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Concerning the Spin-Statistical Factor in the Triplet–Triplet Annihilation of Anthracene Triplets†[1a]

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Abstract: Rate constants for triplet–triplet annihilation (TTA) of anthracene triplets were determined in toluene and in benzene as a function of temperature, using flash kinetic spectroscopy. Plots of observed constants, κ, vs. T/η are linear as expected for a diffusion-controlled process. Effective rate constants k_2 for TTA, calculated from κ, are linearly dependent on experimental rate constants for fully diffusion-controlled triplet excitation transfer from ideno[2,1-*a*]indene to azulene in toluene, $k_2 = 0.57k_{\mathrm{dif}}$. This ratio and known delayed fluorescence efficiencies from TTA events in ethanol give $p_s = 0.046$ as the fraction of triplet–triplet (TT) encounters which generate excited anthracene singlets, $^1A^*$. The k_2/k_{dif} and p values lead to $p_t = 1.40$, the average number of triplets produced directly, by dissociation or decay of a given TT encounter pair (triplets formed through $^1A^*$ are excluded). It is suggested that part of the inefficiency in TTA of anthracene is due to rapid internal conversion of doubly excited triplet pairs to fully dissociative triplet excimers, and that the remaining inefficiency is due to dissociation of quintet pair states back to triplets. Quintet pair states are the probable source of $^1A^*$ and delayed monomer fluorescence, while singlet pair states probably give singlet excimer and anthracene dimer.

Spin-statistical factors are considered to play an important role in determining the efficiency of diffusion-controlled processes of reactants having electronic spins greater than zero. The quenching of triplet states of organic molecules by ground-state molecular oxygen[2-4] and coupling/disproportionation reactions of alkyl radicals[5,6] are important examples.

Interaction of two triplets of the same molecule in solution is known as triplet–triplet annihilation (TTA) because it provides an important triplet decay pathway. It often gives rise to monomer and excimer delayed fluorescence.[7,8] Rate constants for TTA are conveniently obtained from an analysis of the second-order component of the decay of triplet–triplet absorption following flash excitation.[9-13] The magnitude[9-13] and the temperature[10] and viscosity[12] dependence of these rate constants, k_2, suggest strongly that TTA is diffusion controlled and efficiency factors, p, have been calculated by using the Debye equation to estimate the rate constant for a diffusion-controlled reaction, k_{dif},

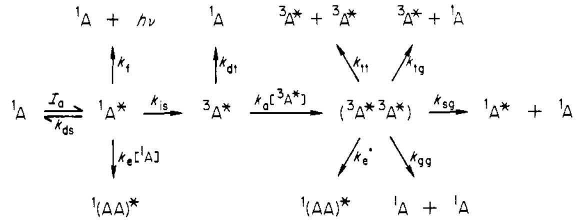
$$k_2 = pk_{\mathrm{dif}} = p8RT/\alpha\eta \tag{1}$$

Different authors have used either the standard Debye equation,[13] $\alpha = 3000$ (stick limit: large solutes, small solvents), or its modification,[12] $\alpha = 2000$ (slip limit: small solutes, large solvents). The limitations of this approach for obtaining p have been pointed out by Meyer and Nickel, who suggested using empirical rate constants, e.g., from triplet excitation transfer, for k_{dif} instead of theoretical values based on "the simplest conceivable model".[14]

In the course of a flash kinetic study of the temperature dependence of rate constants for endothermic triplet excitation transfer from anthracene to the stilbenes,[15] we have determined the temperature dependence of the second-order decay component of anthracene triplets. This paper describes an analysis of these results based on the Meyer and Nickel suggestion.

Kinetics and Results

Scheme I. Kinetics for Triplet Formation and Decay



^1A, ground-state singlet anthracene; $^1A^*$, lowest excited singlet state; $^3A^*$, lowest triplet state; $^1(AA)^*$, singlet excimer of anthracene; $(^3A^{*3}A^*)$, paired triplet state resulting from the encounter of two $^3A^*$

Kinetic Scheme I was used to represent the photophysical processes for anthracene. Applying the steady state approximation on $^1A^*$ and $(^3A^{*3}A^*)$ and assuming $I_a = 0$, following flash excitation, gives

$$-\frac{d[^3A^*]}{dt} = k_{dt}[^3A^*] + k_a(2 - p_t - p_s\phi_{is})[^3A^*]^2 \tag{2}$$

where k_{dt} represents all first-order and pseudo-first-order triplet anthracene decay processes, $p_t = (2k_{tt} + k_{tg})/(k_{tt} + k_{tg} + k_{sg} + k_{gg} + k_e')$ and $p_s = k_{sg}/(k_{tt} + k_{tg} + k_{sg} + k_{gg} + k_e')$are the probabilities that the paired triplet will give directly $^3A^*$ and $^1A^*$, respectively, and $\phi_{is} = k_{is}/(k_{ds} + k_f + k_{is} + k_e[^1A])$ is the intersystem crossing yield of $^1A^*$. Equation 2 has normally been expressed[9-13] as

