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trans-Stilbene–Amine Exciplexes. Photochemical Addition of Secondary and Tertiary Amines to Stilbene

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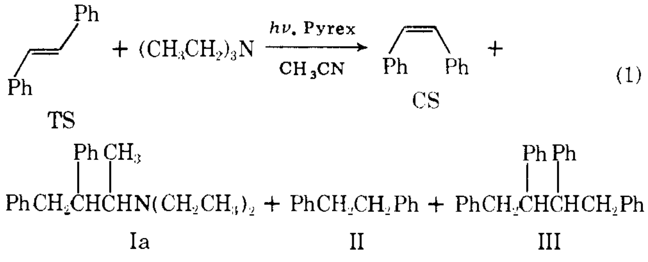
Abstract: The fluorescence of *trans*-stilbene is quenched by several secondary and tertiary amines. Quenching by tertiary amines in nonpolar solvents is accompanied by the appearance of exciplex fluorescence. The temperature dependence of fluorescence quenching by secondary and tertiary amines in polar and nonpolar solvents is indicative of reversible exciplex formation in all cases. Addition of the α C–H bond of tertiary amines to singlet stilbene occurs only in polar aprotic solvents. Electron transfer from the tertiary amine to stilbene apparently must precede proton transfer. The addition of the N–H bond of secondary amines to stilbene occurs in all aprotic solvents. The behavior of exciplexes formed from *trans*-stilbene with secondary and tertiary amines and conjugated dienes is compared.

Stilbene and other diarylethylenes undergo a number of photochemical addition reactions with electron-rich[2,3] and electron-poor[4] alkenes, dienes,[5,6] and amines.[7] We have recently characterized the exciplex intermediates in the photochemical [$_{\pi}2_s + _{\pi}2_s$] cycloaddition reactions of *trans*-stilbene and diphenylvinylene carbonate with conjugated dienes.[6] Frontier orbital interactions in these π-donor–π-acceptor exciplexes appear to determine product stereochemistry and regiochemistry. Recent investigations of the reactions of singlet *trans*-stilbene with amines have established that secondary amines add to stilbene in nonpolar solvents, whereas no reaction occurs with primary or tertiary amines.[7] Exciplex fluorescence has been observed from *trans*-stilbene–*N*-methylpyrrole and exciplex intermediates postulated for the addition of secondary amines.[7b] We were interested in comparing the behavior of n-donor–π-acceptor type exciplexes with our results for π–π type exciplexes and thus have investigated the interactions of singlet *trans*-stilbene with several secondary and tertiary alkyl amines.

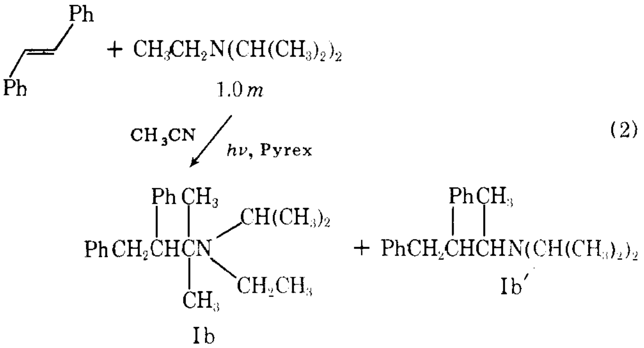
Results

Product Studies. Irradiation of an acetonitrile solution of *trans*-stilbene (0.01 *m*) and triethylamine (1.0 *m*) results in the formation of diastereomeric *N,N*-diethyl-1-methyl-2,3-diphenylpropylamine (Ia), 1,2-diphenylethane (II), and 1,2,3,4-tetraphenylbutane (III) along with isomerized stilbene (eq 1). The diastereomeric amine adducts were not separable by vapor phase or column chromatography; however, the ^{13}C NMR spectrum of the mixture showed two signals of approximately equal intensity for all saturated carbons, indicating the formation of a mixture of diastereomers. The mass spectrum of Ia and other stilbene–amine adducts are remarkably simple and of considerable value in confirming structure assignments (see Experimental Section). Quantum yields for product formation at several amine concentrations are given in Table I. Formation of addition (Ia) and reduction (II, III) products was not detected when photolyses were carried out in hexane, diethyl ether, or ethyl acetate solvents. Quantum yields for formation of Ia in mixed ether–acetonitrile solvent increase with acetonitrile content (Table II). The failure of Kawanisi and Matsunaga[7a] to observe products from irradiation of stilbene in neat triethylamine (ϵ = 2.4 D) is consistent with these observations.



$$\text{TS} + (CH_3CH_2)_3N \xrightarrow[CH_3CN]{h\nu,\ \text{Pyrex}} \text{CS} + \underset{\text{Ia}}{PhCH_2\overset{Ph}{C}H\overset{CH_3}{C}HN(CH_2CH_3)_2} + \underset{\text{II}}{PhCH_2CH_2Ph} + \underset{\text{III}}{PhCH_2\overset{Ph}{C}H\overset{Ph}{C}HCH_2Ph} \quad (1)$$

Irradiation of *trans*-stilbene and diisopropylethylamine in acetonitrile solution similarly results in addition of an amine α C–H bond to stilbene. The complicated ^{13}C NMR spectrum of the amine addition product indicated the formation of both possible adducts, one as a pair of diastereomers (eq 2). Quantum yields for formation of amine adduct (Ib and Ib′), diphenylethane, and tetraphenylbutane are given in eq 2.



