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Chain-Length- and Solvent-Dependent Intramolecular Proton Transfer in Styrene–Amine Exciplexes

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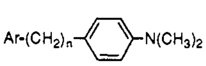
Abstract: The photochemical and photophysical behavior of several ((*N*,*N*-dimethylamino)alkyl)styrenes in which the amino group is attached to the styrene α- or β-carbon by a methyl, ethyl, propyl, or butyl polymethylene chain has been investigated. Efficient intramolecular addition of an aminomethyl C–H to styrene is observed in nonpolar solvents for the (aminoethyl)styrenes, and addition of an aminomethylene C–H is observed for the (aminobutyl)styrenes. However, the (aminomethyl)- and (aminopropyl)styrenes do not undergo intramolecular addition reactions. Both the reactive and unreactive (aminoalkyl)styrenes form fluorescent singlet exciplexes in nonpolar and polar solvents. The results of exciplex and product quenching by an added primary amine indicate that the fluorescent exciplex is an intermediate in the addition reactions of the (aminoalkyl)styrenes. Activation parameters for both exciplex formation and exciplex proton transfer have been determined. Highly regioselective intramolecular proton transfer is proposed to occur via least motion pathways from the lowest energy folded conformations of the singlet exciplex intermediates in nonpolar solvents. The solvent dependence of exciplex proton transfer, fluorescence, intersystem crossing, and nonradiative decay is attributed to a change in exciplex conformation from folded in nonpolar solvents to extended in solvents more polar than diethyl ether.

Introduction

The formation and photophysical behavior of intramolecular exciplexes in which the electron acceptor is connected to a tertiary amine donor by a flexible polymethylene chain have been the subject of numerous investigations.[1–9] Of particular relevance to our investigations of intramolecular styrene–amine exciplexes[2] are the studies of arene–*N*,*N*-dialkylaniline (**I**, Ar = 9-anthryl or 1-pyrenyl, *n* = 0, 1, 2, 3) exciplexes,[3,4] arene–(*N*-methylanilino)alkane (II, Ar = 9-anthryl, *n* = 3) exciplexes,[5,6] and arene–(*N*,*N*-dimethylamino)alkane (**III**, Ar = phenyl, 1-naphthyl, 2-naphthyl, 1-pyrenyl, *n* = 2, 3, 4) exciplexes.[7–9] These studies have established that the rate constants for intramolecular electron transfer are dependent upon the redox properties of the excited-singlet arene acceptor and ground-state amine donor, the solvent polarity, the length of the polymethylene chain separating the donor and acceptor, and the point of attachment of the polymethylene chain to the arene. In nonpolar solvents, the arene–aniline exciplexes are proposed to adopt a sandwich-type geometry, when the polymethylene chain is sufficiently long (three or more carbons), and the arene–trialkylamine exciplexes are proposed to adopt specific folded conformations which maximize orbital overlap and Coulombic attraction while minimizing nonbonded inter-



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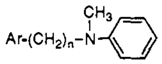

II

$Ar\text{-}(CH_2)_n\text{-}N(CH_3)_2$

III

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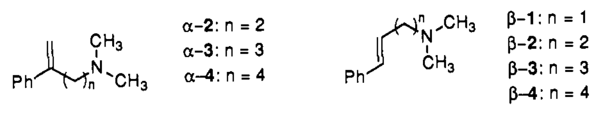
Chart 1



actions in the polymethylene chain. In polar solvents arene–amine exciplexes are proposed to adopt "looser" or more extended conformations.[3,9] Solvent-induced changes in exciplex conformation may be responsible for the solvent dependence of exciplex radiative and nonradiative rate constants.

The conformation of chemically reactive intramolecular exciplexes might be expected to control the regioselectivity of intramolecular addition reactions. However, most intramolecular arene–amine and arylolefin–amine exciplexes investigated to date have not been reported to be photochemically reactive. This lack of reactivity stands in contrast to the behavior of the intermolecular exciplexes of singlet arenes and arylolefins with tertiary amines, many of which have been reported to undergo photoaddition reactions.[10-12] The α- and β-((*N*,*N*-dimethylamino)alkyl)styrenes (Chart 1) constitute an interesting exception in which intramolecular addition is, under certain conditions, far more efficient than intermolecular addition.[2d,13] We report here the results of our detailed investigation of the chain-length and solvent dependence of the photophysical and photochemical behavior of these (aminoalkyl)styrenes. The regioselectivity and rate constant of intramolecular exciplex proton transfer are found to be highly dependent upon the length of the polymethylene chain, the point of attachment (α vs β), and solvent polarity. These results are attributed to exciplex conformational control of photochemical reactivity.

Results

Absorption and Fluorescence Spectra. The α- and β-(aminoalkyl)styrenes were prepared by standard literature procedures (see Experimental Section). The absorption spectra of the styrenes display forbidden (longest wavelength) and allowed transitions. The allowed transition of α-methylstyrene (α-MS) in hexane solution is at higher energy than that of β-methylstyrene (β-MS) (242 vs 248 nm), and the forbidden transition of α-MS appears as a structureless shoulder while that of β-MS displays vibrational structure. The absorption spectra of the α- and β-(aminoalkyl)-styrenes are similar to those of α-MS and β-MS, respectively, with enhanced intensity below 280 nm due to the absorption of the tertiary amine. The absence of enhanced long-wavelength absorption indicates that there is no strong ground-state interaction between the styrene and amine, a conclusion which is corroborated by the appearance of the ^{1}H NMR spectra, specifically the absence of shielding of the *N*-methyl protons by the styrene π electrons.

The fluorescence of α-MS in hexane solution occurs at higher energy than that of β-MS (304 vs 308 nm) and has a shorter lifetime (1.9 vs 11.6 ns). Quenching of the fluorescence of α-MS or β-MS by triethylamine (TEA) is accompanied by the appearance of structureless, long-wavelength exciplex fluorescence. As reported elsewhere,[14] analysis of the kinetics of exciplex formation and decay are complicated by the occurrence of both partially reversible exciplex formation and exciplex quenching by ground-state amine. Exciplex fluorescence maxima for α-MS–TEA and β-MS–TEA in several solvents are reported in Tables 1 and 2 along with the fluorescence decay times of α-MS and β-MS (unquenched) and of the styrene–TEA exciplexes. The latter were determined at low amine concentration (0.005 M) in order to minimize exciplex quenching by ground-state amine.[14]

Table 1. Fluorescence and Product Quantum Yield Data for α-Methylstyrene and α-(Aminoalkyl)styrene Exciplexes

exciplex	solvent	$10^{-3}\nu_{ex}$,[a] cm^{-1}	τ_s,[b] ns	τ_{ex},[c] ns	Φ_F[d]	Φ_{add}[e]
α-MS–TEA	hexane	25.0	(1.9)	6.8		0.08
	dibutyl ether	24.0				
	diethyl ether	23.8		6.6		0.01
	tetrahydrofuran	22.3		12.8		<0.05
	acetonitrile	20.6				<0.05
α-2	hexane	27.0	0.1	0.5	0.012	0.19
	dibutyl ether	24.3		1.9		0.07
	diethyl ether	24.0	<0.1	1.6	0.026	0.05
	ethyl acetate	22.3		3.7		
	tetrahydrofuran	22.4		3.8	0.021	0.02
	acetonitrile	20.6		2.6	0.015	<0.05
α-3	hexane	26.3	0.25	5.8	0.13	<0.05
	diethyl ether	23.9		19.6	0.091	
	tetrahydrofuran	22.6		18.4	0.065	
	acetonitrile	20.0	<0.1	3.2	0.009	
α-4	hexane	26.2	0.4	1.2	0.016	0.20
	diethyl ether	23.8	0.2	5.3	0.073	0.06
	tetrahydrofuran	22.9		8.6	0.30	<0.05
	acetonitrile	20.0		1.3	0.002	

[a] Exciplex fluorescence maxima. [b] Styrene fluorescence decay time in deoxygenated solution (value in parentheses measured in the absence of amine). [c] Exciplex fluorescence decay time. [d] Quantum yield for exciplex fluorescence. [e] Quantum yield for adduct formation.

