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Intramolecular Electron Transfer in Donor−Spacer−Acceptor Systems with Alkylamide Spacers

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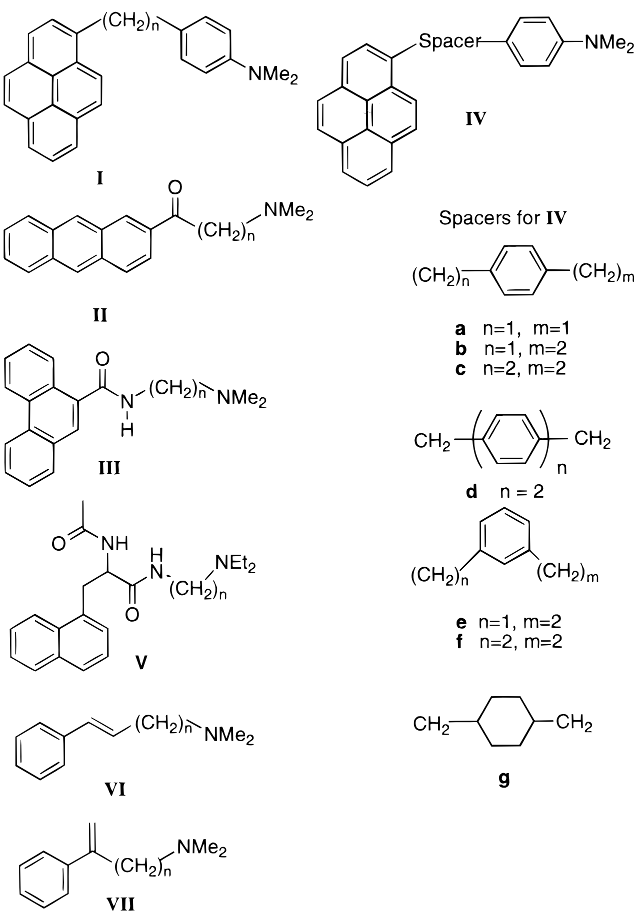
Intramolecular electron transfer and exciplex formation have been investigated for a family of styrene−spacer−amine molecules in which the spacer consists of a rigid amide group in the middle of a flexible alkane chain. The amide is connected to the styrene by either one or two methylene units and to a trialkylamine by two to six methylene units. The dependence of electron-transfer kinetics and exciplex formation have been investigated as a function of the length of the spacer, the orientation of the amide, and the amine oxidation potential. Intramolecular quenching of the styrene fluorescence intensity and lifetime is observed for all of the styrene−spacer−amine molecules. Quenching of styrene fluorescence is accompanied by the appearance of intramolecular styrene−amine exciplex fluorescence in nonpolar solvents. The low energy of the exciplex fluorescence emission maximum in nonpolar solvents is attributed to internal solvation by the polar amide group. A maximum in the quantum yield for exciplex fluorescence and minimum in the styrene lifetime is observed for spacers with a total length of seven atoms, including the amide group. This unusual chain length dependence is attributed to the conformational requirements of the amide group.

The formation of intramolecular exciplexes and the dynamics of photoinduced electron transfer in donor−spacer−acceptor systems is a topic of continuing interest.[1] Rigid spacers such as polycyclic hydrocarbons[1c] and α-helical polypeptides[1d] provide well-defined geometries, facilitating investigation of the distance dependence of electron-transfer processes. For systems with flexible polymethylene spacers, both intramolecular exciplex formation in nonpolar solvents and the kinetics of electron transfer in polar solvents are dependent upon the chain length.[2−6] Numerous donor−acceptor systems with short linear chain polymethylene spacers (four or fewer saturated carbons) have been investigated. In general, these systems display a maximum in the intramolecular exciplex fluorescence intensity for chain lengths of three carbons, similar to that observed for intramolecular arene−arene excimer formation (Hirayama's rule).[7] There have been only a few reports of exciplex fluorescence for systems with spacers containing more than five saturated carbons[2a−c] and no systematic studies of the effect of longer chains on exciplex formation and stability.

Rate constants for exciplex formation decrease markedly with increasing chain length for spacers consisting of chains of one to four atoms, in accord with an increasing entropic requirement for chain folding.[2−5] Staerk and co-workers[4] have investigated the chain length dependence of the pyrene singlet lifetime in acetonitrile solution for pyrene−dimethylaniline systems (Chart 1, system **I**) with 5−16-carbon chain linkers. They observe only a modest increase in the pyrene singlet lifetime from 1.1 to 2.3 ns over this range of chain length. The observed chain length dependence was found to correlate with the probability distributions of donor−acceptor separations, as calculated using the Monte Carlo method. An increase in chain length results in only a small decrease in the probability that the donor and acceptor are within 10 Å and a small increase in the mean donor−acceptor distance. These results are consistent with a through-space electron-transfer mechanism for spacers comprised of five-carbon or longer chains.