$$-\frac{d[^3A^*]}{dt} = k_1[^3A^*] + k_2[^3A^*]^2 \tag{3}$$

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Table I. Temperature and Viscosity Dependence of κ in Toluene, Using Wide Band-Pass

set 1[c]			set 2[d]		
T, K	$T/\eta \times 10^{-4}$,[a] K/P	$\kappa \times 10^{-4}$,[b] s^{-1}	T, K	$T/\eta \times 10^{-4}$,[a] K/P	$\kappa \times 10^{-4}$,[b] s^{-1}
258.2	2.64	0.95	207.3	0.592	0.246
263.2	2.92	1.07 ± 0.07 (6)	218.1	0.863	0.349
268.2	3.22	1.24 ± 0.06 (8)	235.1	1.47	0.520
278.2	3.88	1.42 ± 0.10 (6)	246.7	2.03	0.760
288.2	4.62	1.75 ± 0.08 (8)	262.1	2.87	1.00
298.2	5.40	1.86 ± 0.10 (15)	279.6	3.97	1.39
308.2	6.29	2.26 ± 0.10 (8)	292.3	4.92	1.73
318.2	7.26	2.40 ± 0.10 (9)			

[a] See ref 6, Table I, for pertinent literature. [b] Limits are average deviations from the mean; given in parentheses are numbers of independent determinations. [c] This work. [d] Reference 10c, see text, band-pass not specified.

Analogy with eq 2 gives $k_1 = k_{dt}$ and $k_2 = k_a(2 - p_t - p_s\phi_{is})$, so that k_2 is not a proper rate constant as has often been assumed. Integration of eq 3 gives

$$[^3A^*]_t = k_1[^3A^*]_0/\{(k_1 + k_2[^3A^*]_0)e^{k_1t} - k_2[^3A^*]_0\} \quad (4)$$

where $[^3A^*]_0$ is the concentration of triplet anthracene at an arbitrary zero time and $[^3A^*]_t$ is the concentration at a later time t.[16] Substituting absorbances, A, for concentration terms in eq 4 yields

$$A_t = k_1A_0/\{(k_1 + \kappa A_0)e^{k_1t} - \kappa A_0\} \quad (5)$$

where $A = \epsilon_t[^3A^*]l$ and $\kappa = k_2/\epsilon_tl$.

Five solutions of anthracene in toluene (3.0, 5.0, 5.0, 5.0, and 7.5 × 10^{-5} M) were flashed and the decay of triplet anthracene absorbance recorded for temperatures ranging from 258 to 323 K. Since, initially, the aim was to obtain k_1 values,[15] wide slit widths on the monochromator which selected monitoring wavelengths were employed and no attempt was made to determine these wavelengths with precision. Consequently conversion of the resulting κ values to k_2 would require multiplication by an unknown effective extinction coefficient, $\bar{\epsilon}_t$. Two more anthracene solutions, one in toluene, 5.4 × 10^{-5} M, and one in benzene, 3.3 × 10^{-5} M, were therefore studied, using a 20 nm band-pass centered at 429 nm on the monochromator. Transient measurements for the toluene solution were also recorded, using a 6 nm band-pass centered at 429 nm. Values of k_1, κ, and A_0 were determined by iteratively fitting the predicted values of A_t from eq 5 to the observed values of A_t, using GENLSS, a general least-squares computer program.[17] A_0 was treated as a variable because it represents the absorbance at an arbitrary zero time and is no more reliable than the subsequent A_t values. Values of κ were independent of anthracene concentration and are reported in Tables I and II. As expected from previous work,[9-13] k_1 values did not show a consistent anthracene concentration dependence. Their range, <10^2 to 10^3 s^{-1}, was determined primarily by adventitious quenchers or residual oxygen.

Discussion

Livingston and Ware measured the temperature dependence of κ in several solvents, including toluene.[10c] The close correspondence of the slopes of Arrhenius plots of κ to the activation energies for viscous flow of each solvent provided strong support for the conclusion that TTA is diffusion controlled.[10c] Unfortunately, the values of κ were given in a figure in arbitrary units. The plots of κ vs. T/η (Figure 1) are consistent with eq 1 as expected for a diffusion-controlled process. The least-squares fit of our wide-band measurements to $\kappa = mT/\eta$ gives m = 0.353 ± 0.021 s^{-1} P K^{-1}.[18] Values of κ obtained from Figure 1 of ref 10c were adjusted to conform to m = 0.353 s^{-1} P K^{-1} by multiplying each value by the factor 0.67_1 (Table I). The two sets of data treated together give m = 0.353 ± 0.009 s^{-1} P K^{-1}, the smaller standard deviation apparently reflecting the greater precision of the earlier data.

