time advantage over spectroscopic methods for determining the rotational barrier of a methyl top.

Finally, it should be noted that some degree of caution should be exercised when comparing gas phase spectroscopic barrier values with those determined in the liquid and solid phases. We have recently measured the methyl barriers for isobutene, *trans*-2-butene, and *cis*-2-butene and found some variance between published gas phase values[36] and the values we determined in the liquid phase. However, in all cases the values fell between the published gas and solid phase values.[33-35]

Summary and Conclusions

From the above discussion it is concluded that $T_{1,\mathrm{SR}}$ values for methyl tops are strongly influenced by their internal barrier to rotation. The use of eq 13 for determining barriers to rotation for the compounds under investigation yielded an average deviation from the reported spectroscopic values of ±0.10 kcal/mol. This result has prompted further and continuing investigation into the feasibility and application of this method to methyl tops. It is also noted that similar applications should be feasible with other threefold rotors, e.g., CF_3, SiH_3, and SiF_3 groups.

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Exciplex and Triplex Emission in the System 9,10-Dichloroanthracene–2,5-Dimethyl-2,4-hexadiene[1a,b]

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Abstract: Steady-state and transient fluorescence measurements have been made using mixtures of 9,10-dichloroanthracene and 2,5-dimethyl-2,4-hexadiene in benzene and acetonitrile. In benzene a fluorescent exciplex, $\lambda_{\max}$ ~485 nm, τ 7.4 nsec, forms reversibly with an estimated equilibrium constant for exciplex formation at room temperature of 20 ± 1 M^{-1}. In contrast, no exciplex fluorescence is observed from acetonitrile solutions at intermediate diene concentrations, but triplex fluorescence $\lambda_{\max}$ ~543 nm and τ 3.6 nsec, is observed at higher diene concentrations. Steady-state fluorescence observations in the presence of air are also described.

The green luminescence observed upon excitation of 9,10-dichloroanthracene (DCA) in benzene solutions containing 2,5-dimethyl-2,4-hexadiene (DMH) has been attributed to fluorescence from a DCA-DMH exciplex.[1b] Exciplexes are thought to arise generally from the interaction of aromatic hydrocarbons and dienes,[2] and have been postulated to collapse to adducts[3-5] and to provide additional pathways for reaction of one of the partners with other molecules.[1b] Since such exciplexes are rarely fluorescent[6] a more detailed study of the DCA-DMH system was under-

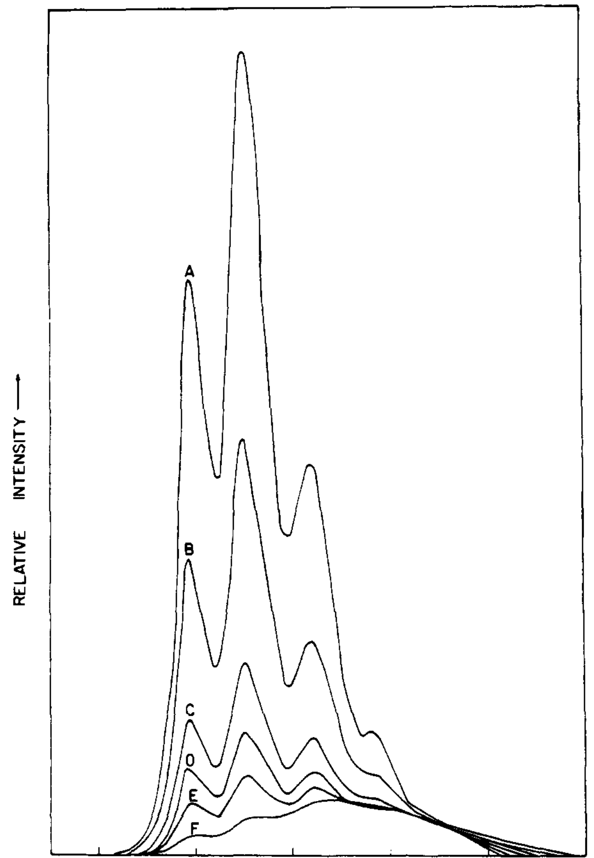

Figure 1. Fluorescence spectra of benzene solutions of DCA and varying amounts of DMH. Curves A-F correspond to 0, 0.069, 0.207, 0.345, 0.69, and 2.76 *M* diene, respectively.

taken employing the methods suggested by Lewis and Ware.[8]

Results

Steady-State Measurements. Fluorescence spectra, corrected for nonlinearity of instrumental response of degassed benzene and acetonitrile solutions containing DCA and varying amounts of DMH are shown in Figures 1 and 2, respectively. In benzene the blue DCA fluorescence is replaced by a green structureless emission at high diene concentrations, while in acetonitrile the new emission is significantly red shifted and has a yellow-golden appearance. The ratios of the area of the corrected spectra of DCA fluorescence in the absence of DMH to the areas of the total emissions recorded in the presence of 2.76 *M* DMH are 7.1 in benzene and 70 in acetonitrile. Relative fluorescence areas from solutions with matched optical densities at the excitation wavelength of anthracene in benzene, and DCA in benzene and acetonitrile, were found to be 0.42:1.00:0.93. Relative DCA fluorescence yields in the presence of DMH were obtained at 23.5 and 23.2° for benzene and acetonitrile solutions, respectively, and are reported in Table I as I_0/I ratios. Table I includes data obtained from air-saturated solutions, reported relative to I_0 for degassed solutions. No fluorescence could be detected under these conditions from a benzene solution containing only 2.76 *M* DMH.

Ultraviolet absorption spectra measured using 1 mm path lengths of the acetonitrile solutions labeled *f* in Table I and of a similar solution containing 2.09 *M* DMH show subtle changes as the amount of DMH is increased. The λ_{max} of the 0-0 band shifts from 401.4 nm in the presence of 0.075 *M* DMH to 402.4 nm in the presence of 2.09 *M* DMH, while the ratio of the optical densities of the first maximum (402.4 nm) to the first minimum (~390 nm) in the spectra decreases from 3.22 to 2.84. The change in optical density at 340 nm upon increasing [DMH] from 0.075 to 2.09 *M* is from 0.182 to 0.220. The optical density at 340 nm of a 2.7 *M* DMH solution in acetonitrile containing no DCA is 0.029 (1 mm path length).

