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ARTICLES

Effects of the Exciting Wavelength and Viscosity on the Photobehavior of 9- and 9,10-Bromoanthracenes

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The widely investigated photobehaviors of 9-bromo and 9,10-di-bromoanthracenes have been revisited here to clarify the competition among different relaxation paths of their lowest two electronic excited states. The results obtained show that these two molecules exhibit a parallel photobehavior, which depends on the excited electronic and vibronic transition, the medium viscosity, and the temperature. The first electronic state of either of these does not exhibit photochemistry in fluid solution or rigid matrices (80 K). The fluorescence emission occurs with a very low quantum yield ($\sim 10^{-2}$) at room temperature but with a very high quantum yield (0.9 to ∼ 1) at 80 K. When exciting in the second electronic transition, the fluorescence intensity is lower than when exciting in S_1 at both room temperature and low temperature due to competition with the observed photocleavage of the C−Br bond. The reaction yield decreases as the temperature decreases and depends on the viscosity of the solvent; the higher the viscosity, the lower the observed yield of photochemistry. Temperature and viscosity effects are a consequence of the fact that the radicals produced by C−Br bond breakage cannot escape from the solvent cage and, moreover, quickly recombine within the cage giving the appearance that no photochemistry occurred. The presence of photochemistry in S_2 and its absence in S_1 is principally due to the fact that S_2 has a π,σ^* character in the C−Br bond, whereas the S_1 state has its origin from a π,π^* delocalized configuration.

Introduction

We have demonstrated that the quantum yields of photochemistry and fluorescence of some organic molecules can drastically change depending upon the vibrational mode, vibrational level, and electronic state that is excited. This has been shown to be true for seven different benzo- and naphthopyrans. The term “vibronic effect in photochemistry” has been given by us to describe this phenomenom.[1−5] Some other type molecules have been shown to have a similar behavior.[6−8] All of the above results are a direct consequence of competition between vibrational relaxation and photochemistry.

Despite the observation of the excitation wavelength dependence of photochemistry and/or fluorescence and in classes of molecules other than those with a core pyran moiety, no quantitative data have been forthcoming. Therefore, to broaden the basis set for such information and to further verify the generality of the “vibronic effect in photochemistry”, we have examined fluorescence and photochemical aspects of both 9,10-dibromoanthracene (DBA) and 9-bromoanthracene (MBA) because they exhibit wavelength-dependent fluorescence and well-resolved absorption spectra suitable for selective vibronic excitation. For the purpose of comparison, we have also examined the photobehavior of anthracene (A) under the same conditions.

It has been noted that the quantum yield of fluorescence of DBA in fluid media at room temperature (∼293 K) was not changed as a function of the wavelength of the exciting light when exciting into S_1.[9] However, exciting in S_2, the quantum yield of fluorescence decreased to about one-half of the value of S_1. It was believed that this decrease was the result of intersystem crossing to a triplet state.[9]

Later, others[10] studied the triplet−triplet absorption of both DBA and MBA in rigid matrices at 80 K. Excitation into S_1 indicated very little intersystem crossing ($\Phi_T \sim 0.001$) for either compound. Moreover, the fluorescence quantum yield was reported to be 1.00 ± 0.05 for each compound. With excitation into S_2 at 261 nm for DBA, no triplet formation was observed, but there was a decrease in the quantum yield of fluorescence by ∼35%. It was suggested that the excitation wavelength dependence of the fluorescence of DBA in S_2 was likely caused by (undefined) photodecomposition. However, for MBA at 80 K, the fluorescence yield was 1.00 ± 0.05 whether excitation occurred in S_1 or S_2 (as seen by the authors[10] for other 9-substituted anthracenes).