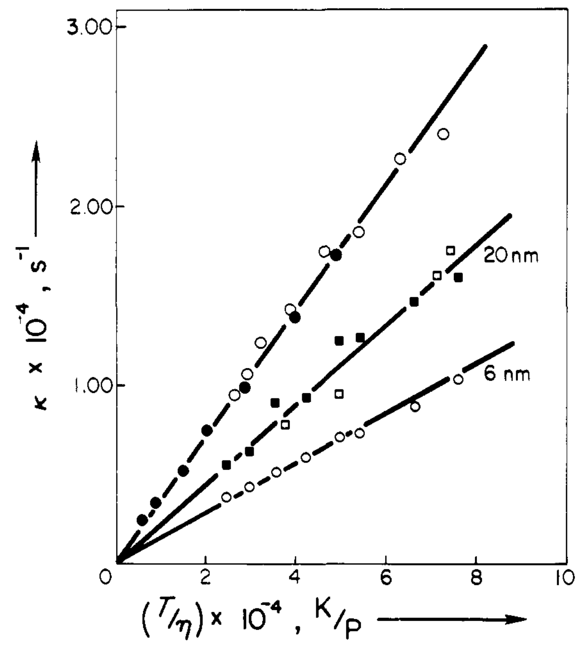

Figure 1. The dependence of κ on T/η in toluene: ○, this work, ●, ref 10c, see text; □, benzene; ■, toluene.

The good adherence of κ to the straight lines in Figure 1 suggests that the effective molar absorptivity for triplet anthracene, $\bar{\epsilon}_t$, which is contained in κ, is temperature independent in the 208–323 K range. The value of ϵ_t appears to be strongly solvent dependent.[20] In particular, the triplet–triplet absorption spectrum of anthracene in benzene is red shifted and exhibits broader, less intense absorption bands than in cyclohexane.[21,22] Ledger and Salmon's λ_{max} and ϵ_t values, 428.5 nm and (5.30 ± 0.19) × 10^4 M^{-1} cm^{-1}, and 422.5 nm and (8.57 ± 0.32) × 10^4 M^{-1} cm^{-1} in benzene and cyclohexane, respectively, seem to be the most reliable.[22] Somewhat larger λ_{max} and lower ϵ_t values were obtained earlier for these solvents by a less direct method.[21] The triplet–triplet absorption spectrum of anthracene in toluene (λ_{max} = 429 ± 1 nm, under our conditions) was assumed to be identical with the published spectrum in benzene.[22] Experimental support for this assumption is provided by the adherence of the T/η plots for benzene and toluene κ's, Table II, to the same line, Figure 1, when the same band-pass is employed. The effective transmittances, T_{eff}, were calculated from the measured band-passes and the triplet–triplet absorption spectrum, using

$$T_{eff} = \frac{\int_{-\infty}^{\infty} I_{0\lambda}10^{-\epsilon_{t\lambda}[^3A^*]l}\, d\lambda}{\int_{-\infty}^{\infty} I_{0\lambda}\, d\lambda} \quad (6)$$

for an arbitrary $[^3A^*]l$ value.[23] Effective extinction coefficients,

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Table II. Temperature and Viscosity Dependence of κ, Using Narrower Band-Pass[a]

toluene				benzene		
T, K	$T/\eta \times 10^{-4}$, K/P	$\kappa \times 10^{-4}$, s^{-1} (20 nm)[b]	$\kappa \times 10^{-4}$, s^{-1} (6 nm)[b]	T, K	$T/\eta \times 10^{-4}$,[c] K/P	$\kappa \times 10^{-4}$, s^{-1} (20 nm)[b]
253.2	2.39	0.56 ± 0.02 (3)	0.37 ± 0.02 (4)	283.2	3.74	0.79 ± 0.01 (2)
263.2	2.92	0.63 ± 0.02 (5)	0.45 ± 0.02 (4)	298.2	4.92	0.95 ± 0.03 (3)
273.2	3.54	0.91 ± 0.08 (3)	0.53 ± 0.03 (4)	313.2	6.33	1.61 ± 0.04 (2)
283.2	4.23	0.93 ± 0.12 (3)	0.58 ± 0.04 (4)	323.2	7.41	1.75 ± 0.03 (2)
293.2	4.99	1.25 ± 0.02 (2)	0.64 ± 0.03 (4)			
298.7	5.44		0.74 ± 0.02 (4)			
299.2	5.49	1.26 ± 0.03 (3)				
313.2	6.76	1.47 ± 0.13 (3)	0.87 ± 0.04 (4)			
323.2	7.75	1.60 ± 0.10 (7)	1.11 ± 0.10 (4)			

[a] See footnotes *a* and *b* in Table I. [b] Monitoring beam band-pass, see Experimental Section. [c] Viscosities from Lange, N. A., Ed. "Handbook of Chemistry," 9th ed.; Handbook Publishers: Sandusky, Ohio, 1956.