$$\text{TS} + \underset{1.0\,m}{CH_3CH_2N(CH(CH_3)_2)_2} \xrightarrow[CH_3CN]{h\nu,\ \text{Pyrex}} \underset{\text{Ib}}{PhCH_2\overset{Ph}{C}H\overset{CH_3}{C}(CH_3)N(CH(CH_3)_2)(CH_2CH_3)} + \underset{\text{Ib}'}{PhCH_2\overset{Ph}{C}H\overset{CH_3}{C}HN(CH(CH_3)_2)_2} \quad (2)$$

Ib + Ib′ (Φ = 0.088) + II (Φ = 0.15) + III (Φ = 0.030)

Kawanisi and Matsunaga[7a] have reported the formation of *N,N*-diethyl-1,2-diphenylethylamine (Ic) and 1,2-diphenylethane (II) from the photolysis of stilbene in neat diethylamine. These products, alone with tetraphenylbutane (III), were isolated from photolyzed hexane solutions of 0.01 *m trans*-stilbene and 1.0 *m* diethylamine (eq 3). Quantum yields for formation of both addition and reduction products decrease

Table I. Quantum Yields for Products Formation from *trans*-Stilbene and Triethylamine in Acetonitrile Solution[a]

Et_3N, *m*	Φ_{add} (Ia)	Φ_{rdn} II	Φ_{rdn} III	Φ_{CS}
0.0	0	0		0.50
0.10	0.009	0.007		0.45
0.125	0.013	0.009		0.42
0.20	0.017	0.012		
0.25	0.022	0.017		0.40
0.50	0.038	0.023		0.32
0.75		0.030		0.26
1.0	0.052	0.036	0.020	0.23

[a] Degassed solutions containing 0.015 *m* *trans*-stilbene and 10^{-4} *m* octadecane internal standard.

Table II. Relative Quantum Yields for *trans*-Stilbene–Triethylamine Adduct Formation in Diethyl Ether–Acetonitrile Mixed Solvents[a]

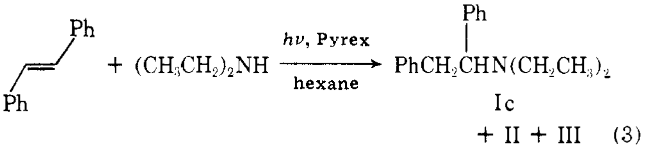
Solvent % CH_3CN	ϵ^b	Φ_{rel} (Ia)
0	3.9	0
20	7.6	0.1
40	15.4	0.5
60	21.2	0.8
80	26.9	1.0
100	32.6	1.0

[a] Table I, footnote *a*, 1.0 *m* amine. [b] Dielectric constant of ether–acetonitrile–1.0 *m* amine mixtures calculated assuming $\epsilon = \Sigma_i \epsilon_i V_i$, where V_i is the volume fraction of component *i*.

Table III. Quantum Yields for Product Formation from *trans*-Stilbene and Diethylamine[a]

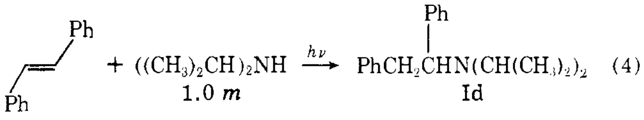
Solvent	Φ_{add} Ic	Φ_{rdn} II	Φ_{rdn} III
Hexane	0.091	0.060	0.026
Ethyl acetate	0.069	0.058	0.021
Acetonitrile	0.041	0.054	

[a] Table I, footnote *a*, 1.0 *m* amine.



$$\text{PhCH=CHPh} + (CH_3CH_2)_2NH \xrightarrow[\text{hexane}]{h\nu,\ \text{Pyrex}} \underset{\text{Ic}}{PhCH_2CH(Ph)N(CH_2CH_3)_2} + \text{II} + \text{III} \quad (3)$$

with increasing solvent polarity (Table III). Analogous products are obtained, albeit in lower quantum yield, with diisopropylamine (eq 4). Low molecular weight, nitrogen-con-



$$\text{PhCH=CHPh} + \underset{1.0\ m}{((CH_3)_2CH)_2NH} \xrightarrow{h\nu} \underset{\text{Id}}{PhCH_2CH(Ph)N(CH(CH_3)_2)_2} \quad (4)$$

$$\text{Id}\ (\Phi = 0.0094) + \text{II}\ (\Phi = 0.012) + \text{III}\ (\Phi = 0.0018)$$

taining products were present in all the photolysis mixtures but were not isolated or characterized.

Fluorescence Quenching and Exciplex Fluorescence. *trans*-Stilbene fluorescence[5d,6,8] is quenched by secondary and tertiary alkyl amines,[7b] but not by primary alkyl amines. Stern–Volmer plots for fluorescence quenching are linear for amine concentrations below 1.0 *m*, but display upward curvature at higher concentrations. Values of $k_q\tau$ obtained from the least-squares slopes of Stern–Volmer plots are given in Table IV along with the results of Kubota and Sakurai[7b] for quenching by pyrrole and *N*-methylpyrrole and the amine ionization potentials. For secondary amines, $k_q\tau$ values are slightly higher in hexane than in acetonitrile, whereas the opposite is observed for tertiary amines. Values of $k_q\tau$ for triethylamine are somewhat lower in alcohol solvents than in aprotic solvents (Table V). The effect of temperature on $k_q\tau$ values for stilbene fluorescence quenching by diisopropylamine and triethylamine was determined in hexane and acetonitrile solution (Table VI).

