then be dc coupled to an oscilloscope thereby avoiding any distortion caused by ac coupling. The oscilloscope was triggered 300-1000 μs and 5-30 ms following the flash in order to record both a trace of the decay of the transmission signal and the 100% transmission signal. The relatively short delay (up to 30 ms) used between the recording of the two traces ensures that errors introduced by slow variations in analyzing beam intensity, and hence in the 100% transmission signal, are avoided. After each flash a shutter on the analyzing beam was activated and the offset voltage, used above to null the 100% transmission signal, was recorded. The oscilloscope traces were photographed by using a polaroid camera, the photographs projected, and the values of the signal as a function of time measured with a ruler. From the value of the offset signal (V_0) and the difference between the signal trace and the 100% transmission trace (V_t), absorbances were calculated as a function of time,

$$A_t = \log\,[V_0/(V_0 - V_t)] \tag{8}$$

Analysis of the Decay of 1-Phenyl-2-(2-naphthyl)ethene Triplets. A Nanosecond Laser Pulse Study[†]

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Contribution from the Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a.d. Ruhr, West Germany, and the Department of Chemistry, Florida State University, Tallahassee, Florida 32306. *Received April 13, 1981. Revised Manuscript Received June 24, 1981*

Abstract: Transients in the 100-ns range, observed by time-resolved laser irradiation of *trans*-1-phenyl-2-(2-naphthyl)ethene (*trans*-2-NPE) under triplet-sensitized excitation conditions in benzene at 25 °C, are assigned to 2-NPE triplets. The energy of the lowest triplet of 2-NPE is determined to be ~49 kcal/mol. Application of high energy sensitizers (e.g., xanthone, benzophenone) yields two transients of 2-NPE with T–T absorption maxima at ~400 and ~500 nm and lifetimes of 150 and 80 ns, respectively, whereas only one transient is observed by using fluorenone and benzanthrone as sensitizers. The transients are tentatively assigned to two sets of conformationally distinct triplet states. The triplets are efficiently quenched by azulene and oxygen. Analysis of the decay of 2-NPE triplets in the absence and presence of quenchers is based on a recently suggested model involving an equilibrium between trans and twisted triplet states ($^3t \rightleftarrows {}^3p$). The equilibrium constants (K) and the rate constants of intersystem crossing ($^3p \xrightarrow{k_d} \alpha{}^1t + (1-\alpha){}^1c$) are determined.

Involvement of triplet states in the direct cis–trans photoisomerization of 1-phenyl-2-(2-naphthyl)ethene (2-NPE) has been suggested by several authors.[1-7] However, strong evidence against a triplet mechanism for this reaction was presented recently.[8] Contrary to a proposed triplet lifetime of ~20 ns,[3] considerably longer lifetimes (104–150 ns) were inferred from the effects of azulene and oxygen on photostationary trans/cis ratios in the sensitized photoisomerization.[8] Azulene and oxygen effects have been demonstrated to provide a useful approach for determining the mechanism of stilbene triplet decay.[9,10] The effects of these quenchers on 2-NPE photostationary compositions were analyzed by using a model involving a rapidly established equilibrium between trans and twisted triplet states, eq 1, which was first

$$^3t \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^3p \tag{1}$$

proposed for stilbene by Hammond and co-workers.[11] Nanosecond pulse excitation of suitable sensitizers in the presence of either stilbene isomer gives transients with lifetimes in the vicinity of 60 ns which have been assigned to stilbene triplets.[12,13] For stilbene[12] and 4-nitrostilbene[14,15] the decay behavior of these transients has been shown to be consistent with eq 1.

In this work we report on the observation of the 2-NPE triplets following nanosecond laser irradiation using several high-energy triplet donors. Lifetimes of 2-NPE triplets measured as a function of oxygen and azulene concentrations give values for equilibrium constants, $K = k_1/k_{-1}$, and rate constants, k_d, for intersystem crossing, $^3p \rightarrow \alpha{}^1t + (1-\alpha){}^1c$, which are in good agreement with data from steady-state irradiation measurements obtained for the sensitized photoisomerization of 2-NPE.[8]

Experimental Section

The third harmonic of a nanosecond Nd laser (pulse width 10 ns, pulse energy ≤50 mJ) was used for excitation at 353 nm. For excitation at 420 nm a dye laser (dye: Stilben 3 in methanol, Lambda Physik), pumped by the 353-nm pulse of a Nd laser (J.K. Lasers), was used.[16] Transient absorptions were monitored on a transient digitizer (Tektronix R 7912), data analyses were carried out on a PDP 11 computer, and the laser flash photolysis system was the same as described elsewhere.[12,15] Unless otherwise indicated the samples were deoxygenated either by purging with argon or by three freeze–pump–thaw cycles on a vacuum line. Air- and oxygen-saturated solutions were prepared by purging with the respective gases. *trans*-2-NPE was the same as in ref 8, and azulene (Aldrich 99.6%) was used as received. The sensitizers were purified by zone refining (z) or recrystallization (r) or were used as received, and the purity was determined by GC analysis: xanthone (EGA, 99.8%), benzophenone (EGA, z, 99.5%), anthraquinone (J. Hinton, z, 99.6%), 2-