Table 2. Fluorescence and Product Quantum Yield Data for β-Methylstyrene and β-(Aminoalkyl)styrene Exciplexes

exciplex	solvent	$10^{-3}\nu_{ex}$,[a] cm^{-1}	τ_s,[b] ns	τ_{ex},[c] ns	Φ_{add}[d]	Φ_i[e]
β-MS–TEA	hexane	25.6	(11.6)	11.5		
	dibutyl ether	24.5				
	diethyl ether	24.0				
	ethyl acetate	22.6	(10.7)	14.5		
	acetonitrile	21.3	(8.9)	4.2		
β-1	hexane	*f*				0.35
β-2	hexane	28.0	0.1	2.2	0.07	0.048
	dibutyl ether	25.3				
	diethyl ether	24.6		8.2	0.01	0.058
	tetrahydrofuran	23.0		8.3	<0.005	0.13
	acetonitrile	21.3		4.3		0.10
β-3	hexane	26.4	0.4	1.5	<0.005	0.035
β-4	hexane	*f*	1.5		0.21	

[a–d] See footnotes to Table 1. [e] Quantum yield for photoisomerization. [f] Exciplex emission too weak to resolve.

The fluorescence spectra of the β-(aminoalkyl)styrenes have previously been described.[2a] The spectra of **β-2** and **β-3** consist of weak residual styrene fluorescence and broad, structureless exciplex emission that shifts to longer wavelength with increasing solvent polarity. In the case of **β-4** the styrene fluorescence is more intense; however, the exciplex fluorescence is very weak at room temperature in both nonpolar and polar solvents. In the case of **α-1** both styrene and exciplex fluorescence are very weak in both nonpolar and polar solvents. The fluorescence spectrum of **α-2** in several solvents is shown in Figure 1. As is the case for **β-2** and **β-3**, the residual styrene fluorescence is very weak and, in some solvents, obscured by scattered light or impurity fluorescence from the solvent. Quantum yields for exciplex fluorescence from **α-2**, **α-3**, and **α-4** in several solvents are reported in Table 1.

Fluorescence decay curves for the (aminoalkyl)styrenes were recorded near both the styrene (310 nm) and exciplex (Tables 1 and 2) emission maxima. In the case of **α-2** the residual styrene decay time is near the time resolution of our instrumentation (0.1 ns) in hexane solution and is too short to measure in more polar solvents. In the case of **α-3** and **α-4** the residual styrene fluorescence exhibits monoexponential decay in hexane solution with an amplitude of >0.99 for the major component, as previously

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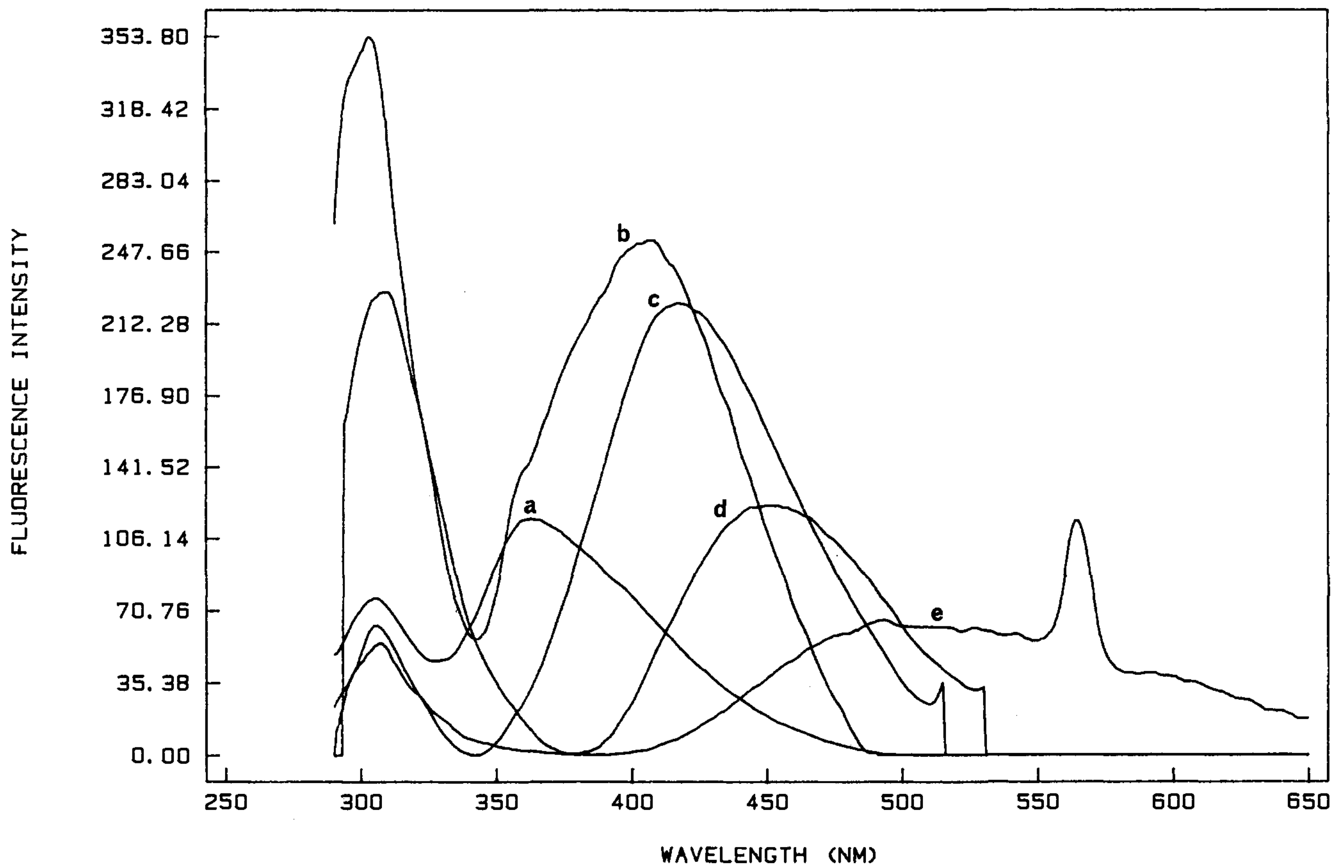


Figure 1. Fluorescence spectra of α-((*N*,*N*-dimethylamino)ethyl)styrene (α-**2**) in hexane (a), dibutyl ether (b), diethyl ether (c), tetrahydrofuran (d), and acetonitrile (e) solution.

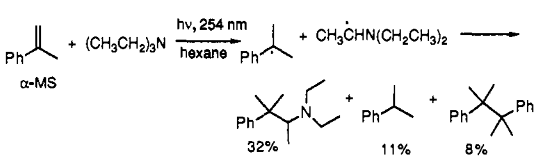
reported for β-**3** and β-**4**.[2a] The exciplex emission of α-**3** and α-**4** displays a rising component with a time constant similar to that of the residual styrene decay and a decaying component which can be fit either to a single exponential or to a dual exponential decay dominated (preexponential >0.95) by a single component. In the case of α-**2** a rising component cannot be resolved, presumably due to its rapid rise time. The exciplex fluorescence decay of α-**2** was monitored at several wavelengths and found to be independent of observation wavelength. This data indicates that exciplex formation is irreversible for the α-(aminoalkyl)-styrenes, as previously reported for the β-(aminoalkyl)styrenes.[2a] The resulting styrene decay times, τ_s, and exciplex decay times, τ_{ex}, are reported in Tables 1 and 2. Exciplex fluorescence rate constants ($k_f = \Phi_f\tau^{-1}$) for the α-(aminoalkyl)styrenes are reported in Table 1. The temperature dependence of the residual styrene and exciplex fluorescence decay of α-**4** was determined in hexane solution between 200 and 300 K. Analysis of the fluorescence decays indicates that exciplex formation is irreversible over the entire temperature range. Values of τ_s, obtained from the monoexponential decay of the styrene monomer fluorescence (amplitude >0.95 except at 200 K), and of τ_{ex}, obtained from the dominant decaying component of the exciplex fluorescence, are reported in Table 3.

Photochemical Reactions. Toki et al.[11b] have reported that 254-nm irradiation of α-MS and TEA hexane solutions results in the formation of a single adduct, *N*,*N*-diethyl 1,2-dimethyl-2-phenylpropylamine (Φ_{add} = 0.04), along with lesser amounts of cumene and bicumyl (eq 1).[15] Quantum yields for adduct formation from 281-nm irradiation of α-MS (0.01 M) with TEA (0.035 M) in several solvents are reported in Table 1. The quantum yield in hexane solution is higher than that reported by Toki et. al.[11b] and decreases with increasing solvent polarity. Irradiation of β-MS (0.01 M) and TEA (0.035 M) in either hexane or acetonitrile solution (>290 nm) results in the formation of a single adduct, *N*,*N*-diethyl-3-phenyl-2-pentylamine, accompanied by comparable amounts of 1-propylbenzene and 3,4-diphenylhexane (eq 2).[2f] Quantum yield measurements for β-MS–TEA were complicated by the occurrence of competing cis,trans isomerization and are not reported.

