portions of CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated under vacuum to give 0.264 g of crude material that was chromatographed on a 100-Å gel permeation column in CH_2Cl_2. Fraction A, retention volume 192 mL, contained little compound, whereas fraction B, retention volume 215 mL, contained 0.156 g (54%) of **6**, which was submitted to molecular distillation (200 °C at 4×10^{-5} mm), mp 123–126 °C; ^{19}F NMR ($CDCl_3$) δ −109.58 (F, 1), −113.51 (F, 2); MS, M^+ 414. Anal. C, H.

49,50,51,52,53,54-Hexafluoro-13,16,19,37,40,43-hexaoxaheptacyclo[43.3.1.1^{2,6}.1^{7,11}.1^{21,25}.1^{26,30}.1^{31,35}]tetrapentaconta-1(49),2,4,6(54),7,9,11(53),21,23,25(52),26,28,30(51),31,33,35(50),45,47-octadecaene (**7**). Procedure B was applied to 0.171 g of 50% NaH (pentane washed, 3.62 mmol) in 80 mL of THF, 0.295 g (0.75 mmol) of diol **21**, and 0.311 g (0.75 mmol) of diethylene glycol ditosylate in 100 mL of THF. The addition of the diol and ditosylate took 9 h, and refluxing was continued for an additional 32 h. The reaction product was chromatographed on a 100-Å gel permeation column with CH_2Cl_2 as the mobile phase. The fraction with a retention volume of 178 mL, 0.140 g, proved to be crude **7**. The powder was recrystallized from hot absolute ethanol to give 0.057 g (18.4%) of **7**, mp 150–154 °C; ^{19}F NMR ($CDCl_3$) δ −115.87 (F, 2), −120.70 (F, 4); MS, M^+ 828; osmometric molecular weight in CH_2Cl_2, 822. Anal. C, H.

Attempts To Complex Cycle ($(CH_3C_6H_2F)_6$) (5). A solution of 10.0 mg of **5** was dissolved in 5.00 mL of $CDCl_3$ to give a 0.0031 M solution. Solutions in $(CD_3)_2SO$ were prepared that were 1.54 M in each of the following salts: $LiClO_4$, $NaClO_4{\cdot}H_2O$, $KClO_4$, $RbClO_4$, and $CsClO_4$. In each of six 5-mm NMR tubes was placed 500 μL of the solution of **5** (0.00155 mmol per tube). To each of the five tubes was added 10 μL of a different salt solution, and the six tubes were sonicated for 10 min and allowed to stand for 24 h at ambient temperature. The ^{19}F NMR spectra gave singlets at δ −112.917 (blank tube), −122.963 (Li^+ tube), −112.917 (Na^+ tube), −112.963 (K^+ tube), −112.917 (Rb^+ tube). The ^{1}H NMR spectrum of each of the six solutions were identical: δ 2.44 (s, 36, CH_3), 7.30 (s, 18, ArH).

Attempts To Detect Complexation of Cycle ($(CH_3C_6H_2F)_8$) (8) with Various Solvents. Approximately 2×10^{-3} M solutions of **8** in five different solvents were prepared and their ^{19}F NMR spectra determined as temperatures were varied between 258 and 335 K, except for the $(CD_3)_2SO$ solution in which the temperature limits were 315 and 371 K. Although the activation energy barriers for ring inversion at 315 K were within error limits of one another and $^5J_{FF}$ remains constant at 32.5 Hz in all solvents, the fluorine chemical shift differences, $\Delta\delta$ (Hz), at 470.56 MHz were remarkably dependent on solvent for unexplained reasons: 131, CD_2Cl_2 (258 K); 230, $(CD_3)_2SO$ (315 K); 422, $CDCl_3$ (258 K); 465, $(CD_3)_2CO$ (258 K); 244, $CDCl_2CDCl_2$ (258 K).

The ^{19}F NMR spectra at 258 K were simulated with the PANIC program (Bruker software of the Aspect 2000 computer). The $^5J_{FF}$ coupling between fluorine neighbors and the chemical shift difference were varied until the theoretical line shapes matched the experimental spectrum. All other coupling constants were fixed at values less than 1 Hz. The exchange-broadened spectra at 315 K were then simulated with the same program adjusting the chemical shifts and increasing the line width. Rate constants, k, for ring inversion were derived from the line widths due to exchange $\Delta\nu$, with $k = \pi\Delta\nu$. This method is exact as long as exchanging NMR signals do not overlap.[17] There is considerable overlap *within* the ^{19}F triplets but not *between* the two triplets in our system (see Figure 1). We estimate the error in k to be ±50% ($\Delta(\Delta G^{\ddagger})$ ±0.3 kcal mol^{-1}) to account for the systematic errors introduced. A complete line-shape analysis is too complicated for the eight-spin system.

Crystal Structure Determination. The crystals of $(CH_3C_6H_2F)_6$ were prepared by slow evaporation of a CH_2Cl_2 solution. A single crystal (0.35 × 0.40 × 0.50 mm) was used in the diffraction study. The space group is *Pa3* (cubic), four molecules per unit cell, a = 15.621 (4) Å, V = 3812 (2) Å^3, μ = 3.21 cm^{-1}, final R = 0.12, R_w = 0.102, 736 reflections with $F \geq 3\sigma(F)$. Disordered CH_2Cl_2 was present but the rest of the structure refined well. Besides the structural parameters given in the text, additional parameters follow. Deviations of the six fluorine atoms of one molecule from their best plane are ± 0.919 Å. Each CH_3 is bent 0.114 Å out of the best plane of its attached benzene ring. The angle between the normal to the best plane of the benzene ring and the best plane of the six fluorines is 26°.[18]

Registry No. 5, 88229-90-7; **6**, 88229-95-2; **7**, 88229-96-3; **8**, 88229-91-8; **9**, 388-82-9; **10**, 88229-82-7; **11**, 88229-83-8; **12**, 88229-85-0; **13**, 88229-86-1; **15**, 88229-81-6; **16**, 88229-84-9; **17**, 88229-87-2; **18**, 88229-88-3; **19**, 88229-89-4; **20**, 88229-92-9; **21**, 88229-93-0; **22**, 88229-94-1; C_6H_5F, 462-06-6; 4-$CH_3C_6H_4F$, 352-32-9; diethylene glycol, 111-46-6; diethylene glycol ditosylate, 7460-82-4.

Supplementary Material Available: Tables of atomic positional parameters and thermal parameters and of interatomic distances and angles of $(CH_3C_6H_2F)_6$ (2 pages). Ordering information is given on any current masthead page.