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[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

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Table I. Quenching Rate Constant of the Triplet of Several Sensitizers by *trans*-2-NPE and Transient Lifetimes in the Absence and Presence of Oxygen[a]

no.	sensitizer (E_T, kcal/mol)	λ_{obsd}, nm	$10^9 k_q$, M^{-1} s^{-1}	τ_0,[b] ns	τ_a, ns	τ_{ox}, ns
1	xanthone (74)	630	7			
		500, 550		77[c] (70)[d]	45	18
		400, 440		152[c] (120)	62	22
2	benzophenone (68.5)	535, 650	6			
		500		87[c] (70)	48	19
		400, 440		143[c] (140)	67	21
3	anthraquinone (62.4)	650	4			
		550		~100	~50	
		430		160		
4	2-acetonaphthone (59.3)	600	5			
		500		~110	75	
		400		160	70	
5	2-nitronaphthalene (56.8)	650	6			
		550		80	50	
		420		150	62	
6	fluorenone (53.3)	435, 700	3			
		450, 550		90	~50	~20
	fluorenone (53.3)[e]	450, 500		~83		
7	pyrene (48.7)	415	1.5			
8	benzanthrone (47)[e]	460, 500	0.6	~100	~60	
9	acridine (45.3)	430	⩽0.08			
10	anthracene (42.5)	420	⩽0.04			

[a] In benzene solutions at 25 °C; λ_{exc} = 353 nm unless otherwise indicated. [b] Experimental error for τ_0 of ±10% from the average deviation from the mean of at least 10 determinations. [c] Samples were degassed by three freeze-pump-thaw cycles (1 × 10^{-5} torr). [d] Values in parentheses refer to 70 °C. [e] λ = 420 nm.

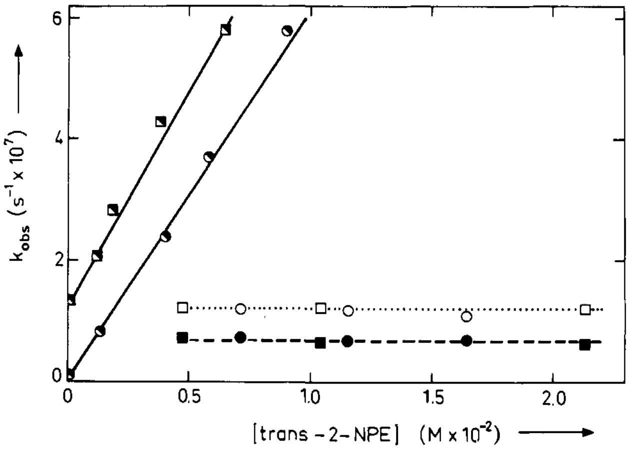

Figure 1. First-order decay rate constants of the transients plotted as a function of the concentration of *trans*-2-NPE at 630 nm (□, ○, full line), 500 nm (□, ○, dotted line), and 400 nm (■, ●, dashed line) in benzene solutions at 25 °C using 2 × 10^{-2} M xanthone (squares) and 2 × 10^{-2} M benzophenone (circles) as sensitizers (λ_{exc} = 353 nm).

acetonaphthone (Eastman, 99.9%), 2-nitronaphthalene (K. and K. Lab., 99.6%), fluorenone (Fluka, r, 99.5%), pyrene (Fluka, z, 98%), acridine (Fluka, 99%), anthracene (EGA, z, 99%), and benzathrone (r, 99%) [supplied by H. Gruen]. Benzene (thiophene-free) was purified by distillation over sodium.

Results

Benzophenone and Xanthone. Results for these two sensitizers are described separately because they are considered to be the most reliable. Pulsed excitation of benzene solutions of benzophenone or xanthone, (1–5), × 10^{-2} M, at 353 nm gives ketone triplet state transient absorptions which exhibit first-order decay in the presence of *trans*-2-NPE. Rate constants, k_{obsd}, obtained by monitoring decay at the wavelengths of maximum sensitizer T–T absorption, λ_{obsd}, depend linearly on the concentration of added *trans*-2-NPE. The slopes of plots of k_{obsd} vs. [*trans*-2-NPE] (Figure 1) give quenching rate constants, k_q, which are close to the diffusion-controlled limit (Table I).