CHART 1: Arene−Spacer−Amine Systems



The use of spacers containing both flexible and rigid elements has also been investigated. A rigid ester or amide group at one end of the spacer in the (aminoalkyl)anthracenecarboxylates[8]

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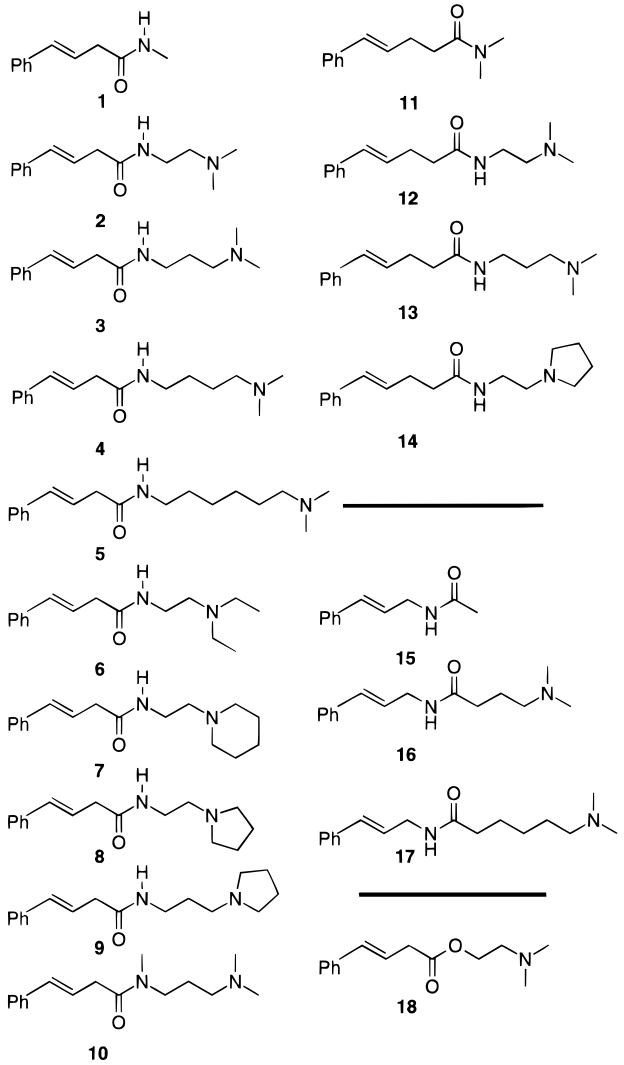
CHART 2: (Aminoalkyl)styrylamides



(Chart 1, system **II**) or (aminoalkyl)phenanthrenecarboxamides[9] (Chart 1, system **III**) prevents arene exciplex formation with short polymethylene chains; however, exciplex fluorescence has been observed for **II** with longer alkyl chains ($n = 9$ or 11). The use of spacers containing flexible methylene groups interrupted by a rigid benzene or cyclohexane ring (Chart 1, system **IV**) has been investigated by Michel-Beyerle[10] and co-workers and by Staerk and co-workers.[11] For the para-substituted molecules **IVa**−**d** the electron-transfer rate constant decreases with spacer length, indicative of a predominantly through-bond interaction. Exciplex fluorescence is observed for the meta-substituted **IVe**, and the electron-transfer rate increases with spacer length, indicative of through-space interaction. Sakurai et al.[12] have recently investigated several (aminoalkyl)naphthalenes **V** in which the dipeptide interrupts a polymethylene chain. Variation of the spacer length ($n = 2-4$) has only a modest effect on the rate constant for exciplex formation.

We report here the results of our investigation of electron transfer and exciplex formation in a family of styrene−spacer−amine molecules in which the spacer consists of a rigid amide group in the middle of a flexible polymethylene chain (Chart 2). The amide group facilitates the construction of donor−spacer−acceptor molecules and is commonly encountered both in the form of peptide linkages in proteins and as a spacer or linker in synthetic diads and larger donor−acceptor systems.[1,13] We find that a secondary amide incorporated into a polymethylene spacer with three to seven methylenes facilitates exciplex formation in nonpolar solvents and electron transfer in polar solvents. A maximum in the exciplex fluorescence quantum yield and electron-transfer rate is observed for a total spacer length of seven atoms. This unusual chain length dependence is attributed to both the rigidity and conformational preferences of the amide group and to the ability of the polar amide group to stabilize an adjacent exciplex or radical ion pair. Variation in the amine oxidation potential and amide orientation has only minor effects on the electron-transfer process.

Experimental Section

Materials. All solvents used were spectral grade. Benzene (Aldrich) was refluxed over sodium metal and distilled prior to use. Hexane (Aldrich), anhydrous diethyl ether (Fisher), acetonitrile (Aldrich), methanol (Fisher), chloroform (Fisher), and triethylamine (Fisher) were used without further purification. The synthesis, purification, and spectroscopic characterization of compounds **1**−**18** are provided as Supporting Information.