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trans-Stilbene–Amine Exciplexes. Stereoelectronic Control of Amine Dimer Cation Radical Formation

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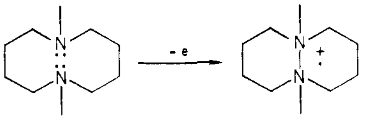
Abstract: The interaction of singlet *trans*-stilbene with several trialkylamines, α,ω-diaminoalkanes, and the bicyclic diamine Dabco in benzene solution has been investigated. The rate constants for fluorescence quenching equal or exceed the rate of diffusion and are not subject to steric hindrance. Exciplex energies and monoamine oxidation potentials show little variation with structure, suggesting that steric destabilization and inductive stabilization counterbalance each other. Intersystem crossing to yield triplet *trans*-stilbene is the predominant exciplex decay pathway at low amine concentrations. At higher amine concentrations, exciplex quenching by ground-state amines occurs and is subjected to a pronounced steric effect in the case of monoamines and a chain-length effect in the case of diiaminoalkanes. On the basis of these effects, exciplex quenching is proposed to occur by the interaction of cation radical and neutral amines to yield a triplex of *trans*-stilbene anion radical and a three-electron, σ-bonded amine dimer cation radical. The energy of this triplex is estimated to be lower than that of triplet *trans*-stilbene.

The interaction of nitrogen lone pairs in monocyclic and bicyclic diamines is destabilizing in the neutral form but stabilizing in the radical cation due to the formation of a three-electron σ bond (eq 1).[1,2] While the formation of diamine monocation radicals from



(1)

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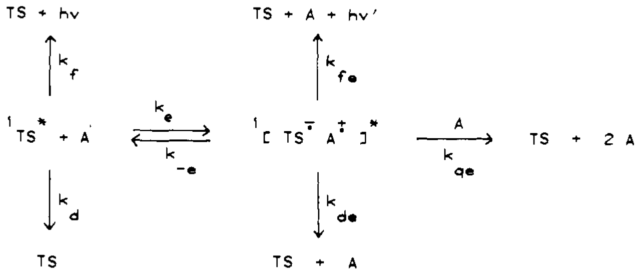
Scheme I. Simplified Exciplex Quenching Mechanism



conformationally restricted diamines (and disulfides[3]) is well documented, little information is available concerning the formation of diamine cation radicals from conformationally mobile acyclic diamines or amine dimer cation radicals from the reaction of a monoamine cation radical with a neutral amine.

It occurred to us that the formation of amine dimer cation radicals might account for numerous reports concerning the efficient quenching of the singlet exciplexes of aromatic hydrocarbons (ArH) with tertiary amines (R_3N) by ground-state amine (eq 2).[4-8] Van and Hammond[7] proposed several years ago that

$$^1ArH^* + R_3N \rightleftarrows {}^1(ArH^{-}\cdot R_3N^{+}\cdot)^* \xrightarrow{R_3N} ArH + R_3N \qquad (2)$$

amine quenching of a naphthalene–amine exciplex involved the formation of a "$(Et_3N)_2^{+}\cdot$ aggregate" but offered no evidence pertaining to the formation or structure of the aggregate. Related to the termolecular interaction of eq 2 is the quenching of aromatic hydrocarbon singlets by α,ω-diaminoalkanes and by 1,4-diazabicyclo[2.2.2]octane (Dabco).[7,9-15] The diaminoalkanes and Dabco display enhanced quenching rates compared to monoamines. While fluorescence has been reported for the exciplexes of singlet aromatic hydrocarbons with diaminoalkanes,[9,10] there has been no report to date of fluorescence from aromatic hydrocarbon–Dabco exciplexes.[11-15] The absence of aromatic hydrocarbon–Dabco exciplex fluorescence is found experimentally to result from anomalously rapid nonradiative decay or intersystem crossing.

We report here the results of our investigations of the quenching of singlet *trans*-stilbene by several monoamines, α,ω-diaminoalkanes, and Dabco in the nonpolar solvent benzene. The observed structure–reactivity relationships for inter- and intramolecular exciplex quenching clearly implicate the formation of amine dimer cation radicals as intermediates in the exciplex quenching process and established a pronounced stereoelectronic effect upon amine dimer cation radical formation.

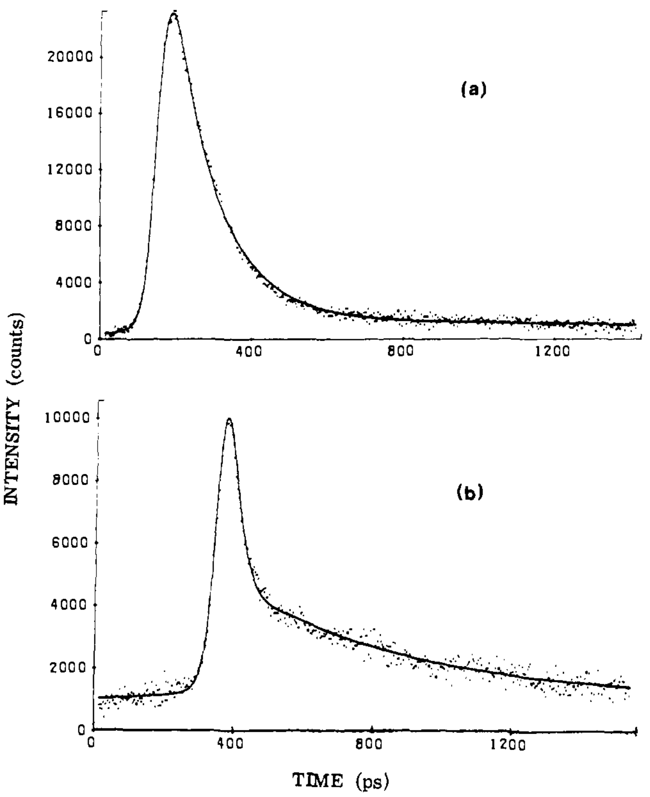


Figure 1. (a) Decay of *trans*-stilbene fluorescence in benzene solution (300 °K) fitted with a lifetime of 105 ps. (b) Decay of *trans*-stilbene fluorescence and of *trans*-stilbene–Abco exciplex fluorescence in benzene solution (300 °K) of 10^{-3} M *trans*-stilbene and 0.6 M Abco. The double exponential fit with τ_1 = 18 ps and τ_2 = 355 ps is drawn as a full line.

Results

Fluorescence Quenching and Exciplex Fluorescence. The fluorescence of *trans*-stilbene is quenched by all of the amines investigated. The short singlet lifetime of *trans*-stilbene in benzene solution requires the use of high amine concentrations for the observation of appreciable fluorescence quenching. Stern–Volmer plots for fluorescence quenching are linear over the concentration range investigated. The values for $k_{qs}\tau_s$ are given in Table I. The fluorescence quenching constants (k_{qs}) reported in Table I are calculated from the least-squares slopes of the Stern–Volmer plots ($k_{qs}\tau_s$) and the singlet lifetime of *trans*-stilbene in benzene solution (τ_S = 105 ± 15 ps) measured with a synchroscan streak camera using picosecond excitation at 300 nm (Figure 1a).[16] For all amines, the values of k_{qs} are approximately equal to or greater than the rate of diffusion in benzene solution (1×10^{10} M^{-1} s^{-1}).[17]

Weak exciplex emission can be detected with a standard commercial fluorimeter for the monoamines ethyldiisopropylamine (EDA),[18,19] triethylamine (TEA), trimethylamine (TMA), and 1-azabicyclo[2.2.2]octane (Abco) but not for the diaminoalkanes. More sensitive photon counting detection allows the observation

