Chemistry of Exciplexes. 5. Photochemistry of Anthracene in the Presence and Absence of Dimethylaniline

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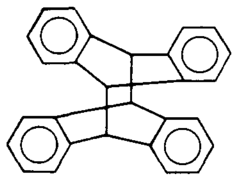
Abstract: Dimethylaniline (DMA) exerts a marked influence on the photochemistry of anthracene (A) in benzene. In the absence of DMA, anthracene undergoes photodimerization which is first order in anthracene concentration. In the presence of DMA, a competing reaction occurs which involves the electron transfer from DMA to excited anthracene as the initiating step. The effect of anthracene concentration on the photochemistry of anthracene in benzene containing 0.1 and 1.0 M DMA was analyzed mechanistically. It was also found that the quantum yield of anthracene consumption, the Stern–Volmer quenching constant of anthracene fluorescence, and the lifetime and quantum yield of the exciplex fluorescence all depend markedly on the DMA concentration. The roles of excimer and exciplex of anthracene in these reactions are discussed. The results indicate there is an interaction between [A*:DMA] exciplex and another molecule of DMA. Such an interaction may take place via a triple exciplex, [A*:2DMA], as the intermediate.

Photodimerization of anthracene and its derivatives is a well-known chemical reaction, yet many of its mechanistic aspects remain to be clarified.[1] Photoexcited anthracene may be self-quenched and quenched by oxygen,[2] amines,[3] and dienes.[4] Excimers and exciplexes have been suggested as intermediates in these processes. Since an important mode of decay of excimers and exciplexes is the formation of photochemical products, it is of particular interest to determine the role that excimers and exciplexes may play in the photochemistry of anthracene.

Bowen and Tanner investigated the photodimerization of anthracene in the presence of air or oxygen and suggested that the complex of an excited anthracene and a ground-state anthracene molecule, later known as the excimer, is the intermediate in the quenching process and the precursor of the photodimer **1**.[2] Suzuki studied the photodimerization of anthracene in toluene at various temperatures, but he did not mention whether his investigations were carried out in the presence or absence of oxygen.[5] Birks subsequently suggested that the excimer is the intermediate in photodimerization, but no published experimental details are available.[6] Recently, the role of excimer in the photodimerization of anthracene has been investigated in several other laboratories.[7-9] Campbell and Liu reported that 9-phenylanthracene is photostable, but will undergo photodimerization in the presence of 1,3-dienes.[10] From the kinetic analysis of photodimerization of anthracene in the presence of *trans,trans*-2,4-hexadiene, Saltiel and coworkers suggested that the arene–diene exciplex may be an intermediate in the photodimerization.[11] Pioneering work by Weller and his associates demonstrated that excited anthracene forms well-characterized exciplexes with aromatic tertiary amines in nonpolar solvents.[3] Reports by Pac and Sakurai and by Davidson stated that anthracene photodimer was the only product formed under such conditions.[12,13] However, an aminated anthracene (**2**) is formed as the major product when the reaction is carried out in acetonitrile, a solvent of high dielectric constant.[12] In connection with our interest in the chemistry of exciplexes,[14-17] the photochemistry of anthracene in benzene both in the presence and absence of dimethylaniline was investigated. We found that a novel reaction competing against photodimerization occurs in the presence of dimethylaniline (DMA). The products isolated were 9-*N*-methylanilino-9,10-dihydroanthracene (**3**) and 9,9′,10,10′-tetrahydro-9,9′-bianthryl (**4**). The mechanisms of these reactions were investigated by both kinetic and spectroscopic methods.



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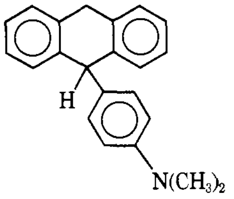

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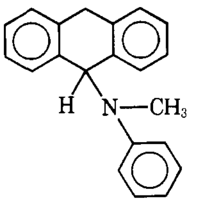

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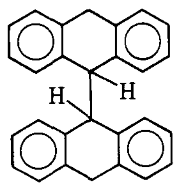

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Experimental Section

Apparatus. A merry-go-round apparatus similar to those described elsewhere was used.[18-20] The light source was a Hanovia medium-pressure Hg lamp with immersion fittings in a quartz cooling well (Ace Glass Catalog No. 6515). The lamp was cooled by circulating through the well a filter solution precooled with a heat exchanger. Corning 2 × 2 in. filters were mounted into four filter holders flush against the well. The rest of the well was taped to eliminate stray light. The sample tube holder (14 cm in diameter) with a capacity of 16 sample tubes was mounted on a turntable capable of rotating around the well at 15 rpm. The samples are approximately 7.0 cm from the lamp. Rotation of the samples around the lamp achieved uniform light intensity for each of the sample tubes during the irradiation. The whole assembly was kept in a room maintained at 21.0 ± 1.0 °C and the light intensities did not vary appreciably throughout this investigation.

The 313-nm line of Hg was isolated from a 450-W Hanovia Hg lamp, No. 679-A-36, by a combination filter consisting of a precooled solution containing 0.6 g/l. of potassium chromate and 0.17 g/l. of sodium hydroxide and a set of four Corning 7-54 filters. Analysis of the light purity indicated that the filtered light consisted of approximately 3% contribution from the 334-nm line of Hg.[21] The average light intensity at 313 nm was approximately 6.0×10^{-7} einstein/min for a 2.5-ml sample. The 366-nm line of Hg was isolated from a 200-V Hanovia Hg lamp, No. 654-A-36, by a set of four Corning 7-39 filters. The light source was cooled by precooled distilled water. Empirical analysis from the data supplied by the manufacturers of filter and lamp indicated that the filtered light contained approximately 3.5% contribution from the 334-nm line and 0.5% from the 313-nm line of Hg. The average total light intensity was approximately 9.0×10^{-7} einstein/min for a 2.5-ml sample. The addition of Corning 0-52 filters to this system was found to have a negligible effect on our results.

Table I. Photodimerization of Anthracene in Benzene[a]

[Anthracene], 10^{-4} M	1/[Anthracene], M^{-1}	Φ	$1/\Phi$
100	100	0.139 ± 0.019	7.19
100	100	0.128 ± 0.009	7.81
50	200	0.0734[b]	13.6
50	200	0.0684 ± 0.0045	14.6
25	400	0.0444 ± 0.0044	22.5
20	500	0.0387 ± 0.0017	25.8
15	667	0.0298 ± 0.0013	33.6
12.5	800	0.0236 ± 0.0041	42.4
10	1000	0.0192 ± 0.0052	52.2
50[c]	200	0.0706 ± 0.0059	14.2

[a] Exciting light at 313 nm. [b] One determination. [c] Exciting light at 365 nm.

Table II. Photoconsumption of Anthracene in Benzene in the Presence of 1.0 M Dimethylaniline[a]

[Anthracene], 10^{-4} M	1/[Anthracene], M^{-1}	Φ	$1/\Phi$
40	250	0.170 ± 0.015	5.88
25	400	0.178 ± 0.010	5.62
20	500	0.175 ± 0.010	5.71
16.7	600	0.167 ± 0.015	5.99
13.3	750	0.181 ± 0.025	5.52
11.1	900	0.182 ± 0.023	5.49
10	1000	0.161 ± 0.008	6.21
8.33	1200	0.160 ± 0.005	6.25
6.67	1500	0.180 ± 0.023	5.56
5.71	1750	0.161 ± 0.014	6.02

[a] Exciting light at 365 nm.

The sample tubes were constructed from right-angle high-vacuum stopcocks with Teflon plugs manufactured by Ace Glass, Inc., No. 8193 or 8195, size 0-3. The stopcock was sealed to a 5-cm section of precision bore borosilicate glass tubing, 12.5-mm o.d. and 9.5-mm i.d. The samples could be conveniently degassed by the common freeze-thaw technique. The sample tubes were shown to be vacuum tight over an 8-h period. The absorption characteristics of round sample tubes have been analyzed recently by Vesley[22] and Shetlar.[23] In order to minimize the error which may be introduced by the difference in refractive indices between the actinometer and the sample, benzophenone-benzhydrol system[24] was selected, since the same solvent (benzene) would be used in our kinetic analysis. The absorption characteristics of our sample tubes were further analyzed by using a series of benzophenone-benzhydrol actinometer solutions containing different concentrations of benzophenone. We found that the absorption characteristics of our sample tubes were approximately the same as rectangular tubes of the same dimension within experimental error.