Two new transients, one in the range of about 380–450 nm and the other one in the range of about 490–550 nm, appear in the presence of *trans*-2-NPE (Figure 2). With use of [*trans*-2-NPE] = 1 × 10^{-2} M, the same transient spectra are obtained after ~30 ns with either benzophenone or xanthone as triplet excitation donors while at shorter times the spectra differ due to (1) different T–T absorption maxima and triplet decay of the two sensitizers within the duration of the laser pulse (~10 ns) and (2) transient absorption at λ > 550 nm owing to direct excitation of *trans*-2-NPE at 353 nm (Figure 2). At [*trans*-2-NPE] > 1 × 10^{-2} M competing absorption by *trans*-2-NPE at 353 nm significantly reduces the optical density of the sensitizer triplet. In the absence of sensitizers a weak transient at ~430 nm (lifetime >1 ms) and a further short-lived (lifetime ≤10 ns) transient at λ > 550 nm ($\lambda_{max} \gtrsim$ 750 nm) are observed. The latter absorption is tentatively assigned to an $S_n \leftarrow S_1$ transition since lifetimes of 3–5 and 25–28 ns have been reported for the short- and long-lived components of fluorescence decay of *trans*-2-NPE in hydrocarbon solutions, respectively.[17,18] The transient absorption spectra presented in

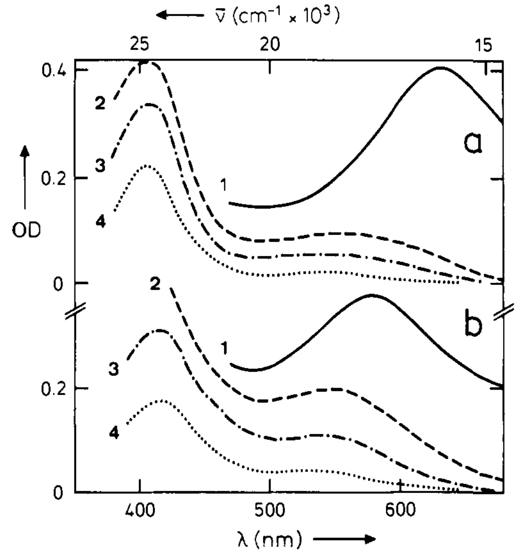

Figure 2. Time-resolved transient absorption spectra of *trans*-2-NPE, 7 × 10^{-3} M, in benzene solutions at 25 °C under (a) xanthone- and (b) benzophenone-sensitized excitation conditions, 2 × 10^{-2} M, (λ_{exc} = 353 nm) at the maximum of optical density (1, —) and 50 ns (2, ---), 100 ns (3, -·-), and 200 ns (4, ···) after the laser pulse.

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Table II. Data Obtained from Quenching of the 2-NPE Transients by Oxygen and Azulene[a]

no.	sensitizer	λ_{obsd}, nm	$10^9 s_{ox}$, M^{-1} s^{-1}	r_{ox}, M^{-1}	$10^9 s_{az}$,[b] M^{-1} s^{-1}	r_{az}, M^{-1}
1	xanthone	500, 550	5.6	430	3.6	280
		400, 440	5.2	790	2.7	410
2	benzophenone	500	5.6	490	3.6	310
		400, 440	5.2	740	2.7	390
3	anthraquinone	550	~6.2	~620 (875)[c]	~5.0	~500 (322)
4	2-acetonaphthone	500	2.6	290		
		400	5.0	750		
5	2-nitronaphthalene	550	4.6	370		
		420	5.8	880		
6	fluorenone	450, 550	~5.5	~500 (1050)	~3.0	~270 (240)
8	benzanthrone[d]	460, 550	~4.1	~410 (728)	~5.0	~500 (325)

[a] Triplet-sensitized excitation in benzene at 25 °C; λ_{exc} = 353 nm unless otherwise indicated. [b] Experimental error for s_{az} of ±15% and ±30% for sensitizers 1, 2 and 3, 6, 8, respectively. [c] Values in parentheses obtained from photostationary trans/cis ratios, see Table III. [d] λ_{exc} = 420 nm.

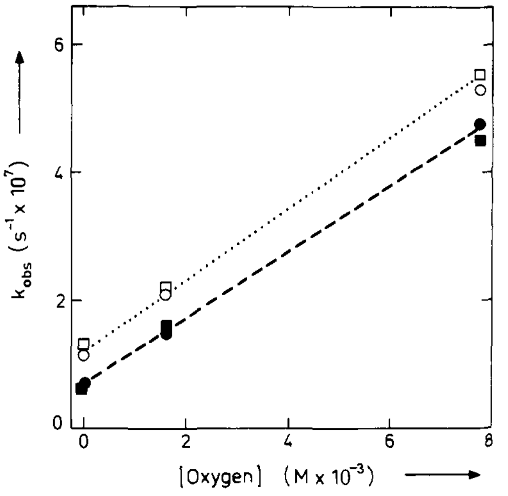

Figure 3. First-order decay rate constants of the transients of *trans*-2-NPE, 2 × 10^{-2} M, as a function of oxygen concentration at 400 nm (■, ●, dashed line) and 500 nm (□, ○, dotted line) under xanthone- (squares) and benzophenone-sensitized (circles) excitation conditions in benzene at 25 °C.