Methods. ^{1}H NMR spectra were recorded on Varian VXR-300 and Varian Gemini 300 MHz spectrometers in $CDCl_3$ and dimethyl-d_6 sulfoxide solvents with TMS as an internal standard. Infrared spectra of 0.005−0.02 M solutions of amines in dichloromethane or chloroform were recorded in 1 mm path length NaCl cells using a Biorad FTS60 spectrometer. Mass spectra were obtained using a Hewlett-Packard 5985 GC/VG70-250E MS system using an ionizing voltage of 70 eV. UV−visible absorption spectra were measured with a Hewlett-Packard Model 8452A diode array spectrophotometer in 1 cm path length quartz cuvettes. Room-temperature fluorescence emission and excitation spectra were recorded using a SPEX Fluoromax spectrophotometer. Solutions were approximately 10^{-4} M and were purged with nitrogen in a 1 cm path length quartz cuvette fitted with a white rubber septum (Aldrich). Fluorescence quantum yields were determined using *trans*-1-phenylpropene ($\Phi_f = 0.35^{14}$) as a reference standard. Fluorescence decays were measured using a Photon Technology International LS-1 single photon counting apparatus with a gated hydrogen arc lamp using a scatter solution to obtain the lamp decay profile. The decays were analyzed using deconvolution and single or multiple exponential least-squares fitting as described by James et al.[15] The reduced χ^2 values, randomness of residuals, and autocorrelation functions were used to determine the goodness of the fit.

Cyclic voltammetric measurements were carried out with a Cypress Systems 1087 computer-controlled potentiostat. A single-compartment cell was used with a platinum disk working electrode, Ag/AgCl reference electrode, and a silver wire as auxiliary electrode. Measurements were made in acetonitrile, freshly distilled over calcium hydride, with twice recrystallized tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Solutions containing approximately 10^{-3} M analyte (0.1 M electrolyte) were deaerated for several minutes by purging with nitrogen. Peak potentials for irreversible amine oxidation were measured at a scan rate of 110 mV s^{-1} with no correction for junction potentials. Ferrocene was added as an internal reference for the final measurement.

Results

The 4-phenyl-3-butenamide derivatives **1**−**10**, 5-phenyl-4-pentenamide derivatives **11**−**14**, the 3-phenyl-2-propenamine derivatives **15**−**17**, and the 4-phenyl-3-butenoic ester **18** were all prepared by standard procedures, purified by column

TABLE 1: Quantum Yields[a] and Decay Times[b] for Styrene Fluorescence

compd	hexane		acetonitrile	
	Φ_f	τ_s, ns	Φ_f	τ_s, ns
4-Phenyl-3-butenamide Derivatives				
1	0.40	8.9	0.32	9.6
2	0.063	1.9	0.053	0.84
3	0.038	0.55	0.046	0.40
4	0.050	0.62	0.092	<0.2
5	0.14	1.5	0.035	1.3
6	0.061	1.1	0.046	0.50
7	0.023	1.8	0.023	0.51
8	0.036	0.44	0.070	0.38
9	0.011	0.55	0.046	<0.2
10	0.024	0.67, 1.0	0.049	0.45, 0.63
5-Phenyl-4-pentenamide Derivatives				
11	0.40	10.4	0.42	9.0
12	0.044	0.50	0.043	0.81
13	0.038	1.2	0.067	0.24
14	0.31	0.55	0.043	0.58
3-Phenyl-2-propenamine Derivatives				
15	0.10	4.0	0.24	1.1
16	0.07	2.3	0.035	0.9
17	0.035	1.0	0.035	0.9
4-Phenyl-3-butenoate				
18	0.039	0.76	0.042	0.87

[a] Fluorescence quantum yields determined using 1-phenylpropene ($\Phi_f = 0.35^{13}$) as actinometer. [b] All fluorescence decays are single exponential except where noted.

TABLE 2: Intermolecular Quenching of Styrene Fluorescence by Triethylamine and Exciplex Emission Maxima

compd	$k_q\tau$,[a] M^{-1}	10^9k_q,[b] $M^{-1}\ s^{-1}$	λ_{fex},[c] nm
1-phenylpropane	49	4.1	378
1	44	4.9	415
11	54	5.2	413
15	63	15.6	418

[a] Slope of Stern−Volmer plot for quenching of fluorescence intensity by triethylamine in deoxygenated hexane solution. [b] Calculated using the lifetime data from Table 1. [c] Maximum of the exciplex fluorescence band in hexane solution.

TABLE 3: Intramolecular Exciplex Fluorescence Maxima, Quantum Yields, and Decay Times[a]

compd	λ_{ex}, nm	Φ_{fex}	τ_{ex}, ns
2	400[b]	≤0.01	
3	419	0.10	2.6
4	413	0.49	7.4
5	415	0.22	12.5
8	397	0.59	1.7
9	414	0.17	7.2
10	410	0.09	3.9, 15.8
13	406	0.18	9.5
16	422	0.11	5.4
17	415	0.25	23.1

[a] Data for deoxygenated solutions at room temperature except as noted. [b] Data for methylcyclohexane solution at 120 K.

chromatography, and characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectroscopy (see Experimental Section). The tertiary amide **10** has two sets of *N*-methyl and (dimethyamino)alkyl resonances of similar integrated area attributed to the *E* and *Z* isomers which interconvert slowly on the NMR time scale.[9] All of the secondary amides possess a single set of resonances, attributed to the *Z* isomers.

The absorption spectra of the model styrylamides **1**, **11**, and **15** display weak long-wavelength bands at 294 nm and stronger bands at 250 nm, essentially identical with those of 1-phenylpropene (β-methylstyrene).[14] Similar absorption spectra are observed for all of the (aminoalkyl)styrylamides. The absence of enhanced long-wavelength absorption indicates that there is no strong ground-state interaction between the styryl chromophore and amide or amine groups in **1**−**18**.