Chemicals. Reagent grade anthracene (fluorescent grade) was recrystallized twice from ethanol, mp 215.0 °C, and reagent grade dimethylaniline (Aldrich) was distilled twice under reduced pressure, bp 95-97 °C (35 mm), for these experiments. Spectrograde benzene (Aldrich) was used as received.

Kinetic Determinations. After stock solutions of samples of appropriate concentrations had been prepared in volumetric flasks, aliquots of 2.5 ml were introduced into the sample tubes. These were degassed by three freeze-thaw cycles at 0.01-0.03 Torr. In order to reduce the possibility of experimental errors, three samples were used for a given concentration of anthracene. Multiples of three samples and one actinometer were irradiated after the lamp had been warmed up for 30 min. Samples were withdrawn at suitable intervals and the extent of reaction was determined by following the decrease in absorbence of anthracene at 379 nm with a Cary-14 spectrophotometer. In order to minimize the error in absorbance determination, the instrument was set at 379 nm and each sample was scanned at that wavelength for 30 s, or 5 cm on the chart paper. The average absorbance over this period was determined visually from the chart. The rate of disappearance of anthracene at a given concentration was determined by plotting the results of three samples withdrawn at different time intervals and obtaining the slope from a least-squares analysis of four points, including the one at time zero. The quantum yield was then calculated from the rate and the light intensity. The average conversion of samples was 15% and in no case did the conversion exceed 28%. The reaction followed zero-order kinetics within the range of reaction examined as indicated by the linearity of our plots by visual examination. Corrections were applied for incomplete light absorption for samples at very low anthracene concentrations.

The 313-nm light was used for the dimerization of anthracene in benzene and the 365-nm light was used for the reaction of anthracene in the presence of dimethylaniline, since the absorption of dimethylaniline at 313 nm interferes with that of anthracene. In a separate determination, we found the quantum yield of dimerization of anthracene in benzene to be the same within experimental error when the sample was excited at either 313 or 366 nm. Tables I, II, and III give the results of photodimerization of anthracene in benzene, the photoconsumption of anthracene in the presence of 1.0 M DMA, and the photoconsumption of anthracene in the presence of 0.1 M DMA, respectively. Table IV gives the results of the photoconsumption of 0.01 M anthracene containing variable concentrations of DMA in benzene, Figure 1 represents graphically the results from Tables I-III, and Figure 2 represents graphically the results from Table IV.

Experimental Uncertainty. The experimental uncertainty in the optical density determination with a Cary-14 spectrophotometer is ±0.002 optical density unit.[25] This, in turn, results in experimental uncertainty in our quantum yield measurements of ±0.01 or ±4% and uncertainty in the slopes of our experimental plots of the order of 5 $\times 10^{-3}$ M^{-1}. Our experimental errors in quantum determinations have an average value of about ±7%, indicating that we have achieved accuracies approaching the limit of experimental conditions.

Table III. Photoconsumption of Anthracene in Benzene in the Presence of 0.1 M Dimethylaniline[a]

[Anthracene], 10^{-4} M	1/[Anthracene], M^{-1}	Φ_{exptl}	Φ_{calcd}	$1/\Phi_{\mathrm{exptl}}$
100	100	0.0762 ± 0.0059	0.0697	13.1
50	200	0.0576 ± 0.0065	0.0548	17.3
40	250	0.0572 ± 0.0046	0.0516	17.5
33.3	300	0.0468 ± 0.0017	0.0494	21.3
25	400	0.0463 ± 0.0016	0.0466	21.6
25	400	0.0518 ± 0.0002	0.0466	19.3
20	500	0.0454 ± 0.0052	0.0449	22.0
16.7	600	0.0424 ± 0.0020	0.0437	23.6
13.3	750	0.0420 ± 0.0011	0.0426	23.8
11.1	900	0.0419 ± 0.0029	0.0418	23.8
10	1000	0.0415 ± 0.0014	0.0414	24.1
8.33	1200	0.0384 ± 0.0022	0.0408	26.0
6.67	1500	0.0381 ± 0.0024	0.0402	26.2
10[b]	1000	0.0404 ± 0.0016		24.8

[a] Exciting light at 365 nm. [b] In benzene containing 8.5% EtOAc.

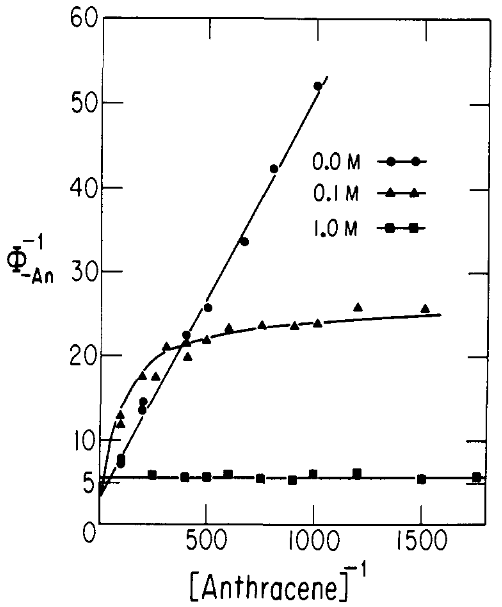


Figure 1. Quantum yield of anthracene consumption in the presence of DMA.

Table IV. Photoconsumption of Anthracene (0.1 M) in the Presence of Dimethylaniline[a]

[DMA], M	ϕ_{exptl}	ϕ_{calcd}
0	0.124 ± 0.006	0.124
0.01	0.106 ± 0.004[b]	0.105
0.025	0.082 ± 0.008[b]	0.089
0.050		0.076
0.10	0.057 ± 0.006[b] 0.076 ± 0.007[c]	0.070

[a] Exciting light at 365 nm. [b] Values are from this run and relative to that in the absence of DMA. [c] Values from Table III.

Fluorescence Determinations. The quenching of anthracene fluorescence by DMA in benzene and the analysis of the exciplex emission were carried out with a Perkin-Elmer MP-4 spectrofluorimeter containing a corrected spectrum system. The samples were degassed by the conventional freeze-thaw technique before the measurements. The results are tabulated in the Table V.

The lifetimes of anthracene fluorescence and the exciplex fluorescence were determined by deconvolution single photon counting.[26,27] We thank Mr. J. K. McVey for these measurements.

Photochemical Reactions between Anthracene and *N,N*-Dimethylaniline in Benzene. A solution of anthracene (5×10^{-3} to 2×10^{-2} M) and dimethylaniline (0.1-1.0 M) in benzene (120-400 ml) was irradiated with a Hanovia 450-W medium-pressure Hg arc through a uranyl glass filter to cut off light emission below 330 nm. The consumption of anthracene was followed by uv-visible spectroscopy. The irradiation was continued until the anthracene absorption at 378 nm had disappeared or was reduced to approximately half of its original intensity. If anthracene photodimer was formed in the reaction, it was isolated by filtration of the reaction mixture. Benzene was then removed under reduced pressure with a rotary evaporator and most of the excess dimethylaniline was removed by distillation at 0.2 Torr with a bath temperature not exceeding 75 °C. The major reaction products, 9-*N*-methylanilino-9,10-dihydroanthracene (**3**, mp 111-113 °C) and 9,9′,10,10′-tetrahydro-9,9′-bianthryl (**4**, mp 235-240 °C) may be isolated by column chromatography on activity II neutral Woelm alumina. The products were identified by comparison with respective authentic samples.[14] Variable amounts (10-20%) of anthracene were recovered in these reactions, presumably from the air oxidation of **4** during the work up. The composition of the reaction mixture was analyzed by NMR spectroscopy after excess dimethylaniline had been removed by distillation. The results of several irradiations are summarized in Table VI and the yields are calculated on the basis of anthracene consumed.

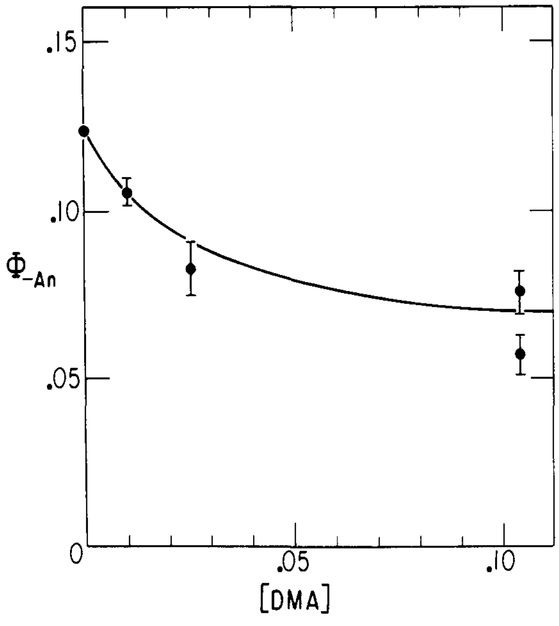
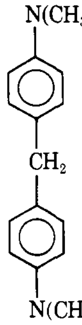


Figure 2. Quantum yield of consumption of anthracene (0.01 M) in the presence of DMA.