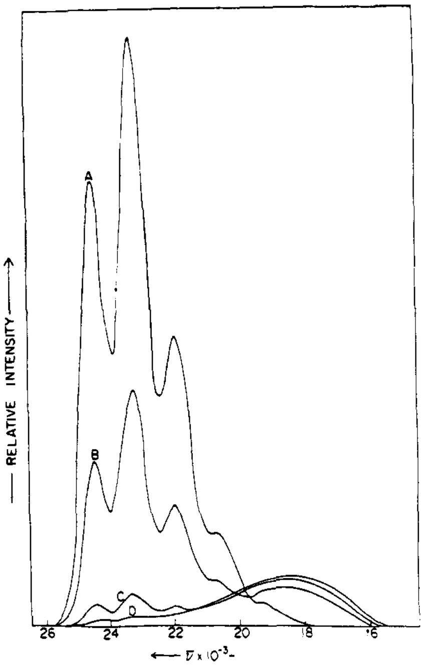

Figure 2. Fluorescence spectra of acetonitrile solutions of DCA and varying amounts of DMH. Curves A-D correspond to 0.069, 0.345, 1.38, and 2.76 *M* diene, respectively.

Table I. Quenching of 9,10-Dichloroanthracene Fluorescence by 2,5-Dimethyl-2,4-hexadiene

	C_6H_6			CH_3CN	
[DMH], *M*	I_0/I[a]	I_0/I_{OX}[b]	[DMH], *M*	I_0/I[c]	I_0/I_{OX}[d]
0	1	1.26	0	1	1.27
0.069	1.88	2.19	0.017	3.01	3.19
0.138[e]	3.25		0.035	4.60	5.22
0.207	4.16	4.41	0.069	9.98	9.83
0.207	4.14		0.075	10.2[f]	
0.345	6.41	6.84	0.104	14.4	15.0
0.690	10.4	11.1	0.150	21.6[f]	
			0.299	49.3[f]	

[a] Degassed solutions, [DCA] = 1.25×10^{-4} *M*, excitation wavelength 340 nm, emission wavelength 414 nm. [b] As in *a*, but air-saturated solutions. [c] Degassed solutions and, unless otherwise noted, [DCA] = 6.40×10^{-5} *M*, excitation wavelength 340 nm, emission wavelength 417 nm. [d] As in *c*, but air-saturated solutions. [e] [DCA] = 2.50×10^{-4} *M*. [f] [DCA] = 7.00×10^{-4} *M*, emission wavelength 430 nm.

Three-milliliter portions of the acetonitrile solutions described in the previous paragraph were irradiated in parallel at 366 nm along with an actinometer solution containing 6.44×10^{-4} *M* anthracene and 0.986 *M* *N,N*-dimethylaniline. Losses of DCA and anthracene were measured by uv spectroscopy. The uv spectra of the irradiated DCA solutions showed a marked decrease in the 0-0 band absorption of DCA (402 nm) and the appearance of a new progression of anthracene-like absorption bands at 389, 369, 351, and 335 nm. The appearance of these bands is concomitant with the appearance of a relatively intense blue-shifted fluorescence from the irradiated solutions. Prolonged irradiation causes a decrease in the optical density of the product(s)

Table II. Effect of DMH Concentration on Photoreactivity of DCA in Acetonitrile[a]

[DMH], *M*	% DCA reacted	[DMH], *M*	% DCA reacted
0.075	23.4	0.299	29.4
0.150	24.0	2.09	24.0

[a] [DCA] = $7.00 \times 10^{-4} M$. Anthracene loss in the actinometer was 18.9%.

Table III. Effective First-Order Decay Constants of Emission from DCA–DMH Solutions[a]

[DMH], $M \times 10^2$	[DCA], $M \times 10^4$	λ, nm	k_{obsd}, $\text{sec}^{-1} \times 10^{-8}$
Benzene			
0	1.32	500	0.97 ± 0.03
		430	1.10 ± 0.08
0	1.25	420	1.05 ± 0.08
1.73	1.25	420	1.12 ± 0.03
3.46	1.25	420	1.16 ± 0.03
		427	1.10 ± 0.03
		500	1.08 ± 0.03
6.92	1.25	420	1.22 ± 0.03
10.4	1.25	420	1.23 ± 0.03
		427	1.23 ± 0.03
		500	1.19 ± 0.03
20.8	1.32	430	1.23 ± 0.03
31.2	1.32	430	1.25 ± 0.03
		500	1.27 ± 0.03
276	1.25	427	1.36 ± 0.03
		480	1.35 ± 0.03
		500	1.35 ± 0.03
Acetonitrile			
0	1.18	430	0.94 ± 0.03
0.104	1.18	430	1.05 ± 0.03
0.520	1.18	430	1.39 ± 0.03
0.780	1.18	430	1.62 ± 0.03
1.04	1.18	430	1.78 ± 0.03
276	0.64	500	2.68 ± 0.04
			3.00 ± 0.04[b]

[a] Measurements made at 25 ± 1° in degassed solutions unless otherwise noted. [b] Air-saturated solution.

which give(s) rise to the above absorption bands. DCA losses for short irradiation periods are given in Table II and are based on the decrease of DCA's 0-0 band absorption.

Lifetime Measurements. Decay rate constants of DCA fluorescence were obtained by monitoring the emission at 420, 427, 430, and/or 500 nm from degassed solutions of DCA and DMH in benzene and acetonitrile. Decay rate constants of the broad new emissions were obtained by monitoring emissions at 480 and/or 500 nm from solutions containing 2.76 *M* DMH. First-order decay rate constants and estimated uncertainties are shown in Table III. These rate constants were obtained from semilog plots of the decaying side of the emission curves. Visual inspection of the plots shows excellent adherence to single exponential decay, except that plots of emissions from benzene solutions showed an additional small shorter-lived exponential component. This component was most pronounced when the emission was monitored at 430 nm, and its contribution diminished with added diene.