Table 3. Temperature Dependence of Fluorescence Decay Times and Adduct Quantum Yields for α-((*N*,*N*-Dimethylamino)butyl)styrene (α-**4**)

temp, K	τ_0,[a] ns	τ_s,[b] ns	τ_{ex},[c] ns	Φ_{ex}[d]	Φ_a[e]	Φ_b[e]
300	1.9	0.29	1.2	0.85	0.042	0.017
280	2.4	0.58	1.9	0.75	0.055	0.021
260	3.6	0.96	3.3	0.73	0.053	0.021
240	5.3	1.7	4.7	0.68	0.039	0.017
220	7.0	2.8	6.7	0.60	0.033	0.016
200	8.7	4.1	7.9	0.53	0.015	0.008

[a] Fluorescence decay time of α-MS in hexane solution. [b] Decay time of residual styrene fluorescence from α-**4**. [c] Exciplex fluorescence decay time of α-**4**. [d] Quantum yield for formation of the exciplex from singlet styrene. [e] Quantum yields for the formation of products α-**4a** and α-**4b** in hexane solution corrected for incomplete exciplex formation.



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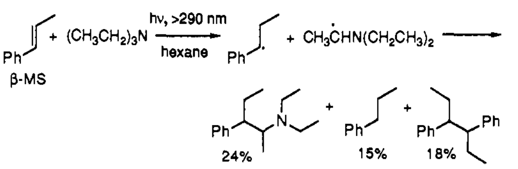

(2)

As previously reported by Aoyama et al.,[13] irradiation of α-**2** (254 nm, hexane solution) results in the formation of a single intramolecular adduct α-**2a** in good preparative yield (eq 3).[15]

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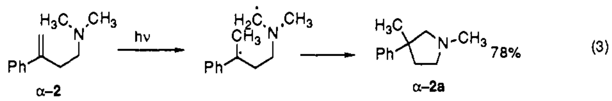
(15) The presumed singlet radical pair and biradical intermediates are shown for purposes of the mechanistic discussion.



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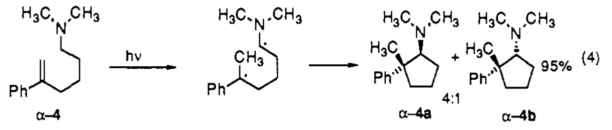

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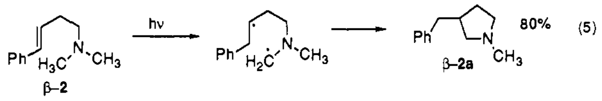

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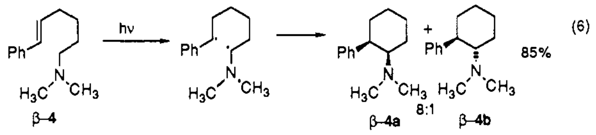

(6)

Prolonged irradiation of α-**3** under similar conditions results in low conversions to several unidentified products. Irradiation of α-**4** in hexane solution results in the efficient formation of a 4:1 mixture of diastereoisomeric adducts α-**4a** and α-**4b** (eq 4). Adduct stereochemistry was assigned on the basis of ^{1}H NMR data. Irradiation of the methine proton adjacent to nitrogen results in a large NOE for the ring methyl of the minor isomer and a small NOE for the major isomer. The photochemical behavior of the β-(aminoalkyl)styrenes is analogous to that of the α-(aminoalkyl)-styrenes in that β-**2** undergoes efficient intramolecular addition to yield a single adduct β-**2a** (eq 5), β-**3** is unreactive (as is β-**1**), and β-**4** yields an 8:1 mixture of diastereoisomeric adducts β-**4a** and β-**4b** (eq 6). The stereochemistry of the major adduct is assigned on the basis of its ^{1}H NMR spectrum. The benzyl proton appears as a broad doublet, consistent with a single axial–axial coupling. Irradiation of the (*E*)-β-(aminoalkyl)styrenes also results in formation of the *Z*-isomers.[2a]

Quantum yields for intramolecular adduct formation in several solvents measured at low conversions on an optical bench using 281-nm irradiation and *trans*-stilbene actinometry are summarized in Tables 1 and 2. Quantum yields decrease with increasing solvent polarity as previously reported for α-**2** by Aoyama et al.[13] In the case of product formation from α-**4**, the product ratio is the same in hexane and diethyl ether solution. The temperature dependence of the quantum yields for the formation of α-**4a** and α-**4b** in hexane solution is reported in Table 3. These values are corrected for incomplete intramolecular quenching of styrene, which becomes significant at lower temperatures. The vanishingly small quantum yields for product formation in acetonitrile solution are consistent with our earlier failure to detect product formation from β-**2** or β-**4** in this solvent.[2a] Triplet-sensitized irradiation of β-**2** or β-**4** in hexane solution (Michler's ketone, 365-nm irradiation) results in styrene trans,cis isomerization but no adduct formation.

Quantum yields for photoisomerization of *E*-β-**2** in several solvents and for *E*-β-**1** and *E*-β-**3** in hexane are reported in Table 2. Since the fluorescence decay time of the residual styrene monomer for these (aminoalkyl)styrenes is very short, exciplex formation must be highly efficient. Thus isomerization is assumed to occur via the singlet exciplex rather than from unquenched singlet styrene.[2a] In the case of α-**4** the quantum yield for formation of the exciplex at room temperature in hexane solution is 0.85 (Table 3). Thus some isomerization may occur via unquenched singlet styrene.

Quenching of Exciplex Fluorescence and Product Formation by Primary Amines. Primary aliphatic amines are much less effective fluorescence quenchers of styrene singlets than are tertiary amines due to their higher ionization potentials.[14] Rate constants for quenching of α- and β-MS by propylamine in hexane solution are 3.1 and 0.36×10^8 M^{-1} s^{-1}, respectively. Addition of propylamine to the (aminoalkyl)styrenes results in quenching of both exciplex fluorescence and product formation but relatively little quenching of the residual styrene monomer fluorescence. Stern–Volmer plots for quenching of α-**2** by propylamine in hexane solution are shown in Figure 2. The least-squares slopes of these plots are reported in Table 4 along with data for other fluorescent (aminoalkyl)styrenes in hexane and more polar solvents. The values of the quenching constants, k_{qf}, in hexane solution are larger for α-**2** and β-**2** than for their longer chain homologs and for α- vs β-(aminoalkyl)styrenes. Values of k_{qf} for both α- and β-(aminoalkyl)styrenes decrease with increasing solvent polarity. Fluorescence quenching of the α-MS–TEA exciplex by added propylamine has also been investigated. Since the α-MS–TEA exciplex is formed reversibly,[14] quenching of both styrene monomer and exciplex fluorescence is observed. However, the slope of the Stern–Volmer plot for quenching of monomer or excimer is larger than that for quenching of α-MS by propylamine. Thus, this slope should approximately equal the Stern–Volmer constant for quenching of the exciplex.

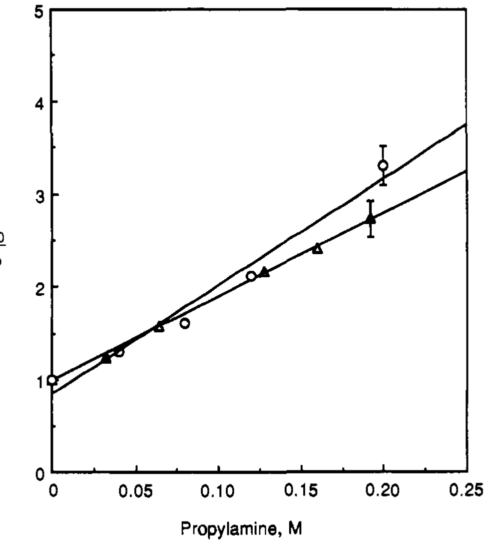

Figure 2. Stern–Volmer plot for quenching of product formation (○) and exciplex fluorescence (△) from α-((*N*,*N*-dimethylamino)ethyl)styrene (α-**2**) in hexane solution.