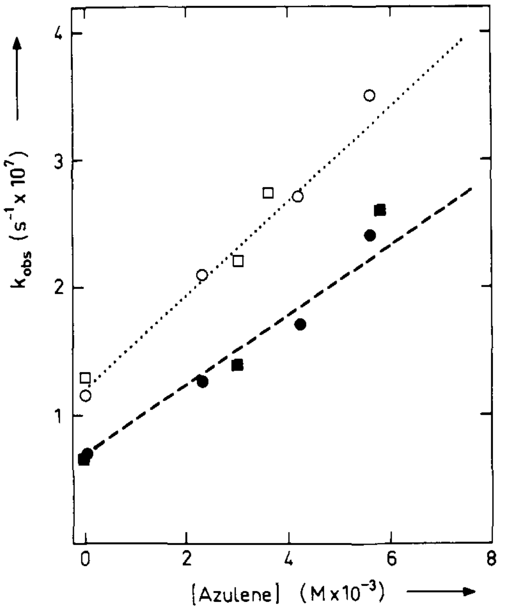

Figure 4. First-order decay rate constant of the transients of *trans*-2-NPE, 2 × 10^{-2} M, as a function of the azulene concentration at 400 nm (■, ●, dashed line) and 500 nm (□, ○, dotted line) under xanthone- (squares) and benzophenone-sensitized (circles) excitation conditions in benzene at 25 °C.

Figure 2 therefore reveal the presence of at least four species: (1) a "400-nm transient" and (2) a "500-nm transient", both formed by transfer of triplet energy from the sensitizer to *trans*-2-NPE, (3) the triplet states of the sensitizers, and (4) a short-lived transient, probably a conformer of the first excited singlet of *trans*-2-NPE.

Decay of the transients at 400 and 500 nm, evaluated at times of ~50 and 20 ns after the laser pulse, respectively, is of first-order; the decay rate constants, $k_{obsd} = \tau^{-1}$, are independent of [*trans*-2-NPE] in the range of 3 × 10^{-3} to 2 × 10^{-2} M and are identical, within experimental error, for the two sensitizers (Figure 1). Substantial fluorescence intensity from *trans*-2-NPE in the 380–450-nm region, even in the presence of sensitizers, gives rise to a large emission signal, $\tau \lesssim 10$ ns, and an additional smaller pulse caused by electronic reflection in the cable between the photomultiplier and the transient digitizer, which reduce the accuracy of measurements in this wavelength range. Only small changes in transient lifetimes are observed at 400 and 500 nm on increasing the temperature up to 70 °C (Table I).

The lifetimes of the 400- and 500-nm transients in argon-, air-, and oxygen-saturated solutions (τ_0, τ_a, and τ_{0x}, respectively) are given in Table I. Plots of k_{obsd} vs. [O_2] are linear within experimental error (Figure 3). No discernible difference is found when xanthone is replaced by benzophenone (Table I). Values of slopes (s_{0x}) and slope/intercept ratios (r_{ox}) from these plots are given in Table II.

The effect of azulene on the 2-NPE transient decay rate constants is shown in Figure 4. Values of slopes (s_{az}) and slope/intercept ratios (r_{az}) obtained from these linear plots are given in Table II. Azulene concentrations were kept below 8 × 10^{-3} M because at higher [Az] absorption by azulene at 350 nm and in the 450–700-nm region severely attenuates excitation of the sensitizer and transmission of analyzing light, respectively. A further transient below 420 nm, which appeared also in the absence of *trans*-2-NPE, has been assigned recently to a T–T absorption of the azulene triplet.[19]

Other Sensitizers. Triplet excitation transfer rate constants to *trans*-2-NPE were determined for a series of donors, $E_T \geq 42.5$ kcal/mol. As described for xanthone and benzophenone, k_q values were set equal to the slopes of linear plots of k_{obsd} vs. [*trans*-2-NPE] (Table I). A plot of log k_q vs. E_T is shown in Figure 5.

With fluorenone as the donor, (1–5) × 10^{-2} M, formation of a 2-NPE transient is observed when [*trans*-2-NPE] is sufficiently large, ≥5 × 10^{-3} M, to reduce the lifetime of fluorenone triplets to well below 100 ns. A single new transient could be discerned whose decay, monitored at 450 or 550 nm, corresponds to a lifetime of ~90 ns which is independent of [*trans*-2-NPE] in the 5 × 10^{-3} to 2 × 10^{-2} M range. However, the presence of a longer lived 400-nm transient cannot be excluded because the fluorenone results are less reliable than those employing either xanthone or benzophenone due to the following complications: (1) pronounced absorption by ground-state fluorenone, whose spectrum extends

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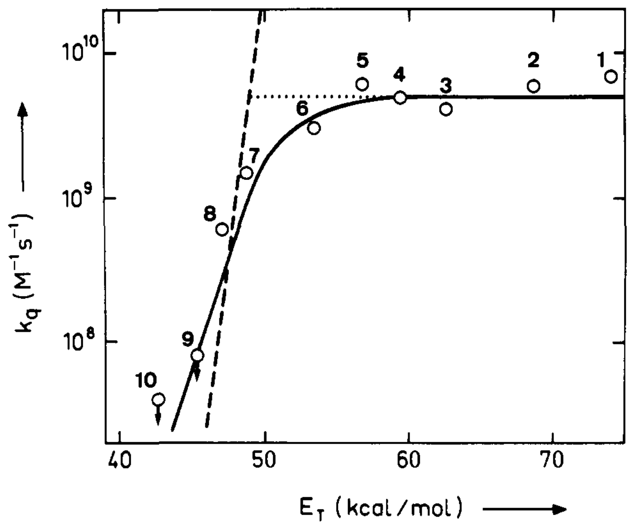