Discussion

The choice of the DCA-DMH system was prompted by observations indicating that the presence of 1,3-dienes opens an additional excited state pathway for dianthracene formation,[1b] even in the case of 9-phenylanthracene,[9] a molecule which does not normally photodimerize. It was our intention to determine whether this pathway is operative in DCA since 9,10-disubstituted anthracenes are known to be particularly resistant to photodimerization.[10-13] Our initial efforts, directed primarily to elucidating the source of the new emissions discovered in benzene and acetonitrile, are described herein.

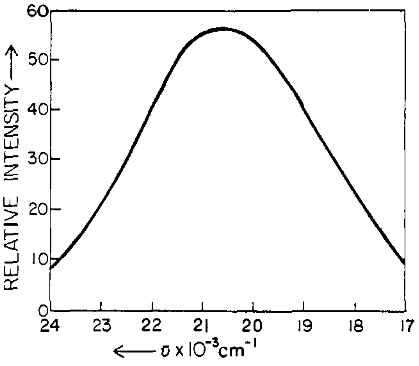

Figure 3. DCA-DMH exciplex fluorescence spectrum in benzene.

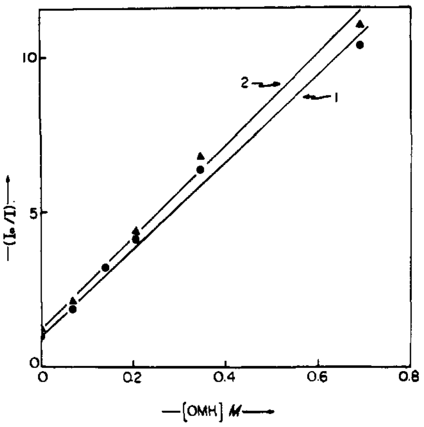

Figure 4. Stern-Volmer plot of the quenching of DCA fluorescence by DMH in benzene: ●, degassed solutions, line 1; ▲, air-saturated solutions, line 2.

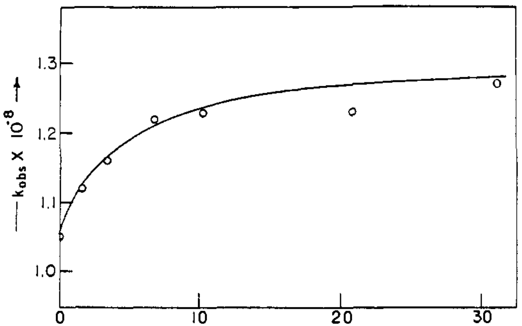

Figure 5. Observed DCA fluorescence decay rate constants in benzene as a function of DMH concentration, $\tau_M = 1/k_{\text{obsd}}$. Solid line was calculated using $p = 0.46$.

Benzene. As can be seen from the spectra in Figure 1, the emission at 2.76 *M* DMH in benzene contains very little DCA fluorescence. Subtraction of the residual DCA emission gives the spectrum shown in Figure 3 with $\lambda_{\max}$ ~485 nm. The presence of an isoemissive point at ~515 nm shows that the lowest excited 9,10-dichloroanthracene singlet state, ^{1}DCA, and the new emitting species which is probably the DCA-DMH exciplex, ^{1}E, form a closed system. The overlapping of curves D, E, and F in Figure 1 at ~480 nm is well within the experimental error of the measurements.

Stern-Volmer plots of I_0/I and τ_0/τ vs. [DMH] are shown in Figures 4 and 5, respectively. The I_0/I plot for degassed samples is linear to 0.69 *M* diene, slope 14.0 M^{-1}. In contrast, ^{1}DCA lifetimes are relatively insensitive to DMH concentration, the slope of the τ_0/τ plot approaching zero at te highest diene concentration employed, 0.312 M.

Sources of curvature in Stern–Volmer plots and discrepancies between I_0/I and τ_0/τ plots are discussed in a recent paper by Lewis and Ware.[8] Upward curvature in I_0/I plots has been associated with (a) transient effects arising due to time-dependent concentration gradients,[14,15] and/or with (b) static quenching arising either from instantaneous quenching of a fluorescent molecule by a quencher already present within its volume of interaction ("active sphere" model[16]) or from ground state complex formation[17-21] which creates a nonrandom initial distribution of quencher and fluorescer, allowing direct excitation of fluorescer molecules already associated with a quencher molecule. The linearity of the I_0/I plot at [DMH] $\leq$ 0.69 M shows that neither transient effects nor static quenching mechanisms need be invoked for [DMH] $\leq$ 0.32 M, the range employed for ^{1}DCA lifetime measurements. In this diene concentration range the striking observation is the downward curvature of the τ_0/τ plot. Lewis and Ware have shown that such behavior is characteristic of systems in which reversible exciplex formation causes a coupling between the decays of the excited monomer and the exciplex.[8,22] In such cases observed decay curves are properly expressed as the sum of the two exponential components whose decay constants are related to the association rate constants and the lifetimes of the two excited species.[8,23]

The following mechanism, eq 1–6, consists of the minimum number of steps needed to account for observations in degassed benzene solutions. The assumption of reversible exciplex formation, eq 4, along with the usual steady-state approximations for all excited species, give modified Stern–Volmer expression 7, where p represents the fraction of exciplexes which do not regenerate excited monomer, eq 8, and τ_m is the monomer singlet lifetime $(k_{fm} + k_{is})^{-1}$ in the absence of quencher. Previous measurements of the lifetime

$$\mathrm{DCA} \xrightarrow{h\nu} {}^1\mathrm{DCA} \qquad (1)$$

$$^1\mathrm{DCA} \xrightarrow{k_{fm}} \mathrm{DCA} + h\nu_1 \qquad (2)$$

$$^1\mathrm{DCA} \xrightarrow{k_{is}} {}^3\mathrm{DCA} \qquad (3)$$

$$^1\mathrm{DCA} + \mathrm{DMH} \underset{k_{-e}}{\overset{k_e}{\rightleftarrows}} {}^1(\mathrm{DCA}\cdot\mathrm{DMH}) \qquad (4)$$