The model styrylamides **1**, **11**, and **15** have fluorescence spectra similar in appearance to that of 1-phenylpropene with emission maxima ~310 nm. Their fluorescence quantum yields (Φ_f) and decay times (τ_s) are reported in Table 1. Values of Φ_f were determined relative to the reported value for 1-phenylpropene ($\Phi_f = 0.35$).[14] Fluorescence decay profiles were obtained using a single photon counting apparatus. The decays were deconvoluted using a single- or multiple-exponential least-squares analysis. Good fits to a single exponential were obtained for **1**, **11**, and **15**. The decay times for **1** and **11** are similar to those for 1-phenylpropene in hexane and acetonitrile solution (11.8 and 10.9 ns, respectively).[14] The decay times for **15** are shorter than those of 1-phenylpropene, especially in acetonitrile solution.

The fluorescence of the styrylamides for **1**, **11**, and **15** is quenched by added triethylamine. The slopes of linear Stern−Volmer plots ($k_q\tau$) obtained in hexane and acetonitrile solution are reported in Table 2 along with the rate constant for singlet quenching calculated using the measured decay times from Table 1. Intermolecular quenching of styrene-like fluorescence in hexane solution is accompanied by the appearance of broad, long-wavelength fluorescence attributed to the styrene−amine exciplex. The exciplex fluorescence maxima (λ_{fex}) are reported in Table 2.

The (aminoalkyl)styrylamides **2**−**10**, **12**−**14**, **16**, and **17** and ester **18** all have significantly weaker 310 nm fluorescence emission and shorter decay times than the styrylamides **1**, **11**, and **15** (Table 1). The residual styrene fluorescence decay can be fit to a single exponential in all cases, except for the decay of **10** which is best fit by a double exponential. The instrumental time resolution is ~0.2 ns. Decay times close to this value should be viewed as approximate, and shorter-lived decay components would not be resolved.

Most of the (aminoalkyl)styrylamides display a second broad emission band at longer wavelengths attributed to an intramolecular styrene−amine exciplex. Exciplex emission maxima, quantum yields, and decay times in hexane solution are reported in Table 3. Only a weak long-wavelength tail attributed to exciplex fluorescence was observed in the fluorescence spectra of **2**, **6**, **12**, and **14** in hexane solution at room temperature, and no exciplex fluorescence was observed for **7**. Well-resolved exciplex emission was detected from **2** in methylcyclohexane solution at 120 K or in a glass at 77 K. As shown for **4** in Figure 1, the exciplex fluorescence intensity decreases, and the emission maxima shift to longer wavelength as the solvent polarity is increased. In no case is exciplex fluorescence detected in acetonitrile solution. In several cases (**4**, **5**, and **17**) the rise time for exciplex emission could be resolved from the lamp profile and was found to be similar to the decay times for the unquenched 1-phenylpropene emission. In these cases, decay of the 1-phenylpropene fluorescence is truly single exponential. Single-exponential exciplex decay was observed in all cases except for the tertiary amide **10**, which displayed dual-exponential decay.

The half-wave potentials for the irreversible oxidation of triethylamine, *N*,*N*-dimethylethylamine, and the model amine−amides **19**−**21** in tetrahydrofuran solution are reported in Chart 3. Compared to the oxidation potential for Me_2NEt, the value

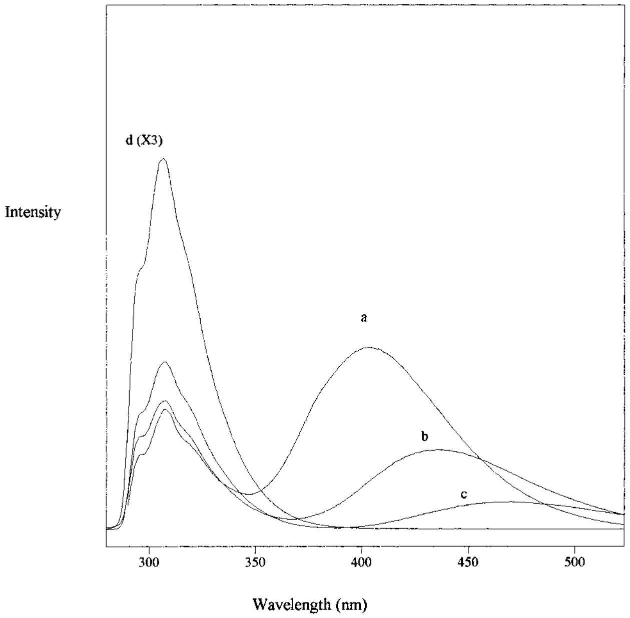
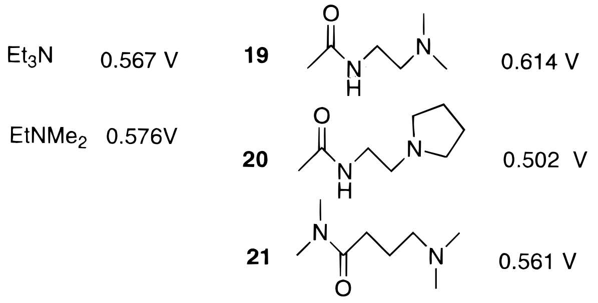


Figure 1. Fluorescence spectra of **4** in (a) hexane, (b) diethyl ether, (c) dichloromethane, and (d) acetonitrile.