When the irradiations were carried out in reagent benzene, no formaldehyde, methylaniline, or bis(4,4′-*N,N*-dimethylaminophenyl)methane (**5**) was detected by gas chromatography or NMR analysis of the reaction mixtures.



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However, a similar irradiation was carried out with a benzene solution of anthracene (6×10^{-3} M) and diethylaniline (0.78 M). The reaction mixture was fractionally distilled at atmospheric pressure with a column rated at eight theoretical plates. In this case, acetaldehyde (7% yield) was detected and identified by gas chromatography and NMR spectroscopy in the forerun of the distillate.

A solution of anthracene (234 mg, 1.34 mmol) and dimethylaniline (0.139 mol) in 120 ml of benzene containing 0.8 ml of water was irradiated as before. After anthracene had been consumed (3 h), a second portion of anthracene (1.34 mmol) was added to the solution. The irradiation was continued for another 4 h. The reaction mixture was then fractionated at atmospheric pressure with a column rated at eight theoretical plates. About 90% of the water was recovered by azeotropic distillation. The presence of formaldehyde in the aqueous layer was established by a purple color test with chromotropic acid and its conversion to the dimedone derivative (mp 188-189 °C). The yield of the dimedone derivative was 5.2%. The reaction mixture was worked up as before. It consisted of recovered anthracene (109.5 mg), anthracene photodimer (16%), **3** (24%), and **4** (48%).

Results

A. Product Analysis. In the absence of DMA, the only photoproduct formed from anthracene is the photodimer. The presence of DMA causes a modification in the photochemical reaction of anthracene, the results of which are tabulated in the Experimental Section. In high concentration of DMA (1.0

Table V. Variation of Stern–Volmer Constant, Maximum of Fluorescence, Fluorescence Quantum Yield, and Lifetime of [^{1}A:DMA] with DMA Concentration in Benzene

[DMA], M	K_{SV}, M^{-1}	λ_{max}	ϕ_f (exptl)[a]	ϕ_f (calcd)[b]	τ_f, ns
0.005–0.03	40.4 ± 1.6	499 ± 2[c]	0.30 ± 0.03[c]		114 ± 5[d]
0.10	50.6	500 ± 2	0.30 ± 0.03		109 ± 4
0.20		501 ± 2	0.30 ± 0.03[e]		
0.30	62.7	501 ± 2	0.33 ± 0.03		
0.70	100.0	502 ± 3	0.28 ± 0.03	0.24	
1.0	133.0	505 ± 3	0.22 ± 0.02	0.21	77 ± 2
1.3	165.4	505 ± 3	0.18 ± 0.02	0.19	
1.7	178.8	506 ± 3	0.14 ± 0.02	0.17	
2.0	212.0	506 ± 3	0.12 ± 0.02	0.15	
0.10[f]	51.0[g]	505 ± 3	0.28 ± 0.03		
0.10[h]	53.3[g]	508 ± 3	0.27 ± 0.03		
0.10[i]	65.7[g]	519 ± 4	0.18 ± 0.02		
0.10[j]	89.4[g]	542 ± 5	0.10 ± 0.01		

[a] The quantum yields given have been corrected for the amount of exciplex existing at the equilibrium. [b] Calculated on the basis of ϕ_f at low DMA concentration to be 0.31. [c] Measured at 0.03 M DMA concentration. [d] Measured at 0.01 M DMA concentration. [e] Assuming K_{SV} to be 56.6 M^{-1}. [f] In benzene containing 8.5% EtOAc. [g] Relative to fluorescence in pure benzene. [h] In benzene containing 18% EtOAc. [i] In 1:1 benzene–EtOAc. [j] In neat EtOAc.

Table VI

				% products	
[Anthracene], M	[Dimethylaniline], M	% conversion	% dimer	**3**	**4**
5×10^{-3}	0.1	Complete	47	35	15
5×10^{-3}	1.0	50		69	31
5×10^{-3}	1.0	Complete	0.5	61	35
2×10^{-2}	1.0	50	46	42	9

M) and relatively low concentration of anthracene (0.005 M or below), little or no photodimer of anthracene is formed, while **3** and **4** are the major reaction products. In either low DMA concentration (0.1 M) or high concentrations of both anthracene (0.02 M) and DMA (1.0 M), both the photodimer and **3** are formed in the reaction.

B. Quantum Yields of Anthracene Consumption. Quantum yields of anthracene consumption under various conditions are presented in Tables I–IV and in Figures 1 and 2. When the reciprocals of the quantum yields of anthracene consumption (ϕ_{-A}^{-1}) are plotted against the reciprocals of anthracene concentrations (A^{-1}), three different lines result, depending upon the DMA concentration. In the absence of DMA, a straight line results, with a slope of (4.80 ± 0.15) × 10^{-2} M^{-1} and an intercept of 3.2 ± 0.9. In 1.0 M DMA, ϕ_{-A} has a value of 0.168 ± 0.013, independent of anthracene concentration from 5.71 × 10^{-4} to 4.0 × 10^{-3} M. In 0.1 M DMA, the case is intermediate between those in the absence of DMA and in 1.0 DMA. As indicated in Figure 1, at high concentrations the quantum yields are less than those in the case of anthracene alone. This is because photodimerization and formation of **3** may compete with each other: the relatively efficient photodimerization is quenched by DMA via exciplex formation, which leads to comparatively inefficient formation of **3**. As the concentration of anthracene is decreased, the quantum yield of photodimerization drops off rapidly, so that eventually the formation of **3** predominates, giving a limiting quantum yield which may be estimated to be 0.038 ± 0.001 (see Discussion). The quenching of photodimerization of anthracene (0.01 M in benzene) by DMA was verified by studying the variation of anthracene consumption with DMA concentration ranging from 0.01 to 0.1 M (Table IV and Figure 2).

The variation in the quantum yield of anthracene consumption from 0.1 M DMA in benzene to 1.0 M DMA is not apparently due to the increase in the dielectric constant of the medium. With the concentration of anthracene at 0.001 M; ϕ_{-A} was measured to be 0.0415 ± 0.0014 in 0.1 M DMA and 0.161 ± 0.008 in 1.0 M DMA. However, ϕ_{-A} in benzene containing 0.1 M DMA and 8.5% of ethyl acetate by volume, which has the same dielectric constant as 1.0 M DMA in benzene,[28] was found to be 0.0404 ± 0.0016. The value is the same within experimental error as that in 0.1 M DMA, but much less than that in 1.0 M DMA.

C. Quenching of Anthracene Fluorescence by DMA in Benzene and the Lifetime of the Exciplex Fluorescence. The fluorescence of anthracene in benzene is efficiently quenched by DMA. Simultaneously, the exciplex fluorescence in the green appears. At low DMA concentrations ranging from 0.005 to 0.03 M, the Stern–Volmer plot is linear with a slope of $k_q\tau$ = 40.4 ± 1.6 M^{-1}. However, as the concentration of DMA increases, the plot rapidly deviates from linearity. The Stern–Volmer quenching constant ($k_q\tau$ or K_{SV}) increases by a factor of more than 5 as the concentration of DMA increases from 0.005 to 2.0 M. The quantum yield and the lifetime of the exciplex fluorescence also vary appreciably with DMA concentration. The quantum yield of the exciplex fluorescence remains constant within experimental error (0.30–0.33 ± 0.03) at low DMA concentrations (0.005–0.03 M), then decreases successively as the concentration of DMA increases (Table V). The lifetime of exciplex fluorescence was found to be 114 ± 5 ns in 0.01 M DMA and 109 ± 4 ns in 0.1 M DNA, but only 77 ± 2 ns in 1.0 M DMA.

These changes in exciplex photophysics are again not caused by the change in the dielectric constant of the medium. We observed no appreciable change in fluorescence behavior of 0.1 M DMA solution in benzene relative to a solution of 0.1 M DMA solution in benzene containing 8.5% of ethyl acetate. The change in fluorescence quantum yield is within the experimental error of our measurements, but there was a slight red shift of exciplex emission maximum from 500 ± 2 to 505 ± 3 nm, which is the same as that in 1.0 M DMA solution.