$$^1(\mathrm{DCA}\cdot\mathrm{DMH}) \xrightarrow{k_{fe}} \mathrm{DCA} + \mathrm{DMH} + h\nu_2 \qquad (5)$$

$$^1(\mathrm{DCA}\cdot\mathrm{DMH}) \xrightarrow{k_{de}} \mathrm{DCA} + \mathrm{DMH} + \text{products} \qquad (6)$$

$$I_0/I = 1 + k_e\tau_m p[\mathrm{DMH}] \qquad (7)$$

$$p = (k_{fe} + k_{de})/(k_{-e} + k_{fe} + k_{de}) \qquad (8)$$

of ^{1}DCA in benzene have yielded values of 10.0[24] and 9.98 nsec[25] in good agreement with the values of 10.3 ± 0.3, 9.1 ± 0.7, and 9.5 ± 0.4 nsec obtained in this work by monitoring the emission at 500, 430, and 420 nm, respectively, Table III. The wavelength dependence observed in τ_m as well as the presence of a second short-lived decay component in the first-order decay plots (especially at 430 nm) is probably associated with the formation of a DCA–benzene exciplex.[26] In the following discussion the introduction of possible complications by the formation of such an exciplex will be neglected and a value of τ_m 9.5 nsec will be assumed, since this was the value obtained at 420 nm where most of the measurements in the presence of diene were made. This lifetime and the initial slope of the Stern–Volmer plot in Figure 4 give $k_e p = 1.47 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$.

The value of p can be estimated from the lifetime measurements by employing a treatment of the kinetics of eq 2–6 which follows Birk's treatment of excimer formation.[8,10] Assuming that an initial excited monomer concentration $^1[\mathrm{DCA}]_0$ is produced by a δ-function excitation pulse, the changes in the concentrations of excited monomer and exciplex with time are described by eq 9 and 10, respectively.

$$-\frac{\mathrm{d}[^1\mathrm{DCA}]}{\mathrm{d}t} = (k_{fm} + k_{is} + k_e[\mathrm{DMH}]) \times [^1\mathrm{DCA}] - k_{-e}[^1(\mathrm{DCA}\cdot\mathrm{DMH})] \qquad (9)$$

$$-\frac{\mathrm{d}[^1(\mathrm{DCA{-}DMH})]}{\mathrm{d}t} = (k_{-e} + k_{fe} + k_{de}) \times [^1(\mathrm{DCA}\cdot\mathrm{DMH})] - k_{-e}[^1\mathrm{DCA}][\mathrm{DMH}] \qquad (10)$$

The time dependences of monomer (I_f^M) and exciplex fluorescence intensity (I_f^E) are obtained by solving eq 9 and 10 and are given by eq 11 and 12, respectively, where the parameters λ_1, λ_2, c_1, and c_2 are described by eq 13–16. Except for k_e and k_{-e} all of the parameters in eq 11–16 are

$$I_f^M = c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t} \qquad (11)$$

$$I_f^E = \frac{k_e[\mathrm{DMH}]}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t} + e^{-\lambda_2 t}) \qquad (12)$$

$$\lambda_{1,2} = \frac{1}{2}[(k_{fm} + k_{is} + k_e[\mathrm{DMH}] + k_{-e} + k_{fe} + k_{de})] \mp \{(k_{-e} + k_{fe} + k_{de} - k_{fm} - k_{is} - k_e[\mathrm{DMH}])^2 + 4k_e k_{-e}[\mathrm{DMH}]\}^{1/2} \qquad (13)$$

$$c_1 = (\lambda_2 - x)/(\lambda_2 - \lambda_1) \qquad (14)$$

$$c_2 = (x - \lambda_1)/(\lambda_2 - \lambda_1) \qquad (15)$$

$$x = (k_{fm} + k_{is} + k_e[\mathrm{DMH}]) \qquad (16)$$

available directly from experimental measurements. The lifetime of ^{1}DCA in the absence of diene gives $k_{fm} + k_{is} = 1.05 \times 10^8\ \mathrm{sec}^{-1}$. Although unnecessary for the present analysis this can be further broken down to $k_{fm} = 6.7 \times 10^9\ \mathrm{sec}^{-1}$ and $k_{is} = 3.8 \times 10^9\ \mathrm{sec}^{-1}$ by using the fluorescence quantum yield of DCA in benzene, $\phi_{fm} = 0.64$.[27] The rate constant of exciplex emission obtained at 2.76 M DMH, Table III, gives $k_{fe} + k_{de} = 1.35 \times 10^8\ \mathrm{sec}^{-1}$, since at this high DMH concentration essentially all excited singlets are present as exciplexes as evidenced by the almost complete absence of monomer emission in the total luminescence spectrum, $I^M/I_0^M \simeq 34$ (Figure 1). Since the value of $k_e p$ has been obtained from the slope of the Stern–Volmer plot in Figure 4, assumption of a value of p defines the values of k_e and k_{-e} and allows an evaluation of the time dependence of I_f^M using eq 11.

A systematic computer variation[32] of p and evaluation of ln I_f^M as a function of time was performed. The simulated decay data obtained were treated by least-squares analysis and plotted for visual observation of the linearity of the first-order plots over the time range corresponding to the experimental measurements. Since experimental first-order plots are linear, only those values of p which predicted linearity were considered realistic and a final value of p was selected which gives the best agreement between calculated and experimental lifetimes at all quencher concentrations. The latter condition allows p to be rather narrowly defined as 0.46 ± 0.01. The internal consistency of the calculations was checked by calculating the exciplex lifetime at 2.76 M

diene using eq 12. The value of τ_e 7.46 nsec obtained for $p = 0.46$ is in excellent agreement with the observed value of 7.4 nsec and supports the assumption that $\tau_e = (k_{fe} + k_{de})^{-1}$ at 2.76 M diene. The calculated ^{1}DCA lifetimes are compared with the experimental data in Figure 5.