Table 4. Exciplex Quenching Data

exciplex	solvent	$k_{qf}\tau_{ex}$,[a] M^{-1}	$10^{-9}k_{qf}$, M^{-1} s^{-1}	$k_{qp}\tau_{ex}$,[b] M^{-1}	$10^{-9}k_{qp}$, M^{-1} s^{-1}
α-MS–TEA	hexane	17	2.6		
α-**2**	hexane	10	20	12	25
	diethyl ether	7.3	4.5		
	THF	2.8	0.74		
	acetonitrile	1.0	0.38		
α-**3**	hexane	18	2.9		
	diethyl ether	20	1.0		
α-**4**	hexane	7.7	3.1		
	diethyl ether	13	2.4		
β-**2**	hexane	23	10	29	13
	diethyl ether	35	4.3		
β-**3**	hexane	<1	<0.7		

[a] Slopes of Stern–Volmer plots for quenching of exciplex fluorescence by propylamine. [b] Slopes of Stern–Volmer plots for quenching of product formation by propylamine.

Discussion

The photochemical behavior of the α- and β-((*N*,*N*-dimethylamino)alkyl)styrenes displays remarkable structural and solvent dependence. Efficient product formation is observed for the (aminoethyl)- and (aminobutyl)styrenes (eq 3–6) but not for the (aminomethyl)- or (aminopropyl)styrenes. Furthermore, C–H bond breaking involves the *N*-methyl in the (aminoethyl)styrenes and the *N*-methylene in the (aminobutyl)styrenes, while C–H bond making involves styrene C_β for α-**2**, α-**4**, and β-**4** and styrene

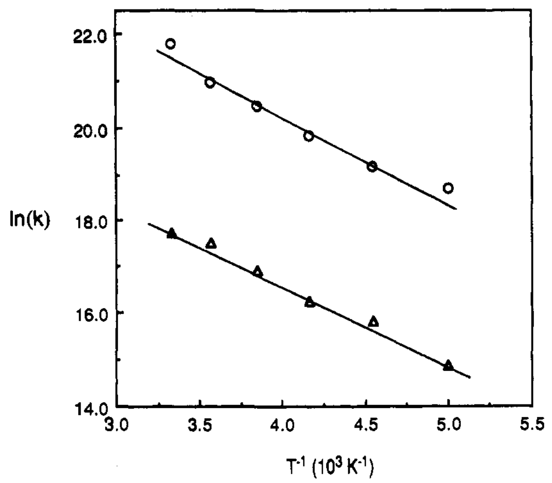

Figure 3. Temperature dependence of the rate constant for exciplex formation (○) and product formation (△) for α-((*N*,*N*-dimethylamino)butyl)styrene (α-**4**) in hexane solution.

C_α for β-**2**. Product formation is observed only in solvents less polar than tetrahydrofuran. The occurrence of product formation via intramolecular proton transfer in fluorescent exciplex intermediates can be established by means of exciplex-quenching studies. This permits the first detailed investigation of the relationship between arene–amine intramolecular exciplex photophysical and photochemical behavior and their dependence upon chain length and solvent polarity. The behavior of some structurally related nonfluorescent exciplexes can also be elucidated by comparison to these results.

Exciplex Photophysics. The kinetics of formation and the photophysical behavior of the intermolecular α-MS–TEA exciplex and intramolecular α-(aminoalkyl)styrene exciplexes are, in most respects, similar to those of β-MS–TEA and β-(aminoalkyl)styrene exciplexes which were previously investigated in our laboratories.[2] There is no evidence for ground-state styrene–amine association, and thus we assume that the (aminoalkyl)styrenes exist as mixtures of gauche and anti conformers in the ground state. Both α- and β-MS excited singlets undergo diffusion-controlled quenching by TEA, resulting in the partially reversible formation of long-lived fluorescent exciplexes (Tables 1 and 2).[14] The styrene decay times for both the α- and β-(aminoalkyl)styrenes (τ_s, Tables 1 and 2) decrease with decreasing polymethylene chain length and with increasing solvent polarity, as is the case for other intramolecular arene–amine exciplexes.[3-9] The slightly larger rate constants for the α- vs β-(aminoalkyl)styrenes are consistent with a larger driving force for exciplex formation in nonpolar solvents, as calculated using eq 7,[16] the singlet energies of α- and β-MS (4.43 and 4.25 eV),

$$\Delta G_{ex} = E_D^{ox} - E_A^{rdn} - E_S + 0.38 \text{ eV} \qquad (7)$$

their reduction potentials (2.39 and 2.54 V vs SCE),[17,18] and the oxidation potential of TEA (0.78 V vs SCE).[19] The resulting values of ΔG_{ex} are –0.88 and –0.55 eV, respectively. In the case of α-**4**, the residual styrene fluorescence is sufficiently long-lived to permit measurement of its temperature dependence (Table 3). The resulting Arrhenius plot (Figure 3) provides values of E_{act} = 3.7 kcal/mol and $\Delta S^\dagger$ = –5.6 eu for exciplex formation, similar to those reported for formation of the ((*N*,*N*-dimethylamino)butyl)benzene exciplex.[9e]

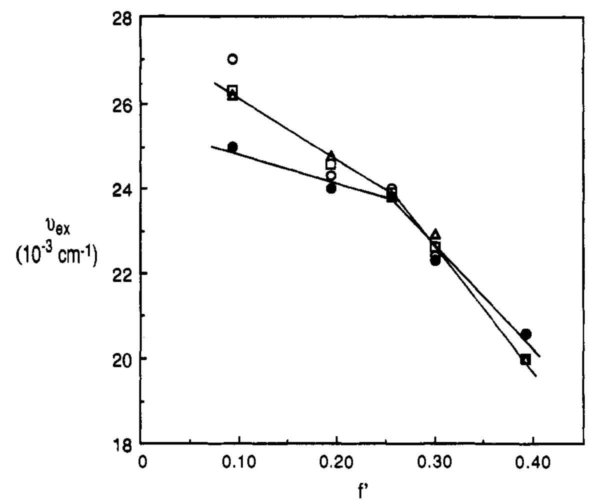

Figure 4. Solvent polarity dependence of the exciplex fluorescence maxima for α-MS–TEA (●), α-**2** (○), α-**3** (□), and α-**4** (△).

The exciplex fluorescence maxima are at lower energy for α-MS–TEA vs β-MS–TEA and for the α- vs β-(aminoalkyl)styrenes (Tables 1 and 2), in accord with the lower reduction potential of α- vs β-MS.[17] The fluorescence maxima for both the inter- and intramolecular exciplexes display large solvent shifts. A Lippert–Mataga[20] plot of exciplex energy vs solvent polarity (eq 8)for the three α-(aminoalkyl)styrene intramolecular exciplexes and the α-MS–TEA intermolecular exciplex is shown in Figure 4. In hexane solution, the fluorescence maxima of α- and β-**2** are at higher energies than those for their longer chain homologs, while the maxima for the intermolecular exciplexes are at lower energies. These differences are less pronounced in more polar solvents. The slopes of the Lippert–Mataga plots (Figure 4) appear to increase in solvents more polar than diethyl ether, indicative of the formation of a more polar exciplex in polar vs nonpolar solvents. Similar Lippert–Mataga plots have been observed for semiflexible (aminoalkyl)arene exciplexes by Verhoeven and co-workers[21] and attributed to a change in exciplex conformation from folded or compact in nonpolar solvents to extended in polar solvents.

$$f' = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/2(2n^2 + 1) \qquad (8)$$

The exciplex decay times (Tables 1 and 2) of both the inter- and intramolecular exciplexes are longer in moderately polar vs alkane solvents or acetonitrile. This increase is much larger in the case of α- and β-**2** than in their longer chain homologs or the intermolecular exciplexes. Fluorescence rate constants ($k_f = \Phi_f\tau^{-1}$) for the α-(aminoalkyl)styrenes, calculated from the exciplex fluorescence quantum yields and decay times (Table 1 and 2), are reported in Table 5. The values of k_f are not strongly dependent upon chain length but decrease with increasing solvent polarity. As discussed by Birks,[22a] the fluorescence rate constant can be expressed as the sum of the Einstein *A* coefficients summed over the entire fluorescence spectrum (eq 9)

$$k_F = A_{u0\to l} = \sum_m A_{u0\to l^m} \qquad (9)$$

where *u* and *l* refer to the upper and lower excited states and the summation is over the vibronic levels *m* of *l*. Equation 9 can be expressed in terms of the mean value of the electronic transition moment, $\overline{M_{ul}}$, and the reciprocal of the mean value of ν^{-3} over