Discussion

A. Photodimerization of Anthracene in the Absence of DMA. The results of photodimerization of anthracene in benzene may be analyzed by the following equations:

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

$${}^1A \xrightarrow{k_1 \text{ or } 1/\tau} A + h\nu' + \text{heat} \qquad (2)$$

$${}^1A + A \xrightarrow{k_2} [{}^1A{:}A] \qquad (3)$$

$$[{}^1A{:}A] \xrightarrow{k_3} A_2 \qquad (4)$$

$$[{}^1A{:}A] \xrightarrow{k_4} 2A \qquad (5)$$

where A, ^{1}A, [^{1}A:A], A_2, and τ are anthracene, singlet excited anthracene, the excimer, photodimer of anthracene, and the lifetime of excited anthracene, respectively. For the sake of simplicity, the rate constant k_1 includes both rates of fluorescence and nonradiative decay of singlet excited anthracene and the dissociation of excimer to its components (the reverse of reaction 3) has been neglected, since it has been shown to be insignificant in the gas phase.[29] Since the photodimer is the only product of this reaction, the quantum yield of anthracene disappearance is twice that of photodimerization to account for the two molecules of anthracene consumed in the dimerization. On the basis of above kinetic equations, the quantum yield of anthracene disappearance may be written as

$$\phi_{-A} = 2\phi_{\text{dim}} = 2\left[\frac{k_2[A]}{k_1 + k_2[A]}\right]\left[\frac{k_3}{k_3 + k_4}\right]$$

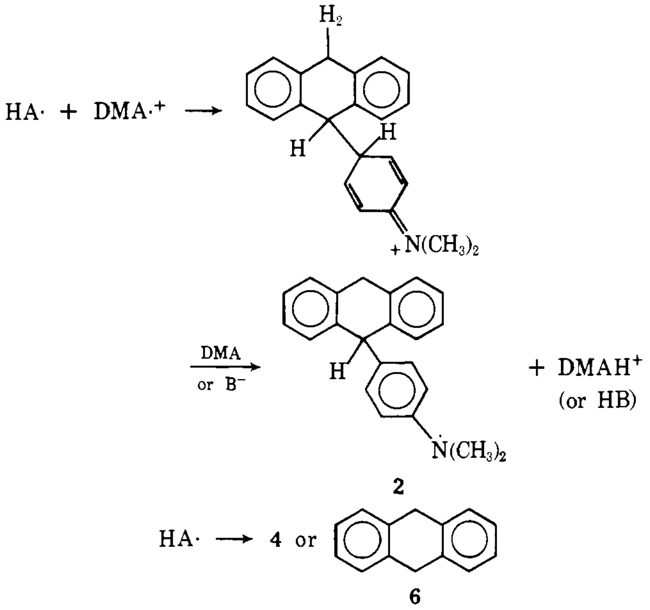
$$2\phi_{-A}^{-1} = 1/\phi_{\text{dim}} = [1 + (k_4/k_3)][1 + (1/k_2\tau[A])]$$

where $\tau = 1/k_1$. Since ϕ_{-A}^{-1} is plotted against $[A]^{-1}$ in Figure 1, the intercept for ϕ_{-A} is 3.2 ± 0.9 or that for ϕ_{dim} is 6.4 ± 1.8. The limiting quantum yield of photoconsumption is 0.31 ± 0.09 and that for photodimerization is thus 0.16 ± 0.05. This is below the literature values of 0.3[1] and 0.338,[5] but is in fair agreement with the values of 0.22[2] and 0.24.[7] The slope of the plot corrected for dimerization was (9.6 ± 0.3) × 10^{-2} M, which may be compared with the literature values of 1.9 × 10^{-2} M in the presence of oxygen and 3.1 × 10^{-2} M in the presence of air.[2]

The intercept of 6.4 ± 1.8 may be taken as $(k_3 + k_4)/k_3$, or the reciprocal of the fraction of excimer which will decay to give the photodimer. This implies that only 16 ± 5% of the excimer will go on to form the photodimer, while the majority of it will undergo radiationless decay to ground-state anthracene. The slope, on the other hand, may be taken as the intercept divided by the product of the rate of excimer formation and the lifetime of singlet excited anthracene. Since the lifetime of singlet excited anthracene is 4.8 ns, the calculated value for k_2 is (1.39 ± 0.48) × 10^{10} M^{-1} s^{-1}, which is in good agreement with the literature value of 0.93 × 10^{10} M^{-1} s^{-1} [5] and the calculated rate for a diffusion-controlled process in benzene of 1.0 × 10^{10} M^{-1} s^{-1}.[30] These results confirm the idea that the rate of anthracene excimer formation is, within experimental error, a diffusion-controlled process.

$${}^1A + DMA \xrightarrow{CH_3CN} A\cdot^- + DMA\cdot^+$$

$$A\cdot^- + DMAH^+ \text{ (or HB)} \longrightarrow HA\cdot + DMA \text{ (or } B^-)$$



B. Photochemistry of Anthracene in the Presence of DMA. Anthracene reacts photochemically with DMA in acetonitrile, a polar solvent, to give **2**, **4**, and **6** in high efficiency (ϕ_{-A} = 0.58);[12,14] however, anthracene photodimer is the only product reported when anthracene is irradiated with DMA in benzene, a nonpolar solvent.[12,13] Therefore, DMA has apparently no effect on the photochemistry of anthracene in nonpolar solvents. In an effort to relate our mechanistic investigation to the product analysis, we found that anthracene reacts photochemically with DMA in benzene at high DMA concentrations to give **3**, the adduct of *N*-methylaniline to anthracene, and **4**, the bimolecular reduction product of anthracene. Both **3** and **4** had been isolated and characterized in our laboratory previously,[14] and they were readily identified. Since the DMA used has been purified and analyzed by gas chromatography to exclude the contamination by *N*-methylaniline, **3** is formed from DMA and not *N*-methylaniline, which might be present as a contaminant. DMA is apparently demethylated and the cleaved methyl group functions as a reducing agent for anthracene. We encountered a considerable amount of experimental difficulty in tracing the fate of the "missing" methyl group in the formation of **3** from DMA. We systematically eliminated many derivatives of methanol and formaldehyde, such as bis(4,4′-dimethylaminophenyl)methane (**5**), alkylated anthracene, and alkylated DMA as possible products in our reaction. Finally, we detected qualitatively the cleaved methyl group as formaldehyde from the DMA reaction with anthracene and the cleaved ethyl group as acetaldehyde from the DEA reaction. Since only a trace of water is needed for these reactions, i.e., about 0.01% by weight in benzene, there is apparently enough moisture in the reaction mixture for this reaction to occur.[31] Stoichiometrically, the reaction may be expressed as

$$3C_{14}H_{10} + DMA + (H_2O) \xrightarrow{h\nu} \mathbf{3} + \mathbf{4} + CH_2O$$

This reaction is analogous to the photoreduction of aromatic ketones in the presence of tertiary amines, which may also proceed via an exciplex intermediate.[32] Cohen and his coworkers suggested that [ketone*-amine] exciplex decays to give a ketyl radical and an aminoalkyl radical as the initial step of the photoreduction. The presence of such radicals in this reaction has been confirmed by spectroscopic methods.[32]

$$[Ar_2C{=}O]^* + R_2NCH_3 \rightarrow [\text{exciplex}] \rightarrow Ar_2\dot{C}OH + R_2N\dot{C}H_2$$

$$2Ar_2\dot{C}OH \rightarrow Ar_2C(OH)C(OH)Ar_2$$

$$R_2NCH_2\cdot \xrightarrow[(H_2O)]{\text{many steps}} R_2NH + CH_2O$$

or overall,

$$2Ar_2C{=}O + R_2NCH_3 + (H_2O) \xrightarrow{h\nu} Ar_2C(OH)C(OH)Ar_2 + R_2NH + CH_2O$$

Although the abstraction of a hydrogen atom by an excited carbonyl compound, either directly or via an exciplex, is a well-known chemical reaction, the analogous reaction by an excited anthracene molecule has not been documented. The decay of [^{1}A:DMA] to give chemical products is found by us to be inefficient; however, the bimolecular decay of the exciplex with another molecule of DMA is apparently quite efficient, $\phi_{-A} = 0.168$.