Table III. Temperature Dependence of k_2 and k_{dif} in Toluene

set 1[b]			set 2[c]		
T, K	$k_2 \times 10^{-9}$, $M^{-1}\,s^{-1}$	$k_{\text{dif}} \times 10^{-9}$,[a] $M^{-1}\,s^{-1}$	T, K	$k_2 \times 10^{-9}$, $M^{-1}\,s^{-1}$	$k_{\text{dif}} \times 10^{-9}$,[a] $M^{-1}\,s^{-1}$
258.2	2.74	4.76	207.3	0.71	1.30
263.2	3.09	5.26	218.1	1.01	1.80
268.2	3.58	5.80	235.1	1.50	2.83
278.2	4.10	6.97	246.7	2.19	3.72
288.2	5.04	8.26	262.1	2.90	5.15
298.2	5.37	9.69	279.6	3.99	7.14
308.2	6.53	11.2	292.3	4.97	8.83
318.2	6.93	12.9			

[a] From Arrhenius parameters in ref 6, see text. [b] This work. [c] From ref 10c, see text.

$\bar{\epsilon}_t$, were then obtained from the transmittance at $\lambda_{\max}$, $T_{\min}$, for the same $[^3A^*]l$ value, using

$$\bar{\epsilon}_t = \epsilon_{t\,\max} \frac{\log (1/T_{\text{eff}})}{\log (1/T_{\min})} \tag{7}$$

where $\bar{\epsilon}_{t\,\max} = 5.3 \times 10^4$ M^{-1} cm^{-1}.[22] This procedure gives $\bar{\epsilon}_t = 3.0_5 \times 10^4$ and $\bar{\epsilon}_t = 4.9_3 \times 10^4$ M^{-1} cm^{-1} for the 20 and 6 nm band-pass conditions. The ratio of these $\bar{\epsilon}_t$ values, 0.61_9, is in excellent agreement with the ratio of the slopes of the 6 and 20 nm band-pass lines in Figure 1, $(0.138 \pm 0.007)/(0.220 \pm 0.030) = 0.62_7$. The relative slope of the wide band-pass line in Figure 1 gives $\bar{\epsilon}_t = 1.9_2 \times 10^4$ M^{-1} cm^{-1} under these conditions. This value was used to convert the κ values in Table I to k_2's, Table III.

Evidence was recently presented suggesting strongly that triplet energy transfer from indeno[2,1-*a*]indene to azulene is fully diffusion controlled in toluene.[6] Arrhenius parameters obtained from measured rate constants (228–309 K)[6] were used to inter- and extrapolate the set of empirical k_{dif} values given in Table III: $k_{\text{dif}} = 10^{11.98} \exp(-1.36_9 \times 10^3/T)$. Since Figure 1 and previous work (see especially ref 10c and 12) establish that TTA is a diffusion-controlled process, $k_a = k_{\text{dif}}$. Substitution in the equation derived above gives $k_2 = k_{\text{dif}}\,(2 - p_t - p_s\phi_{is})$. A plot of k_2 vs. k_{dif} is shown in Figure 2. The slope of the best line through the origin is 0.57 ± 0.02.

Since $(2 - p_t - p_s\phi_{is}) = 0.57$ over the entire temperature range, either p_t, p_s, and ϕ_{is} are all insensitive to the temperature change or there is fortuitous compensation between changes in p_t and in $p_s\phi_{is}$. The results of several determinations give $\phi_f = 0.27 \pm 0.02$[24] and $\phi_{is} = 0.72 \pm 0.02$,[25] independent of solvent, for the fluorescence

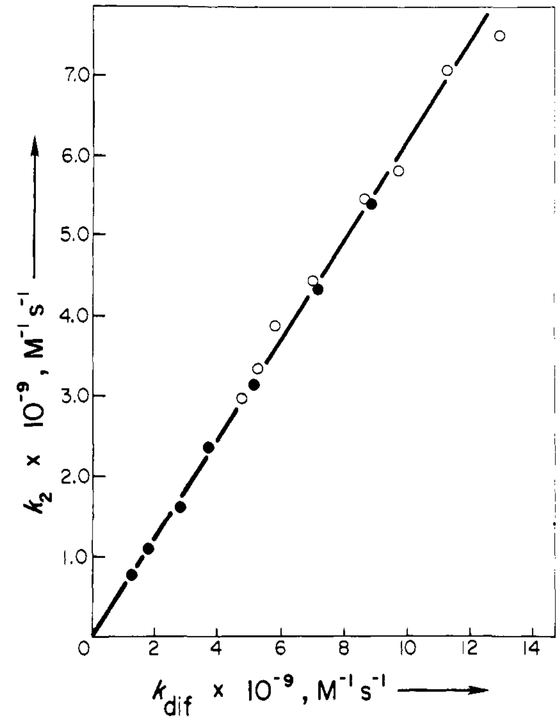

Figure 2. The dependence of k_2 on k_{dif} in toluene: ○, this work, ●, ref 10c, see text.