The quantum yields of triplet formation and fluorescence have been determined by others at room temperature and/or 80 K for both DBA and MBA.[11−16] At room temperature, DBA is

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reported to have a Φ_T of ~0.9 in 3-methylpentane (3MP)[11] as well as in acetonitrile[12] when exciting into S_1, while in toluene,[13] a value of 0.7 is reported; Φ_T in 3MP at 80 K decreases but it is still detectable, ~0.1.[11] The fluorescence yield of DBA has been reported to be ~0.1 in heptane[14] and petroleum ether[15] at room temperature (all presumably excited in S_1). For MBA, with excitation into S_1, the triplet yield is reported to be ~0.99[11,12,16] in 3MP at room temperature and ~0.001 at 80 K. The fluorescence yield of MBA is reported as 0.01 in heptane[14] and ~0.02 in petroleum ether[15] at room temperature with excitation into S_1. Photochemical debromination with excitation into S_1 of both MBA and DBA has been observed in acetonitrile only in the presence of amines.[12]

The existence and cause of the wavelength dependence of the fluorescence of DBA and MBA is the focal issue of this paper. However, our concern is much broader than considerations of just the electronic state dependence of the yields of fluorescence. We will not only reveal the crucial importance of the excitation of particular electronic states, vibrational modes, and vibrational levels on fluorescence yields, but on the complementary process, photochemistry, that occurs in both DBA and MBA. Moreover, the unique role solvent viscosity plays in observing photochemistry will be elucidated.

We will show that the fluorescence yield at 80 K of DBA and MBA when exciting anywhere within S_1 is constant and large, ~1, and, thereby, is independent of the vibrational mode or excited level. However, when exciting into S_2 where photochemistry exists, the fluorescence yield is a function of the wavelength of excitation (vibrational mode/level excited) at 80 K. At room temperature, lower yields but parallel trends are observed to those at 80 K. We will also show and discuss the behavior of anthracene at 80 K that shows a similar wavelength dependence for fluorescence despite the absence of photoreaction. In conclusion, comparison with other works of any nature is difficult because of the lack of data from excitation into the second excited state.

Experimental Section

Materials. DBA and MBA (from Aldrich) and anthracene (A; J. T. Baker Chemical Co.) were purified through HPLC. The solvents used were 3MP (Acros Organics, 99%), which was distilled before use, whereas heptane (Aldrich, 99%), decane (Aldrich, 99%), dodecane (Aldrich, 99%), hexadecane (Sigma−Aldrich, 99%), and methylcyclohexane (J. T. Baker Chemical Co.) were used as received. Other compounds used as fluorescence standards were 9,10-diphenylanthracene (Baker) and *trans*-stilbene (Fluka), which were used as received. The 2,3′-dithienylketone, used as triplet sensitizer, was synthesized and purified for a previous work.[17]

Apparatus and Methods. The absorption spectra were recorded on a Perkin-Elmer Lambda 800 spectrophotometer or a Perkin-Elmer Lambda 5 spectrophotometer or using a HP 8453 diode-array spectrophotometer. Irradiation of the samples was carried out in a 1 cm cell path in the spectrophotometer holder, at a right angle to the monitoring beam, using a fiber-optic system. A Hg medium-pressure lamp (Applied Photophysics) with interferential filters and a 125 W Xe lamp, coupled with a Jobin-Yvon H10 UV monochromator, were used for irradiation. The band pass was 4 nm. An Oxford Instruments cryostat was used for the temperature control. A gray filter (10% transmittance) was inserted between the sample cell and the diode-array spectrophotometer source to avoid a fraction of the UV light intensity that might reach the sample, thus inducing photochemistry.

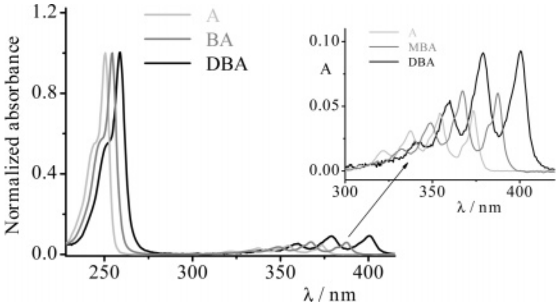

Figure 1. Absorption spectra of A, MBA, and DBA in 3MP at room temperature. Inset: zoom on the lowest energy electronic transition (S_1).