Although photoexcited anthracene is known to undergo efficient electron transfer with DMA in polar solvents such as acetonitrile to form radical ions as intermediates in chemical reactions,[12,14] DMA has only a slightly higher dielectric constant ($\epsilon = 5.03$) than benzene ($\epsilon = 2.28$).[28] The presence of 1 M DMA in benzene only increases the dielectric constant slightly; therefore, the modification of reaction pathway from a low concentration DMA solution to a higher one is unlikely to be due to the minor increase in the dielectric constant of the reaction medium. This is verified by our experiment that when ethyl acetate is added to benzene to adjust the dielectric constant of 0.1 M DMA solution to that of 1.0 M DMA solution, there is practically no change in photophysical behavior of the exciplex and photochemistry of the system (Tables III and V). The results implied that the interaction between the exciplex and the second molecule of DMA must occur in a very specific manner, and such an interaction may well be the formation of a triple exciplex or [^{1}A:2DMA]. The formation of triple exciplexes from one molecule of excited aromatic hydrocarbon and two molecules of a ground-state donor has been demonstrated spectroscopically[33,34] and is also supported by kinetic evidence from other laboratories.[34,35] Suckow and Grellmann have shown that the quantum yield and lifetime of [^{1}A:DEA] emission decrease with decreasing temperature and suggested that the formation of the triple exciplex is favored at lower temperature, which decays mainly via "intersystem crossing".[33] The results are completely compatible with the interpretation that the triple exciplex may decay efficiently via electron transfer and chemical reactions. Such an interpretation is further supported by our kinetic results (vide infra).

By analogy with the photoreduction of aromatic ketones by tertiary amines, we propose that the photoreduction of anthracene by DMA proceeds via the triple exciplex with the electron transfer as the initiating and the rate-determining step.

$$[^1A{:}2DMA] \rightarrow A\cdot^- + DMA\cdot^+ + DMA$$

The presence of a second molecule of DMA in the close proximity of [^{1}A:DMA] induces the electron transfer and the result will be the formation of the radical ion pair with another molecule of DMA in close proximity. Since DMA is a base and DMA$\cdot^+$ is an electron-deficient molecule, an acid-base reaction is expected to occur

$$DMA + DMA\cdot^+ \rightarrow DMAH^+ + PhN(CH_3)CH_2\cdot$$

In a nonpolar medium like benzene, DMAH$^+$ may react with A$\cdot^-$ to give AH$\cdot$ and DMA,

$$DMAH^+ + A\cdot^- \rightarrow DMA + AH\cdot$$

or overall,

$$[^1A{:}DMA] + DMA \rightleftharpoons [^1A{:}2DMA] \rightarrow AH\cdot + DMA + PhN(CH_3)CH_2\cdot$$

The nonradiative decay processes may thus include

$$AH\cdot + PhN(CH_3)CH_2\cdot \rightarrow A + DMA$$

$$DMA\cdot^+ + A\cdot^- \rightarrow A \text{ or } {}^3A + DMA$$

and AH$\cdot$ may dimerize to give **4**.

$$2AH\cdot \rightarrow \mathbf{4}$$

Subsequent steps in the formation of **3** are, however, less well understood, as in the case of photoreduction of aromatic ketones by tertiary amines. We wish to suggest that following reactions may be involved

$$PhN(CH_3)CH_2\cdot + [^1A{:}DMA] + (H_2O) \rightarrow PhN(CH_3)CH_2OH + AH\cdot + DMA$$

$$PhN(CH_3)CH_2OH + [^1A{:}DMA] \rightarrow \mathbf{3} + CH_2O + DMA$$

C. Kinetic Analysis of the Equilibrium of Exciplex Formation and Exciplex Lifetime. Judging from the results summarized in Table V, the behavior of the anthracene-dimethylaniline exciplex depends markedly on the concentration of DMA in solution. Kinetically, the effect of DMA on the photochemistry of anthracene may be expressed by the following scheme:

$$^1A + DMA \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [^1A{:}DMA] \qquad (6)$$

$$[^1A{:}DMA] \xrightarrow{k_6} A + DMA + h\nu \qquad (7)$$

$$[^1A{:}DMA] \xrightarrow{k_7} A + DMA + \text{heat} \qquad (8)$$

$$[^1A{:}DMA] \xrightarrow{k_8} \text{products} \qquad (9)$$

$$[^1A{:}DMA] + DMA \xrightarrow{k_9} \text{products} \qquad (10)$$

$$[^1A{:}DMA] + DMA \xrightarrow{k_{10}} A + 2DMA + \text{heat} \qquad (11)$$

where [^{1}A:DMA] represents the anthracene-dimethylaniline exciplex; k_6, k_7, and k_8 represent the rates of unimolecular decay of the exciplex via exciplex fluorescence, nonradiative decay, and chemical product formation, respectively; k_9 and k_{10} represent the rates of bimolecular decay of the exciplex via product formation and nonradiative decay. Alternatively, we may assume [^{1}A:DMA] may interact reversibly with another molecule of DMA to form a 1:2 exciplex, [^{1}A:2DMA], which may subsequently decay to form either products or starting material.

$$[^1A{:}DMA] + DMA \rightleftharpoons [^1A{:}2DMA] \begin{array}{l} \nearrow \text{products} \\ \searrow A + 2DMA + \text{heat} \end{array} \qquad (11a)$$

By carefully analyzing the decay characteristics of [^{1}A:DMA] fluorescence at room temperature (23 ± 1 °C), we found that the decay follows simple first-order kinetics over many decades of mean lifetimes; that is, there was no experimental evidence of nonexponential decay. A similar observation has been made by Suckow and Grellmann on the decay of the anthracene-diethylaniline exciplex,[33] [^{1}A:DEA]*. These results indicate that, if the triple exciplex is formed under these conditions, there is an equilibrium between the two exciplexes which is much more rapid than the decay of either species. The exciplex fluorescence from [^{1}A:2DEA] has been detected at low temperatures and its lifetime was found to be shorter than the 1:1 exciplex even at these temperatures. Therefore, kinetically the bimolecular decay of the exciplex may be represented equally well by eq 10 and 11 or by eq 11a.

Since the exciplex has a much longer lifetime than the uncomplexed excited arene and the exciplex formation is a reversible process, the fluorescence of the parent arene will decay nonexponentially. It will decay initially with a rate of $k_1 + k_5[\mathrm{DMA}]$ and subsequently with a rate which is the reciprocal of the lifetime of the exciplex, τ_{ex}^{-1}, or the sum of k_{-5}, k_6, k_7, and k_8, at low DMA concentrations. The slower decay is due to the fluorescence of excited anthracene regenerated by the dissociation of $[^1\mathrm{A{:}DMA}]$. Such a phenomenon has been noted earlier by Ware and his co-workers.[36,37]

Under our experimental conditions of deconvolution photon counting, when DMA is present only at low concentrations, the bimolecular decay of $[^1\mathrm{A{:}DMA}]$ by interaction with DMA is unimportant. Hence τ_{ex}^{-1} may be given by the following expression:

$$\tau_{\mathrm{ex}}^{-1}[^1\mathrm{A{:}DMA}] = (k_{-5} + k_6 + k_7 + k_8) \times [^1\mathrm{A{:}DMA}] - k_5[^1\mathrm{A}][\mathrm{DMA}] \quad (12)$$

Since $[^1\mathrm{A}]$ decays so much faster than $[^1\mathrm{A{:}DMA}]$, i.e., $k_1 + k_5[\mathrm{DMA}]$ is much larger than τ_{ex}^{-1}, during the lifetime measurement of $[^1\mathrm{A{:}DMA}]$, virtually all $[^1\mathrm{A}]$ formed by initial excitation has already decayed and the concentration of $^1\mathrm{A}$ in solution may be adequately represented by the $[^1\mathrm{A}]$ regenerated from the dissociation of $[^1\mathrm{A{:}DMA}]$. The regenerated $[^1\mathrm{A}]$ decays with a lifetime of τ_{ex}, as has been shown experimentally.[37] Thus,

$$\tau_{\mathrm{ex}}^{-1}[^1\mathrm{A}] = k_5[^1\mathrm{A}][\mathrm{DMA}] + k_1[^1\mathrm{A}] - k_{-5}[^1\mathrm{A{:}DMA}] \quad (13)$$