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Table I. Fluorescence Quenching and Stilbene Isomerization Data

amine	$k_{qs}\tau_s$,[a] M^{-1}	$10^{-10}k_{qs}$,[b] $M^{-1}\ s^{-1}$	$k_{qe}\tau_{ex}$,[c] M^{-1}	$\phi_{cs}'(^1/_2)$[d]	$\phi^0{}_{cs}'$[e]	$k_{qe}\tau_{ex}$,[f] M^{-1}
ethyldiisopropylamine (EDA)	3.6	3.6	<1	0.51	0.51	<1
triethylamine (TEA)	2.0	2.0	3.5	0.15	0.29	3
trimethylamine (TMA)	1.0	1.0	8.0			
1-azabicyclo[2.2.2]octane (Abco)	1.7	1.7	4.0	0.21		
1,4-diazabicyclo[2.2.2]octane (Dabco)	4.5	4.5		0.17	0.5	12
tetramethyl-1,2-ethanediamine	2.1	2.1		0.06	0.43	13
tetramethyl-1,3-propanediamine	2.4	2.4		0.09	0.15	2
tetramethyl-1,4-butanediamine	2.2	2.2		0.09	0.09	<1

[a] Least-squares slope of Stern–Volmer plot. Limits of error ±5%. [b] Calculated from Stern–Volmer slope and measured *trans*-stilbene singlet lifetime. Limits of error ±10%. [c] Values calculated from the data in Figure 2, according to eq 4. Limits of error ±20%. [d] Quantum yield for *cis*-stilbene formation from the singlet exciplex at the half-quencher concentration, calculation from eq 6. Limits of error ±20%. [e] Quantum yield for *cis*-stilbene formation from the exciplex in the limit of low amine concentration. Limits of error ±20%. [f] Least-squares slopes of data in Figure 5, according to eq 6. Limits of error ±10%.

Table II. Amine Oxidation and Exciplex Fluorescence Data

amine[a]	IP, eV[b]	$E_{1/2}$, V[c]	$-\Delta G_{ex}$, eV[d]	ν_{ex}, cm^{-1}[e]	obsd E_{ex}, eV[f]	calcd E_{ex}, eV[g]	τ_{ex}, ns[h]	$10^{-8}k_{qe}$[i]
EDA	7.64	0.76	0.18	21 100	2.61	2.87	14 (14)	<0.1
TEA	8.06	0.78	0.16	21 000	2.60	2.89	8 (12)	3
TMA	8.52	0.82	0.12	21 100	2.61	2.93		
Abco	8.03	0.82	0.12	21 700	2.69	2.93	0.42 (0.8)	16
Dabco	7.51	0.57	0.37	17 500	2.12	2.68	<2[j]	>40

[a] See Table I for full names of amines. [b] Vertical-ionization potentials from ref 25 and 27. [c] Oxidation potential vs. SCE in acetonitrile solution. [d] Calculated free energy for electron transfer, eq 7. [e] Exciplex emission maxima. [f] Exciplex state energy, determined from emission maxima. [g] Exciplex state energy, calculated from eq 8. [h] Lifetimes at the amine concentration which quenches 50% of the *trans*-stilbene fluorescence (and in the limit of low amine concentration). Limits of error ±10%. [i] Rate constant for exciplex quenching by amine from eq 3. Limits of error ±10%. [j] Limit of pulse fluorimeter time resolution. The fluorescence intensity is too low to allow measurement with the picosecond apparatus.

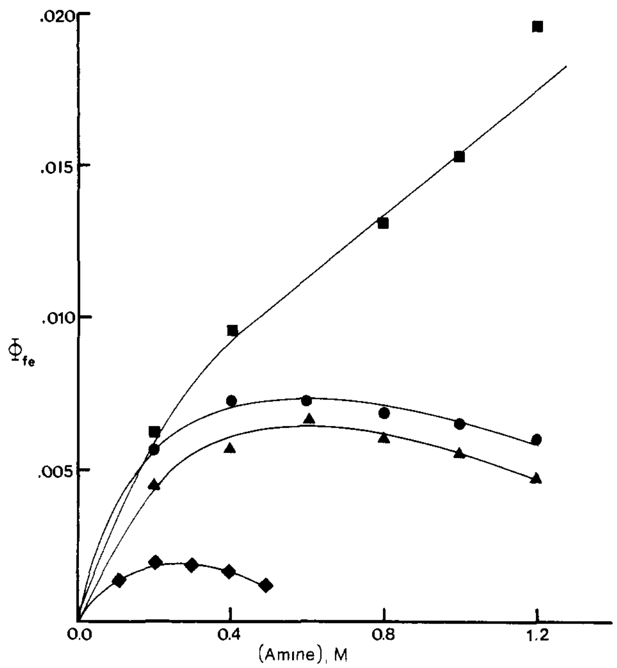


Figure 2. Amine concentration dependence of the exciplex fluorescence quantum yield for *trans*-stilbene with ethyldiisopropylamine (■), triethylamine (▲), trimethylamine (♦) and Abco (●).

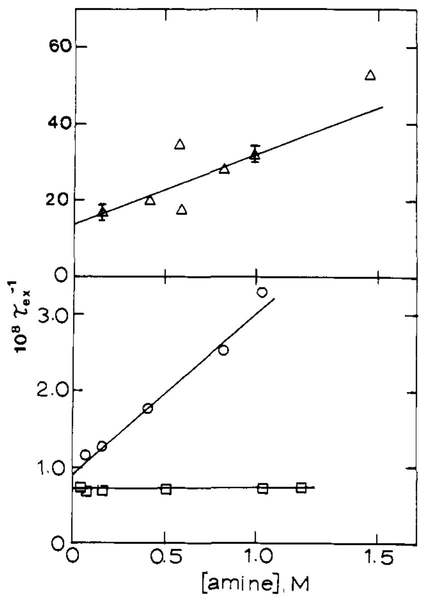


Figure 3. Amine concentration dependence of the *trans*-stilbene–ethyldiisopropylamine (□), triethylamine (○), and Abco (△) exciplex lifetime. The error bars indicate the time resolution of 20 ps due to trigger jitter in the synchroscan streak camera.

of very weak ($\phi < 10^{-4}$) emission from the *trans*-stilbene–Dabco exciplex. The positions of the exciplex fluorescence maxima are given in Table II. Plots of the exciplex emission quantum yields (ϕ_{fe}) vs. amine concentration are shown in Figure 2. Values of ϕ_{fe} increase with increasing amine concentration for EDA, but display maxima at ca. 0.6 M for TEA, 0.2 M for TMA, and 0.4 M for Abco.