Using $p = 0.46$, values of k_e and k_{-e} of $3.2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ and $1.6 \times 10^8\ \mathrm{sec}^{-1}$ are predicted, respectively, which give an equilibrium constant, K_e, for the quenching process of $20 \pm 1\ M^{-1}$.

The presence of oxygen is expected to introduce additional decay channels as shown in eq 17 and 18. Inclusion of eq

$$^1(\mathrm{DCA}) + \mathrm{O_2} \xrightarrow{k_{qm}} \text{quenching} \qquad (17)$$

$$^1(\mathrm{DCA \cdot DMH}) + \mathrm{O_2} \xrightarrow{k_{qe}} \text{quenching} \qquad (18)$$

17 in the mechanism predicts an increase in the intercept of the Stern–Volmer plot, Figure 4, by $k_{qm}\tau_m[\mathrm{O_2}]$. The observed intercept of 1.26 along with the concentration of oxygen, $[\mathrm{O_2}] = 1.5 \times 10^{-3}\ M$,[33] and the value of τ_m measured in this work give $k_{qm} = 1.8 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ in benzene at 23°, a somewhat lower value than those usually found for the interaction of aromatic hydrocarbon singlets with oxygen, $k_{qm} \simeq 3.0 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$.[32,34-36] Inclusion of eq 18 in the mechanism predicts that the slope of the Stern–Volmer plot in the presence of air, s_{ox}, should be larger than the slope, s, of the plot obtained from data for degassed solutions as shown in eq 19, where τ_e is the lifetime of the exciplex, $(k_{fe} + k_{de})^{-1}$.

$$s_{ox}/s = (1 + k_{qe}\tau_e[\mathrm{O_2}])\frac{1 + k_{-e}\tau_e}{1 + k_{-e}\tau_e + k_{qe}\tau_e[\mathrm{O_2}]} \qquad (19)$$

Since the slope ratio reduces to unity when exciplex formation is not reversible, $k_{-c} = 0$, deviation of s_{ox}/s from unity provides an additional criterion for reversibility. This will not always be a definitive criterion, because, as is evident from eq 19, the maximum deviation of the slope ratio from unity equals $k_{qe}\cdot\tau_e[\mathrm{O_2}]$, and can be vanishingly small for systems with short exciplex lifetimes. For the DCA-DMH case in benzene assuming $k_{qe}[\mathrm{O_2}] \simeq k_{qm}[\mathrm{O_2}] = 3.6 \times 10^7\ \mathrm{sec}^{-1}$,[35] substitution of the values of τ_e and k_{-e} in eq 19 gives $s_{ox}/s = 1.13$ in fair agreement with the experimental s_{ox}/s ratio of 1.06 ± 0.05.

Quantum yields of exciplex fluorescence, ϕ_{fe}, of 0.029, 0.041, 0.047, 0.059, and 0.071 were obtained at diene concentrations of 0.069, 0.207, 0.345, 0.69, and 2.76 M, respectively, using DCA fluorescence in the absence of diene as standard, $\phi_{fm} = 0.64$ (see above). The proposed mechanism predicts the diene concentration dependence of exciplex fluorescence quantum yields shown in eq 20. The exciplex fluorescence quantum yields can be used along with the known constants in eq 20, to calculate the maximum possible exciplex fluorescence quantum yield, $\phi_{fe}{}^{max} = k_{fe}\tau_e$. Alternatively, $\phi_{fe}{}^{max}$ values can be calculated using the I_0/I values in Table I. Using the latter method the values of $k_{fe}\tau_e$ obtained are 0.062, 0.054, 0.056, 0.065, and 0.074 at [DMH] = 0.069, 0.207, 0.345, 0.69, and 2.76 M, respectively, and give $k_{fe} = 8.4 \pm 0.8 \times 10^6\ \mathrm{sec}^{-1}$.

$$\phi_{fe} = \frac{k_e\tau_m[\mathrm{DMH}]k_{fe}\tau_e}{1 + k_{-e}\tau_e + k_e\tau_m[\mathrm{DMH}]} = (1 - I/I_0)k_{fe}\tau_e \qquad (20)$$

Acetonitrile. The effect of solvent dielectric on the behavior of exciplexes has been studied extensively.[40-42] Increasing the dielectric constant, ϵ, of the solvent generally shifts the exciplex emission to the red and causes a decrease in τ_e. In order to determine such effects in the DCA-DMH system, the experiments described in the previous section were repeated in acetonitrile. Corrected total emission spectra as a function of diene concentration are shown in Figure 2. At the highest diene concentrations the decrease in DCA fluorescence intensity is accompanied by the appearance of a new golden, broad structureless fluorescence, λ_{max} ∼543 nm. The lifetime of the excited species giving rise to this emission, 3.6 nsec, was determined by monitoring the emission decay at 500 nm as a function of time, using 2.76 M DMH. Estimates of the rate for oxygen quenching of the new emission of $k_q[\mathrm{O_2}] = 4.4 \times 10^7$ and $2.2 \times 10^7\ \mathrm{sec}^{-1}$, obtained from $I_0/I = 1.16$ and $\tau_0/\tau = 1.08$ ratios for degassed and air-saturated solutions, respectively, suggest that the value of the rate constant for interaction with oxygen must be close to the diffusion-controlled limit.

The Stern–Volmer plots of DCA fluorescence quenching by DMH in degassed and air-saturated acetonitrile solutions are shown in Figure 6 and the plot of ^{1}DCA lifetimes in degassed solutions is shown in Figure 7. The I_0/I Stern–Volmer plots start showing upward curvature at [DMH] $\simeq$ 0.04 M. The initial slope of the plot for data obtained in degassed solutions, Figure 6, gives $k_e\tau_m p = 106\ M^{-1}$, eq 7, from which a value of $k_e p = 1.00 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ can be calculated using the observed DCA lifetime, 10.6 nsec, in the absence of DMH, Table III. In contrast to the observations for benzene solutions, the lifetime Stern–Volmer plot is essentially linear and its slope, 89.5 M^{-1}, is only ∼20% smaller than the initial slope of the I_0/I plot, suggesting that exciplex formation in acetonitrile is not freely reversible.