and intersystem crossing quantum yields of anthracene at room temperature. The temperature dependence of ϕ_{is} can be inferred from the temperature dependence of ϕ_f since $\phi_{is} = 1 - \phi_f$. Early work in several solvents was scantily presented, but suggests a small decrease in ϕ_f in toluene,[26] $\phi_f \simeq 0.36$ at 207 K and $\phi_f \simeq 0.26$ at 318 K.[27] A small decrease in ϕ_f as the temperature is raised above 250 K has been reported in 3-methylpentane.[28] However, in tetrahydrofuran ϕ_f is temperature independent for $T > 200$ K.[29]

The efficiency of delayed fluorescence of anthracene has been measured in ethanol by several groups.[30-33] Three independent flash spectroscopic determinations of the ratio, p_e, of the rate of excited singlet generation to the effective rate of triplet annihilation are in remarkable agreement yielding values of 0.077,[31] 0.08,[32] and 0.080.[33] According to our kinetic scheme $p_e = p_s k_a/k_2$. Using $p_e = 0.080$ and the ratio $(k_2/k_a) = 0.57$ from the preceding

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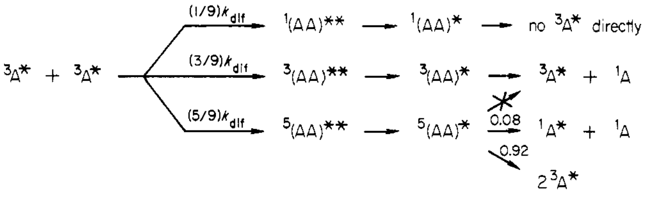
paragraph gives $p_s = 0.046$. In applying the p_c value obtained in ethanol to our results in toluene we rely on Parker's report that delayed fluorescence results obtained for anthracene in cyclohexane are similar to those obtained in ethanol,[8c] cf. also below.

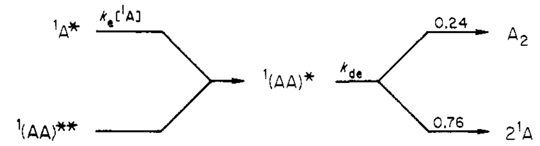
In Parker's experiments steady-state irradiation and choppers were employed to determine the ratio of prompt to delayed fluorescence.[8] From this ratio the fraction, p_c, of $^3A^*,^3A^*$ encounters yielding $^1A^*$ was calculated. The standard form of the Debye equation [eq 1, $\alpha = 3000$] was used to estimate k_{dif} which is needed for the calculation of p_c. The effect of solvent on p_c was evaluated for perylene triplets for which p_c values of 0.013, 0.006, and 0.006 were reported for ethanol, *n*-hexane, and cyclohexane.[30,34] At first glance these values suggest a large decrease in p_c on going from ethanol to a hydrocarbon solvent. However, the larger value of p_c in ethanol is probably due to the use of $\alpha = 3000$ in eq 1 which is known to underestimate k_{dif} for alcohols by at least a factor of 2.[5,6,35] In fact, adjusting the ethanol value by the 2.2 factor suggested by Ware and Novros (for isobutyl alcohol relative to *n*-heptane)[35] renders p_c for perylene solvent independent. Since, by definition, $p_c/p_s = k_a/k_{dif}$ (see, for example, ref 33 where the symbol p_0 is used instead of p_s) and since the experimental evidence discussed above suggests strongly that $k_a = k_{dif}$, as assumed by Parker, p_c should equal p_s. It is pleasing, therefore, that the p_c value for anthracene in ethanol, 0.04,[30,36] is very close to the p_s value calculated above. As described for perylene, however, use of a more realistic value for k_{dif} in ethanol would render p_c more than a factor of 2 smaller than p_s. Naqvi has argued that Parker's method for calculating p_c gives results which are low by a factor of 4,[36] but this criticism was apparently discounted because it was due to different definitions for the rate of light absorption.[30,38] The possibility that anthracene TTA is not diffusion controlled in ethanol, in contrast to toluene, is not attractive because the activation energies for viscous flow nicely predict the temperature dependence of κ in either solvent.[10c] Thus, the origin of the discrepancy between the adjusted p_c and p_s remains unclear. We note that the p_s value calculated for toluene solutions is well below previously estimated limits for this quantity in ethanol, probably because these were based on incorrect simplifying assumptions.[32,33]