Table IV. Quenching of *trans*-Stilbene Fluorescence by Secondary and Tertiary Amines[a]

Amine	IP, eV[b]	$k_q\tau$, m^{-1} Hexane	$k_q\tau$, m^{-1} Acetonitrile
Dimethylamine	8.24	2.50	
Diethylamine	8.01	1.88	1.48
Diisopropylamine	7.73	0.74	0.57
Pyrrole	8.20	3.6[c]	
Trimethylamine	7.82	1.58	
Triethylamine	7.50	2.20	2.80
N,N-Diisopropylethylamine	7.2[d]	3.89	4.89
N-Methylpyrrole	7.8[d]	2.2[c]	

[a] Degassed solutions containing 1 × 10^{-4} *m* TS and 0.1–0.5 *m* amine excited at 320 or 322 nm (25 ± 2 °C). [b] K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26,** 1773 (1957). [c] Data from ref 7b, cyclohexane solution. [d] Estimated value.

Table V. Solvent Dependence of *trans*-Stilbene Fluorescence Quenching by Triethylamine[a]

Solvent	ϵ^b	$10^{10}k_{diff}$, m^{-1} s^{-1} [c]	$k_q\tau$, m^{-1}
Hexane	1.88	2.1	2.20 ± 0.09
Ethyl acetate	6.02	1.4	3.28 ± 0.08
Ethanol	24.5	0.55	0.54 ± 0.04
Methanol	32.7	1.1	0.47 ± 0.05
Acetonitrile	38.8	1.9	2.80 ± 0.3

[a] See Table I. [b] Dielectric constant of pure solvent. [c] Rate of diffusion at 20 °C.

Table VI. Temperature Dependence of *trans*-Stilbene Fluorescence Quenching by Diisopropylamine and Triethylamine[a]

	$k_q\tau$, diisopropylamine, m^{-1}		$k_q\tau$, triethylamine, m^{-1}	
Temp, °C[b]	Hexane	Acetonitrile	Hexane	Acetonitrile
5		0.27		
15			1.5	3.3
25	0.74	0.57	2.2	2.8
35	0.73	0.62	1.9	4.2
45	0.67	0.28	1.5	3.4
55	0.59		1.5	4.0

[a] See Table I. [b] ±1 °C.

Quenching of *trans*-stilbene fluorescence by tertiary alkyl amines or *N*-methylpyrrole[7b] in nonpolar solvents is accompanied by the appearance of structureless exciplex fluorescence at longer wavelengths than the residual stilbene fluorescence. No exciplex emission is observed for quenching by secondary alkyl amines or pyrrole.[7b] The quantum yield for exciplex fluorescence from *trans*-stilbene–diisopropylethylamine in hexane solution increases with amine concentration to a maximum value of 0.01 ± 0.005 at 1.0 *m* amine (83% quenching). The solvent dependence of the relative fluorescence intensity (I_{fex}) and position of the fluorescence maximum (ν_{max}) for this exciplex are given in Table VII. Exciplex fluorescence from *trans*-stilbene–1 *m* triethylamine in hexane is less intense and appears as a poorly resolved shoulder on the residual stilbene fluorescence (76% quenching). A discrete maximum can be observed for the weak exciplex fluorescence

Table VII. Solvent Dependence of *trans*-Stilbene-*N*,*N*-Diisopropylethylamine Exciplex Fluorescence in Ethyl Acetate-Hexane Mixed Solvent[a]

Solvent % ethyl acetate	ϵ^b	ν_{max}, cm^{-1} [c]	I_{fex}[d]
0	1.91	23 300	(1.0)
20	2.66	21 500	0.48
40	3.35	20 600	0.21
60	4.03	20 100	0.18
80	4.72	19 600	0.15
100	5.41	19 200	0.12

[a] Degassed solutions containing 1.0 *m* amine and 1 × 10^{-4} *m* trans-stilbene, λ_{ex} = 320 nm. [b] Dielectric constant of ethyl acetate-hexane-amine mixtures calculated assuming $\epsilon = \Sigma_i \epsilon_i V_i$, where V_i is the volume fraction of component *i*. [c] Maximum of exciplex fluorescence, ±500 cm^{-1}. [d] Relative intensity of exciplex fluorescence.

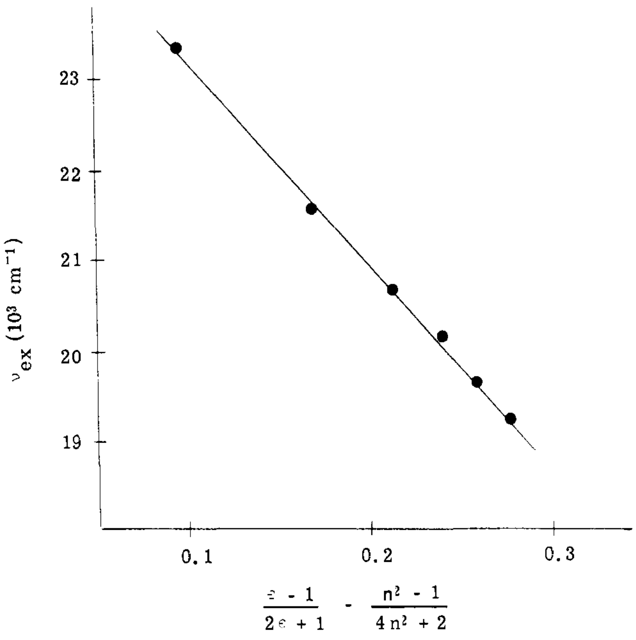


Figure 1. Frequency of *trans*-stilbene-diisopropylethylamine exciplex fluorescence maxima vs. solvent polarizability (eq 8).