Figure 5. Logarithmic plot of the quenching rate constants of the triplets of various sensitizers by *trans*-2NPE vs. sensitizer triplet energy in benzene at 25 °C. The sensitizers and λ_{obsd} are as indicated in Table I; the dashed line refers to $\Delta\log k_q = \Delta E/2.3RT$ where ΔE is the difference in triplet energies between the sensitizers and 2-NPE.[20]

to ~440 nm, prevents transient absorption measurements at $\lambda \leq 430$ nm; (2) fluorenone fluorescence, ranging from 430 to 660 nm, interferes with monitoring of transient absorptions at times shorter than 20 ns following the excitation pulse; (3) the T–T absorption spectrum of fluorenone, extending from 420 to 700 nm with a significant maximum at ~435 nm, strongly overlaps the region of 2-NPE T–T absorption making the assignment of absorption to a specific transient difficult. To varying degrees, these difficulties were also encountered with 2-acetonaphthone, anthraquinone, and benzanthrone as sensitizers. Nevertheless, the approximate results obtained in these cases are important because they involve sensitizers employed in steady-state measurements and are included in Tables I and II.

As with xanthone and benzophenone, two 2-NPE transients, one in the 400–450 nm and the other in the 500–550 nm range, are observed with anthraquinone, (1–3) × 10^{-2} M, 2-acetonaphthone, (1–3) × 10^{-3} M, and 2-nitronaphthalene, (1–3) × 10^{-3} M as sensitizers. With benzanthrone, as with fluorenone, only one transient in the 430–550-nm range and $\tau_0 \approx 90$ ns could be assigned to 2-NPE. That the same transient is obtained from these two sensitizers is suggested by oxygen and azulene quenching observations which are independent of sensitizer within experimental error (Table II). The significance of the observation of a single 2-NPE transient is unfortunately clouded by the difficulties described in the preceding paragraph. In an attempt to improve the reliability of these results, fluorenone and benzanthrone were also excited at 420 nm by using Nd laser-pumped dye laser.[16] Since *trans*-2-NPE does not absorb at 420 nm, neither the short-lived transient at $\lambda > 550$ nm nor *trans*-2-NPE fluorescence are observed. Although, due to a low pulse energy of ~1 mJ, the optical density of the 2-NPE transient was small (≤ 0.1), the lifetime and quenching data obtained are practically the same as those obtained with $\lambda_{exc} = 353$ nm.

Discussion

Transient Observations. The transients observed at 400 and 500 nm with use of high-energy triplet sensitizers are assigned to triplet states of 2-NPE. This assignment is based on the following results. (1) The transients are formed by energy transfer from triplet donors to *trans*-2-NPE. Values of k_q are close to the diffusion-controlled limit for high-energy sensitizers and decrease markedly below $E_T \simeq 50$ kcal/mol (Figure 5). (2) The transient lifetimes at 400 and 500 nm are strongly reduced by azulene, $E_T = 39$ kcal/mol,[20] and oxygen (see Figures 3 and 4 and Table II). (3) Quenching data obtained for 2-NPE by laser flash kinetic spectroscopy are in satisfactory agreement with photochemical quenching results obtained under steady-state irradiation conditions employing triplet excitation donors[8] (see below).

Table III. Data Obtained from the Effect of Azulene and Oxygen on Photostationary Trans/Cis Ratios of 2-NPE[8]

sensitizer (E_T, kcal/mol)	r_0,[a] M^{-1}	$k_c\alpha/k_t(1-\alpha)$[b]	k_{ox}/k_d,[c] M^{-1}	k_{az}/Kk_d,[d] M^{-1}
anthraquinone (62.4)	644	0.90	875	322
fluorenone (53.3)	480	0.51	1050	240
benzanthrone (47)	650	0.30	728 868[e]	325

[a] Slope/intercept ratios of the plots of $([t]/[c])_s$ vs. [Az], eq 7, in the absence of oxygen. [b] Intercepts of the plots of $([t]/[c])_s$ vs. [Az], eq 7. [c] From oxygen attenuation of the azulene effect, eq 8, unless otherwise indicated. [d] Obtained from r_0 and assuming $\alpha = 0.5$, see text. [e] From oxygen attenuation of the benzanthrone effect.

It has been shown by several authors that noninterconverting conformers of the excited singlet state play an important role in the fluorescence behavior of 1,2-diarylethylenes.[17,18,21-23] By analogy, the existence of two different conformers of trans as well as twisted triplet states of 2-NPE has been suggested recently.[8] In view of this and the recent spectroscopic observation of the trans triplet state of stilbene[12] the 400- and 500-nm transients are tentatively assigned to the two conformers of the *trans*-2-NPE triplet state.