TABLE 1: Spectral Characteristics of DBA and MBA in 3MP and A in Hexane at Room Temperature

	DBA		MBA		A[a]	
transition	λ_{max} nm	ϵ_{max} M^{-1} cm^{-1}	λ_{max} nm	ϵ_{max} M^{-1} cm^{-1}	λ_{max} nm	ϵ_{max} M^{-1} cm^{-1}
S_0-S_1	400.5	12 600	387.5	3150	374.5	8500
S_0-S_2	258.5	121 700	254.5	75 100	252	220 000

[a] In hexane, from ref 18.

TABLE 2: Spectral Characteristics of DBA and MBA in 3MP at 80 K

	DBA		MBA	
transition	λ_{max} nm	ϵ_{max} M^{-1} cm^{-1}	λ_{max} nm	ϵ_{max} M^{-1} cm^{-1}
S_0-S_1	405.5[a] (441)	18 300[b] (0.21)	392	4900
S_0-S_2	263[a] (264)	191 000[b] (2.38)	258.5	109 000

[a] Wavelengths obtained from AM1 calculations. [b] Calculated oscillator strength values using AM1 method.

The emission spectra were taken using a Spex Fluorolog-2 1680/1 spectrofluorimeter; the fluorescence quantum yields were determined using 9,10-diphenylanthracene in cylohexane and *trans*-stilbene in trimethylpentane as standards. The uncertainty in the quantum yield determinations was estimated to be about 10%.

For laser flash photolysis measurements in nanosecond time-resolution, the third ($\lambda = 355$ nm) and fourth ($\lambda = 267$ nm) harmonic from a Continuum Surelite Nd:YAG laser were used with fluence less than 10^6 J cm^{-2} s^{-1} per pulse and time resolution of about 30 ns. Q-switch delays were used to reduce the laser intensity. For the spectrophotometric analysis, a 150 W xenon source, a Baird-Tatlock monochromator blazed at 500 nm, a Hamamatsu R928 photomultiplier, and a Tektronix DSA 602 digitized analyzer were used. The data were processed by a Tektronix PEP 301 computer.

The quantum yields of the photoreaction were determined by spectrophotometry, using potassium ferrioxalate actinometry to measure the radiation intensity, typically on the order of $2-3 \times 10^{-7}$ moles of photons dm^{-3} s^{-1}. The uncertainty in the quantum yield determination was within 10%.

Results and Discussion

Absorption and Fluorescence Spectra. The absorption spectra of A, MBA, and DBA at room temperature (~293 K) are given in Figure 1.

Note the progressive blue shift of the bands from DBA to MBA to A. Spectral data concerning the two lowest spectrally detectable electronic transitions of MBA and DBA are collected and compared with those of A in Table 1 at room temperature and in Table 2 at 80 K.

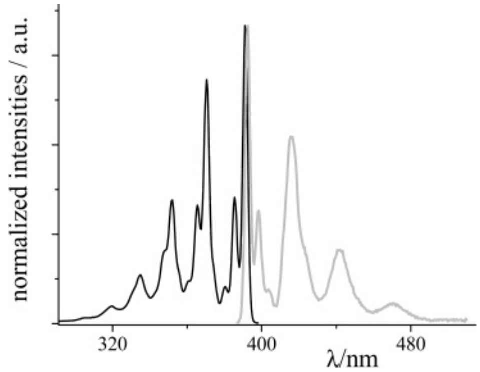

Figure 2. Normalized excitation (S_1) and emission spectra of MBA in 3MP at 80 K.