CHART 3: Oxidation Potentials of Amines and (Aminoalkyl)amides



for **19** is 38 mV larger, whereas that for **20** is slightly smaller and that for **21** is 74 mV smaller.

Discussion

Previous investigations of intramolecular electron transfer in aminoalkyl systems with short flexible spacers ($n \leq 5$) have established that fluorescent exciplexes with partial charge-transfer character and compact folded structures are formed in nonpolar solvents.[2,5] In polar solvents such as acetonitrile, electron transfer occurs to yield intramolecular radical ion pairs that possess more extended structures and are, in most cases, nonfluorescent. The dynamics of singlet quenching is often complex in nonpolar solvents due to reversible exciplex formation,[16a] whereas electron transfer is normally irreversible in polar solvents. The amide-linked (aminoalkyl)styrenes (Chart 2) display solvent-dependent exciplex fluorescence (Figure 1) similar to that of the (aminoalkyl)styrenes (Chart 1, systems **VI** and **VII**).[5a,b] Thus, we have focused this investigation on the structure dependence of exciplex formation in the nonpolar solvent hexane and the dynamics of electron-transfer quenching in the polar solvent acetonitrile.

The model styrylamides **1** and **11** are homologues of the cinnanamides, which have very short singlet lifetimes and are nonfluorescent.[16b] Both **1** and **11** have fluorescence spectra, quantum yields, and lifetimes (Table 1) similar to that of 1-phenylpropene.[14] Thus, a single methylene serves to effectively isolate the styrene and amide chromophores. Shorter lifetimes and lower quantum yields are observed for the model compound **15**, particularly in the polar solvent acetonitrile. Stronger interaction of the styrene and amide chromophores in **15** vs **1** may result from bonding to the N-terminus rather than the central carbon of the amide chromophore, for which the highest occupied molecular orbital has a node at carbon.[17] Aoyama and co-workers[18] have observed intramolecular addition reactions between styrenes and amides, processes that do not have intermolecular counterparts. They have attributed this to weak intramolecular interactions between the singlet styrene and amide chromophores. Thus, the amide group in the styrene–spacer–amine molecules that we have investigated may influence excited-state behavior directly as well as by influencing the spacer geometry.

The rate constants for bimolecular fluorescence quenching of the model compounds **1** and **11** by Et_3N (Table 2) are slower than the rate constant for diffusion in hexane solution ($\sim 2 \times 10^{10}$ M^{-1} s^{-1}).[19] A similar rate constant was observed for bimolecular quenching of singlet 1-phenylpropene by Et_3N and attributed to reversible exciplex formation.[16a] The larger rate constant observed for the model compound **15** plausibly reflects less reversible exciplex formation. The intermolecular exciplex fluorescence maxima of all three model compounds with Et_3N are at significantly longer wavelength than that of 1-phenylpropene in hexane solution (Table 2). This might result from an inductive electron-withdrawing effect of the amide group which would render the styrylamides better electron acceptors than 1-phenylpropene.[20] However, such an inductive effect would be expected to be larger for **1** than for **11** and to result in an increase the values of k_q as well as the red shift in λ_{ex}, contrary to observation. It seems more likely that the amide serves to stabilize the styrene–amine exciplex by means of internal solvation. A similar effect can be seen in the data of Sakurai et al.[12] for the bimolecular exciplex analogue of **V**. Chandross[21] has reported that low concentrations (<1%) of polar solvents such as propionitrile or hexamethylphosphoramide can effect substantial shifts in the fluorescence of intramolecular naphthalene–amine exciplexes. The value of λ_{ex} for the **1**/Et_3N exciplex in hexane solution is similar to that of the 1-phenylpropene/Et_3N exciplex in diethyl ether,[5b] suggesting that internal solvation by a single amide group results in exciplex stabilization similar to that observed in a moderately polar solvent.

The styrene–spacer–amine molecules under investigation all display styrene-like fluorescence with lower fluorescence yields and shorter lifetimes than the corresponding model compounds (Table 1). In addition, intramolecular exciplex fluorescence is observed at room temperature in hexane solution for most of the (aminoalkyl)styrylamides (Table 3). The exciplex emission maxima for molecules with five-atom spacers (**2**, **6**, and **8**) are at shorter wavelengths than those for molecules with longer spacers. A similar increase in λ_{ex} is observed for (aminoalkyl)-styrenes (Chart 1, systems **VI** and **VII**) with 3- or 4-atom vs 2-atom spacers and has been attributed to better arene–amine orbital overlap with the longer spacer.[5b] The values of λ_{ex} for six-atom or longer spacers (Table 3) are similar to those for the intramolecular exciplexes of the model compounds with Et_3N (Table 2), indicative of good orbital overlap in the intramolecular exciplexes.