The observed decay rate constants of the 2-NPE transients can be interpreted by using eq 2 which is based on the simplified

$$k_{obsd} = \frac{Kk_d}{1+K}\left(1 + \frac{k_{ox}}{k_d}[O_2] + \frac{k_{az}}{Kk_d}[Az]\right) \tag{2}$$

reaction scheme used in the analysis of the steady-state irradiation observations obtained for 2-NPE, eq 1 and 3–5. Equation 2,

$$^3p \xrightarrow{k_d} \alpha{}^1t + (1-\alpha){}^1c \tag{3}$$

$$^3t + Az \rightarrow {}^1t + {}^3Az \tag{4}$$

$$^3p + O_2 \xrightarrow{k_{ox}} \alpha{}^1t + (1-\alpha){}^1c + O_2 \tag{5}$$

where $K = k_1/k_{-1}$, obtains provided that equilibration between (^3t) and perpendicular (^3p) triplet conformations is fast relative to triplet decay, i.e., $k_1, k_{-1} >> k_d, k_{az}[Az], k_{ox}[O_2]$. This reaction scheme has also been applied to the interpretation of steady-state and transient kinetic observations involving triplet states of stilbene[11,12] and 4-nitrostilbenes.[14,15] According to eq 2 the slopes of Figures 3 and 4 give $s_{ox} = k_{ox}K/(1+K)$ and $s_{az} = k_{az}/(1+K)$, respectively, and the reciprocals of the intercepts give 2-NPE triplet lifetimes (eq 6).

$$\tau_0 = (1+K)/Kk_d \tag{6}$$

Previously, estimates of $1/k_d$ were assumed to give effective triplet lifetimes of stilbene[24] and the 2-NPE's.[8] As is clear from eq 6 that assumption holds only when the equilibrium in eq 1 strongly favors twisted conformations, i.e., $K >> 1$.

Comparison with Steady-State Observations. Slope/intercept ratios from the plots in Figures 3 and 4 give r_{ox}/k_d and $r_{az} = k_{az}/Kk_d$ values, respectively (Table II), which can be compared with corresponding parameters derived from steady-state observations. The mechanism in eq 1 and 3–5 predicts that for sensitized cis–trans photoisomerization stationary trans/cis ratios should vary with azulene and oxygen concentrations as shown in eq 7, where k_c and k_t are rate constants for triplet excitation transfer from the sensitizer to *cis*- and *trans*-2-NPE, respectively. When excitation transfer from the sensitizer (e.g., benzanthrone,

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(24) Saltiel, J.; Thomas, B. *J. Am. Chem. Soc.* **1974**, *96*, 5660.

$$\left(\frac{[\mathrm{t}]}{[\mathrm{c}]}\right)_{\mathrm{s}} = \left(\frac{k_{\mathrm{c}}}{k_{\mathrm{t}}}\right)\left(\frac{\alpha}{1-\alpha}\right)\left(1 + \frac{k_{\mathrm{az}}}{\alpha K(k_{\mathrm{d}} + k_{\mathrm{ox}}[\mathrm{O_2}])}[\mathrm{Az}]\right) \tag{7}$$

E_T = 47 kcal/mol) to *trans*-2-NPE is reversible, a more complete expression is required for data analysis.[8] In such cases eq 7 can be applied following extrapolation to the zero sensitizer concentration limit. Photostationary state data plotted according to eq 7 give straight lines with intercepts $k_c\alpha/k_t(1-\alpha)$ and slope/intercept ratios $r_0 = r_{az}/\alpha$ and r_a for degassed and air-saturated solutions, respectively. Ratios k_{ox}/k_d are calculated by using eq 8. Results obtained for anthraquinone, fluorenone, and benzanthrone as sensitizers are shown in Table III.[8]

$$\frac{k_{\mathrm{ox}}}{k_{\mathrm{d}}} = \frac{r_0 - r_{\mathrm{a}}}{r_{\mathrm{a}}[\mathrm{O_2}]} \tag{8}$$

The constants K, k_d, k_{az}, and k_{ox} in the quantities in Table III represent weighted averages of the corresponding rate constants defined by the transient kinetic measurements because the mechanism in eq 1 and 3–5 does not distinguish between the two sets of isomeric 2-NPE triplet states. It is more proper, therefore, to compare ranges of rate constant ratios rather than specific values. The range k_{ox}/k_d values, 730–1050 M^{-1}, obtained from the steady-state measurements (Table III), is clearly in satisfactory agreement with the range, 400–800 M^{-1}, obtained from the transient measurements (Table II). Comparison of r_{az} and r_0 values is hampered by the fact that the effective decay fraction α is not known. As with other constants in eq 7 α reflects the weighted decay behavior of two sets of 2-NPE triplets, and since weighting factors can differ from sensitizer to sensitizer, it need not be a constant. Of the sensitizers employed in the steady-state irradiation measurements, only anthraquinone can be considered to behave as a "high-energy sensitizer", i.e., $k_c = k_t$ (Table I and Figure 5). Since its stationary trans/cis ratio is nearly unity in the absence of azulene,[4,8,25] a value of $\alpha = 0.5$ is tentatively applied to the r_0 values to generate the entries in the last column of Table III. In view of the experimental uncertainties involved and the assumption of a constant α, the agreement between the range of k_{az}/Kk_d values estimated from the steady-state observations, 240–325 M^{-1} (Table III), with the range of values obtained from the transient observations 300–500 M^{-1} (Table II), is again satisfactory.