In 0.01 M DMA, τ_{ex} is 114 ns, $k_1 = 1/\tau = 2.08 \times 10^8\ \mathrm{s}^{-1}$, and k_5 is assumed to be the diffusion-controlled rate of $1.0 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. Substituting these values into eq 13,

$$8.77 \times 10^6\ \mathrm{s}^{-1}\ [^1\mathrm{A}] = 1.0 \times 10^8\ \mathrm{s}^{-1}\ [^1\mathrm{A}] + 2.08 \times 10^8\ \mathrm{s}^{-1}\ [^1\mathrm{A}] - k_{-5}[^1\mathrm{A{:}DMA}]$$

or

$$k_{-5}[^1\mathrm{A{:}DMA}] = 2.99 \times 10^8\ \mathrm{s}^{-1}\ [^1\mathrm{A}]$$

Substituting the value of $[^1\mathrm{A}]$ in terms of $[^1\mathrm{A{:}DMA}]$ derived from eq 14 into eq 12,

$$8.77 \times 10^6\ \mathrm{s}^{-1} = (k_6 + k_7 + k_8) + (k_{-5} - 0.334k_{-5}) = (k_6 + k_7 + k_8) + 0.666k_{-5} \quad (15)$$

Since the Stern-Volmer quenching constant ($k_q\tau$) of $^1\mathrm{A}$ by DMA at 0.01 M DMA is 40.4 M^{-1} and τ is 4.8 ns,

$$k_q = 8.32 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

and

$$k_q = k_5(k_6 + k_7 + k_8)/(k_{-5} + k_6 + k_7 + k_8) \quad (16)$$

or

$$(k_5/k_q) - 1 = k_{-5}/(k_6 + k_7 + k_8)$$

therefore,

$$4.95k_{-5} = k_6 + k_7 + k_8$$

Substituting this value into eq 15,

$$5.62k_{-5} = 8.77 \times 10^6\ \mathrm{s}^{-1}$$

or

$$k_{-5} = 1.56 \times 10^6\ \mathrm{s}^{-1}$$

and

$$k_6 + k_7 + k_8 = 7.73 \times 10^6\ \mathrm{s}^{-1}$$

The equilibrium constant for $[^1\mathrm{A{:}DMA}]$ formation from $^1\mathrm{A}$ is then

$$K_{\mathrm{ex}} = k_5/k_{-5} = 1 \times 10^{10}/1.56 \times 10^6\ \mathrm{M}^{-1} = 6410\ \mathrm{M}^{-1}$$

This value compares well with the value of 2900 M^{-1} obtained in a different manner by Weller and his co-workers for the $[^1\mathrm{A{:}DEA}]$ system.[38]

In 1.0 M DMA, τ_{ex} is 77 ns and the formation of $[^1\mathrm{A{:}DMA}]$ from $^1\mathrm{A}$ is for all practical purposes nonreversible; therefore, the result may be expressed as

$$\tau_{\mathrm{ex}}^{-1} = k_6 + k_7 + k_8 + (k_9 + k_{10})[\mathrm{DMA}] \quad (17)$$

or

$$k_9 + k_{10} = (12.99 - 7.73) \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1} = 5.26 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1} \quad (18)$$

We may now use the results from the 0.1 M DMA case to check the consistency of our calculated values to this point. In 0.1 M DMA, τ_{ex} is 109 ± 4 ns or τ_{ex}^{-1} is $9.17 \times 10^6\ \mathrm{s}^{-1}$. The bimolecular decay of $[^1\mathrm{A{:}DMA}]$ with DMA becomes appreciable, $(k_9 + k_{10})(0.1\ \mathrm{M}) = 5.26 \times 10^5\ \mathrm{s}^{-1}$, and eq 13 may be expressed as

$$9.17 \times 10^6\ \mathrm{s}^{-1}\ [^1\mathrm{A}] = (1 \times 10^9 + 2.08 \times 10^8)\ \mathrm{s}^{-1}\ [^1\mathrm{A}] - k_{-5}[^1\mathrm{A{:}DMA}]$$

or

$$k_{-5}[^1\mathrm{A{:}DMA}] = 1.20 \times 10^9\ \mathrm{s}^{-1}\ [^1\mathrm{A}] \quad (19)$$

Since $(k_5[\mathrm{DMA}] + k_1) \gg \tau_{\mathrm{ex}}^{-1}$, it is worth noting that a minor variation in τ_{ex} will have no measurable effect on the numerical value of $[^1\mathrm{A{:}DMA}]/[^1\mathrm{A}]$.

Equation 12 now has to be modified to include the bimolecular decay terms

$$\tau_{\mathrm{ex}}^{-1}[^1\mathrm{A{:}DMA}] = (k_{-5} + k_6 + k_7 + k_8)[^1\mathrm{A{:}DMA}] + (k_9 + k_{10})[^1\mathrm{A{:}DMA}][\mathrm{DMA}] - k_5[^1\mathrm{A}][\mathrm{DMA}] \quad (20)$$

Substituting the value of $[^1\mathrm{A}]$ in eq 19 into eq 20, we have

$$\begin{aligned}\tau_{\mathrm{ex}}^{-1} &= (k_{-5} + k_6 + k_7 + k_8) + (0.1\ \mathrm{M})(k_9 + k_{10}) - 0.833k_{-5} \\ &= (k_6 + k_7 + k_8) + (0.1\ \mathrm{M})(k_9 + k_{10}) + 0.167k_{-5} \\ &= 5.12k_{-5} + (0.1\ \mathrm{M})(k_9 + k_{10})\end{aligned} \quad (21)$$

Using the values previously obtained for k_{-5} and $k_9 + k_{10}$, we may calculate a value for τ_{ex}, or we may calculate a value for k_{-5} from the experimental value of τ_{ex} and the value of $k_9 + k_{10}$: τ_{ex}(calcd, 0.1 M DMA) = 117 ns, and k_{-5}(calcd) = $1.69 \times 10^6\ \mathrm{s}^{-1}$. Comparing these values to the experimental values of 109 ± 4 ns and $1.56 \times 10^6\ \mathrm{s}^{-1}$, one finds that they are in good agreement with each other.

D. Analysis of Quantum Yields of Anthracene Consumption in the Presence of DMA. In the presence of DMA, anthracene may undergo photoreduction via the exciplex as well as photodimerization via the excimer. Since the rate of anthracene consumption via the exciplex is $k_8 + k_9[\mathrm{DMA}]$ and the rate of anthracene consumption via excimer is $k_2[2\phi_{\mathrm{dim}}^{\mathrm{lim}}][\mathrm{A}]$, where $\phi_{\mathrm{dim}}^{\mathrm{lim}}$ is the limiting value for photodimerization of anthracene, the quantum yield of anthracene consumption in the presence of DMA may be expressed as

$$\phi_{-\mathrm{A}} = \frac{(k_8 + k_9[\mathrm{DMA}])[^1\mathrm{A{:}DMA}] + k_2[2\phi_{\mathrm{dim}}^{\mathrm{lim}}][\mathrm{A}][^1\mathrm{A}]}{\{k_6 + k_7 + k_8 + (k_9 + k_{10})[\mathrm{DMA}]\}[^1\mathrm{A{:}DMA}] + (k_1 + k_2[\mathrm{A}])[^1\mathrm{A}]} \quad (22)$$

We have shown that the photoconsumption of anthracene at very low anthracene concentrations levels off to a constant value in the presence of DMA (Figure 1 and Table II and III). The reults clearly indicate that the bimolecular decay of anthracene via excimer is unimportant under such conditions. Therefore, we shall be able to solve the values of individual rate constants (k_6 to k_{10}) in eq 22 by the application of steady-state analysis (part D-1). Once we have obtained values of all rate constants, the validity of our kinetic analysis will then be tested by two additional experiments: (1) by comparing the experimental values of ϕ_{-A} in 0.1 M DMA solutions in benzene containing a range of anthracene concentrations (6.67×10^{-4} to 0.01 M) with the values calculated from eq 22 (part D-2) and, subsequently, (2) by comparing these values in 0.01 M anthracene solutions in benzene over a range of DMA concentrations (0–0.1 M) (part D-3).