Lifetimes for the fluorescent exciplexes were measured by single photon counting (EDA, TEA) or picosecond spectroscopy (Abco, Figure 1b). Dual component emission is observed for the *trans*-stilbene–Abco system. The major (long-lived) component is assigned to the singlet exiplex while the minor (short-lived) component might be due to a nonrelaxed exciplex. Lifetime values for the *trans*-stilbene–EDA exciplex are independent of amine concentration,[18] while values for the TEA and Abco exciplexes

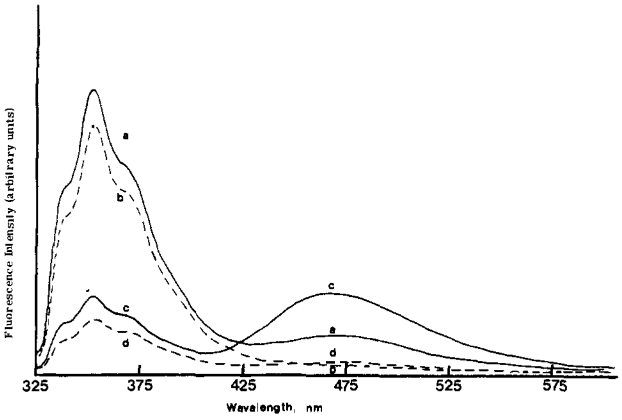


Figure 4. Oxygen quenching (broken curves) of *trans*-stilbene–ethyldiisopropylamine exciplex fluorescence and residual stilbene monomer fluorescence. Curves a and b for 0.2 M amine and c and d for 1.0 M.

decrease with increasing amine concentration as shown in Figure 3.

The fluorescence quantum yield and lifetime data are indicative of exciplex quenching by ground-state amine. A mechanism which adequately accounts for observations of *trans*-stilbene monomer and exciplex fluorescence is given in Scheme I. Complete kinetic analysis of the mechanism shown in Scheme I requires either the measurement of both monomer and exciplex fluorescence decay as a function of amine concentration[20] or the use of various simplifying assumptions.[4–7] Unfortunately, the short singlet lifetime of *trans*-stilbene precludes monomer decay measurement by nanosecond pulse fluorimetry and necessitates the use of high amine concentrations for the observation of monomer as well as exciplex quenching. Approximate kinetic analysis is possible if exciplex formation is assumed to occur irreversibly.[20] Under these conditions the exciplex lifetime can be simply described by eq 3. The

$$\tau_{ex}^{-1} = k_{fe} + k_{de} + k_{qe}[\text{amine}] \qquad (3)$$

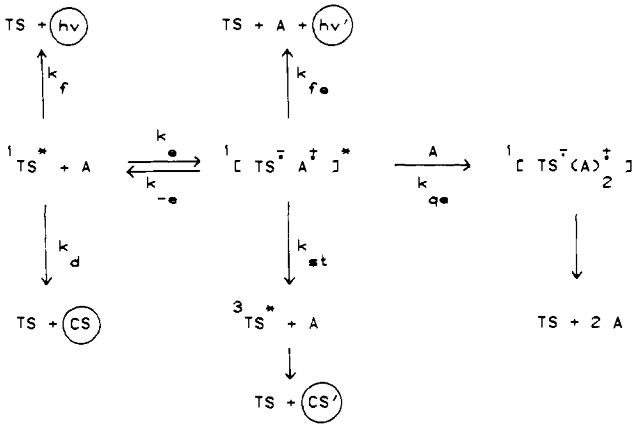
plots of τ_{ex}^{-1} vs. [amine] shown in Figure 3 provide values of $\tau^0_{ex} = (k_{fe} + k_{de})^{-1}$ and k_{qe} (Table II). The values of τ^0_{ex} for EDA and TEA are similar and substantially greater than the value for Abco. For EDA, the exciplex lifetime is independent of amine concentration, indicating that $k_{qe}[\text{amine}] << \tau_{ex}^{-1}$. Approximate values of $k_{qe}\tau_{ex}$ can also be obtained from the dependence of ϕ_{fe} on amine concentration (Figure 2) using eq 4, where ϕ^0_{fe} is

$$\phi^0_{fe}/\phi_{fe} = 1 + k_{qe}\tau_{ex}[\text{amine}] \qquad (4)$$

calculated from the observed fluorescence quantum yield at the lowest amine concentration (Figure 2) and the extent of singlet quenching at that amine concentration. The values of $k_{qe}\tau_{ex}$ obtained using eq 3 and 4 are in good agreement in the case of TEA. The poorer agreement in the case of Abco possibly reflects the uncertainty in the extrapolated value of τ^0_{ex} (Figure 1b).

Qualitative information concerning the extent to which exciplex formation is reversible is provided by oxygen quenching of *trans*-stilbene monomer and exciplex fluorescence (Figure 4). In the absence of amines, *trans*-stilbene fluorescence is not quenched by 1.0 atm of O_2 due to its short lifetime. For 0.2 M and 1.0 M EDA approximately 79% and 88%, respectively, of the exciplex emission is oxygen quenchable, whereas, 13% and 27% of the stilbene monomer emission is oxygen-quenchable fluorescence.

Scheme II. Elaborated Exciplex Quenching Mechanism



The lifetime of the *trans*-stilbene–EDA exciplex fluorescence for 0.2 M EDA is reduced from 14 ns in argon-saturated benzene solution to 9 ns in air-saturated solution. From the lifetime data and the assumption of $[O_2] = 2 \times 10^{-3}$ M, the rate constant for exciplex quenching by oxygen is calculated to be 2×10^{-10} M, in agreement with previous estimates.[18] Even less oxygen-quenchable fluorescence is observed for the exciplexes of TEA and Dabco. Thus the neglect of k_{-e} in the derivation of eq 3 probably has little effect on the lifetime and quenching data in Tables I and II.

Stilbene Isomerization. Quenching of stilbene trans → cis isomerization by amines is less efficient than quenching of *trans*-stilbene fluorescence.[18,19] In the case of EDA quenching, the quantum yield for *cis*-stilbene formation is essentially the same at the half-quencher concentration (0.28 M) as with no quencher. The quantum yield for *cis*-stilbene formation in the presence of amine is given by eq 5, where ϕ_{cs} is the trans → cis isomerization

$$\phi_{obsd} = (1 - a)\phi_{cs} + a(\phi_{cs'}) \qquad (5)$$

quantum yield for 0.05 M *trans*-stilbene (0.45),[21] $\phi_{cs'}$ is the quantum yield for isomerization via the singlet exciplex, and *a* is the fraction of singlet quenched, calculated from the fluorescence quenching data in Table I and the amine concentration. Formation of *cis*-stilbene via the singlet exciplex is known to occur via exciplex intersystem crossing to yield a triplet exciplex which is less stable than triplet *trans*-stilbene.[18,22] Isomerization of triplet *trans*-stilbene occurs with a quantum yield of 0.55,[23] placing an upper limit on the value of $\phi_{cs'}$. Values of $\phi_{cs'}$ measured at the half-quencher concentration are given in Table I. Plots of $(\phi_{cs'})^{-1}$ vs. [amine] are shown in Figure 5 for several mono- and diamines. Assumption of (a) irreversible exciplex formation and (b) intersystem crossing as the predominant pathway for exciplex decay provides the simple relationship given in eq 6, where $\phi^0_{cs'}$ is the

$$(\phi_{cs'})^{-1} = (\phi^0_{cs'})^{-1}(1 + k_{qe}\tau_{ex}[\text{amine}]) \qquad (6)$$

limiting quantum yield for *cis*-stilbene formation via the singlet exciplex in the absence of exciplex quenching by amine and k_{qe} and τ_{ex} are defined as in eq 3. Values of $\phi^0_{cs'}$ and $k_{qe}\tau_{ex}$ are given in Table I. The value of $k_{qe}\tau_{ex}$ obtained by this method for TEA