The Equilibrium Constant *K*. A thorough study of the temperature and viscosity dependence of rate constants, k_{in}, for triplet excitation transfer from indeno[2,1-*a*]indene (a rigid *trans*-stilbene model) to azulene has led to the conclusion that the process is fully diffusion controlled.[26] Adjusting the empirical k_{in} value in toluene for the change in viscosity gives $k_{in} = 8.6 \times 10^9$ M^{-1} s^{-1} for benzene at 25 °C. The conclusion that this value is very close to the diffusion-controlled limit is supported by measurements of the quenching of the triplet states of several aromatic compounds ($E_T \geq 45$ kcal/mol) by azulene which give an average value of quenching rate constants in benzene solutions of 7.4 × 10^9 M^{-1} s^{-1}.[12,19] The 2-NPE results can now be analyzed further by assuming $k_{az} = k_{in} = k_{dif}$ in eq 9.

$$K = (k_{\mathrm{az}}/s_{\mathrm{az}}) - 1 \tag{9}$$

The more precise s_{az} values, determined with xanthone and benzophenone as sensitizers (Table II), give K = 1.4 and 2.2 for the 500- and the 400-nm transients, respectively (Table IV). The approximate s_{az} values listed in Table II for anthraquinone, fluorenone, and benzanthrone give $\sim 0.7 \leq K \leq \sim 1.9$ for molecular species whose decay was monitored in the 450–550-nm region. Both the wavelength region and the range of K are consistent with the tentative conclusion that these species are identical with the 500-nm transient observed with the higher triplet energy donors. The τ_0 values listed in Table I are in good agreement with this conclusion since the average τ_0's are 84 ± 5 ns for the 500-nm transient (sensitizers 1, 2, 5, 6) and 153 ± 5 ns for the 400-nm transient (sensitizers 1–5). The best K's and these narrowly defined average lifetimes substituted into eq 6 give values of intersystem crossing rate constants, k_d, corresponding to ^{3}p decay, of 2.1 × 10^7 and 1.0 × 10^7 s^{-1} for the 500- and the 400-nm transients, respectively. These can be compared with k_d's calculated by using data obtained separately with each sensitizer (Table IV). Also listed in Table IV are rate constants, $k_{ox} = r_{ox}k_d$, for the quenching of twisted 2-NPE triplets by oxygen, 7.5 × 10^9 and 9.6 × 10^9 M^{-1} s^{-1} for the 400- and 500-nm transients, respectively.

Table IV. Conformational Equilibrium Constants and Rate Constants for Radiationless Decay and Quenching by Oxygen for 2-NPE Triplets

sensitizer	λ_{obsd}, nm	K^a	$10^7 k_d$,[b] s^{-1}	$10^9 k_{ox}$,[c] M^{-1} s^{-1}
xanthone	500, 550	1.4 ± 0.4	2.2 ± 0.4	9.5
	400, 440	2.2 ± 0.5	1.0 ± 0.3	7.6
benzophenone	500	1.4 ± 0.4	2.0 ± 0.4	9.8
	400, 440	2.2 ± 0.5	1.0 ± 0.3	7.4
anthraquinone	550	~0.7	~2.4	~15
fluorenone	450, 550	~1.9	~1.7	~8.5
benzanthrone	460, 500	~0.7	~2.4	~9.8

[a] Obtained from s_{az} (Table II) and $k_{az} = k_{in} = 8.6 \times 10^9$ M^{-1} s^{-1}, using eq 9, see text. [b] Obtained from τ_0 (Table I) and K, using eq 6. [c] Obtained from r_{ox} (Table II) and k_d.

It follows from the equilibrium constants that, although the twisted triplet conformations are favored for each isomer, they are not favored as strongly as in the stilbene case.[9,12,13,27] If 30–40% of the 2-NPE triplets, depending on conformation, are transoid, then quenching of ^{3}t by oxygen must be much slower than quenching of ^{3}p in order to account for the absence of oxygen effect on the intercepts of the stationary state plots.[8] Rate constants for the quenching of a series of rigid aromatic hydrocarbon triplet states by oxygen, k_{ox}, are inversely dependent on E_T of the quenched molecules.[28,29] The value of k_{ox} increases as E_T decreases. For pyrene whose triplet energy, 48.7 kcal/mol, is very close to that of ^{3}t (Figure 5) the empirical rate constant in benzene is 2.2 × 10^9 M^{-1} s^{-1}.[29] The k_{ox} values in Table IV are 2–5 times larger than this value, reflecting in part a threefold increase of the spin-statistical factor for spin-exchange vs. electronic energy transfer.[30] This difference is apparently sufficient to make any dependence of trans/cis photostationary states on oxygen difficult to detect experimentally. Such dependence has been detected for 3,3-dimethyl-1-(2-naphthyl)-1-butene[31] where steric hindrance in ^{3}p conformations may cause a further decrease in K. The possibility also exists that changes in trans/cis compositions due to quenching of ^{3}t by oxygen are compensated by changes due to quenching of ^{3}p, i.e., α in eq 3 larger than α in eq 5. A precedent for this suggestion is provided by spin-exchange quenching of stilbene ^{3}p triplets by di-*tert*-butyl nitroxide.[32] The k_d values of 1.0 × 10^7 and 2.1 × 10^7 s^{-1} obtained for the 400- and 500-nm transients, respectively, are very close to k_d = 1.8 × 10^7 s^{-1}, the value determined recently for stilbene.[12]