Substituting $p_s = 0.046$ and $\phi_{is} = 0.72$ into $(2 - p_t - p_s\phi_{is}) = 0.57$ gives $p_t = 1.40$ for toluene. The spin-statistical consequences of TTA in solution were considered by Krishna[39] and, independently, applied to pyrene by Birks.[40] Each TT encounter produces, with equal probability, one of nine spin states: five quintets, $^5(AA)^{**}$, three triplets, $^3(AA)^{**}$, and one singlet, $^1(AA)^{**}$. The double asterisks indicate that these states, having initially the energy content of two monomer triplets, ~85 kcal/mol, do not necessarily represent energy minima in their respective manifolds.[40] Each may undergo internal conversion to give lowest energy states, designated as $^5(AA)^*$, $^3(AA)^*$ (~42.4 kcal/mol) and $^1(AA)^*$ (~75 kcal/mol), from which further decay or dissociation occurs. In order to account for the temperature dependence of the ratio of delayed excimer to delayed monomer fluorescence from pyrene TTA, Birks arbitrarily proposed that $^3(AA)^{**}$ instantaneously dissociates into $^1A^* + {}^1A$, that $^1(AA)^{**}$ gives single excimer $^1(AA)^*$, and that internal conversion of $^5(AA)^{**}$ to $^5(AA)^*$ is followed by a temperature-sensitive partitioning between $^1(AA)^*$ and $^3A^* + {}^1A$.[40] Naqvi criticized this mechanism because it fails to predict exactly the experimental ratio of delayed excimer to delayed monomer fluorescence at the high temperature limit.[41] This criticism, however, while requiring modification of Birks' assumptions concerning the fate of the pair spin states, does not invalidate them as the proper departure point for discussion of the mechanism of TTA. More recently, the spin states of TT encounter pairs were proposed to play a key role in accounting for the influence of external magnetic fields on the delayed fluorescence of aromatic hydrocarbons in solution.[42]

Scheme II. Proposed Mechanism for Anthracene TTA



Scheme III. Formation and Decay of Singlet Excimer



Starting then, with the nine spin states of the TT encounter pairs, the simplest mechanism which is consistent with $p_t = 1.40$ and $p_s = 0.046$ is shown in Scheme II. The first step in this mechanism allows each of the pair states to lose excess energy and relax to corresponding lowest energy states within its respective manifold. In the case of the triplet this decay represents the largest energy loss, ~42.4 kcal/mol, because the energy of the triplet excimer is essentially identical with the energy of one triplet monomer. The triplet excimer is proposed to be totally dissociative giving one triplet and one ground state molecule. This assumption is consistent with results from numerous flash kinetic studies showing that quenching of anthracene triplets by ground state anthracene in several solvents either does not occur or is very inefficient.[9,10,13] The most striking additional requirement is that in toluene nearly all quintet pair states must give back two anthracene triplet molecules. It should be noted that this is a rather stringent requirement which does not permit the sequence: pair quintet → monomer quintet → monomer triplet, which was postulated in accounting for magnetic field effects on the delayed fluorescence of aromatic hydrocarbons.[42] Of course, the energy of the lowest quintet state of anthracene monomer is not known and may be sufficiently high as to be inaccessible from the pair quintet.

Some remarks concerning the generation of singlet excimer and excited singlet monomer are now in order. The most obvious source of singlet excimer is the singlet pair state. It is likely that $^1(AA)^*$ is the anthracene excimer, as initially proposed for pyrene by Birks.[40] Anthracene excimer also forms from anthracene singlets at the diffusion-controlled rate and partitions itself between anthracene dimer, A_2, and ground-state anthracene, Scheme III.[43] The dependence of dimerization quantum yields in toluene on anthracene concentration gives $k_e\tau_m{}^0 = 40.8\ M^{-1}$, where $\tau_m{}^0$ is the lifetime of $^1A^*$, $\tau_m{}^0 = (k_f + k_{is})^{-1}$.[44] Using Ware's value of $\tau_m{}^0 = 4.2$ ns in toluene[45] gives $k_e = 9.7 \times 10^9\ M^{-1}\ s^{-1}$ which is identical to the empirical k_{dif} obtained at 25 °C for triplet excitation transfer from indeno[2,1-*a*]indene to azulene. It follows that formation of $^1(AA)^*$ from $^1A^*$ is strictly irreversible, so that $^1(AA)^*$ cannot be a significant source of $^1A^*$. Since in TTA the initially formed $^1(AA)^{**}$ contains some 10 kcal/mol excess energy than the relaxed singlet excimer $^1(AA)^*$,[33] one may reason that diffusive separation to $^1A^* + {}^1A$ is energetically feasible from this species. Therefore, implicit in Scheme III is the assumption that the lifetime of an encounter complex in toluene, $(1/k_{-dif})$ =