The chain-length dependence of the exciplex fluorescence quantum yield for the homologous series **2**–**5** is shown in Figure 2a along with previously reported values for (aminoalkyl)-styrenes (Chart 1, system **VII**) in hexane solution.[5b] The values of Φ_{fex} for **2**–**5** are corrected for incomplete quenching of

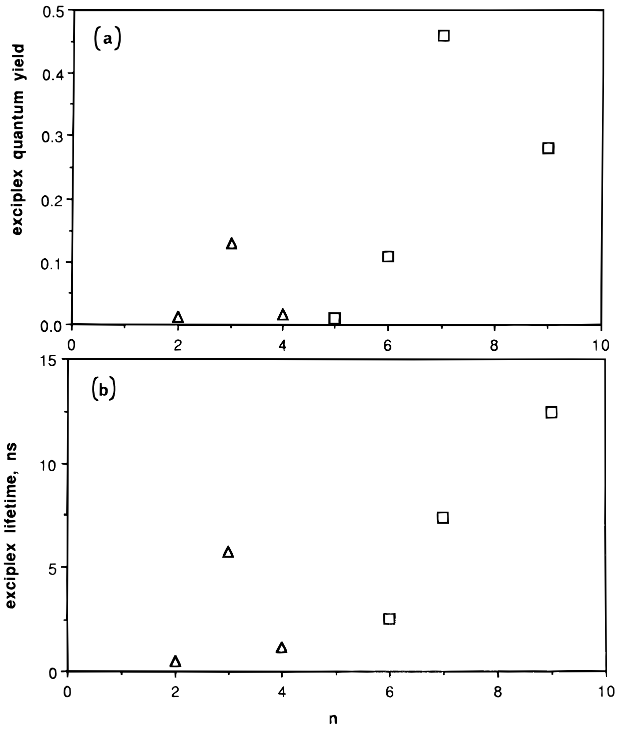


Figure 2. (a) Dependence of the exciplex fluorescence quantum yield (Φ_{fex}) and (b) the exciplex lifetime (τ_{ex}) upon the total spacer chain length for the (aminoalkyl)styrenes (△, Chart 1, system **VI**) and the (aminoalkyl)styrylamides **2**−**5** (☐).

singlet styrene using the measured styrene lifetime data (Table 1). Maximum values of Φ_{fex} are observed when $n = 3$ for the (aminoalkyl)styrenes and when $n = 7$ for the amide-linked systems. The maximum in Φ_{fex} for $n = 7$ corresponds to the minimum in Φ_f for 1-phenylpropene fluorescence (Table 1). The decrease in Φ_{fex} observed for the aminoalkyl(styrene) for $n = 4$ is much larger than the decrease observed for the amide-linked system for $n = 9$. Exciplex lifetime data for these molecules are shown in Figure 2b. The values of τ_{ex} for the (aminoalkyl)styrenes have a maximum for $n = 3$,[5b] whereas the values for the amide linked systems increase continuously with spacer length (Figure 2b). Increases in both Φ_{fex} and τ_{ex} with spacer length are also observed for **13** vs **12** and for **17** vs **16**. An increase in the rate constant for intramolecular quenching was also observed by Sakurai et al. for the amide-linked (aminoalkyl)naphthalenes (Chart 1, system **V**) when $n = 3$ or 4 vs $n = 2$.

Maximum values of Φ_{fex} and τ_{ex} and for $n = 3$ have been observed for a number of arene−spacer−amine systems with short chain spacers ($n \leq 5$).[2−5] The decrease in these values for $n > 3$ has been attributed to the unfavorable enthalpy of formation of medium size rings[4] and to the geometry dependence of the exciplex fluorescence rate constant.[2e] Surprisingly little information is available concerning intramolecular exciplex formation for longer chain spacers. De Schryver and co-workers observed exciplex fluorescence for a phenyl−spacer−amine system with $n = 11$ at room temperature in THF solution[2a−c] but did not detect exciplex fluorescence for a pyrene−spacer−amine system with $n = 8$.[2d] Exciplex fluorescence was also observed for 2-anthracenecarboxylate−spacer−amine systems (Chart 1, system **II**) in which $n = 9$ or 11, but not when $n =$ 2, 3, or 5.[8] Evidently, the longer chains are necessary to allow the amine to overlap the central region of the anthracenecarboxylate. Exciplex fluorescence has been observed by Sakurai et al. for the amide-linked (aminoalkyl)naphthalenes (Chart 1, system **V**, $n = 2$−4). The spacer dependence of intramolecular excimer formation in α,ω-bis(pyrenyl)alkanes in methylcyclohexane solution has been thoroughly investigated by Zachariasse et al.[22] They report a maximum in the ratio of excimer/monomer fluorescence intensity when $n = 3$, a minimum for $n = 5$−8, a second maximum at $n = 13$, and a gradual decrease for longer spacers. The minimum for $n = 5$−8 was attributed to the thermochemical strain associated with the formation of medium-sized rings, which is absent in larger rings. Rate constants for intramolecular excimer formation were found to parallel the ratio of excimer/monomer fluorescence.