The small decreases in τ_0 for each 2-NPE triplet at 70 °C, (Table I) may reflect slight shifts of the equilibrium compositions toward twisted conformations at the higher temperature. With use of eq 6, it can readily be shown that, if the k_d's are temperature independent, a less than twofold increase in the values of K would

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account for the observed changes in τ_0. An even lower sensitivity to a similar temperature increase has been observed for stilbene triplets in several solvents,[12] which may indicate that, in that case, K remains sufficiently large in the 25–100 °C range for τ_0 to be dominated by a temperature independent k_d. A shift of the equilibrium composition toward twisted conformations of the stilbene triplet state can be inferred, however, from an analysis of the temperature dependence of the azulene effect on sensitized cis–trans photoisomerization.[9,33]

The Energy of 2-NPE Triplets. The Sandros plot in Figure 5 indicates an effective energy of ~49 kcal/mol for the lowest *trans*-2-NPE triplets.[20,34] Steady-state measurements indicating that triplet excitation transfer to *trans*-2-NPE is irreversible with fluorenone but reversible with benzanthrone as donor[8] are nicely consistent with this energy. Thus, in addition to strong similarities in decay and quenching behavior, the 2-NPE triplets are very similar to stilbene triplets with respect to energetics.[11,35] This conclusion is consistent with the absorption spectrum of *trans*-2-NPE in ethyl iodide which yielded 53 kcal/mol as an upper limit for its triplet energy.[36] The results clearly show that the lowest 2-NPE triplet states can best be described as substituted olefin triplets rather than as perturbed naphthalene triplets as previously suggested.[36]

It is concluded that the transient kinetic observations confirm several of the key steps of the mechanism proposed for sensitized 2-NPE photoisomerization. Similar measurements using *cis*-2-NPE are planned in order to determine the degree to which the relative population of isomeric triplet states depends on the starting 2-NPE isomer. Isomerization quantum yield measurements, now in progress, may reveal variations of effective α with sensitizer and/or possible excitation transfer inefficiencies in the quenching of sensitizer triplets by the 2-NPE's: cf. ref 37 and 38.

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Liquid Crystalline Solvents as Mechanistic Probes. 6. Dynamic Quenching of Pyrene Fluorescence by 5α-Cholestan-3β-yldimethylamine in the Liquid Crystalline and Isotropic Phases of a Cholesteric Solvent[†,1]

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Abstract: A method is described for determining the specificity of quenching of pyrene singlets by a tertiary alkylamine, 5α-cholestan-3β-yldimethylamine (CA), in a nonpolar cholesteric liquid crystalline solvent [59.5/15.6/24.9 (w/w/w) cholesteryl oleate/cholesteryl nonanoate/cholesteryl chloride]. It is found that the pyrene–amine orientation for quenching resembles closely the probable exciplex geometry. Activation parameters for the quenching process are phase dependent: from Stern–Volmer derived quenching rate constants at low CA concentrations, the Arrhenius activation energies and preexponential factors in the cholesteric phase are calculated to be $E_6 = 9.9 \pm 0.2$ kcal mol^{-1} and $A_6 = (2.1 \pm 1.3) \times 10^{14}$ M^{-1} s^{-1}; the isotropic phase has $E_6 = 5.3 \pm 0.1$ kcal mol^{-1} and $A_6 = (1.8 \pm 0.4) \times 10^{11}$ M^{-1} s^{-1}. The value of E_6(cholesteric) is found to change with CA concentration, approaching E_6(isotropic) at high CA. A cohesive explanation of these and other results, including the previously reported photodimerization of acenaphthylene in a different cholesteric phase, is advanced.

The mechanism responsible for quenching excited singlet states of aromatic molecules by amines has been investigated extensively during the last several years.[2] Of particular interest has been the specific orientation between the lumophore and amine required for efficient quenching and those factors which lead to stable lumophore–amine excited-state complex (exciplex) formation.

The appearance of a new, red-shifted emission attributed to an exciplex accompanies the quenching of fluorescence of pyrene (P) by alkyl tertiary amines in several solvents of very different viscosity and polarity (usually $\epsilon < 8$). A large part of the exciplex stability can be ascribed to excited pyrene–amine charge-transfer interactions. The accepted geometry for the exciplex[3] places the orbital for the nitrogen lone pair of electrons directly above the π lobes of pyrene. Although specific in orientation, the interaction need not be axially symmetric as depicted in E.

The eventual fate of the exciplex is determined by its stabilization energy which mediates dissociation and by the availability of chemical and photophysical pathways (e.g., electron transfer to form separated ion radicals, intersystem crossing leading to triplets of pyrene and dissociated ground-state amine, and emission

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[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

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