Before considering the curvature in the I_0/I plot at [DMH] > 0.04 M the question of the origin of the new emission is addressed. Examination of the data in Table I and the spectra in Figure 2 shows that although 91% of DCa fluorescence is quenched at [DMH] = 0.069 M, no new emission is experimentally discernible at that concentration. In fact the new emission is observed over a diene concentration range where the fraction of quenched DCA singlets is not changing substantially (91 → 100%), suggesting that the emission is not coming from the species formed as a result of the initial quenching process. This conclusion is substantiated by the fact that an isoemissive point is not maintained in the spectra in Figure 2 as would have been expected if the two emitting systems constituted a closed system.[43] Three other systems in which an isoemissive point is not maintained at high quencher concentrations are those of pyrene-*N,N*-dimethylaniline,[44] pyrene-3,5-di-*tert*-butyl-*N,N*-dimethylaniline,[45] and anthracene-*N,N*-dimethylaniline.[32] In these cases a lowering of the intersection point of monomer and exciplex fluorescence is observed which is attributed to interaction of the exciplex with an additional molecule of quencher leading to a nonemitting species. A more striking precedent is provided by the naphthalene-1,4-dicyanobenzene system in which interaction of the exciplex with an additional molecule of 1,4-dicyanobenzene leads to a decrease in the intensity of the exciplex emission as a new red-shifted emission appears which has been assigned to heterotrimer (triplex) species.[46,47]

In view of the above, it seems probable that the new fluorescence in the DCA-DMM system in acetonitrile originates from a triplex formed by the trapping of the nonfluorescing exciplex, eq 21–23, with DMH.[49] Quantum yields

$$^1(\mathrm{DCA \cdot DMH}) + \mathrm{DMH} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^1(\mathrm{DCA \cdot DMH_2}) \qquad (21)$$

$$^1(\mathrm{DCA \cdot DMH_2}) \xrightarrow{k_{f1}} \mathrm{DCA} + 2\mathrm{DMH} + h\nu \qquad (22)$$

$$^1(\text{DCA}\cdot\text{DMH}_2) \xrightarrow{k_{\text{dt}}} \alpha(\text{DCA} + 2\text{DMH}) + (1 - \alpha)\text{products} \tag{23}$$

of the new fluorescence, ϕ_{ft}, were obtained relative to the fluorescence of DCA in acetonitrile, $\phi_{\text{f}} = 0.55$, which was obtained by relating it to the fluorescence of DCA in benzene by applying the usual index of refraction correction.[51] This value, which seems rather low,[52] and the data in Table I and Figure 2 lead to ϕ_{ft} values of 7.9×10^{-3}, 7.1×10^{-3}, and 5.5×10^{-3} for 2.76, 1.38, and 0.345 M DMH concentrations, respectively. Since at these diene concentrations the quenching of DCA fluorescence is almost complete, Table I, triplex emission quantum yields should follow approximately eq 24, where τ_{e} and τ_{t} are k_{de}^{-1} and $(k_{\text{ft}} + k_{\text{dt}})^{-1}$, respectively.

$$[\text{DMH}]/\phi_{\text{ft}} = (1 + k_{-\text{t}}\tau_{\text{t}})/k_{\text{ft}}\tau_{\text{t}}k_{\text{t}}\tau_{\text{e}} + [\text{DMH}]/k_{\text{ft}}\tau_{\text{t}} \tag{24}$$

The plot of $[\text{DMH}]/\phi_{\text{ft}}$ vs. [DMH] is linear its slope giving $k_{\text{ft}}\tau_{\text{t}} = 8.5 \times 10^{-3}$ as the limiting triplex fluorescence quantum yield. A maximum value of $k_{\text{ft}} \leq 2.4 \times 10^6$ sec^{-1} can now be calculated by substituting the observed triplex lifetime, 3.6 nsec at 2.76 M DMH, for τ_{t}. A minimum exciplex lifetime in acetonitrile of $\tau_{\text{e}} \geq 0.4$ nsec can be estimated from the slope–intercept ratio of this plot assuming that the rate constant for triplex formation, eq 21, is less than or equal to the diffusion controlled limit of $\sim 10^{10}$ M^{-1} sec^{-1}. These results are consistent with previous observations showing that exciplex lifetimes decrease drastically with increasing solvent dielectric constant, ϵ.[40,41,44] For example, the lifetime of the pyrene-*N*,*N*-dimethylaniline exciplex decreases from 130 nsec in *n*-hexane (ϵ 1.9) to 47 nsec in pyridine (ϵ 12.3).[41] If the lifetime of the DCA–DMH exciplex were similarly affected, the expected decrease would be from 7.4 nsec in benzene (ϵ 2.3) to slightly less than 1 nsec in acetonitrile (ϵ 38.8). Exciplex fluorescence quantum yields depend even more strongly on ϵ. Thus, the fluorescence quantum yield of pyrene-*N*,*N*-dimethylaniline exciplex decreases by a factor of 44 on changing the solvent from *n*-hexane to pyridine and no exciplex fluorescence is detected in acetonitrile. It is, therefore, not surprising that no fluorescence was observed from the DCA–DMH exciplex in acetonitrile.

The upward curvature in the I_0/I Stern–Volmer plot, Figure 6, is probably due primarily to the formation of ground state complexes, eq 25 and 26, as suggested by the

$$\text{DCA} + \text{DMH} \overset{K_{\text{c}}}{\rightleftarrows} (\text{DCA}\cdot\text{DMH}) \tag{25}$$

$$(\text{DCA}\cdot\text{DMH}) \xrightarrow{h\nu} {}^1(\text{DCA}\cdot\text{DMH}) \tag{26}$$

subtle changes in the absorption spectra of acetonitrile solutions of DCA as DMH is added. With respect to the active sphere model for quenching, it should be noted that the curvature is apparent at 0.04 M DMH where very few excited DCA singlets are expected to form in the presence of a diene nearest neighbor molecule if the diene molecules were randomly distributed in the solution.[54-56] This model could account for some of the curvature at concentrations higher than 0.1 M since in this solvent k_{e} is very close to the diffusion-controlled limit. If all the curvature is assigned to ground state complex formation, eq 25 and 26, a maximum value of $K_{\text{c}} \leq 1.85$ M^{-1} can be calculated using eq 27, which is derived by assuming that the extinction coefficients of monomer and complex are the same at 340 nm.