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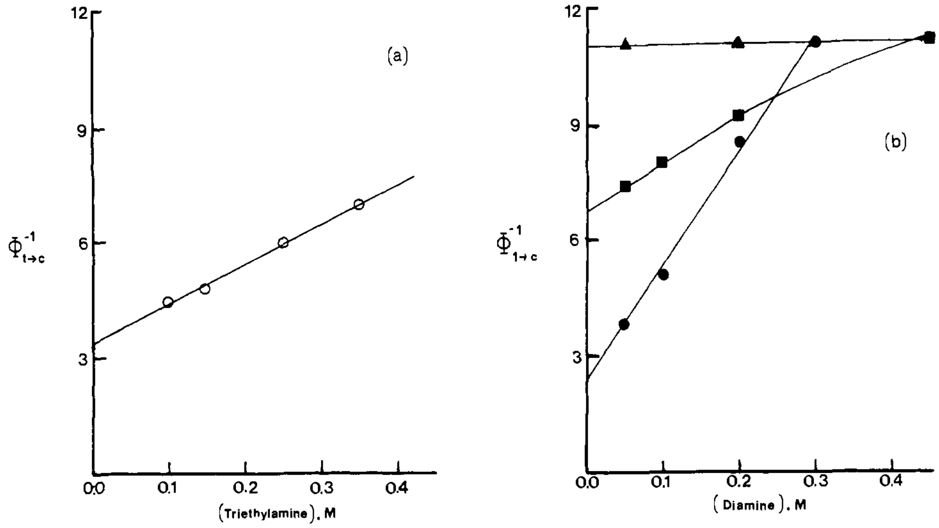

Figure 5. Amine concentration dependence of *cis*-stilbene formation via singlet *trans*-stilbene amine exciplexes (a) with triethylamine (○) and (b) with *N,N,N′,N′*-tetramethylpropanediamine (■), *N,N,N′,N′*-tetramethylethanediamine (●), and *N,N,N′,N′*-tetramethylbutanediamine (▲).

is in good agreement with the values obtained from lifetime data (Table II) and fluorescence quantum yield (Table I) data.

No products other than *cis*-stilbene are formed upon irradiation of mono- or diamines and *trans*-stilbene in benzene solution.

Discussion

Elaboration of the basic exciplex quenching mechanism shown in Scheme I to include exciplex intersystem crossing and plausible pathways for exciplex quenching by amine provides Scheme II. The encircled parameters are those which can be determined experimentally. Monomer ($h\nu$) and exciplex ($h\nu'$) fluorescence can be spectrally (Figure 4) and temporally resolved (Figure 1b). Total *cis*-stilbene formation can be separated into two components, direct isomerization of singlet *trans*-stilbene (CS) and isomerization via the singlet exciplex (CS′), by using eq 5. Ample precedent exists for the processes outlined in Scheme II. The mechanism of *cis*-stilbene formation via intersystem crossing of the singlet exciplex has been established in the case of the stilbene–EDA exciplex.[6,22] Quenching of exciplexes by amines has been frequently observed, both in cases where the amine is also a component of the exciplex (as in Scheme II)[4–7] and where it is not.[8] The novel feature of the present investigation is the marked dependence of exciplex formation, exciplex behavior, and exciplex quenching (k_{qe}) rate constants on amine structure. These structure–reactivity relationships provide evidence concerning the nature of the interaction between neutral and electron-deficient nitrogen for monoamines, Dabco, and α,ω-diaminoalkanes.

Quenching by Monoamines and Dabco. Formation of a "pure" charge-transfer exciplex requires that electron transfer be exergonic.[23] The free energy for exciplex formation in a nonpolar solvent can be calculated from Weller's equation (eq 7), where

$$-\Delta G_{ex} = {}^1E^*_{ts} - (E_A^{ox} - E_{ts}^{red}) - 0.33 \pm 0.1 \text{ eV} \qquad (7)$$

${}^1E_{ts}^*$ and E_{ts}^{red} are the singlet energy (3.53 eV) and reduction potential (−2.26 V) of *trans*-stilbene, E_A^{ox} is the amine oxidation potential, and the constant term corrects for the estimated solvation enthalpy in benzene solution. Values of ΔG_{ex} calculated using eq 7 and amine oxidation potentials (measured by cyclic voltammetry) are exergonic (Table II). Diffusion-controlled quenching is expected for exergonic formation of a charge-transfer stabilized exciplex;[23] however, rate constants for amine quenching of stilbene fluorescence (Table I) exceed the rate of diffusion in benzene solution.

Rate constants exceeding the rate of diffusion could result from ground-state complexation between *trans*-stilbene and amines or from the occurrence of electron transfer over distances somewhat larger than the collision diameter. Ground-state complexation is not supported by spectroscopic evidence[19] and would be expected to be subjected to steric interactions.[24] While modest steric effects have been observed in cases where amines quench singlet aromatic molecules with rate constants less than the rate of diffusion,[25] there is no apparent steric effect on the monoamine quenching data (Table I).

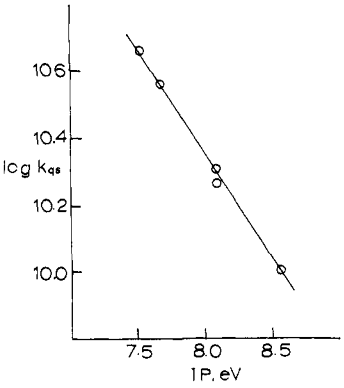

Figure 6. Dependence of fluorescence quenching rate constant upon amine vertical ionization potential.

Recent investigations of exciplex formation by picosecond spectroscopy suggest that electron transfer can occur by initial formation of a solvent-separated ion pair which subsequently forms an exciplex (contact ion pair).[26] Initial formation of a solvent-separated ion pair is consistent with our observations of (a) rate constants for fluorescence quenching which exceed the calculated rate of diffusion, (b) the absence of a pronounced steric effect on fluorescence quenching, even with the hindered amine EDA, and (c) a good correlation between quenching rate constants and amine vertical-ionization potentials (Figure 6).[25,27]

Relaxation of the initially formed solvent-separated ion pair yields the more stable fluorescent exciplex. It is remarkable that

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(24) The association constant for the BF_3 complex of TMA is larger than that for TEA. Brown, H. C.; Taylor, M. D. *J. Am. Chem. Soc.* **1947**, *69*, 1332–1336.