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$(1/\xi k_{\text{dif}}) \simeq 11$ ps,[6] is sufficiently long to allow $^1(AA)^{**} \rightarrow {}^1(AA)^*$ relaxation before appreciable dissociation can occur. In toluene about $^1/_4$ of the singlet excimers give dimer and the other $^3/_4$ give ground state anthracene. Similar $^1(AA)^*$ decay characteristics have been found in other hydrocarbon solvents.[43] According to Scheme III TTA should also result in anthracene dimer formation. This pathway was initially proposed[46] as the mechanism for the biacetyl-sensitized photodimerization of anthracene;[47] it has been confirmed by preliminary observations concerning the dependence of dimerization quantum yields on the intensity of the exciting light.[48] The conclusion that $^1(AA)^*$ formation from the interaction of $^1A^*$ and ^1A is fully diffusion controlled (i.e., occurs with unit efficiency) is relevant to the notion that the probability of $^1(AA)^*$ formation depends on the relative orientation of the two anthracene molecules at the instant of $^1A^*$ generation following a TT encounter.[42,49] The suggestion that attainment of the sandwich excimer geometry via rotational diffusion within the solvent cage can somehow be slower than translational diffusion of the two anthracenes out of the cage is not consistent with fully diffusion-controlled excimer formation from $^1A^*$. Since every $^1A^*$ encounter with ^1A forms excimer, there can be no dependence on the initial orientation of the two partners. The strict proportionalities between κ and T/η, and between k_2 and k_{dif}, Figures 1 and 2, respectively, are also not consistent with the proposal that TTA occurs over larger distances than the normal encounter diameter of the two solutes.[50,51] The latter conclusion can also be drawn from a study of the delayed fluorescence of 1,2-benzanthracene over a wide range of temperature and viscosity.[52] Having eliminated singlet and triplet pair states as significant precursors of anthracene monomer fluorescence, it follows that the major source of $^1A^*$ must be the quintet pair state. Since the above discussion also eliminates the process $^5(AA)^* \rightarrow {}^1(AA)^*$ as a source of $^1A^*$, it is proposed that $^1A^*$ is generated via intersystem crossing from $^5(AA)^*$ to a dissociative excited excimer state $^1(AA)^{*\prime}$. The involvement of such a state in the generation of $^1A^*$ has been discussed by Krishna.[39] The experimental $p_s = 0.046$ value would be accommodated if about 8% of the $^5(AA)^*$ pairs decayed via $^1(AA)^{*\prime}$. Incorporation of this conclusion in Scheme II gives $p_t = 1.36$, which is in excellent agreement with our experimental value of $p_t = 1.40$.

Finally it is important to stress that the above mechanism for anthracene TTA applies to toluene, benzene, and probably other hydrocarbon solvents. Measurements of k_2/ϵ_t for anthracene in ethanol (6.0×10^4[31,32] and 6.3×10^4 cm s^{-1}[33]) suggest a possible solvent effect on the decay of the pair states. Interpretation of k_2/ϵ_t in ethanol is hampered by irreproducibility in determinations of ϵ_t in alcohols [$(5.0 \pm 0.5) \times 10^4$[32] and $(7.5 \pm 0.5) \times 10^4$ M^{-1} cm^{-1}[53] in ethanol at room temperature, and 9.0×10^4 M^{-1} cm^{-1} in ethanol/methanol at 113 K[54]] and the lack of an empirical k_{dif} value in that solvent. Assuming $e_t \leq 10^5$ M^{-1} cm^{-1} gives $k_2 \leq 6 \times 10^9$ M^{-1} s^{-1}. A value of $k_{\text{dif}} \simeq 1.2 \times 10^{10}$ M^{-1} s^{-1} in ethanol at 20 °C can be estimated by adjusting the standard Debye equation [eq 1, $\alpha = 3000$] by the 2.2 factor mentioned above.[6,35] Perhaps the strongest experimental basis for this procedure is provided by k_2 values for 1,2-benzanthracene measured in methanol (−140 to −60 °C) and in ethylene glycol (−90 to 20 °C).[52] Over the entire temperature range in both solvents these k_2's are two to three times larger than twice k_{dif} calculated by using the standard Debye equation.[52] It appears likely, therefore, that $k_2/k_{\text{dif}} \leq 0.5$ in ethanol, which is somewhat smaller than the value of this ratio in toluene. This result together with $p_e = 0.080$ gives $p_s \leq 0.04$ in ethanol. While this limiting value of p_s is more consistent with Parker's p_c value (see above), it brings into question the assumption, used in the analysis of TTA in toluene, that p_e is solvent independent. This is not considered a serious deficiency in the analysis, however, because, the absolute magnitudes of p_c and p_e being small, predicted p_t values are not significantly affected. Using $p_s \leq 0.04$ and $k_2/k_{\text{dif}} \leq 0.5$ gives $1.5 \leq p_t \leq 2$ in ethanol, suggesting that an additional decay channel from pair states to $^3A^*$ must be included for this solvent in Scheme II. It is tentatively suggested that the large energy gap, ~42.2 kcal/mol, between $^3(AA)^{**}$ and $^3(AA)^*$ makes competing dissociation of $^3(AA)^{**}$ to 2^3A^* an attractive possibilty.