in the more polar solvent ethyl acetate (ν_{max} = 19 900 cm^{-1}). No exciplex fluorescence is observed for *trans*-stilbene-1 *m* trimethylamine in hexane (61% quenching). The absorption spectra of *trans*-stilbene (0.01 *m*)-amine (1.0 *m*) solutions showed no evidence for ground state interactions.

The time dependence of the *trans*-stilbene-diisopropylethylamine exciplex fluorescence decay was determined using the single photon counting technique. For amine concentrations of 1.0, 1.2, and 1.4 in hexane solution, single exponential decay was observed in the time interval 15-50 ns following excitation, providing an exciplex lifetime of 16 ± 1 ns. At higher amine concentrations, more rapid and nonexponential exciplex fluorescence decay is observed. The lifetime of the *trans*-stilbene-triethylamine exciplex could not be measured accurately due to its low intensity and overlap with residual stilbene fluorescence, but is estimated to be ≤5 ns.

Discussion

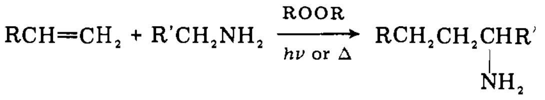
The photochemical reaction products of *trans*-stilbene with triethylamine (eq 1)[9] and diethylamine (eq 3) implicate the presence of free-radical intermediates in these reactions. Combination and disproportionation of the radical pair formed by α C-H homolysis of the tertiary amine (eq 5) and N-H homolysis of the secondary amine (eq 6)

$$PhCH{=}CHPh + (CH_3CH_2)_3N \xrightarrow{h\nu} PhCH_2\dot{C}HPh + (CH_3CH_2)_2N\dot{C}HCH_3 \quad (5)$$

$$PhCH{=}CHPh + (CH_3CH_2)_2NH \xrightarrow{h\nu} PhCH_2\dot{C}HPh + (CH_3CH_2)_2N\cdot \quad (6)$$

can account for the observed products. The ratio of diphenylethane/tetraphenylbutane for the triethylamine reaction is 1.8 (eq 1), much higher than the disproportionation/combination ratio for the diphenylethyl radical (0.113).[10a] Thus most of the diphenylethane must result from disproportionation of the initially formed radical pair (eq 5).

The photochemical reaction of stilbene with tertiary amines is formally analogous to the peroxide-initiated addition of amines to alkenes (eq 7).[10b] However, the latter reaction is a



$$RCH{=}CH_2 + R'CH_2NH_2 \xrightarrow[h\nu \text{ or } \Delta]{ROOR} RCH_2CH_2\underset{NH_2}{\underset{|}{CHR'}} \quad (7)$$

chain process with amine reactivity decreasing in the order primary > secondary > tertiary. Photochemical addition of the amine α C-H bond occurs only with tertiary amines in polar solvents and with quantum yields less than unity (Table I, eq 2). Certain aspects of the reaction of *trans*-stilbene with secondary amines are consistent with rate-determining N-H abstraction (eq 6); namely, the absence of a solvent effect upon reactivity and the decrease in reactivity with increasing size of the alkyl group (Table IV). However, such a mechanism cannot explain the complete lack of reactivity observed for primary alkyl amines.[7d]

The observation of exciplex fluorescence from *trans*-stilbene with trialkylamines in nonpolar solvents (Table VII) suggests that the exciplex may be an intermediate in the photochemical addition reaction[7b] and facilitates characterization of this intermediate. The exciplex dipole moment can be estimated from the variation of the exciplex emission maxima (ν_{max}) with solvent polarity according to

$$\nu_{max} = \nu_0 - \frac{2\mu^2}{hca^3}\left[\frac{\epsilon - 1}{2\epsilon + 1} + \frac{n^2 - 1}{4n^2 + 2}\right] \quad (8)$$

where ν_0 is the hypothetical gas phase emission frequency, μ is the dipole moment, a is the solvent cavity radius (assumed to be 4.5 Å), h is Planck's constant, c is the velocity of light, ϵ is the solvent dielectric constant, and n is the index of refraction.[11] From the plot of the ν_{max} data (Table VII) shown in Figure 1, a dipole moment of 14 ± 1 D is calculated for the *trans*-stilbene-diisopropylethylamine exciplex. This value is similar to those reported for a number of highly polar aromatic hydrocarbon-amine exciplexes.[12] The rate constant for exciplex fluorescence calculated from the limiting lifetime (14 ns) and fluorescence quantum yield is 7 × 10^5 s^{-1}, also in agreement with values for aromatic hydrocarbon-amine exciplexes.[13] The decrease in exciplex fluorescence intensity with increasing solvent polarity is analogous to observations for aromatic hydrocarbon-amine exciplexes.[14] Mataga[14b] has shown that the decrease in fluorescence intensity for the pyrene-*N*,*N*-dimethylaniline exciplex is accompanied by an increase in radical ion formation. Radical ion formation may result from dissociation of the polar exciplex or direct electron transfer from the ground state amine donor to the excited state electron acceptor.