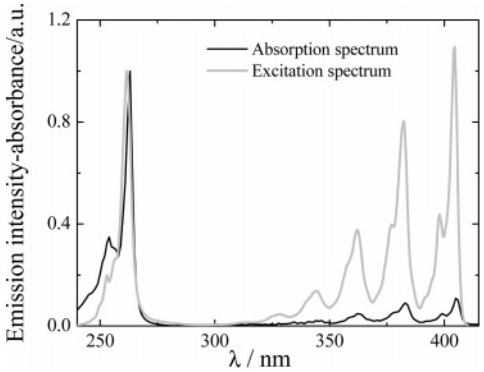

Figure 3. Absorption (black) and fluorescence excitation (gray) spectra of DBA in 3MP at 80 K, normalized in S_2.

Figure 2 demonstrates the excitation (S_1 transition) and fluorescence spectra of MBA at 80 K, whereas in Figure 3 absorption and fluorescence excitation spectra of DBA at 80 K show the dependence of the fluorescence yield on electronic excitation and (for S_2) on vibronic excitation.

Table 3 gives the fluorescence quantum yields (Φ_F) in 3MP at room temperature (~293 K) and 80 K for DBA, MBA, and A. For the foregoing molecules at 293 K, the Φ_F is constant (within 10%) when exciting at any wavelength in S_1, and the same is true at 80 K. Note the dramatic increase in the fluorescence yield when the temperature is lowered from 293 to 80 K. The Φ_F values when exciting into S_2 either at 293 K or 80 K, show a significant decrease compared to exciting into S_1; furthermore, there is a marked dependence of the fluorescence yield on the vibrational level excited in S_2. In general, the fluorescence yield decreased as the excitation energy increased to higher and higher vibrational levels.

The fluorescence yield for DBA is greater than or equal to that for MBA at either 293 K or 80 K. For anthracene, fluorescence is higher than MBA and DBA at room temperature and increases to a lesser extent than for the brominated derivatives at 80 K. The wavelength effect when exciting in S_2 was observed for all three compounds, Table 3. Values reported in Table 3 are in reasonable agreement with those reported by Melhuish in petroleum ether at room temperature by exciting in S_1 (0.088 for DBA, 0.024 for MBA, and 0.22 for A).[15]

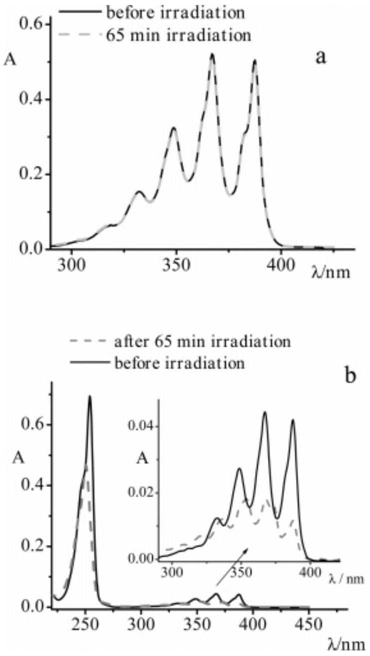

Figure 4. Effect of exciting S_1 (a) and S_2 (b) on the existence of photochemistry for MBA in 3MP at room temperature, as seen by comparison of the relative intensity of the absorption bands before and after irradiation.

Photochemistry. Photochemical reactions of DBA and MBA led to cleavage of the C−Br bond, forming monobromoanthracene and anthracene, respectively. By steady excitation of both compounds at *room temperature* in 3MP solution into the first electronic state, S_1, no photochemistry was detected, whereas by exciting in the second electronic state, photoreaction was observed. As an example, a qualitative comparison of the presence or absence of photochemistry for MBA when irradiating in the S_1 and S_2 states at 293 K is shown in Figure 4. Note that photochemistry existed when excitation was into S_2 but not when exciting into S_1, which is parallel to the same response that was seen for DBA (not shown) at 293 K. This is consistent with AM1 calculations, revealing that S_1 is a pure π,π^* transition, whereas S_2 is π,π^* with notable σ^* character located in the C−Br bond. The photochemical quantum yields of disappearance of the irradiated compounds were independent of the vibrational level excited in S_2. For example, determinations of Φ_{PC} carried out for MBA exciting at two different wavelengths of S_2 (246 and 256 nm) gave values ($\Phi_{PC} = 0.13 \pm 0.02$ at 246 nm and $\Phi_{PC} = 0.14 \pm 0.02$ at 256 nm) averaged over three independent experiments that were coincident within the experimental uncertainty.