D-1. In Benzene Solutions Containing Low Anthracene Concentrations. In benzene solutions containing high concentration of DMA (1.0 M) and low concentrations of anthracene (less than 0.004 M), the decay of uncomplexed excited anthracene becomes unimportant relative to the decay via [^{1}A:DMA]; i.e., k_q[DMA] becomes much larger than $k_1 + k_2$[A]. Therefore eq 22 may be simplified to the following:

$$\phi_{-A} = \frac{[k_8 + (1.0\ \mathrm{M})k_9][^1\mathrm{A{:}DMA}]}{[k_6 + k_7 + k_8 + (1.0\ \mathrm{M})(k_9 + k_{10})][^1\mathrm{A{:}DMA}]} = [k_8 + (1.0\ \mathrm{M})k_9]\tau_{\mathrm{ex}} \quad (23)$$

The ϕ_{-A} in 1.0 M DMA and relatively low [A] is independent of [A] and is 0.168 (Table II and Figure 1), and τ_{ex} is 77 ns. Substituting these values in eq 23, we have

$$k_8 + (1.0\ \mathrm{M})k_9 = 0.168(77\ \mathrm{ns})^{-1} = 2.18 \times 10^6\ \mathrm{s}^{-1} \quad (24)$$

In 0.1 M DMA and very low anthracene concentrations, the rate of excited anthracene decay via exciplex formation is much larger than the rate of excited anthracene via excimer formation, or k_q[DMA] is much larger than k_2[A], but the unimolecular decay of ^{1}A is still significant. Therefore, eq 22 may be simplified to

$$\phi_{-A} = \frac{[k_8 + (0.1\ \mathrm{M})\, k_9][^1\mathrm{A{:}DMA}]}{[k_6 + k_7 + k_8 + (0.1\ \mathrm{M})(k_9 + k_{10})][^1\mathrm{A{:}DMA}] + k_1[^1\mathrm{A}]} \quad (25)$$

Under the experimental conditions of quantum yield determinations, we may apply the steady-state analysis to the rates of formation and decay of [^{1}A:DMA], i.e.,

$$k_5[^1\mathrm{A}][\mathrm{DMA}] = \{k_{-5} + k_6 + k_7 + k_8 + (k_9 + k_{10}) \times [\mathrm{DMA}]\}[^1\mathrm{A{:}DMA}] \quad (26)$$

Since the values of k_{-5}, $k_6 + k_7 + k_8$, and $k_9 + k_{10}$ are already known, we may solve for [^{1}A] in terms of [^{1}A:DMA] at 0.1 M DMA.

$$[^1\mathrm{A}] = 9.82 \times 10^{-3}[^1\mathrm{A{:}DMA}] \quad (27)$$

Assuming the quantum yield of anthracene consumption at 6.67×10^{-4} M anthracene (Table III) and 0.1 M DMA in benzene, 0.038, to be the limiting quantum yield for an infinitely dilute anthracene solution and substituting this value, values of various rate constants, and eq 27 into eq 25, we have

$$0.038 = \frac{k_8 + (0.1\ \mathrm{M})k_9}{[8.26 \times 10^6 + 0.208(9.82 \times 10^6)]\mathrm{s}^{-1}} \quad (28)$$

or

$$k_8 + (0.1\ \mathrm{M})k_9 = 3.90 \times 10^5\ \mathrm{s}^{-1}$$

Combining eq 28, 24, and 18,

$$k_8 = 1.90 \times 10^5\ \mathrm{s}^{-1}$$

$$k_9 = 1.99 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

$$k_{10} = 3.27 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

Since the fraction of [^{1}A:DMA] which decays via fluorescence is 0.31 (Table V), we may also solve for k_6 and k_7,

$$k_6 = 0.31(k_6 + k_7 + k_8) = 2.40 \times 10^6\ \mathrm{s}^{-1}$$

$$k_7 = (7.73 - 2.40 - 0.19)10^6\ \mathrm{s}^{-1} = 5.14 \times 10^6\ \mathrm{s}^{-1}$$

The results indicate that the product formation or anthracene consumption via unimolecular decay of [^{1}A:DMA] is relatively inefficient, i.e., $k_8/(k_6 + k_7 + k_8) = 0.025$, while the product formation via bimolecular decay with another molecule of DMA is appreciable, i.e., $k_9/(k_9 + k_{10}) = 0.38$. Alternatively, the 1:2 exciplex, [^{1}A:2DMA], if formed, decomposed quite efficiently (38%) to give products.

D-2. In Benzene Solutions Containing 0.1 M DMA and Anthracene Concentrations up to 0.01 M. At higher anthracene concentrations, we have shown that the consumption of anthracene will proceed via both the excimer to give the photodimer and the exciplex to give the photoreduction products (**3** and **4**). Values for all rate constants in eq 22 are now available. Applying the steady-state analysis (eq 27), we may solve for ϕ_{-A} as a function of [A] in 0.1 M DMA solutions

$$\phi_{-A} = \frac{3.90 \times 10^5 + 4.23 \times 10^7[\mathrm{A}]}{10.3 \times 10^6 + 13.65 \times 10^7[\mathrm{A}]} = \frac{3.90 + 423[\mathrm{A}]}{103 + 1365[\mathrm{A}]} \quad (29)$$

From eq 29, we may now calculate ϕ_{-A} in 0.1 M DMA for a range of anthracene concentrations. These values are listed with the experimental values in Table III and are used for plotting the curved line in Figure 1. The calculated and the experimental values are in very good agreement with each other, confirming the validity of our kinetic analysis.

D-3. In Benzene Solutions Containing 0.01 M of Anthracene and Variable Concentrations of DMA. Our results indicate that the quantum yield of unimolecular decay of [^{1}A:DMA] to products is inefficient compared to that of photodimerization of anthracene via the excimer. Therefore, ϕ_{-A} will be quenched by the addition of moderate amounts of DMA to a concentrated solution of anthracene in benzene, 0.01 M. By applying the steady-state analysis as given in eq 26, we first solve for [^{1}A] in terms of [^{1}A:DMA]

$$[^1\mathrm{A}] = \left\{\frac{k_{-5} + k_6 + k_7 + k_8}{k_5[\mathrm{DMA}]} + \frac{k_9 + k_{10}}{k_5}\right\}[^1\mathrm{A{:}DMA}] = (5.26 \times 10^{-4} + 9.29 \times 10^{-4}[\mathrm{DMA}]^{-1})[^1\mathrm{A{:}DMA}] \quad (30)$$

Introducing the values of appropriate rate constants and substituting eq 30 into eq 22, we obtain eq 31.

$$\phi_{-A} = \frac{1.90 \times 10^5 + 1.99 \times 10^6[\mathrm{DMA}] + 4.32 \times 10^7(5.26 \times 10^{-4} + 9.26 \times 10^{-4}[\mathrm{DMA}]^{-1})}{7.73 \times 10^6 + 5.26 \times 10^6[\mathrm{DMA}] + 3.47 \times 10^8(5.26 \times 10^{-4} + 9.26 \times 10^{-4}[\mathrm{DMA}]^{-1})} = \frac{21.3 + 199[\mathrm{DMA}] + 4.00[\mathrm{DMA}]^{-1}}{791 + 526[\mathrm{DMA}] + 32.3[\mathrm{DMA}]^{-1}} \quad (31)$$

Both the calculated values and the experimental values are presented in Table IV and Figure 2. They are again in good agreement with each other, which lends further support to the validity of our analytical treatment.

E. The Dependence of [^{1}A:DMA] Fluorescence on DMA Concentration. The quantum yield of [^{1}A:DMA] fluorescence decreases and the maximum shifts to the red as the concentration of DMA increases in benzene solution from 0.005 to 2.0 M (Table V). Pioneering work by Weller and his coworkers showed that both the emissions maximum and efficiency of [^{1}A:DEA] fluorescence depend on the dielectric constant of the medium.[3] Due to the polar charge-transfer character of the exciplex, the maximum shifts to the red as the

Table VII. Values of Rate Constants

Rate constant	Symbol	Value[a]
Total decay rates of singlet excited anthracene in benzene (τ_f^{-1})	k_1	$2.08 \times 10^8\ s^{-1}$
Rate of formation of anthracene excimer	k_2	$1.39 \times 10^{10}\ M^{-1}\ s^{-1}$
Rate of formation of [A*:DMA]	k_5 or k_{diff}	$1.0 \times 10^{10}\ M^{-1}\ s^{-1}$
Rate of dissociation of [A*:DMA]	k_{-5}	$1.54 \times 10^6\ s^{-1}$
Rate of fluorescence of [A*:DMA]	k_6	$2.40 \times 10^6\ s^{-1}$
Rate of nonradiative decay of [A*:DMA]	k_7	$5.14 \times 10^6\ s^{-1}$
Rate of product formation from [A*:DMA]	k_8	$1.90 \times 10^5\ s^{-1}$
Biomolecular rate of product formation from [A*:DMA] and DMA	k_9	$1.99 \times 10^6\ M^{-1}\ s^{-1}$
Biomolecular rate of nonradiative decay from [A*:DMA] and DMA	k_{10}	$3.27 \times 10^6\ M^{-1}\ s^{-1}$