Values of $k_q\tau$ for quenching of *trans*-stilbene fluorescence by tertiary amines increase with decreasing amine ionization potential. Such a trend is expected for formation of a charge-transfer stabilized exciplex. The variation in $k_q\tau$ with amine ionization potential is far too small for rate-determining exciplex formation, but is consistent with reversible exciplex formation.[6,15] For reversible exciplex formation (eq 9), the rate constant for fluorescence quenching is given by eq 10. Fluorescence and nonradiative decay are assumed to be the only deactivation processes occurring in nonpolar solvent. The observed increase in $k_q\tau$ with decreasing amine ionization potential probably reflects a decrease in the rate constant for exciplex dissociation (k_{-e}) rather than an increase in the rate constant for exciplex formation (k_e). The longer exciplex lifetime for stilbene–diisopropylethylamine vs. triethylamine (15 ns vs. ≤5 ns) supports this conclusion. Evidence for reversible exciplex formation is also provided by the temperature dependence of the fluorescence quenching data (Table VI). Unfortunately, analysis of *trans*-stilbene fluorescence quenching data is complicated by the observation of both prompt and delayed fluorescence from *trans*-stilbene,[8] both of which are probably quenched by amines. Assuming that the effective singlet lifetime of *trans*-stilbene either decreases or remains constant with increasing temperature, the data in Table VI indicate a negative or zero Arrhenius temperature coefficient for fluorescence quenching.[6b]

$$\begin{tikzcd} & & h\nu + \mathrm{TS} + \mathrm{R_3N} \\ \mathrm{TS}^* + \mathrm{R_3N} \arrow[r, shift left, "k_e"] & \left[\mathrm{TS}^{\delta}\text{-}\mathrm{R_3N}^{\delta+}\right]^* \arrow[l, shift left, "k_{-e}"] \arrow[ur, "k_f"] \arrow[dr, "k_d"'] & \\ & & \mathrm{TS} + \mathrm{R_3N} \end{tikzcd} \tag{9}$$

$$k_q = k_e\left(\frac{k_d + k_f}{k_{-e} + k_d + k_f}\right) \tag{10}$$

Product formation from stilbene–tertiary amines is only observed in polar aprotic solvents (Table II), whereas exciplex fluorescence is only observed in nonpolar solvents (Table VII). It appears likely that electron transfer to form a solvated ion pair precedes[14] formation of the radical pair responsible for product formation (eq 5). The interaction of *trans*-stilbene with tertiary alkyl amines can be summarized as shown in Scheme I. Plots of Φ_{add}^{-1} and Φ_{rdn}^{-1} vs. $[R_3N]^{-1}$ and Φ_{cs}^{-1} vs. $[R_3N]$ are linear, in agreement with Scheme I. The limiting quantum yield for triethylamine adduct formation in acetonitrile solution is 0.14 ± 0.1. Thus even under conditions of irreversible exciplex formation, one or more decay pathways compete with product formation, rendering fruitless attempts to obtain kinetic information from quantum yield data. The upward curvature of Stern–Volmer plots and decreased exciplex lifetime at high amine concentrations (>1 *m*) indicate that exciplex quenching by amine may occur, as is the case for the anthracene–dimethylaniline exciplex.[16]

Scheme I

$$\begin{tikzcd} \mathrm{TS}^\circ & \mathrm{CS} & \mathrm{TS}^\circ + \mathrm{R_3N} & \mathrm{TS}^\circ + \mathrm{R_3N} & \mathrm{TS}^\circ + \mathrm{R_3N} \\ \mathrm{TS}^* + \mathrm{R_3N} \arrow[u, "k_d"] \arrow[ur, "k_i"] \arrow[d, "k_f"] \arrow[rr, shift left, "k_e"] & & \left[\mathrm{TS}^{\delta}\text{-}\mathrm{RN_3}^{\delta+}\right] \arrow[ll, shift left, "k_{-e}"] \arrow[u, "k_{dex}"] \arrow[d, "k_{fex}"] \arrow[r, "k_{ip}"] & \mathrm{TS}^{-\cdot} + \mathrm{R_3N}^{+\cdot} \arrow[u, "k_{dip}"] \arrow[r, "k_r"] & \text{radicals} \arrow[u, "k_{dr}"] \arrow[d, "k_p"] \\ \mathrm{TS}^\circ + h\nu & & \mathrm{TS}^\circ + \mathrm{R_3N} + h\nu' & & \text{products} \end{tikzcd}$$

The modest increase in $k_q\tau$ values for quenching by tertiary amines in acetonitrile vs. hexane (Table IV) may result from product formation pathways for exciplex decay in the more polar solvent. Values of $k_q\tau$ are distinctly lower in methanol and ethanol than in aprotic solvents. Addition products are not observed in these solvents, whereas addition occurs in ether–acetonitrile mixed solvents with lower dielectric constants (Table II). It appears that hydrogen bonding of the amines with alcohols hinders both the exciplex formation and product formation steps.