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(17) Reduction potentials for α- and β-MS were measured in acetonitrile solution at a glassy-carbon electrode using ferrocene as an external reference. The values reported are obtained from the observed difference in oxidation potentials and the previously reported value for β-MS vs SCE.[18]

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Table 5. Calculated Values for the Rate Constants for Exciplex Fluorescence, Intersystem Crossing, Nonradiative Decay, and Proton Transfer[a]

exciplex	solvent	$10^{-7}k_f$, s^{-1}	$10^{-7}k_f/\nu^3$, s^{-1}	$10^{-7}k_{isc}$, s^{-1}	$10^{-8}k_d$, s^{-1}	$10^{-8}k_H$, s^{-1}
α-MS–TEA	hexane					0.12
	diethyl ether					0.01
α-**2**	hexane	2.4	1.2		16	4.1
	diethyl ether	1.6	1.2		5.8	0.45
	tetrahydrofuran	0.55	0.49		2.5	0.05
	acetonitrile	0.58	0.67		3.8	<0.01
α-**3**	hexane	2.2	1.22		1.5	<0.01
	diethyl ether	0.46	0.34		0.46	<0.01
	tetrahydrofuran	0.35	0.30		0.51	<0.01
	acetonitrile	0.28	0.35		3.0	<0.01
α-**4**	hexane	1.3	0.72		5.9	1.7
	diethyl ether	1.4	1.4		1.6	0.11
	tetrahydrofuran	0.35	0.30		1.1	<0.01
	acetonitrile	0.15	0.18		7.6	<0.01
β-**2**	hexane			4.4	3.8	0.32
	diethyl ether			1.4	1.1	0.01
	tetrahydrofuran			3.2	0.9	<0.01
	acetonitrile			7.6	1.9	<0.01
β-**3**	hexane			4.6	6.2	<0.01

[a] Rate constants calculated from exciplex decay times and quantum yields (Tables 1 and 2).

the fluorescence spectrum, $\langle \nu_F^{-3} \rangle_{Av}^{-1}$ (eq 10)

$$k_F = \frac{64\pi^4 n^3}{3hc^3}|\overline{M_{ul}}|^2 \langle \nu_F^{-3} \rangle_{Av}^{-1} \tag{10}$$

where n is the solvent refractive index. Approximating $\langle \nu_F^{-3} \rangle_{Av}^{-1}$ by $(\nu_{max})^{-3}$ leads to eq 11, relating the mean transition

$$\frac{k_F}{(\nu_{max})^3} = \frac{64\pi^4 n^3}{3hc^3}|\overline{M_{ul}}|^2 \tag{11}$$

moment to the rate constant and emission maximum for exciplex fluorescence. Calculated values of k_F/ν^3 for the exciplexes of α-**2**, α-**3**, and α-**4** are reported in Table 5. While these calculations are subject to accumulated errors, the values for hexane solution are consistently larger than those for tetrahydrofuran or acetonitrile solution. Because $\overline{M_{ul}}$ is related to the electronic coupling matrix between the ground and excited states, it is expected to be particularly sensitive to changes in exciplex geometry and coupling between the locally excited and charge-transfer states. However, since in all cases the charge-transfer state lies well below the locally excited state, variations in k_F/ν^3 predominantly reflect changes in exciplex geometry.[22] Thus the decrease in k_F/ν^3 in moderately polar solvents provides further evidence for a change in exciplex conformation.

An indirect method for estimating the exciplex intersystem crossing rate constant for the β-(aminoalkyl)styrenes is provided by the observation of styrene *E*,*Z*-photoisomerization. Since intramolecular quenching of singlet styrene is essentially quantitative for α-**1**–α-**3**, isomerization must occur via the singlet exciplex rather than unquenched styrene. Singlet stilbene–amine[12c] and β-(aminoalkyl)styrene[2a] exciplexes are known to undergo intersystem crossing to yield locally excited stilbene or styrene triplet states which undergo barrierless *E*,*Z* isomerization. Rate constants for exciplex intersystem crossing calculated from the exciplex decay times and isomerization quantum yields ($k_{isc} = 2\Phi_i\tau^{-1}$) are reported in Table 5. The values of k_{isc} for β-**2** and β-**3** in hexane solution are similar to the value for singlet β-methylstyrene (4.8×10^7 s^{-1})[23] and are not strongly solvent dependent. A lower bound for the value of $k_{isc} > 7 \times 10^9$ s^{-1} can be calculated for β-**1** from the observed value of $\Phi_i = 0.35$ and the assumption of a decay time < 0.1 ns for the nonfluorescent exciplex. Much more rapid intersystem crossing for tertiary (aminomethyl)- vs (aminoethyl)arenes has previously been reported by Okada et al.[3h] and attributed to differences in exciplex conformation. It is interesting to note that ((*N*,*N*-dimethylamino)methyl)arenes in general display very weak monomer and exciplex emission.[7,8] Intersystem crossing quantum yields and rate constants for several other (aminoethyl)- and (aminopropyl)arene exciplexes are reported to display only minor variation with chain length or solvent polarity.[8d,9i]

Rate constants for exciplex nonradiative decay can be estimated from the exciplex decay times and the quantum yields for other decay pathways ($k_d = [1 - (\Phi_i + \Phi_f + \Phi_{isc} + \Phi_{add})\tau^{-1}]$). The values reported in Table 5 display both chain length and solvent dependence. Values of k_d for singlet exciplexes generally increase with increasing solvent polarity, due to a decrease in the energy gap for return electron transfer.[3l,9i] Thus the decrease in k_d from hexane to ether solvents is unusual. If the biradical intermediates formed upon exciplex proton transfer (*vide infra*) partition between product and starting material, proton transfer may contribute to the estimated values of k_d in nonpolar solvents. This possibility is consistent with the observation that the magnitudes of k_H and k_d are roughly proportional in nonpolar solvents (α-**2** > α-**4** > α-**3**) and also with recent reports by Mataga and coworkers[24a–c] that hydrogen-bonding interactions in exciplexes can promote nonradiative decay. In the case of the α-(aminoalkyl)styrenes, values of k_{isc} have not been determined and may contribute to the estimated values of k_d. However, this contribution will be relatively minor if the values of k_{isc} for the α-(aminoalkyl)styrenes are similar to those for β-**2** and β-**3**.

Photochemical Behavior. Singlet exciplexes have been proposed as intermediates in the intermolecular addition reactions of singlet styrenes[2] and stilbenes[11,12] with amines; however, no direct evidence for this proposal has been reported. A singlet-state mechanism is supported by the observation that triplet-sensitized irradiation results in isomerization of *E*-β-**2** but not the formation of adduct β-**2a**. Recent picosecond spectroscopic investigations by Mataga and co-workers[24d–g] have led to the proposal that intermolecular hydrogen transfer from amines to triplet benzophenone occurs via a sequential electron-transfer, proton-transfer mechanism in the case of tertiary amines including N,N-dimethylaniline but that electron transfer and hydrogen transfer are competing processes in the encounter complex of triplet benzophenone with diphenylamine. In the case of linked benzophenone–diphenylamine systems, both direct hydrogen abstraction and sequential electron-transfer, proton-transfer pathways are proposed to be operative.

The use of exciplex quenching to establish the role of singlet exciplex intermediates in photochemical reactions was first employed by Caldwell et al.[25] in their studies of arene–olefin (2 + 2) cycloaddition reactions. Appropriate quenchers which did not quench the singlet arene were found to quench both exciplex fluorescence and product formation with similar rate constants. Aoyama et al.[13] employed biacetyl as a quencher of exciplex emission and the photoreaction (consumption of starting material) of α-**2** and observed unequal extents of quenching. On this basis, they concluded that formation of the fluorescent exciplex and the 1,5-biradical intermediate (eq 3) are competing processes in a singlet encounter complex rather than sequential processes. While biacetyl has previously been used as an exciplex quencher by McCullough et al.[26] in their investigations of intramolecular arene–olefin (2 + 2) photoaddition reactions, it's use as an exciplex quencher of styrene–amine exciplexes is problematic, since it is

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a competitive absorber at wavelengths absorbed by styrene and emitted by singlet styrene and styrene–amine exciplexes.

