 (obsd).

9-((N,N-Dimethylamino)propyl)phenanthrene (9P3): 9-(2-Chloroethyl)phenanthrene was reacted with sodium cyanide to give 9-(2-cyanoethyl)phenanthrene in nearly quantitative yield. Several recrystallizations from methanol afforded light tancolored crystals; mp 96-97 °C (lit.³² mp 101-102 °C). The crude nitrile was dissolved in anhydrous diethyl ether and added dropwise with stirring to a solution of LiAlH₄ (1 equiv) in anhydrous diethyl ether under nitrogen at room temperature. After addition was complete, the solution was gently refluxed for 16 h. Cold water was added dropwise to quench any unreacted LiAlH₄. The amine was extracted from the organic phase with aqueous acid. After basification, the amine was reextracted with a mixture of diethyl ether and ethyl acetate. Evaporation of the solvent under reduced pressure produced the pure primary amine as a colorless crystalline solid in 59% yield; mp 98-100 °C. The ¹H NMR spectrum of the amine was similar to that previously reported.²² Reductive alkylation provided the tertiary amine.²⁸ After extractions, the amine was purified by preparative thick-layer chromatograhy (eluent: MeOH, 1% ammonium hydroxide) to give a colorless oil in 37% yield. ¹H NMR δ 8.70 (dd, 2H); 8.13 (d, 1H); 7.84 (d, 1H); 7.57-7.67 (m, 5H); 3.16 (t, 2H); 2.45 (t, 2H); 2.27 (s, 6H); 2.00 (quin, 2H). ¹³C NMR (decoupled) δ 136.47, 131.90, 131.28, 130.72, 129.67, 128.09, 126.69, 126.59, 126.20, 126.09, 125.99, 124.50, 123.26, 122.49, 59.70, 45.66, 31.17, 28.29. HRMS 263.1674 (calcd) and 263.1673 (obsd).

1-((N,N-Dimethylamino)propyl)phenanthrene (1P3): 1-(Bromomethyl)phenanthrene was synthesized from 1-methylphenanthrene using the procedure from Harmon and co-workers.³² Purification by flash chromatography (eluent: 50% CHCl₃, 50% hexane) gave 1-(bromomethyl)phenanthrene in 37% yield. The bromide was converted to 3-(1-phenanthrene)propionic acid in 68% yield using the method of Bachmann³³ modified by using the procedure Clarke and Murray³⁴ for hydrolysis and decarboxylation of the diester. Purification of the resulting acid by base extraction and reacidification followed by recrystallization several times from dilute acetic acid gave a colorless crystalline solid; mp 185-187 °C (lit.33 189-189 °C). The acid was converted to the amide via the acid chloride by reaction with thionyl chloride followed by reaction with dimethylamine (a 40% solution was used with 1 equiv of potassium carbonate rather than anhydrous amine).³⁵ Purification by flash chromatography (eluent: 2% MeOH, 98% CHCl₃) provided the amide 71% yield. Reduction of the amide with LiAlH₄ followed by acid/base extractions gave the desired tertiary amine in 58%

yield. The amine was further purified by preparative thicklayer chromatography (eluent: 5% MeOH, 95% CH₂Cl₂) and distilled under vacuum to give a colorless oil: ¹H NMR δ 8.65 (dd, 2H); 8.0 (d, 1H); 7.87 (d, 1H); 7.75 (d, 1H); 7.52-7.68 (m, 3H); 7.45 (d, 1H); 3.15 (t, 2H); 2.42 (t, 2H); 2.25 (s, 6H); 1.94 (quin, 2H). HRMS 263.1674 (calcd) and 263.1671 (obsd).

Photochemical Reaction of 9-((N,N-Dimethylamino)methyl)phenanthrene (9P1): A hexane solution of 9P1 (0.02 M) was irradiated to 91% conversion of starting material (as determined by GC). Removal of the solvent under nitrogen and ¹H NMR analysis of the residue dissolved in CDCl₃ revealed peaks assignable to the starting material, 9-methylphenanthrene, and 1,2-di-9-phenanthrylethane. 9-Methylphenanthrene was isolated by acid/base extraction (to remove amine impurities) and identified by comparison of its ¹H NMR and GCMS to those of an authentic sample. The ¹H NMR of 1,2-di-9phenanthrylethane is similar to that reported previously.³⁶

Acknowledgment. We thank G. D. Reddy for some preliminary observations and A. V. Satish for assistance with the electrochemical measurements. Financial support for this research has been provided by the National Science Foundation.

Supplementary Material Available: Table of fluorescence decay data (decay times for locally excited and exciplex fluorescence, preexponentials, χ^2 , and Durbin Watson fits) (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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