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the emission maxima of the exciplexes of *trans*-stilbene and all of the monoamines occur at approximately the same energy, whereas the vertical-ionization potentials of EDA and TMA differ by nearly 1.0 eV. Weller[23] has found that the emission maxima of numerous exciplexes can be related to the redox potentials of the donor (D) and acceptor (A) molecules using eq 8. Values

$$h\nu^{\max} = E_D^{\mathrm{ox}} - E_A^{\mathrm{red}} - 0.15 \pm 0.1 \text{ eV} \tag{8}$$

calculated for the four monoamines using eq 8, the amine oxidation potentials in Table II, and the reduction potential of *trans*-stilbene are ca. 0.2 eV greater than the experimental values. Formation of a "heteroexcimer" in which the charge-transfer state interacts with locally excited states can account for this difference.[23] A plausible explanation for the small variation in monoamine oxidation potential and exciplex energy with amine structure is that steric interactions between the alkyl groups of the sp^2 hybridized amine cation radical and the anion radical lead to a larger equilibrium distance between the cation radical and anion radical (or anode surface) for more hindered than less hindered amines. The resulting steric destabilization may effectively counterbalance the inductive stabilization of electron deficient nitrogen.

The observed emission maximum for the *trans*-stilbene–Dabco exciplex indicates that this exciplex is 0.56 eV more stable than the Abco exciplex. This value is double the energy difference calculated from the difference in amine oxidation potentials (eq 8); however, it is in good agreement with both the recently determined resonance stabilization energy of the Dabco cation radical (0.4 eV)[1] and the difference in Dabco vs. Abco vertical-ionization potentials. We thus would caution that the use of eq 8 to estimate the energy of nonfluorescent aromatic hydrocarbon–Dabco exciplexes may grossly underestimate the stability of such species.

The quantum yields for *cis*-stilbene formation via the monoamine and Dabco exciplexes at low amine concentrations (Table I) are nearly as large as the reported value for trans → cis isomerization of triplet *trans*-stilbene.[28] Thus intersystem crossing must be the predominant pathway for decay of the monoamine and Dabco exciplexes. Rate constants for intersystem crossing ($k_{st} \sim 5 \times 10^7$ s^{-1}) obtained from the measured *trans*-stilbene–EDA and –TEA exciplex lifetimes (Table II) are similar to those observed for the exciplexes of TEA with naphthalene[7] and pyrene.[15] The rate constant for intersystem crossing of the short-lived *trans*-stilbene–Abco exciplex is evidently faster than those for the other monoamine exciplexes, perhaps reflecting a difference in exciplex structure. The acyclic amines should yield planar cation radicals while Abco should yield a pyramidal cation radical.[1,2]

The rate constant for intersystem crossing of the short-lived *trans*-stilbene–Dabco exciplex is also substantially greater than the values for the EDA or TEA exciplexes. This difference might reflect either a change in exciplex structure or a change in the energy gap between the singlet exciplex and *trans*-stilbene triplet states. A state energy diagram for *trans*-stilbene with TEA is shown in Figure 7. The triplet energy of *trans*-stilbene (2.12 eV) is ca. 0.5 eV lower than in the energy of the TEA exciplex but is only slightly lower than that of the Dabco exciplex. Adams and Cherry[29] have recently reported that the rate constant for production of triplet stilbenes from the singlet exciplexes of substituted stilbenes with fumaronitrile increases with decreasing energy gap, from 1.8×10^7 s^{-1} for an energy gap of 0.5 V to 2.9×10^8 for an energy gap of 0.2 V. It thus appears likely that previously reported failures to observe fluorescence from aromatic hydrocarbon–Dabco exciplexes[7,11-15] may be due to the exceptionally low energy of these exciplexes. Dabco singlet exciplexes have been observed to decay via both very rapid intersystem crossing and internal conversion.[12,13] Both processes are known to display pronounced energy gap dependence.[29,30]

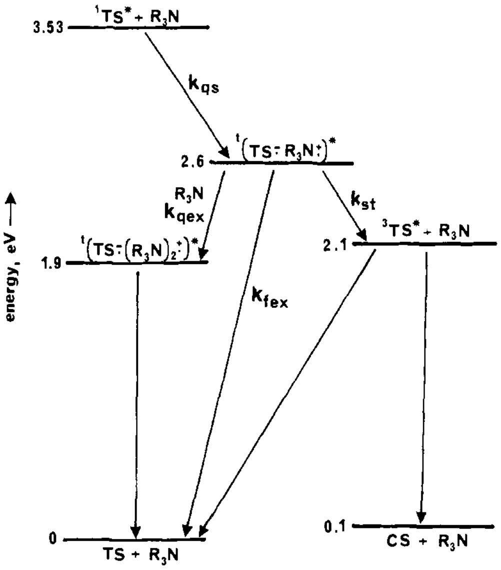

Figure 7. Energy level diagram for *trans*-stilbene locally excited singlet and triplet states and stilbene–triethylamine exciplex and triplex.

While the unimolecular decay processes of the stilbene–monoamine exciplexes are similar, their rate constants for quenching by ground-state amine (Table II) are markedly different. For the stilbene–EDA exciplex, the exciplex fluorescence intensity increases almost linearly with the amine concentration (Figure 2), while its lifetime (Figure 3) and quantum yield for *cis*-stilbene formation (Table I) are independent of amine concentration. Thus exciplex quenching by this amine is not a kinetically significant process ($k_{qe} < 1 \times 10^7$ M^{-1} s^{-1}). In contrast, the lifetime, fluorescence intensity, and quantum yield for *cis*-stilbene formation from the stilbene–TEA, –TMA, and –Abco exciplexes are highly dependent upon amine concentration. Rate constants for exciplex quenching obtained from exciplex lifetime data for TEA and Abco are 3×10^8 and 1.6×10^9 M^{-1} s^{-1}, respectively. The value for TEA is similar to that reported for the naphthalene–TEA exciplex.[7] On the basis of the dependence of exciplex fluorescence quenching upon amine concentration (Figure 2), exciplex quenching by TMA is even more rapid than for Abco.

While quenching of singlet exciplexes by ground-state amines has been frequently observed,[4-8,15] the pronounced effect of amine structure on reactivity observed with the four monoamines is without precedent. The observed order of reactivity (TMA > Abco > TEA > EDA) is suggestive of stereoelectronically controlled nucleophilic attack of the tertiary amines on the exciplex.[31] The most likely target for nucleophilic attack is the positively charged amine nitrogen, leading to the formation of a triplex (Scheme II) in which the two amines exist as an amine dimer cation radical (eq 1). Quenching of donor–acceptor exciplexes by ground-state donors is known to occur from the donor side.[8,23a] The interaction of both nitrogen lone pairs with stilbene, either on the same or opposite sides, would not be expected to give rise to a steric effect of the magnitude observed. Three-electron bonding in diamines and disulfides is known to require close approach of the two nuclei.[1-3] Close approach of two EDA molecules is prevented by the nonbonded interaction of the isopropyl groups, which are restricted to conformations in which methyl groups flank the lone pair.[32] In TEA two of the three methyl groups can rotate away from the lone pair,[31,33] while in Abco the bicyclic structure minimizes nonbonded interactions in the cation radical.