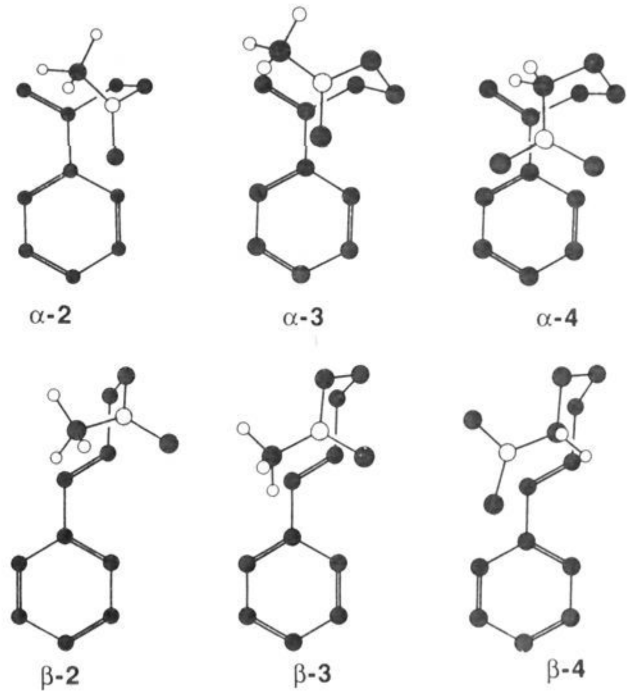
We have previously reported the use of primary amines as quenchers of intermolecular stilbene–tertiary amine exciplexes.[27] Primary amines do not absorb above 280 nm, are inefficient quenchers of singlet stilbene, and are efficient quenchers of stilbene–amine exciplex fluorescence. The mechanism proposed for exciplex quenching is nucleophilic attack of the primary amine on the electron-deficient tertiary amine of the stilbene–amine exciplex followed by nonradiative decay of the resulting triplex. We have investigated the use of propylamine ($PrNH_2$) as a quencher of singlet styrenes and styrene–amine exciplex fluorescence and product formation (Table 4). $PrNH_2$ is a moderately efficient quencher of singlet α- and β-MS. However, the short decay times of the residual styrene fluorescence from the (aminoalkyl)styrenes (Table 1) and the very efficient quenching of exciplex fluorescence by $PrNH_2$, particularly in the case of α-**2** and β-**2** in hexane solution, are consistent with selective exciplex quenching. Thus the observation of similar slopes for Stern–Volmer plots for exciplex fluorescence intensity quenching and product formation quenching by added $PrNH_2$ (Figure 2) supports the role of the singlet exciplex as an intermediate in the photoaddition process.

Rate constants for exciplex quenching, k_{qf}, in hexane solution are similar for α-**3**, α-**4**, and α-MS–TEA (Table 4). The much larger value of k_{qf} for α-**2** vs α-**3** or α-**4** (and for β-**2** vs β-**3**), like the higher energy of its fluorescence maximum, may reflect a greater degree of exciplex charge separation in the (aminoethyl)-styrenes vs their longer chain homologs. The larger values of k_{qf} for the α- vs β-(aminoalkyl)styrenes may also reflect the greater degree of exciplex charge separation in the exciplexes of the stronger acceptor. We[27] and others[28] have observed that rate constants for quenching of intermolecular exciplexes increase as the free energy for exciplex formation (eq 7) is increased either by changing the redox properties of the donor or acceptor or by increasing the solvent polarity. Rate constants for (aminoalkyl)-styrene exciplex quenching decrease with increasing solvent polarity. This unusual trend may reflect the change in intramolecular exciplex structure with solvent polarity indicated by the fluorescence rate data (Table 5).

With this support for an exciplex mechanism (sequential electron-transfer, proton-transfer) for styrene–amine intramolecular photoaddition in hand, the selectivity of product formation can be related to the regioselectivity of exciplex proton transfer and the efficiency of product formation can be related to the exciplex decay time and proton-transfer rate constant. The intermolecular exciplexes of both α- and β-MS undergo regioselective proton transfer to styrene C_β (eqs 1 and 2). Selective formation of a benzyl vs secondary alkyl radical would be expected both on the basis of product stability and the larger charge density at C_β vs C_α in the styrene anion radical.[29] The intramolecular α-**2** and β-**2** exciplexes undergo regioselective 1,6-proton transfer from *N*-methyl to styrene C_β and C_α, respectively. The resulting singlet 1,5-biradical intermediates cyclize to yield the *N*-methylpyrrolidines α-**2a** and β-**2a** (eqs 3 and 5). The α-**4** exciplex undergoes 1,6-proton transfer from *N*-methylene to styrene C_β, yielding a 1,5-biradical which cyclizes to yield a mixture of cyclopentanes α-**4a** and α-**4b** (eq 4), while the β-**4** exciplex undergoes 1,5-proton transfer from *N*-methylene to styrene C_β, yielding a 1,6-biradical which cyclizes to yield a mixture of cyclohexanes β-**4a** and β-**4b** (eq 6).

The failure of the (aminopropyl)styrenes to form intramolecular adducts is every bit as intriguing as the remarkable proton-transfer regioselectivity displayed by the (aminoethyl)- and (aminobutyl)-styrenes. The observation of the formation of longer-lived fluorescent exciplexes in hexane solution from α-**3** and β-**3** than from their ethyl or butyl analogs indicates that the absence of adduct formation is a consequence of inefficient proton transfer and not inefficient exciplex formation or rapid exciplex decay. The exciplexes of both α-**3** and β-**3** have available several intramolecular proton-transfer processes, including 1,5-proton transfer from *N*-methylene to styrene C_β in α-**3** and 1,6-proton transfer from *N*-methyl to styrene C_β in β-**3**. These processes should be comparable to those of the (aminoethyl)- and (aminobutyl)styrenes in terms of the energetics of bond making and bond breaking. The failure of α-**1** to form intramolecular adducts may be attributed to either its exceptionally short exciplex decay time or to an unfavorable trajectory for intramolecular proton transfer.

Chart 2



De Schryver and Van der Auweraer[9] have proposed that ((*N*,*N*-dimethylamino)ethyl)arene exciplexes adopt a conformation in nonpolar solvents in which the ethane C–C bond is nearly eclipsed so as to position the nitrogen above the arene plane near the ipso carbon. Analogous conformations for the exciplexes of α-**2** and β-**2** would place an *N*-methyl hydrogen above the styrene C_β in α-**2** and styrene C_α in β-**2** (Chart 2).[30] Least motion pathways for 1,6-proton transfer lead to the 1,5-biradical intermediates shown in eqs 3 and 5. The singlet exciplexes of ((*N*,*N*-dimethylamino)propyl)arenes are proposed to adopt a folded g^+g^- conformation in which nitrogen lies beyond the ipso carbon toward the center of the aromatic ring.[9] Analogous conformations for α-**3** and β-**3** would place the *N*-methyl hydrogens beyond the styrene C_β in α-**3** and styrene C_α in β-**3** and the *N*-methylene hydrogens oriented away from the styrene double bond. The absence of a least motion pathway for proton transfer in these exciplexes may account for their lack of reactivity and longer exciplex decay times. Finally, the ((*N*,*N*-dimethylamino)butyl)-arene exciplexes are proposed to adopt a folded $g^+g^-g^-$ conformation in which nitrogen lies near the center of the aromatic ring.[9] Analogous conformations for α-**4** and β-**4** place an *N*-methylene hydrogen above the styrene C_β in both α-**4** and β-**4**. Least motion pathways for 1,6-proton transfer in α-**4** and 1,5-proton transfer in β-**4** lead to the 1,5- and 1,6-biradical intermediates shown in eqs 4 and 6.

Rate constants for inter- and intramolecular proton transfer can be calculated from the exciplex decay time and quantum yield for product formation ($k_H = \Phi_{add}\tau_{ex}^{-1}$, Table 5), assuming the biradical intermediates cyclize and do not disproportionate

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[29] AM1 Hückel semiempirical calculations on the β-MS anion radical provide electron spin densities of 0.24 at C_β and 0.04 at C_α.