TABLE 3: Fluorescence Quantum Yields of DBA, MBA, and A in 3MP at Room Temperature and 80 K[a]

	room temperature (~293K)			80 K		
excited state	DBA	MBA	A	DBA	MBA	A
S_1[b]	0.07	0.006	0.18	0.9	~1	0.53
S_2	0.012	0.0009	0.035	0.45	0.32	0.12
	(258.5 nm)	(254.5 nm)	(250.5 nm)	(263)	(258.5 nm)	(254 nm)
	0.008	0.0005	0.017	0.28	0.17	0.062
	(250.5 nm)	(247.5 nm)	(243.5 nm)	(253.5 nm)	(249.5 nm)	(246 nm)
				0.075	0.036	
				(244.5 nm)	(241 nm)	

[a] Excitation wavelengths are given in parenthesis. [b] Values constant over all excitation wavelengths used.

TABLE 4: Temperature−Viscosity Effect on the Observed Quantum Yield of the Photochemistry (Φ_{PC}) of DBA and MBA (λ_{exc} = 254 nm, S_2) in 3MP[a]

T (K)	viscosity (cp)	Φ_{PC} of DBA	Φ_{PC} of MBA
319	0.255	0.040	
312	0.270	0.039	0.17
305	0.287	0.037	
298	0.306	0.034	0.15
283	0.354	0.030	0.14
268	0.417	0.028	0.11
253	0.500		0.093
238	0.615	0.024	0.081
223	0.776		0.073
208	1.01	0.019	0.053
195	1.32	0.014	0.048
185	1.66	0.012	

[a] Viscosities at the different temperatures were calculated using the relationship: $\eta_T = \eta_0 e^{\Delta E/RT}$.

TABLE 5: Parameters Obtained from Eq 1 for DBA and MBA in 3MP

	DBA	MBA
E_a/kJ mol^{-1}	4.25	6.20
Φ_{PC}^{lim}	0.17	0.68

TABLE 6: Viscosity Effect on the Reaction Quantum Yield of DBA (λ_{exc} = 254 nm, S_2)

	other solvents		3MP		
solvent	η/cp (298 K)	Φ_{PC} of DBA	η/cp	*T*/K	Φ_{PC} of DBA
3MP	0.31	0.034			
heptane	0.39	0.025	0.35	283	0.030
decane	0.85	0.018	0.61	238	0.024
dodecane	1.40	0.015	1.32	195	0.014
hexadecane	3.34[a]	0.012			

[a] 293 K.

The reaction quantum yields determined in 3MP were found to decrease with decreasing temperature for both the bromoderivatives. No photochemistry was observed for both compounds when exciting at 80 K even though *it actually did occur*, see later in the Discussion section. Table 4 shows the effect of some selected temperatures on the observed photochemical yield in 3MP as well as the viscosities of 3MP at those temperatures. The reaction yields as a function of temperature were treated according to the Arrhenius type eq 1.

$$\ln (1/\Phi_{PC} - 1) = E_a/RT + C \tag{1}$$

"Apparent" activation energies and "limit" yields, Table 5, were determined from the slope and intercept, respectively, of linear plots of ln ($1/\Phi_{PC}$ − 1) versus T^{-1}. A graphical example is shown in Figure 5.