Experimental Section

Materials. *Toluene* (Fisher or Mallinkrodt reagent grade) was stirred at 100 °C with concentrated sulfuric acid and this repeated four times until no further discoloration of the acid layer occurred. After being washed with water and dilute aqueous sodium bicarbonate the toluene was distilled twice from phosphorous pentoxide and either used immediately or stored over molecular sieves. *Benzene* (Mallinkrodt reagent grade) was purified by the Metts exhaustive photochlorination procedure.[55] A 2-L portion of benzene was placed in a Hanovia reactor fitted with a water cooled Pyrex lamp probe, a 450W medium-pressure Hanovia Hg lamp, and a fritted glass bubbler. Chlorine gas (Matheson) was bubbled through the benzene until a yellow solution was obtained. The reaction mixture was irradiated until it became colorless (~5 min), and the procedure repeated three more times. The progress of the chlorination of impurities was monitored by GLC, using a 10% Carbowax 400 on Chromosorb W, $^1/_8$ in. × 12 ft column, 90 °C. The photochlorination reaction mixture was extracted twice with saturated aqueous sodium bicarbonate, then with aqeous sodium chloride, passed through a 3 cm o.d. × 12 cm column of alumina, and distilled. A final distillation was carried out by using a 1.3 cm o.d × 100 cm vacuum jacketed fractionating column packed with stainless steel helices (Helipac, Podbielniac Corp.). *Anthracene* (Eastman, blue violet fluorescent) was used as received, Table I, or was obtained in high purity by thermally splitting anthracene photodimer.

Flash Kinetic Analysis. A Northern-Precision kinetic flash photolysis apparatus and a Bausch and Lomb monochromator with a 33-86-07 UV–visible grating having a reciprocal dispersion of 7.4 nm per 1 mm were employed. Wavelength calibration of the monochromator was achieved by using the 404.5 and 435.8 nm lines of a Hg pen-ray lamp and the 422.6 nm line of a Westinghouse Ca hollow cathode lamp.[56] The position of the $\lambda_{\max} = 429 \pm 1$ nm for anthracene TT absorption was determined by noting maximum absorbance as the monitoring wavelength of the monochromator was stepped through a series of wavelengths around 430 nm while holding the flash energy and V_0 (see below) constant. To achieve a 6 nm band-pass at $^1/_2$ intensity the monochromator entrance and exit slits were set at 1.40 and 0.80 mm, respectively. The band-pass was determined by using the 422.6 nm line of the Ca lamp. For the 20-nm band-pass entrance and exit monochromator slits were set at 6.00 and 1.00 mm, respectively. Use of the Ca lamp under these conditions confirmed the 20-nm band-pass at $^1/_2$ intensity but at low intensities was hampered due to detection of other Ca and Ca$^+$ lines at 393.4, 396.8, 442.5, and 443.5 nm. A much better defined profile of the band-pass was obtained by recording the actual output of the monitoring lamp through the monochromator, using a Perkin-Elmer Hitachi MPF-2A spectrophotometer (Phototube Hitachi R-106, 2 nm emission slit width). In applying eq 6 to obtain T_{eff} for each band-pass, plots of I_0 and I vs. λ were Xeroxed in triplicate and the areas under each curve determined by cutting and weighing. The density of each Xerox page was similarly determined by weighing a 6 × 6 cm square. It was assumed to be uniform. Reproducibility of separate weighings of the same area, corrected for changes in paper density, was generally better than or equal to ±1.5%. The variable temperature cells, $l = 15.0$ cm, have been described in ref 6 (see also ref 10b). Solutions were rigorously degassed, using 6–10 freeze-pump-thaw cycles to less than 10^{-5} mm Hg. The decay of anthracene triplets was monitored by measuring the transmission of the solution at 429 nm. Delayed fluorescence, which is also present at 429 nm, was monitored by measuring the emission from the cell at right angles to the analyzing beam. The two signals were preamplified in clipping (±2 V), variable offset, dc amplifiers and then coupled in a differential mode such that the delayed fluorescence component in the analyzing beam signal was exactly cancelled. The offset was adjusted to make the output 0.0 V at 100% transmission. The output signal could

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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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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

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

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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