[30] The structures shown in Chart 2 were obtained using Chem 3D Plus assuming standard ground-state bond lengths and bond angles except for nitrogen, which is assumed to be planar rather than pyramidal. Torsional angles have been adjusted to attain folded conformations whose energies have not been minimized.

to re-form starting materials.[31] Values of k_H are dependent upon the chain length (α-**2** > α-**4** > α-**3**), point of attachment (α-**2** vs β-**2**), and solvent polarity. The larger value of k_H for 1,6-proton transfer from *N*-methyl to styrene C_β in α-**2** vs 1,6-proton transfer from *N*-methylene to styrene C_β in α-**4** may reflect the greater kinetic acidity of methyl vs methylene protons. We previously observed a 5:1 ratio of methyl/methylene adducts in the intermolecular addition of singlet *trans*-stilbene with *N,N*-dimethylbutylamine, somewhat larger than the 3:1 ratio expected on a purely statistical basis.[12c] The larger value of k_H for 1,6-proton transfer from *N*-methyl to C_β in α-**2** vs C_α in β-**2** may reflect the greater basicity of C_β vs C_α.[29]

Activation parameters for the exciplex proton transfer process in α-**4** can be obtained from the temperature dependence of the exciplex decay time and quantum yield data for adduct formation ($\Phi_a + \Phi_b$) in hexane solution (Table 3). The Arrhenius plot shown in Figure 3 provides values of E_{act} = 3.5 kcal/mol and $\Delta S^\dagger$ = −14 eu. These values are similar to those reported by Caldwell and co-workers[32] for intermolecular exciplex (2 + 2) cycloaddition. The activation parameters for exciplex proton transfer can also be compared to those for the γ-hydrogen abstraction of triplet valerophenone (E_{act} = 3.3 kcal/mol, $\Delta S^\dagger$ = −24 eu).[33] While the activation energies for the two processes are similar, the entropy of activation for exciplex proton transfer is less negative than that for γ-hydrogen abstraction. Presumably, formation of the exciplex intermediate results in a less negative entropy of activation for the subsequent proton-transfer process. The activation energy for exciplex proton transfer in α-**4** is slightly larger than that for exciplex formation while the entropy of activation is more negative. In the context of these activation parameters, the failure of the exciplexes of α-**3** or β-**3** to undergo measurable proton transfer might reflect either a slightly higher activation energy (>5 kcal/mol) or a less favorable entropy of activation. The smaller proton-transfer rate constant for α-MS–TEA vs α-**4** could reflect a more negative entropy of activation for inter- vs intramolecular proton transfer.

The ratio of adducts α-**4a**/α-**4b** decreases slightly with decreasing temperature but is the same in hexane and diethyl ether solution. We assume that both adducts are formed from a common singlet 1,5-biradical intermediate with slightly different activation parameters. However, it is possible that the two products are formed from two different folded exciplex conformations. Additional studies are needed to establish the role of biradical intermediates in both the formation of products and the nonradiative decay of these exciplexes.

Rate constants for exciplex proton transfer decrease with increasing solvent polarity (Figure 5) and are too slow to compete with nonradiative decay in solvents more polar than diethyl ether. Both stabilization of the compact exciplex by moderately polar solvents and a change in exciplex conformation from compact to extended in more highly polar solvents may be responsible for these results. On the basis of our analysis of exciplex fluorescence energies and rate constants (Figure 4 and Table 5), a change in exciplex conformation was proposed to occur in solvents more polar than diethyl ether. Diethyl ether would be expected to stabilize the compact exciplex more than the biradical intermediate, resulting in an increased activation energy for proton transfer even in the absence of a change in exciplex conformation. More polar solvents would effect a change in exciplex conformation from compact to extended, resulting in a less favorable trajectory for proton transfer and an increase in the solvent reorganization energy for proton transfer.

Related Systems. In comparison to the behavior of the tertiary (aminoalkyl)styrenes, the photoaddition reactions of the analogous secondary (aminoalkyl)styrenes display much lower chain-length dependence, regioselectivity, and solvent dependence.[2a,e] Secondary α- and β-((*N*-methylamino)alkyl)styrenes with ethyl, propyl, and butyl polymethylene chains all undergo intramolecular addition with comparable efficiencies. In the case of the β-((*N*-methylamino)alkyl)styrenes, mixtures of regioisomers resulting from N–H transfer to both styrene C_α and C_β are formed.[2a] For example, irradiation of β-((*N*-methylamino)propyl)styrene yields mixtures of pyrrolidine and piperidine adducts with comparable efficiencies in polar and nonpolar solvents. We have proposed that the two regioisomers are formed via exciplex proton transfer to styrene C_α or C_β from folded exciplex conformations in which the N–H is either equatorial or axial (Scheme 1).

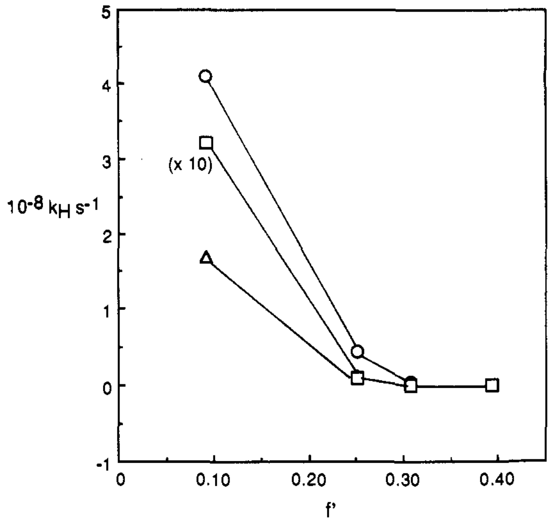
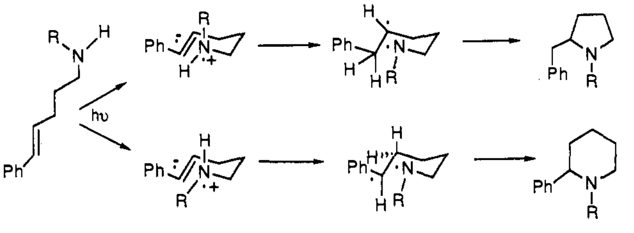


Figure 5. Solvent dependence of the exciplex proton-trasfer rate constant for α-**2** (○), α-**4** (△), and β-**2** (□).

Scheme 1



The exclusive formation of N–H vs C–H adducts for the secondary (aminoalkyl)styrenes and the absence of exciplex fluorescence indicate that the rate constants for N–H proton transfer are much larger than those for C–H proton transfer. An estimate of the activation energy for N–H proton transfer can be obtained from our previously published data for the temperature dependence of the quantum yield for intramolecular addition of β-((*N*-methylamino)propyl)styrene (233–303 K)[2a] and the knowledge that the singlet decay time of β-MS is independent of temperature over this temperature range.[23] The resulting activation parameters are E_{act} = 2.2 kcal/mol and $\Delta S^\dagger$ = −21 eu. Since either exciplex formation or proton transfer could be the rate-determining step for product formation, these values represent an upper limit for the activation energy and a lower limit for the activation entropy for N–H proton transfer. The lower activation energy for N–H proton transfer vs C–H proton transfer in α-**4** is consistent with the failure to observe either C–H transfer or exciplex fluorescence from the secondary (aminoalkyl)styrenes. The quantum yield for adduct formation for the secondary (aminoalkyl)styrenes is only slightly lower in acetonitrile vs hexane solution. This suggests the absence of a solvent-induced change in exciplex conformation or a significant solvent-induced barrier for the secondary (aminoalkyl)styrenes. It seems likely that intramolecular N–H–styrene hydrogen bonding may prevent a change in exciplex conformation from folded to extended in polar

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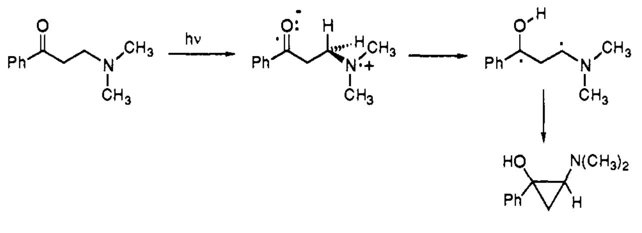
(31) Biradical disproportionation would result in lower quantum yields for product formation than for exciplex proton transfer and, thus, higher rate constants for proton transfer than those reported in Table 5.

(32) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45.

(33) Lewis, F. D.; Johnson, R. W.; Kory, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 6100.