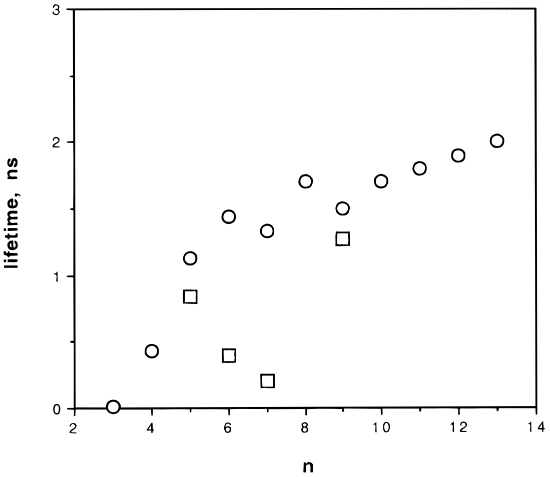


Figure 3. Dependence of the locally excited singlet lifetime upon total spacer chain length for the (aminoalkyl)pyrenes (○, Chart 1, system **IV**) and the (aminoalkyl)styrylamides **2**−**5** (☐).

Electron-transfer quenching of singlet styrene by trialkylamines is highly exergonic in acetonitrile solution and thus presumably irreversible.[16a] Under these circumstances, lifetime of the residual styrene fluorescence should be determined by the rate constant of electron transfer. The values of τ_s in acetonitrile solution for homologous series **2**−**5** are shown in Figure 3 along with the part of the extensive data set reported by Staerk and co-workers[4] for the pyrene−dimethylaniline systems with polymethylene spacers (Chart 1, system **I**). Very short singlet lifetimes ($\tau_s < 0.1$ ns) are observed in acetonitrile solution for both (aminoalkyl)styrenes[5] and pyrene−spacer−dimethylaniline systems[4] with $n \leq 4$. When $n > 4$ through-space interactions are thought to dominate the electron-transfer process.[2−5] The data for the pyrene−dimethylaniline systems display a continuous increase in τ_s with increasing spacer length, with a superimposed odd−even effect for $n < 10$.[4] The absence of a minimum for $n = 5$−8 suggests that electron transfer does not require the formation of a strained medium-sized ring as in the case of pyrene excimer formation.[22] Our lifetimes for $n =$ 5 and $n = 9$ are similar to those for the pyrene−dimethylaniline systems.[4] However, we observe a minimum value of τ_s for $n = 7$ (Figure 3). Our more limited data for the 5-phenyl-4-pentenamide (**12** vs **13**) and the 3-phenyl-2-propenamine derivatives (**16** vs **17**) are consistent with a minimum value of τ_s for $n \sim 7$.

The maximum in Figure 2a and minimum in Figure 3 for $n = 7$ indicate that intramolecular exciplex formation and electron-transfer quenching are particularly favorable for this spacer. This seven-atom-spacer effect is not observed for polymethylene spacers and presumably reflects the special conformational requirements of the amide group. Gellman and co-workers[23] have reported that an amide-containing spacer promotes folding of a triamide into a stable conformation possessing a nine-membered-ring hydrogen bond. The stability of the folded

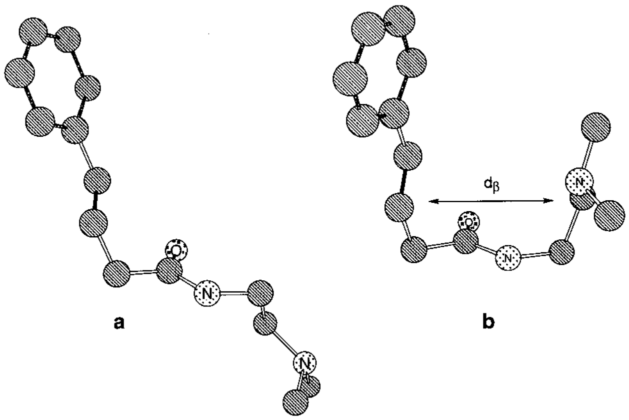


Figure 4. MM2 calculated structure of **2** (a) anti conformation and (b) syn conformation (d_β is the distance between β-carbons).

TABLE 4: Calculated Spacer Length and Singlet Lifetime

molecule, spacer[a]	d_β,[b] Å	τ_s,[c] ns (CH_3CN)
2, amide	4.7	0.84
12, amide		0.81
IVe, *m*-benzene	6.15	1.05
IVf, *m*-benzene		0.95
IVa, *p*-benzene	6.7	1.2
IVb, *p*-benzene		2.0
IVc, *p*-benzene		3.9
IVd, *p*-biphenyl	11.3	28.5
IVg, 1,4-cyclohexyl	8.0	29.0

[a] See Charts 1 and 2 for structures. [b] Calculated distance between atoms β to the spacer (see text and Figure 4). [c] Singlet lifetime of styrene or pyrene chromophore.

conformation was attributed to the central nonrotating amide segment and "more subtle torsional restrictions about sp^3-sp^2 bonds". Amides display a preference for conformations in which the β-carbons on both the carbonyl and nitrogen side are perpendicular to the amide plane.[9,24] Thus, the styryl and amine groups in the amide-linked (aminoalkyl)styrenes are either syn or anti with respect to the amide plane (Figure 4) and can be interconverted via a low-barrier rotation. MM2 (gas phase) calculations indicate that the minimized syn conformer is several kcal/mol more stable than the anti; however, solvation may eliminate this difference. A syn conformer with $n = 7$ needs no more than one or two rotations about an aminoalkyl C−C bond to achieve a folded conformation in which the styrene and amine groups are in close proximity.