The reactions of *trans*-stilbene[7b] and aromatic hydrocarbons[17] with secondary amines are thought to occur via exciplex intermediates, even though spectroscopic evidence for exciplex intermediates has been lacking. Zachariasse[18] has recently observed weak, short-lived exciplex fluorescence from pyrene with primary and secondary aryl amines. The short lifetimes (<3.5 ns) of these exciplexes result from rapid hydrogen transfer to form the dihydropyrenyl radical. The requirement of exciplex formation prior to hydrogen transfer offers an attractive explanation for the lack of reactivity of primary amines with *trans*-stilbene. The free energy for electron transfer from ground state amine to singlet stilbene can be calculated according to

$$\Delta G = E(\mathrm{D/D^+}) - E(\mathrm{A^-/A}) - E_s - \text{const} \tag{11}$$

where E_s is the stilbene singlet energy (3.53 eV) and the constant term is the energy required to bring the radical ions to the encounter distance (0.05 eV in acetonitrile).[19a] Using amine ionization potentials in place of oxidation potentials ($E(\mathrm{D/D^+}) = \mathrm{IP} - 6.5$ eV) electron transfer is calculated to be exothermic by 0.4 eV for triethylamine, slightly endothermic (0.1 eV) for diethylamine, and highly endothermic (0.8 eV) for ethylamine. Thus formation of a charge-transfer stabilized exciplex is unlikely for primary amines.

Evidence for exciplex formation from *trans*-stilbene with diisopropylamine is provided by the temperature dependence of the fluorescence quenching data (Table VI). Exciplex formation followed by hydrogen transfer (eq 12) provides an expression for the fluorescence quenching rate constant (eq 13) similar to eq 10. Rate constants for fluorescence quenching via exciplex formation are expected to increase with ground-state electron donor ability.[6,15,19] The results for the secondary amines in Table IV provide a unique exception to this generalization. A possible explanation for this observation is that the electron-deficient amine nitrogen in the exciplex is stabilized by electron-releasing alkyl groups, thus diminishing its acidity and the rate of proton transfer (k_H). The most stable exciplex is, in this case, the least reactive.[20] The decrease in product quantum yields for diisopropylamine (eq 4) vs. diethylamine (Table III) is even larger than the decrease in $k_q\tau$ value (Table IV). The diisopropylamino radical is known to disproportionate almost exclusively at low temperatures whereas the diethylamino radical yields comparable amounts of combination and disproportionation products.[21] Polar solvents are observed to decrease both the $k_q\tau$ value (Table IV) and the quantum yield for adduct formation with secondary amines (Table III). The solvent effects could again reflect a decrease in k_H upon solvent stabilization of the polar exciplex.

$$\begin{tikzcd} & & \text{radicals} \\ \mathrm{TS}^* + \mathrm{R_2NH} \arrow[r, shift left, "k_e"] & \left[\mathrm{TS}^{\delta}\text{-}\mathrm{R_2NH}^{\delta+}\right]^* \arrow[l, shift left, "k_{-e}"] \arrow[ur, "k_H"] \arrow[dr, "k_d"'] & \\ & & \mathrm{TS} + \mathrm{R_2NH} \end{tikzcd} \tag{12}$$

$$k_q = k_e\left(\frac{k_H + k_d}{k_{-e} + k_H + k_d}\right) \tag{13}$$

The reactions of *trans*-stilbene with secondary and tertiary amines are, in their gross mechanistic features, similar to those observed by Yang and Libman[17] for anthracene–amine reactions. Reversibly formed exciplexes are intermediates in both the secondary and tertiary amine reactions. Exciplex fluorescence is observed only when product formation is slow or absent, as is the case for tertiary amines in nonpolar solvents. Exciplex fluorescence ($k_f \sim 10^6$ s^{-1}) is too slow to compete efficiently with N–H hydrogen transfer from secondary amines. An important consequence of reversible exciplex formation is that fluorescence quenching does not provide the rate of exciplex formation, but rather a complex kinetic expression (eq 13).[15] As previously discussed, the normal increase in tertiary amine $k_q\tau$ values and abnormal decrease in secondary amine $k_q\tau$ values with decreasing amine ionization potential as well as the small solvent effects are consequences of reversible exciplex formation. Comparison of secondary and tertiary amine $k_q\tau$ values is most interesting in this context. Dimethylamine (IP = 8.24 eV) and triethylamine (IP = 7.50 eV) have nearly identical $k_q\tau$ values in spite of the substantial difference in their electron donor abilities. The greater stability (k_e/k_{-e}) of the tertiary amine exciplex is apparently offset by the greater reactivity (k_H) of the secondary amine exciplex. We suspect that a similar explanation can account for observations of carbonyl n,π^* triplet and singlet quenching by secondary vs. tertiary amines.[19c,22]

A comparison of the behavior of exciplexes formed by *trans*-stilbene with tertiary amines and conjugated dienes is given in Table VIII. The energies of the fluorescence maxima in hexane and the exciplex dipole moments indicate that the tertiary amine complex is more polar and more stable, as expected on the basis of its lower ionization potential. The larger $k_q\tau$ value for diene quenching and the shorter exciplex lifetime again illustrate the importance of product formation pathways in determining exciplex kinetics. On the basis of our results for stilbene and diarylethylene exciplexes, we propose that exciplex formation and stability are primarily functions of ground-state electron donor ability rather than donor type (n vs. π). Exciplex behavior, on the other hand, is highly dependent on the molecular structure of the electron donor.