Quenching of the *trans*-stilbene–Dabco exciplex by ground-state Dabco is even more efficient than exciplex quenching by mono-

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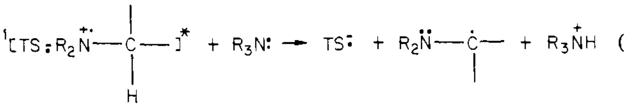
amines (Table I). The rate constant for exciplex quenching by Dabco obtained from the exciplex lifetime and $k_{qe}\tau_{ex}$ values (Tables I and II) is 4×10^9 M^{-1} s^{-1}, approximately double the value for Abco (Table II). Clearly the weak thru-bond interaction present in the cation radical of Dabco does not inhibit the interaction with a second molecule of Dabco. This interaction presumably results in the formation of a triplex consisting of a stilbene anion radical and a cation radical complex involving the four nitrogen atoms of the two Dabco molecules. Analogous complexes have been proposed for the interaction of neutral and cation radical disulfides.[3]

One consequence of the large k_{qe} value for Dabco is that the relative exciplex fluorescence intensity attains a maximum value when [Dabco] ~ 0.1 M and decreases at higher amine concentrations. Thus reported failures to observe aromatic hydrocarbon–Dabco exciplex emission might result from efficient exciplex quenching as well as rapid intersystem crossing or nonradiative decay.[7,11–14]

An alternative pathway which might be considered for exciplex quenching by amine is proton transfer from the cation radical α-carbon to the neutral amine lone pair (eq 9). Since the cation



$$^1[\mathrm{TS}^{\overset{\cdot}{\cdot}}\,\mathrm{R_2}\overset{+\cdot}{\mathrm{N}}\!-\!\underset{\mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}\!-\!]^* + \mathrm{R_3N}: \rightarrow \mathrm{TS}^{\overset{\cdot}{\cdot}} + \mathrm{R_2}\ddot{\mathrm{N}}\!-\!\underset{|}{\dot{\mathrm{C}}}\!- + \mathrm{R_3}\overset{+}{\mathrm{N}}\mathrm{H} \quad (9)$$

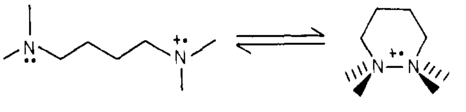
radical of EDA is readily deprotonated in polar solvents,[19,32] while that of Abco is not,[34] this pathway cannot account for the observed order of exciplex quenching reactivity.

Quenching by Diaminoalkanes. Davidson and co-workers[9] have reported that α,ω-diaminoalkanes are more efficient quenchers of napthahalene fluorescence than the corresponding monoamines, but give rise to less intense exciplex emission. In agreement with these results we find the three tetramethyl-α,ω-diaminoalkanes investigated to be more efficient quenchers of stilbene fluorescence than TMA (Table I). The absence of exciplex fluorescence for the diaminoalkanes is not surprising in view of the very weak emission observed in the presence of TMA.

The dependence of $\phi_{cs'}$ on amine concentration for the diaminoethane (Figure 5) is similar to that observed for TEA. The limiting quantum yield ($\phi^0_{cs'} = 0.4 \pm 0.1$) indicates that intersystem crossing is the predominant exciplex decay pathway in the absence of exciplex quenching by a second molecule of diamine. Thus the interaction of the two nitrogens of one diaminoethane molecule with singlet stilbene does not result in quenching of the exciplex intersystem crossing pathway which leads to stilbene isomerization: The slope/intercept ratio of the data for the diaminoethane (Figure 5) provides a value of $k_{qe}\tau_{ex} = 12$ for exciplex quenching by ground-state diamine, a value somewhat larger than that for TMA (Table I). Since it is unlikely that τ_{ex} is longer for the nonfluorescent stilbene–diamine exciplex than the fluorescent stilbene–TMA exciplex, k_{qe} must be greater for the diamine than the monoamine. The 2:1 statistical factor may account for part or all of the reactivity difference in this case as well as for Dabco vs. Abco.

In contrast to the behavior of the diaminoethane, the diaminopropane and butane display limiting quantum yields for *cis*-stilbene formation, $\phi^0_{cs'}$, substantially lower than the monoamine values (Table I). Thus the presence of the second nitrogen does result in quenching of the exciplex intersystem crossing process. In the case of the diaminobutane, the value of $\phi_{cs'}$ is low and independent of amine concentration. For the diaminopropane, values of $\phi_{cs'}$ decrease slightly with increasing amine concentration reaching the same limiting value as for the diaminobutane (Figure 5).

The contrasting behavior of the three diaminoalkanes can be readily explained by stereoelectronic control of intramolecular amine dimer cation radical formation. Optimum orbital overlap for three-electron σ bonding can be achieved in a six-membered ring without the introduction of ring strain (eq 10). Modest ring



(10)

strain would be expected for the five-membered ring and substantial ring strain for the four-membered ring. For the corresponding disulfides the order of stability of the intramolecular disulfide cation radicals with ring size is five > six >> four.[3] The enhanced stability of the five- vs. six-membered ring is consistent with the larger C–S vs. C–N bond distance.

The observation of an unquenchable component of *cis*-stilbene formation in the reactions of the diaminopropane and butane suggests that ca. 20% of the stilbene–diamine excited complex undergoes intersystem crossing. This plausibly reflects the initial interaction of a single nitrogen lone pair with singlet stilbene to form an exciplex which must undergo a conformational change (eq 10) prior to triplex formation (Scheme II). Assuming that the rate of intersystem crossing is the same as that for monoamine exciplexes, the rate constant for the conformational change is ca. 4×10^7 s^{-1}. This value is similar to the rate constant for γ-hydrogen abstraction in triplet valerophenone, a process with low activation energy (ca. 0.13 eV) which also requires the freezing out of several rotational degrees of freedom in the transition state.[35]

Exciplex Quenching Mechanism. The inter- and intramolecular quenching of the exciplexes of singlet *trans*-stilbene with monoamines and diaminoalkanes is proposed to occur via the formation of a triplex in which the two nitrogen atoms interact to form a three-electron σ bond (eq 1 and 10). This proposal is uniquely consistent with the observation of a steric effect on the quenching reactivity of monoamines and the effect of chain length on the reactivity of diaminoalkanes. The results for both monoamines and diaminoalkanes indicate that the quenching mechanism involves the interaction of two nitrogen atoms on the same (rather than opposite) side of the stilbene molecular plane. Furthermore the higher rate constant for the exciplex quenching by Abco vs. TEA establishes that triplex formation need not occur by back-side attack of neutral nitrogen on positively charged nitrogen. Thus the stilbene–amine exciplex does not have a well-defined geometry, requiring overlap of the stilbene-π and amine lone pair orbitals, like that of aromatic hydrocarbon–aniline exciplexes.[36]

Decay of the singlet triplex without formation of *cis*-stilbene might occur either directly via internal conversion, or via a triplet triplex which does not form triplet stilbene (Scheme II). Intersystem crossing is the predominant pathway for decay of the exciplex of stilbene both with monoamines and with diamines which cannot form a three-electron σ bond (Dabco and the diaminoethane). It seems unlikely that the increased interaction between nitrogens in the triplexes vs. Dabco exciplex would result in a total change in the decay pathway from intersystem crossing to nonradiative decay. Grellmann and Suckow[4] have in fact observed enhanced intersystem crossing for the anthracene–diethylaniline triplex vs. exciplex.