$$I_0/I = \frac{(1 + k_{\text{e}}\tau_{\text{m}}p[\text{DMH}])(1 + K_{\text{c}}[\text{DMH}])}{1 + (1 - p)K_{\text{c}}[\text{DMH}]} \tag{27}$$

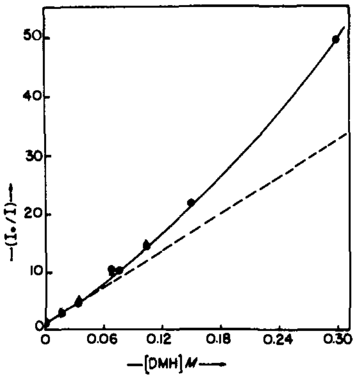

Figure 6. Stern–Volmer plot of the quenching of DCA fluorescence by DMH in acetonitrile; ●, degassed solutions; ▲, air-saturated solutions. The dashed line represents the initial slope.

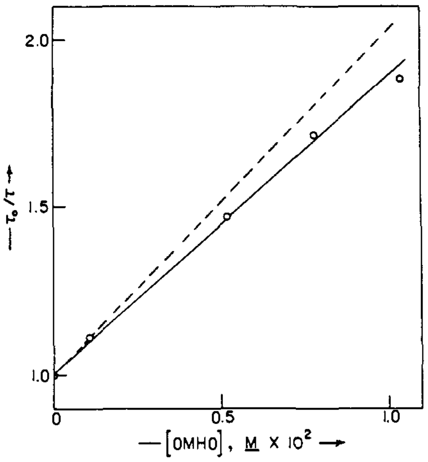

Figure 7. The effect of DMH on the observed fluorescence lifetime of DCA in acetonitrile. The dashed line is the same as in Figure 6.

The small deviation between the initial slope of the I_0/I plot, 106 M^{-1}, and the slope of the τ_0/τ plot, 89 M^{-1}, may be indicative of some reversibility in exciplex formation despite the short exciplex lifetime. It could also be due to the fact that the I_0/I measurements were obtained at a lower temperature, 23°, than the τ_0/τ measurements, 25°.[57] Deviations between the I_0/I and I_0/I_{ox} values are small, Table I, being almost within the range of experimental uncertainty, and thus provide no evidence for reversibility in exciplex formation (see discussion concerning eq 22). Since, furthermore, only a limit has been placed on τ_{e} in acetonitrile, application of the procedure used to obtain the value of p from the data for benzene solutions does not seem justified. However, it is important to recognize that if p were less than unity, the diene-concentration-dependent quenching of the exciplex would cause p to increase with increasing diene concentration thus providing an additional mechanism for explaining the upward curvature of the I_0/I plots in Figure 6.

Photochemical Considerations. Exciplexes are often postulated as intermediates in photochemical reactions.[58] In the above, spectroscopic evidence has been described indicating the presence of singlet (DCA·DMH) exciplexes in benzene and acetonitrile and (DCA·DMH$_2$) triplexes in acetonitrile. While the photochemistry of these systems has not been thoroughly studied,[59] it may be appropriate at this time to consider implications of preliminary findings in acetonitrile. The results in Table II can be converted to quantum yields for DCA disappearance, $\phi_{-\text{DCA}}$, using the quantum yield for anthracene disappearance, $\phi_{-\text{A}} = 0.17$, in the actinometer.[60] The $\phi_{-\text{DCA}}$ values are 0.23, 0.24, 0.29, and 0.24 for [DMH] = 0.075, 0.150, 0.299, and 2.09 M, respectively, and the uv spectra of the reaction mixtures are remarkably similar indicating that the same major reaction, probably the formation of a new anthracene system, is occurring in each of the four solutions. Since exciplex formation is essentially complete (≥90%) throughout the selected concentration range, while efficiency of triplex formation varies from ~25% at 0.075 *M* DMH to ~90% at 2.09 *M* DMH, a strong dependence of $\phi_{-\mathrm{DCA}}$ on [DMH] might have been expected. This is especially so since in benzene, where a long exciplex lifetime is observed, preliminary observations indicate that there is little or no loss of DCA in the presence of DMH under conditions for which large amounts of anthracene dimer are produced in the anthracene-*trans,trans*-2,4-hexadiene (A–HD) system.[1b,61] The observed insensitivity of $\phi_{-\mathrm{DCA}}$ to [DMH] in acetonitrile may therefore suggest that a significant decay pathway of the triplex involves reversal of step 21 and reaction of the exciplex in the polar medium. This interpretation seems preferable to one which would require identical product formation efficiencies for both $^{1}(\mathrm{DCA}\cdot\mathrm{DMH})$ and $^{1}(\mathrm{DCA}\cdot\mathrm{DMH}_2)$. Finally, the possibility must now be considered that the ultimate electronically excited intermediate leading to enhanced anthracene dimerization in the A–HD system is an $^{1}(\mathrm{A}_2\cdot\mathrm{HD})$ triplex.[1b]

Experimental Section

Materials. 9,10-Dichloroanthracene, K & K, was twice recrystallized from benzene, mp 208.0–208.9°. 2,5-Dimethyl-2,4-hexadiene, Aldrich, was bulb-to-bulb distilled under vacuum immediately prior to use. *N,N*-Dimethylaniline, Aldrich reagent, was purified by distillation over mossy zinc under reduced pressure, bp 90.2–90.5° (29 Torr). Benzene, spectral grade from Mallinckrodt, Baker, or Fisher, was used without purification. Acetonitrile, spectral grade, from Aldrich or Eastman, was used without purification.