Experimental Section

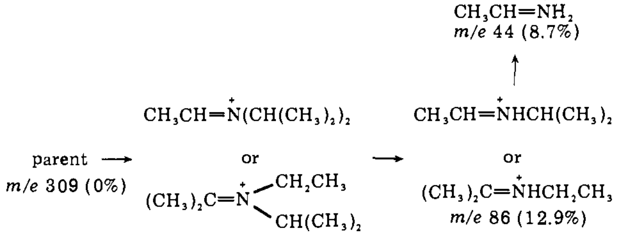
General Procedures. *trans*-Stilbene (Aldrich) was recrystallized twice from benzene and twice from 95% ethanol. Trimethylamine and dimethylamine (Eastman) and all other amines (Aldrich) were fractionally distilled prior to use. Solvents were purified and dried by standard techniques. Preparative photolyses were carried out under a nitrogen atmosphere using a Hanovia medium-pressure mercury lamp in a water-cooled Pyrex lamp well. Quantum yields were determined on degassed samples contained in sealed 15-mm o.d. Pyrex test tubes and irradiated on a merry-go-round apparatus, maintained at 25 ± 2 °C, using monochromatic 313-nm light, isolated using a potassium chromate solution filter. Irradiated solutions were analyzed by GC with a Hewlett-Packard 5750 dual-flame gas chromatograph using either a 5% SF-96 or 5% FFAP on Chromosorb G $^1/_8$ in. column.

Fluorescence spectra were recorded on a Perkin-Elmer MPF-2A spectrophotometer. The exciplex fluorescence quantum yield was determined using quinine bisulfate as a primary standard. Fluorescence lifetimes were measured using the single photon counting apparatus of Professor R. P. Van Duyne. NMR spectra were recorded on a Varian CFT 20 spectrometer and mass spectra on a Hewlett-Packard 5930A mass spectrometer using an ionizing voltage of 10 eV.

Irradiation of Stilbene and Triethylamine. A solution of 1.55 g (8.6 mmol) of *trans*-stilbene and 86 g (0.86 mol) of triethylamine in 860 mL of acetonitrile was irradiated for 12 h. Removal of most of the volatile components resulted in precipitation of 1,2,3,4-tetraphenylbutane. Fractional crystalization from benzene–hexane gave the pure meso isomer: mp 178–180 °C (lit.[23] 183–185 °C); ^{1}H NMR (CDCl$_3$) δ 2.3–3.3 (m, 6 H), 6.6–7.4 (m, 20 H). Chromatography of the photolysis mixture on 48 g of silica gel (2% ethyl acetate–hexane) afforded a pure sample of diastereomeric *N,N*-diethyl-1-methyl-2,3-diphenylpropylamine: ^{1}H NMR (CDCl$_3$) δ 0.6–1.2 (m, 9 H), 2.1 –3.9 (m, 8 H), 7.0 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 11.1, 12.4 (CH*C*H$_3$), 14.3, 15.2 (CH$_2$*C*H$_3$), 39.9, 40.6 (Ph*C*H), 43.6, 43.8 (Ph*C*H$_2$), 53.4, 54.0 (N*C*H$_2$CH$_3$), 58.9, 59.3 (NCH), 129–124 (aromatic); mass spectrum, eq 14.

$$\begin{tikzcd}
\underset{m/e\ 281\ (0\%)}{\text{parent}} \arrow[r] & \underset{m/e\ 100\ (100\%)}{CH_3CH{=}\overset{+}{N}(CH_2CH_3)_2} \arrow[dr] & \\
& \underset{m/e\ 44\ (6.9\%)}{CH_3CH{=}\overset{+}{N}H_2} & \underset{m/e\ 72\ (6.2\%)}{CH_3CH{=}\overset{+}{N}HCH_2CH_3} \arrow[l]
\end{tikzcd} \tag{14}$$

Irradiation of Stilbene and Diisopropylethylamine. A solution of 1.55 g (8.6 mmol) of *trans*-stilbene and 71 g (0.64 mol) of amine in 860 mL of acetonitrile was irradiated for 13 h. Removal of the volatile material followed by vacuum distillation of the residue yielded a yellow oil. Preparative gas chromatography gave a pure sample of amine adducts: ^{1}H NMR (CDCl$_3$) δ 0.6–1.3 (m, 15 H), 2.3–3.8 (m, 6 H), 7.1 (m, 10 H); mass spectrum, eq 15.



(15)

Irradiation of Stilbene and Diethylamine. A solution of 1.55 g (8.6 mmol) of *trans*-stilbene and 62.9 g (0.86 mol) of diethylamine in 860 mL of hexane was irradiated for 10.5 h. Removal of the volatile components followed by thick layer chromatography (Quanta PLQF 1000, ethyl acetate) of the residual oil afforded a pure sample of *N,N*-diethyl-1,2-diphenylethylamine: ^{1}H NMR (CDCl$_3$) δ 0.98 (t, 6 H), 2.52 (q, 4 H), 2.9–4.1 (m, 3 H), 7.0–7.2 (m, 10 H); mass spectrum, eq 16.

$$\underset{m/e\ 253\ (0\%)}{\text{parent}} \longrightarrow \underset{m/e\ 162\ (100\%)}{PhCH{=}\overset{+}{N}(CH_2CH_3)_2} \longrightarrow \underset{m/e\ 134\ (2.9\%)}{PhCH{=}\overset{+}{N}HCH_2CH_3} \tag{16}$$