[a] All values are calculated from experimental results at 22 ± 2 °C except that of k_5, which is assumed to be the rate of diffusion-controlled process in benzene at the value given.

dielectric constant of the medium increases. The red shift is accompanied by a decrease in quantum efficiency, which may be attributed to the increase in the rates of nonradiative decay processes. The decrease in fluorescence efficiency of [^{1}A:DEA] in cyclohexane with increasing DEA concentration was reported by Selinger and MacDonald[39] and they suggested that the decrease may be attributed to the increase in the dielectric constant of the medium. Alternatively, Chandross and Thomas, by studying the interaction between an intramolecular naphthalene–amine exciplex with another donor molecule, suggested that the decrease in the quantum efficiency of exciplex fluorescence with increasing donor concentration may be due to the formation of a new stoichiometric complex between the exciplex and another donor molecule.[40]

Since DMA has a higher dielectric constant (ϵ = 5.03) than benzene (ϵ = 2.28),[28] we desired to separate the effect of increasing dielectric constant from the effect of bimolecular quenching of [^{1}A:DMA] by another molecule of DMA. In order to accomplish this, the effect of variable amounts of ethyl acetate (ϵ = 6.0) on the exciplex fluorescence of [^{1}A:DMA] in benzene containing 0.1 M DMA was investigated. We observed a definite trend in the red shift of fluorescence maximum and decrease in fluorescence efficiency as the proportion of ethyl acetate in benzene increased (Table V). The extent of red shift of fluorescence maximum from a dilute solution of DMA in benzene to a more concentrated solution is the same as that caused by the addition of an equivalent amount of ethyl acetate to the dilute solution to adjust the dielectric constant to that of the more concentrated solution, e.g., λ_{max} of fluorescence of 0.1 M solution of DMA in benzene containing 8.5% ethyl acetate is approximately the same as that of a 1.0 M DMA solution. Therefore, the red shift of exciplex fluorescence in a nonpolar solvent is caused by the increase of dielectric constant of the medium. However, the presence of ethyl acetate up to 18% by volume in a 0.1 M solution of DMA in benzene caused only a minor decrease in the quantum yield of exciplex fluorescence.

We have shown that [^{1}A:DMA] may react with another molecule of DMA (eq 10 and 11); therefore, the fluorescence of [^{1}A:DMA] may be quenched by a bimolecular process with another molecule of DMA. The fraction of [^{1}A:DMA] which decays via fluorescence (ϕ_f') may be given by the following expression:

$$\phi_f' = k_6/\{k_6 + k_7 + k_8 + (k_9 + k_{10})[\mathrm{DMA}]\}$$

The values of ϕ_f' calculated from this expression at different concentrations of DMA are listed in Table V. The results indicate that the bimolecular quenching of [^{1}A:DMA] by another molecule of DMA is the major factor for the decrease in fluorescence efficiency with increasing DMA concentration. The increase in DMA concentration will cause an additional minor decrease in fluorescence efficiency due to the increase in the dielectric constant, and, although the available information is insufficient for us to treat this effect quantitatively, the inclusion of this change in our calculation would bring the calculated quantum yields closer to the experimental values.

F. The Variation of the Stern–Volmer Constant (K_{SV}) with DMA Concentration. The Stern–Volmer constant for the quenching of anthracene fluorescence by DMA (K_{SV}) remains invariable, within experimental error, in DMA concentration ranging up to 0.03 M ($K_{SV} = k_q\tau = 40.4 \pm 1.6\ M^{-1}$). However, it increases by a factor of more than 5 as the concentration of DMA increases to 2.0 M. Since the rate for a diffusion-controlled process in benzene at room temperature is estimated to be $k_{diff}\tau$ or 48 M^{-1}, the results indicate that k_q has apparently exceeded the diffusion-controlled limit or that a static quenching process is involved at high DMA concentrations. Static quenching of excited molecules has been discussed by Weller[41] and Wagner.[42] Such quenching processes involve either the complexation between the quenchee and quencher in the ground state before excitation or a diffusion-controlled thermodynamically favorable energy transfer from the excited molecule to a quencher molecule which exists as a nearest neighbor at the instant of excitation. Careful examinations of the absorption spectra and fluorescence excitation spectra of our anthracene–DMA system failed to reveal the formation of any ground-state complex between them. On the other hand, exciplex formation from ^{1}A and DMA does not involve a thermodynamically favorable energy transfer and is not a diffusion-controlled process. In fact, the exciplex formation has a large negative entropy, indicating that a rather restricted geometry is required for the formation.[38] Therefore, the static quenching of aromatic hydrocarbon fluorescence by amines, which has been observed in our and other laboratories, cannot be accounted for by the existing theories of static quenching.[41,42]

Weller and co-workers suggested that the exciplex formation may involve a two-stage process: the formation of an encounter exciplex at an encounter distance of 7–8 Å, followed by the formation of the exciplex[3]

$$^1\mathrm{A} + \mathrm{D} \overset{K_1}{\rightleftharpoons} [\text{encounter exciplex}] \overset{K_2}{\rightleftharpoons} [^1\mathrm{A{:}D}] \qquad (32)$$

The existence of encounter exciplexes has been recently demonstrated in our laboratory.[15] The equilibrium constant for the formation of the encounter exciplex from its components (K_1) as well as the heat and entropy of its formation have been found to be relatively small, indicating only very loose geometrical requirements. The interconversion between encounter exciplex and exciplex involves the rotation between the component molecules, which may be extremely rapid, the equilibrium constant of interconversion (K_2) depending on the nature of component molecules involved. Since the overall equilibrium constant for the exciplex formation from ^{1}A and DMA and related systems (K_1K_2) is usually very large, e.g., K_1K_2 for [^{1}A:DMA] formation is 6410 (vide supra), the formation of the exciplex from the encounter exciplex in our system is expected to be highly favorable compared with dissociation to its component molecules. The steady-state concentration of encounter exciplex in [^{1}A:DMA] and related systems will thus be too low to be detected spectroscopically. Since the formation of the encounter exciplex occurs at the encounter distance of 7–8 Å, the formation of the exciplex may also occur at this same distance in spite of its restricted geometrical requirement. As the concentration of DMA increases in solution. a growing fraction of anthracene molecules has DMA molecules within the encounter distance at the instant of excitation, thus forming the encounter exciplex immediately. This instantaneous formation of the encounter exciplex, then, permits quenching and exciplex formation to proceed faster than the diffusion-controlled rate.

Conclusions

Our experimental results provide the basis for a quantitative understanding of the behavior of photoexcited singlet anthracene in the presence and absence of DMA in benzene.

(1) **Unimolecular Decay.** This well-documented process consists of fluorescence and radiationless decay.

(2) **Bimolecular Decay via the Excimer.** At high anthracene concentrations the diffusion-controlled formation of excimer becomes important and leads to the formation of anthracene photodimer (16%) and radiationless decay to ground-state anthracene (84%).

(3) **Bimolecular Decay via the Exciplexes.** If DMA is present, quenching may occur by interaction between photoexcited anthracene and DMA at nearly the diffusion-controlled rate. This interaction may lead initially to the formation of a loose encounter exciplex, which undergoes very rapid geometric reorientation to result in the well-defined exciplex, [^{1}A:DMA]. The overall equilibrium constant for the formation of [^{1}A:DMA] from its components is 6410 M^{-1}. At low DMA concentrations, this exciplex undergoes mainly unimolecular decay by dissociation to its components, fluorescence, and nonradiative decay. The product formation from the exciplex, however, is relatively inefficient. The competition between exciplex formation and excimer formation depends on the concentrations of anthracene and DMA and causes variations in the quantum yield of anthracene consumption and in the proportion of anthracene photodimer formed.

(4) **Termolecular Decay via the Exciplex.** At high DMA concentrations, interaction between the exciplex and a second DMA molecule is an important mode of decay. The interaction results in an appreciable reduction in the fluorescence efficiency and lifetime of the exciplex, but an increase in the efficiency of product formation. The formation of products, **3** and **4**, may be rationalized via an electron-transfer process between [^{1}A:DMA] and another molecule of DMA. This termolecular decay may result from a rapid equilibrium between the exciplex and a triple exciplex, [^{1}A:2DMA].

We have thus examined the photochemistry of anthracene in the absence and presence of DMA in benzene and simultaneously analyzed the photophysical behavior of excited anthracene, its excimer, and its exciplexes with DMA. As a result, we have established the relationship between the photochemistry and photophysics of these systems. The values of the rate constants for the important photochemical and photophysical processes are presented in Table VII.

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