Fluorescence Measurements. Steady-state fluorescence measurements were made using a Perkin-Elmer Hitachi MPF-2A spectrophotometer. The instrument was employed in the ratio recording mode. Pyrex cells constructed from 1 cm square tubing were employed. The cells were fitted to degassing bulbs equipped with 10/30 standard taper joints and grease traps. Solutions were degassed using five to six freeze-pump-thaw cycles to about 10^{-6} Torr and the ampoules were flame sealed at a constriction. The solutions were transferred from the degassing bulb to the square cell and the cell was flame sealed at a second constriction. In obtaining relative fluorescence intensities the emission from each of the four cell faces was recorded for each sample and the average value was employed. The maximum deviation in the four measurements was 2%. Fluorescence measurements were also made using air-saturated samples. Total fluorescence spectra were corrected at each wavelength using the procedure described by Parker.[51,62] Relative fluorescence quantum yields were obtained by cutting and weighing Xerox copies of the spectra.

Fluorescence Lifetimes. Fluorescence decay profiles were determined by time correlated single photon counting. The excitation source was a free-running spark lamp whose arc formed between two sharpened tungsten or molybdenum wire electrodes separated by 0.5 mm in air at atmospheric pressure. One electrode was connected through a 66 MΩ resistor chain to the −HV output of a TRW Nanosecond Spectral Source apparatus and the other electrode was grounded. The half-peak width of the excitation source was ~2.5 nsec. The excitation flash was monitored with an RCA 1P21 photomultiplier and sample fluorescence was monitored with an RCA 8850 photomultiplier operated at −2200 V. The 12th dynode output was amplified and analyzed for single-photon response by a single channel analyzer (SCA). Conversion pulses from an Ortec 457 time-to-pulse height converter (TAC) were allowed to enter a coincidence pulse-gated TMC CN-1024 multichannel analyzer where the gating pulses were produced when TAC busy signals were coincident with SCA logic output pulses. Later in this work an equivalent but simpler method was used, that of strobing the TAC output with the SCA logic pulses (representing receipt of single photons).

Sample cells were constructed from 4 mm × 8 cm Pyrex tubing which was flattened at one end and was formed into the shape of a hemispherical lens at the other. A solution reservoir was laterally attached at the flattened end. Samples were degassed using five to six freeze-pump-thaw cycles to about 10^{-6} Torr and the ampoules were flame sealed at a constriction. The spark lamp output was filtered with a Corning 7-60 filter and was focused onto the flat end of the cell with a TRW Model 38A Relay Lens System. Fluorescence detection was enhanced due to complete trapping of the excitation light and partial trapping of the emission by total internal reflection. The rounded end of the sample cell was positioned directly at the entrance slit (1 mm) of a Jarrell-Ash 1/4 M monochromator. The emitted light was filtered with a Corning 3-72 filter mounted flush with the entrance slit. The RCA 8850 photomultiplier was mounted at the exit slit of the monochromator. Lifetimes were obtained from the slopes of first-order plots of the decay of fluorescence intensity. Least-squares fit calculations were performed on a CDC-6500 computer. With few exceptions (see the Results section) first-order plots exhibited excellent linearity.

Absorption Measurements. Ultraviolet absorption spectra were obtained using a Cary 14 recording spectrophotometer.

Irradiation Procedure. Quantum yield measurements were performed using a Moses merry-go-round apparatus[63] immersed in a water bath thermostated at 30.0°. A 200 W Hanovia mercury lamp in a Pyrex cooling probe was employed. The 366 nm mercury line was isolated using Corning filters CS 7-37 and 0-52. Samples (3 ml) of solutions containing the desired substrates were introduced into 13 × 60 mm Pyrex ampoules equipped with grease traps and 10/30 female joints. The solutions were degassed using four freeze-pump-thaw cycles to about 10^{-6} Torr, and the ampoules were flame sealed at a constriction. Analyses were by uv.

References and Notes

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Transition State Energy Stabilization in the Reactions Allyl + Propene and Methyl + 1,3-Butadiene

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Abstract: Critical energies (E_0) for reactions involving resonance stabilized reactants and/or products were measured by studying the β scission decomposition of chemically activated alkyl and alkenyl radicals. For the reverse process, addition of a radical to a double bond was obtained by microscopic reversibility. For these β scission decompositions, 67% of the TS stabilization energy is obtained from the reactants and the remaining 33% from the products. It was found that the reaction allyl + propene has a critical energy, E_0, approximately 6.8 ± 0.3 kcal/mol greater than that for the reaction propyl + propene. The critical energy for the anti-Markovnikov addition of methyl to 1-butene relative to that for the Markovnikov addition is discussed.

The question has often been asked as to the amount of stabilization which occurs in the transition state (TS) for reactions involving either resonance stabilized reactants or products. The inherent energy stabilization can only be measured in the gas phase where solvent perturbations are absent since solvent stabilization energies in solution may or may not be equal in the reactant and transition states. Energy stabilization of either the reactant or the TS will directly affect the critical energy of the reaction (E_0) which in turn appears in the temperature dependence of the rate constant, i.e., the experimentally observed activation energy. For a given reaction, energy stabilization of reactants will increase the observed activation energy while if only the TS is stabilized the observed activation energy will decrease. The absolute amount of stabilization in either reactant or TS can be obtained by measuring the difference in critical energy of two analogous reactions, one of which involves stabilization in either the reactant or product state.

The absolute amount of TS stabilization will depend on whether the TS is best characterized by the reactant or product state. Thus the position of the TS on the reaction coordinate and the contribution of stabilization from reactants and products can be determined from relevant activation or critical energy measurements. In this work the unimolecular decomposition of chemically activated radicals (R*), produced by the addition of thermalized hydrogen atoms to an olefin (Ol), results in the production of two fragments: a smaller radical (R′) and olefin (Ol′).

$$\mathrm{H + Ol \longrightarrow R^* \longrightarrow R' + Ol' + \Delta E}$$

Rate constants relative to a standard reaction [the decomposition of 2-methylbutyl-2 (2MB2)] were measured. The observed unimolecular rate constant, k_a, is related to the following fundamental quantities: the energy of excitation, the vibrational frequency pattern of the radical and decomposition TS, and the critical energy for the reaction, by the quantum statistical formulation of unimolecular reactions developed by Marcus and Rice[1] (RRKM). The first three

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