The effect of an amide group in our spacers should be similar to that of the benzene ring in the spacers investigated by Michel-Beyerle and by Staerk (Chart 1, system **IV**). As is the case for amides, the β-carbons of an alkylbenzene have lowest energy conformations perpendicular to the benzene plane.[25] The distances between the β-carbons (d_β, Figure 4) of the syn conformers of *N*-ethylpropanamide, *m*-diethylbenzene, and *p*-diethylbenzene as calculated by MM2 are shown in Table 4 along with the arene singlet lifetime data in acetonitrile solution for arene−spacer−acceptor systems with one or two methylenes attached to the amide or benzene. Lifetimes are seen to increase with the value of d_β; however, the increases are quite modest. Larger increases in lifetime are observed for the biphenyl- and cyclohexyl-linked molecules **IId** and **IIg** (Chart 1), which have much larger d_β values (Table 4). The similar values for amides and *m*-benzenes with $n = 1$ or 2 may reflect a decrease in the through-bond interaction which compensates for an increase in the through-space interaction. On the basis of our results with a more extended set of linkers (Table 1), we anticipate that the probability of conformations in which the donor and acceptor are in close proximity is greater when $n = 1$ and $m \geq 3$ than when both n and $m \geq 2$. Thus, shorter lifetimes in acetonitrile solution and exciplex formation in nonpolar solvents might be observed for disubstituted benzenes in which $n = 1$ and $m \geq 3$. Additional experiments are needed to confirm these predictions.

We have investigated several structural variables in addition to the spacer chain length. The effect of amine substitution was investigated for the series **2** and **6**−**8**. The pyrrolidine **8** has the shortest styrene lifetime in hexane solution (Table 1) and is the only member of this series to form a strongly fluorescent exciplex at room temperature in hexane solution (Table 2). Exciplex formation is presumably favored by the low oxidation potential (Chart 3) and smaller steric demand of pyrrolidine compared to the other members of this series. Singlet lifetimes in acetonitrile solution are similar for all four members of this series (Table 1). Evidently, photoinduced electron transfer is sufficiently exergonic in acetonitrile solution to render insignificant the differences in amine oxidation potential. Increasing the spacer length also appears to eliminate the advantage of a pyrrolidine vs dimethylamine donor as seen by comparing the data for **3** vs **9** and **12** vs **14** in Table 1.

The behavior of the styrene−spacer−amine systems is also dependent upon amide orientation. As mentioned previously, inverting the orientation of amide group results in a decrease in the lifetime of the model compound **15** vs **1**. The amine oxidation potential (Chart 3) and styrene reduction potential may also be dependent upon amide orientation. The styrene lifetimes for **16** and **17** ($n = 6$ and 8) are longer than those for **3** and **4** ($n = 6$ and 7), indicative of less effective intramolecular quenching in both hexane and acetonitrile solution (Table 1). Curiously, intermolecular quenching is more efficient for **15** vs **1** (Table 2). The inter- and intramolecular exciplex fluorescence λ_{ex} and τ_{ex} values are similar for both amide orientations (Tables 2 and 3). Amide orientation is known to affect the rate constants of photoinduced electron transfer in porphyrin-containing diad and triad systems.[13]

We have briefly investigated two spacers structurally related to the secondary amides. The tertiary amide **10** displays dual-exponential decay of the styrene fluorescence with decay times similar to those of its secondary amide analogue **3** (Table 1). The two decay components are attributed to the ground-state *E* and *Z* conformers which have similar ground-state populations based on integration of the NMR spectrum. We have previously observed a large difference in the decay rates of several *N*-(aminoalkyl)-9-phenanthrenecarboxamides (Chart 1, system **III**) and attributed the shorter and longer decays to the *Z* and *E* conformers, respectively.[9] Because of their similar decay times, we have not attempted to assign the two decay components to specific conformers of **10**. The exciplex fluorescence observed for **10** in hexane solution also exhibits dual-exponential decay with one decay time similar to that of **3** and one that is longer-lived (Table 3). The ester **18** displays values of Φ_f and τ_s similar to those of the analogous secondary amide **2** (Table 1). As is the case for **2**, the exciplex fluorescence of **10** in hexane solution consists of a weak long-wavelength tail.

In summary, we find that a rigid amide group in the middle of a flexible alkane chain can facilitate intramolecular exciplex formation and electron transfer. The amide group serves both to limit the conformational degrees of freedom of the linker and to stabilize the adjacent exciplex by means of internal solvation. The amide linker facilitates the synthesis of donor−spacer−acceptor molecules and offers an advantage over benzene-containing spacers in this respect. Finally, we find that the (aminoalkyl)styrylamides undergo intramolecular styrene amine addition reactions to yield medium-ring lactams in fair to good yields. The synthetic aspects of our investigation will be described elsewhere.

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Supporting Information Available: Methods used for the synthesis of **1**−**21** and their spectroscopic characterization (8 pages). Ordering information is given on any current masthead page.

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