Irradiation of Stilbene and Diisopropylamine. GC–mass spectral analysis of the photolysis mixture showed the major product to be the amine adduct: mass spectrum, eq 17.

$$\begin{tikzcd}
\underset{m/e\ 281\ (0\%)}{\text{parent}} \arrow[r] & \underset{m/e\ 190\ (100\%)}{PhCH{=}\overset{+}{N}(CH(CH_3)_2)_2} \arrow[r] & \underset{m/e\ 148\ (28\%)}{PhCH{=}\overset{+}{N}HCH(CH_3)_2} \arrow[d] \\
& & \underset{m/e\ 106\ (10.5\%)}{PhCH{=}\overset{+}{N}H_2}
\end{tikzcd} \tag{17}$$

Table VIII. Summary of *trans*-Stilbene–Tertiary Amine and Diene Exciplex Behavior

	Donor	
	Diisopropylethylamine	Diene[a]
Ionization potential, eV	7.2	7.8
$k_q\tau$, m^{-1} (hexane, 25 °C)	3.9	4.5
Exciplex ν_{max}, cm^{-1} (hexane)	23 300	23 800
Exciplex μ, D	14	<7
Exciplex τ, ns (hexane)	14	~1
Φ_{adduct} (hexane)	<0.001	0.83
(acetonitrile)	0.14	~0.5

[a] Data for 2,5-dimethyl-2,4-hexadiene from ref 6b.

Acknowledgment. Support of this work by the National Science Foundation (MPS 75-07181) is gratefully acknowledged. The authors thank R. P. Van Duyne for use of the single photon counting apparatus and B. Holman for the lifetime measurements.

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Chiroptical Properties of 1-Methyl-1,2,3,4-tetrahydroisoquinolines. A Semiempirical Quadrant Rule Based on One-Electron Theory[1]

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Received March 29, 1976

Abstract: Chiroptical properties of 1-methyl-1,2,3,4-tetrahydroisoquinolines are reviewed. Previously proposed empirical quadrant and segment rules for these compounds are discussed and some of the difficulties involved in their application pointed out. A semiempirical quadrant rule based on one-electron theory is developed, which is independent of the substitution pattern in the benzene ring. It is shown to apply correctly to twelve 1-methyltetrahydroisoquinolines of known absolute configuration, and is used to assign this in two cases where it is unknown.

The 1,2,3,4-tetrahydroisoquinolines comprise an important group of natural products[2] because of their biogenetic relationships to the morphine alkaloids. Many of the simple tetrahydroisoquinolines bear a substituent (usually methyl or benzyl) in the 1 position, and are optically active. Although ORD and CD spectra have been reported[3] for some of these compounds, there is no simple method which allows a correlation of chiroptical properties with their absolute configuration. Several quadrant and segment rules have been proposed,[4-6] utilizing different approaches, but none has, so far, proved to be generally applicable and independent of the substitution pattern in the benzene ring. The reasons for this are briefly discussed, and a semiempirical rule based on one-electron theory is outlined below.

Ultraviolet Spectra. Aromatic compounds usually show three major transitions between 180 and 300 nm; two strong absorption bands appear near 180 and 200 nm; and a weak band, usually showing considerable fine structure, appears at ~260 nm. These three transitions are designated ^1B_a, ^1L_a, and ^1L_b, respectively, in the Platt notation.[7] Since the intensity of an electronic transition is proportional to the square of the transition dipole moment vector, for the symmetric benzene itself the intensity of the ^1L_b transition is zero and is thus said to be "forbidden". Vibrational perturbations cause small distortions in the molecule resulting in a small net transition dipole moment, which accounts for the low intensity actually observed. The ^1L_a transition is only partially forbidden, and its intensity is therefore ~10 to 100 times higher. ^1B_a is an electronically "allowed" transition and is of far stronger intensity.

Substitution on the benzene ring results in changes of both the intensities and positions of the absorption bands. The simple tetrahydroisoquinoline alkaloids usually bear oxygen substituents at positions 6 and 7, and occasionally at 5 and 8. This substitution pattern results in a big change of the UV spectrum in comparison with benzene itself. Generally, the ^1L_b transition is shifted to 280 nm (20-nm bathochromic shift), while the ^1L_a transition is moved to 235 nm (35-nm bathochromic shift). Both shifts are accompanied by an increase in the extinction coefficient and loss of fine structure.

Theoretical studies[8,9] showed that such changes of intensity are caused by substitution perturbations so that the lower energy transitions mix with the allowed ^1B_a transition. The resultant electronic contribution to the intensity is of the same order of magnitude as the vibrationally induced ^1L_b intensity. Therefore, the effect is proportionately much greater for the ^1L_b transition than for the ^1L_a transition. The wavelength shift, however, is considered to arise from two different sources.[8,9] The first-order contribution comes from interactions of the lower energy transitions (^1L_a or ^1L_b) with a higher energy "charge-transfer" state of the substituent, i.e., overlap of the π orbital of benzene with the nonbonding p orbital of oxygen, and this effect is larger for ^1L_a than for ^1L_b. The second-order contribution again comes from the mixing of the ^1B_a transition with the ^1L_a or ^1L_b transition. In most cases, the net result is that the ^1L_a shift is greater than the ^1L_b shift and this is what