If the singlet triplex decays via intersystem crossing to the triplet triplex, the question remains as to why triplet stilbene is formed efficiently from the *trans*-stilbene exciplexes (including that with Dabco) but not from the *trans*-stilbene triplexes (Scheme II). Efficient formation of triplet *trans*-stilbene from the singlet exciplex is expected in cases where the triplet energy of *trans*-stilbene (2.12 eV) lies below the triplet exciplex or ion pair state energy.[4,37] As shown in Figure 7, this is the case for monoamine exciplexes. Alder, et al.[1b] have estimated the bond dissociation energy for the three-electron σ bond of the diamine in eq 1 as 0.67 eV. If triplex formation lowers the exciplex energies (Table II) by this amount,

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then the triplex energies will be lower than the *trans*-stilbene triplet energy (Figure 7).

Concluding Remarks. The results of this investigation demonstrate that the photophysical behavior of stilbene–amine exciplexes in nonpolar solvent is highly dependent upon amine structure and concentration due to varying degrees of interaction between positively charged and neutral nitrogen. For the sterically hindered amine EDA there is no evidence for nitrogen–nitrogen interaction. For the 1,2-diaminoalkanes Dabco and tetramethyl-1,2-diaminoethane, weak thru-bond interactions[1] result in enhanced exciplex intersystem crossing without diminishing the efficiency of triplet *trans*-stilbene formation. For the less hindered monoamines TEA, TMA, and Abco and the 1,3- and 1,4-diaminoalkanes, formation of a triplex in which the two amine nitrogens form a strong three-electron σ bond accounts for exciplex quenching and the concomitant quenching of triplet *trans*-stilbene formation. In the accompanying paper our investigations of the interactions of singlet stilbene with monoamines and diaminoalkanes in polar solvent are described.

Experimental Section

Materials. *trans*-Stilbene (Aldrich) was recrystallized once from benzene and twice from absolute ethanol. Diisopropylethylamine, triethylamine, *N,N,N',N'*-tetramethyl-1,4-butanediamine, *N,N,N',N'*-tetramethyl-1,3-propanediamine, and *N,N,N',N'*-tetramethylethanediamine (all Aldrich) were distilled under reduced pressure. 1,4-Diazabicyclo[2.2.2]octane (Aldrich) and 1-azabicyclo[2.2.2]octane (Aldrich) were sublimed. Spectroquality benzene (Aldrich) was refluxed over sodium and distilled.

Stilbene Isomerization. Oxygen-free samples were prepared by purging with prepurified nitrogen. Samples were irradiated on a merry-go-round apparatus immersed in a water bath. Monochromatic 313-nm light was provided by a potassium chromate filter solution. Light intensities were measured by stilbene actinometry.[21] The extent of *trans*-stilbene isomerization was determined with a Varian 3700 dual flame ionization gas chromatograph with a 6 ft × $^1/_8$ in. column containing 5% SF-96 on Chromasorb G.

Spectroscopic Studies. Fluorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrofluorimeter. Oxygen quenching of fluorescence was investigated by first purging the samples with nitrogen, followed by extended oxygenation (1 atm). Nanosecond exciplex lifetimes were determined via single photon counting techniques with excitation wavelength at 315 nm and observation at $\lambda > 455$ nm.[38] Subnanosecond fluorescence decay kinetics were studied by means of a "Synchroscan" streak camera, in conjunction with UV picosecond pulses (2 ps) for excitation ($\lambda = 300$ nm; frequency doubled output of a rhodamine 6G dye laser synchronously pumped by an acoustooptically mode-locked Ar^+ laser). The streak image was monitored by an optical multichannel analyzer and the decay curve stored in a minicomputer.[39] Due to abnormal electronic jitter in the oscillator of the streak camera, the time resolution was limited to about 60 ps. The deconvolution of the decay curve with the exciting laser pulse (half-width 60 ps) profile still allowed determination of lifetimes of the order of 20 ± 5 ps. Fluorescence lifetimes and amplitude ratios were derived by a least-square fit procedure.[40] To distinguish between *trans*-stilbene and exciplex fluorescence Kodak wratten filters have been applied in the detection channel.

Acknowledgment. Financial support of the Deutsche Forschungsgemeinschaft and the National Science Foundation (CHE80-26020) and compensation of travel expenses by NATO Research Grant No. 1911 are gratefully acknowledged. We thank Dr. G. Woolfe and P. Geiselhart for their assistance in the picosecond measurements and Professor A. Weller for illuminating discussions and correspondence.

Registry No. EDA, 7087-68-5; TEA, 121-44-8; TMA, 75-50-3; Abco, 100-76-5; Dabco, 280-57-9; tetramethyl-1,2-ethanediamine, 110-18-9; tetramethyl-1,3-propanediamine, 110-95-2; tetramethyl-1,4-butanediamine, 111-51-3; *trans*-stilbene, 103-30-0.

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trans-Stilbene–Amine Exciplexes. Behavior of the Exciplex, Solvent-Separated Radical Ion Pair, and Free Radical Ions

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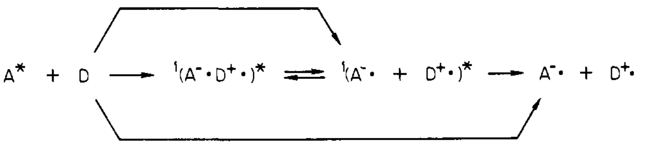
Abstract: The interaction of singlet *trans*-stilbene with several trialkylamines and diamines in acetonitrile solution has been investigated by a combination of steady-state measurements and time-resolved resonance Raman spectroscopy. Adduct formation between *trans*-stilbene and acyclic monoamines is proposed to occur via a short-lived exciplex (contact radical ion pair) intermediate, which is not quenched by ground-state amine. A solvent-separated radical ion pair is formed either directly from an encounter complex or via the exciplex and decays by intersystem crossing to yield triplet *trans*-stilbene, dissociation to yield free radical ions, or quenching by ground-state amine. Intersystem crossing is more rapid for the diamines vs. monoamines, resulting in a lower yield of free radical ions. Quenching of the solvent-separated radical ion pair by ground-state amine is subject to the same stereoelectronic effect as observed for exciplex quenching in nonpolar solvent. Free *trans*-stilbene anion radical decay is by recombination with amine cation radical and is independent of amine structure or concentration.

Photoinduced electron transfer between neutron electron donor (D) and acceptor (A) molecules leads to the formation of a pair of radical ions, $A^{-}\cdot$ and $D^{+}\cdot$.[1,2] As is the case for classical ion pairs,[3] it is possible to distinguish spectroscopically between contact radical ion pairs (exciplexes), solvent-separated ion pairs, and separated free radical ions. Time-resolved spectroscopic investigations have established that diffusive encounter of an excited singlet state acceptor and ground-state donor in polar solvent can result in initial formation of either an exciplex $^1(A^{-}\cdot D^{+}\cdot)^*$ or solvent-separated $^1(A^{-}\cdot + D^{+}\cdot)^*$ ion pair (Scheme I).[1,2] Long-

Scheme I. Formation of Radical Ion Pairs and Free Radical Ions



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