Scheme 2



solvents. Okada et al.[24a] have observed that hydrogen bonding in the intermolecular pyrene–*N*-ethylaniline exciplex can result in rapid nonradiative decay and intersystem crossing, as well as N–H proton transfer.

A further indication of the often complex relationship between exciplex conformation and the regioselectivity of product formation is provided by a comparison of the photochemical behavior of α-((*N*,*N*-dimethylamino)alkyl)styrenes and that of the analogous phenyl ketones.[34,35] DeVoe et al.[34b] have observed that β-(*N*,*N*-dimethylamino)propiophenone undergoes regioselective *N*-methylene vs *N*-methyl proton transfer via a triplet exciplex intermediate (Scheme 2) with a quantum yield which is only moderately sensitive to solvent polarity (0.59 in benzene and 0.23 in acetonitrile solution). Proton transfer is proposed to occur from the *N*-methylene to the oxygen nonbonding lone pair via an extended conformation of the triplet exciplex, rather than the folded conformation proposed for α-**2** (Chart 2). The much larger driving force for electron transfer from the triplet ketone vs the singlet styrene may be responsible for the difference in exciplex conformation. The triplet exciplexes formed via photoinduced electron transfer in the homologous tertiary aminobutyrophenone and valerophenone are chemically unreactive.[35] Presumably the extended conformations of these exciplexes do not provide a least motion pathway for *N*-methylene proton transfer.

While the focus of this investigation has been on the mechanistic aspects of intramolecular exciplex proton transfer, the synthetic aspects of these reactions should not be overlooked. The preparative yields of the intramolecular reactions (eqs 3–6) are substantially higher than those for the intermolecular reactions (eqs 1 and 2). This difference results mainly from the competition of cage escape with radical pair combination in the intermolecular reaction. Thus the connecting polymethylene chain in the (aminoalkyl)styrenes serves both to control the regioselectivity of intramolecular proton transfer and to prevent separation of the resulting radical centers.

Experimental Section

General Methods. NMR spectra were recorded in $CDCl_3$ solution using a Gemini 300 or Varian XLA 400 spectrometer with TMS as an internal standard. High-resolution mass spectra were determined with a Hewlett-Packard 5985 GC/VG70-250SE MS system using an ionizing voltage of 70 V. IR spectra were recorded using a Mattson FT-IR. Ultraviolet absorption spectra were obtained using a Hewlett-Packard 8452 diode-array spectrophotometer. Steady-state fluorescence spectra were obtained using a Perkin-Elmer MPF-44A or a PTI-LS1 spectrometer. Fluorescence decay times were measured with two different single-photon counting apparatuses with different excitation sources, one with a gated arc lamp (PTI-LS1, time resolution ca. 0.2 ns) and the other with a mode-locked dye laser (time resolution ca. 50 ps). The method of analysis of the fluorescence decay curves has previously been described.[2a,14]

Preparative-scale irradiations were carried out under nitrogen in Pyrex test tubes using a Rayonet reactor fitted with RPR 3000 lamps or in quartz test tubes using RPR 2537 lamps. Hexane solutions (0.01 M styrylamine) were irradiated to >95% conversion of starting material while monitoring the progress of the reaction by GC. Product yields are based on GC integration. Products were isolated by either preparative thick-layer chromatography or column chromatography followed by bulb-to-bulb distillation. Quantum yield measurements were carried out using an optical bench (200-W xenon–mercury high-pressure lamp and 0.25-m high-intensity monochromator at 281 nm) with conversions limited to 10%. Light intensities were determined using *trans*-stilbene actinometry.[36] Irradiated solutions were analyzed by gas chromatography (Hewlett-Packard 5890 equipped with a flame ionization detector) with a 10 × 0.53 mm^2 fused silica column coated with polymethyldisiloxane.

Materials. α-Methylstyrene (Aldrich), β-methylstyrene (Aldrich), triethylamine (Aldrich), and propylamine (Aldrich) were distilled prior to use. Hexane, ethyl acetate, tetrahydrofuran, acetonitrile (Aldrich, spectrograde), and diethyl ether (Fisher) were used as received. Dibutyl ether (Aldrich) was passed through a column of alumina and distilled prior to use. The β-(aminoalkyl)styrenes[2a] and α-((*N*,*N*-dimethylamino)ethyl)styrene α-**2**[13] were prepared using published procedures. The other α-(aminoalkyl)styrenes were prepared from the corresponding secondary amines, whose syntheses have been reported,[2e] by means of the Eschweiler–Clarke procedure.[37]

α-((*N*,*N*-Dimethylamino)propyl)styrene (α-3). ^{1}H NMR δ 7.32 (m, 5H); 5.27 (s, 1H); 5.08 (s, 1H); 2.52 (t, 2H, J = 7.5 Hz); 2.29 (t, 2H, J = 7.5 Hz); 2.20 (s, 6H); 1.63 (quintet, 2H, J = 7.5 Hz). IR (film) 2943, 2765, 1634, 1455 cm^{-1}. MS (*m*/*e* 189 (M$^+$, 46), 70 (100). HRMS 189.1517 (calcd) and 189.1512 (obsd).

α-((*N*,*N*-Dimethylamino)butyl)styrene (α-4). ^{1}H NMR δ 7.32 (m, 5H); 5.27 (s, 1H); 5.06 (s, 1H); 2.52 (t, 2H); 2.22 (t, 2H); 2.19 (s, 6H); 1.48 (m, 4H). IR (film) 2924, 2765, 1634, 1464 cm^{-1}. MS (*m*/*e*) 203 (M$^+$, 62), 84 (100). HRMS 203.1674 (calcd) and 203.1685 (obsd).

***trans*-1-(*N*,*N*-Dimethylamino)-2-methyl-2-phenylcyclopentane (α-4a).** GC analysis of the irradiated solution of α-**4** showed the formation of two products with similar retention times in a 4:1 ratio, independent of the extent of conversion. Both products have similar MS fragmentation patterns and are inseparable by column chromatography. NMR spectra for the major isomer, α-**4a**, were assigned from data obtained for the isomer mixture. ^{1}H NMR δ 7.46 (d, 2H); 7.30 (t, 2H); 7.16 (t, 1H); 2.78 (t, 1H); 2.14 (m, 1H); 1.97 (s, 6H); 1.76 (m, 4H); 1.40 (s, 3H). ^{13}C NMR 150.0 (s), 128.3 (d), 128.2 (d), 126.0 (d), 125.9 (d), 77.2 (s), 48.3 (t), 46.6 (q), 46.5 (q), 46.0 (d), 31.2 (t), 21.2 (t), 19.25 (q). MS 203 (M$^+$, 8%), 91 (5), 85 (17), 84 (53), 58 (15). HRMS 203.1673 (calcd) and 203.1680 (obsd). Partial ^{1}H NMR data for the minor isomer, which is tentatively assigned the structure α-**4b**, was obtained from the spectrum of the mixture. δ 2.64 (t, 1H, *N*-methine); 1.94 (s, 6H, N-methyl).

***N*-Methyl-3-benzylpyrrolidine (α-2a).** ^{1}H NMR δ 7.2 (m, 5H); 2.46–2.75 (m, 6H); 2.33 (s, 3H); 2.22 (m, 1H); 2.0 (m, 1H); 1.52 (m, 1H). ^{13}C NMR 141.3 (s), 128.7 (d), 128.3 (d), 125.8 (d), 62.3 (t), 56.2 (t), 42.4 (q), 41.8 (t), 39.5 (d), 31.3 (t). MS 175 (M$^+$, 12%), 174 (64), 97 (42), 83 (100), 57 (76). HRMS 175.1361 (calcd) and 175.1385 (obsd).

***cis*-1-(*N*,*N*-Dimethylamino)-2-phenylcyclohexane (β-4a).** GC analysis of the irradiated solution of β-**4** showed the formation of two products with similar retention times in an 8:1 ratio, independent of the extent of conversion. Both products have similar MS fragmentation patterns and are inseparable by column chromatography. NMR spectra for the major isomer, β-**4a**, were assigned from data obtained for the isomer mixture. ^{1}H NMR δ 7.25 (m, 5H); 2.92 (d, 1H, J = 12 Hz); 2.32 (s, 6H); 2.20 (m, 2H); 1.82 (m, 3H); 1.6 (m, 4H). MS 203 (M$^+$, 35%), 160 (10), 111 (4), 84 (100). HRMS 203.1673 (calcd) and 203.1669 (obsd).

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