Basic information to understand the meaning of these parameters came from measurements of quantum yields in different hydrocarbons. Table 6 provides data on the yield of photochemistry (λ_{exc} = 254 nm, S_2) as a function of viscosity for a group of aliphatic hydrocarbon solvents at the same temperature. Photochemical yields decreased as the viscosity increased. In the last three columns of Table 6, some Φ_{PC} values in 3MP are given at temperatures at which the 3MP viscosity was close to that of the coupled hydrocarbon. The correspondence of Φ_{PC} values at essentially iso-viscous conditions but at different temperatures indicates that the process is intrinsically barrierless. The dependence on temperature is essentially a consequence of viscosity changes of the solvent and not because of changes in any intramolecular dynamics. Perhaps the clearest way to see the correlation of the yield of photochemistry and viscosity is in Figure 6, where the viscosity is modified by changing the solvent at a given temperature versus being modified by varying the temperature for a given solvent (3MP).

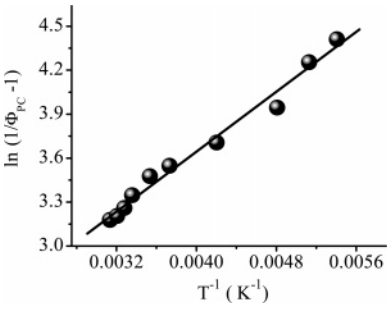

Figure 5. Quantum yield data of DBA in 3MP treated according to eq 1.

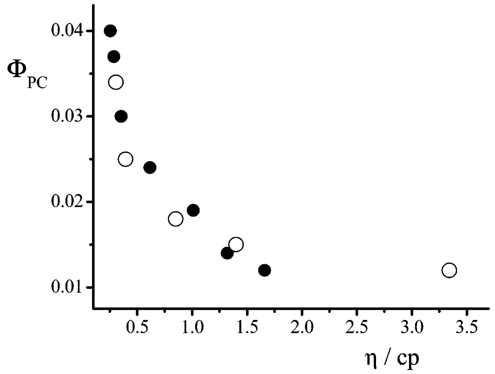

Figure 6. Quantum yield of photochemistry as a function of viscosity generated by solvent change at the same temperature (○) versus that generated by a temperature change for 3MP (●).

Based on the foregoing, the activation energies determined (eq 1) are *not* due to an energy barrier in the solute, but to the temperature dependence of the viscosity of the solvent, $\eta_T = \eta_0\, e^{\Delta E/RT}$. The dependence of PC on the temperature in 3MP, Tables 4 and 5, can be explained by the fact that even at low viscosity, escape of the unbound $Br^\bullet$ from the solvent cage is strongly hindered and the limit yields, determined from the Arrhenius type treatment, correspond to the photoreaction occurring in a nonviscous medium and represent the "true" quantum yield of the photoprocess. The escape of radicals with rate constant (k_η), produced from the reaction cage (for example $A^\bullet$ and $Br^\bullet$ from MBA), should be the viscosity-dependent process, whereas the back recombination of radicals that occurs within the cage can be largely considered as a temperature- and viscosity-independent process.

Laser Flash Photolysis. Laser flash photolysis experiments on DBA carried out at room temperature also confirmed that only the second electronic state was photoreactive. Excitation in the S_1 produced the triplet state that totally decayed to the ground state, a lifetime of 3.9 μs, and no photochemistry was observed, Figure 7. Excitation in the second transition also led to triplet population, but there was not complete decay to the ground state when monitoring at 320 nm, Figure 8. The residual absorption was assigned to the photochemical formation of anthracene based on the spectrum recorded after flashing at the 267 nm (see the spectrum of A in Figure 1).

Parallel results were obtained for MBA at room temperature; the triplet showed a spectrum with the maximum at 430 nm and a lifetime of 7 μs.

We have also observed that at 293 K the phosphorescence of a triplet donor was efficiently quenched by MBA (2,3′-

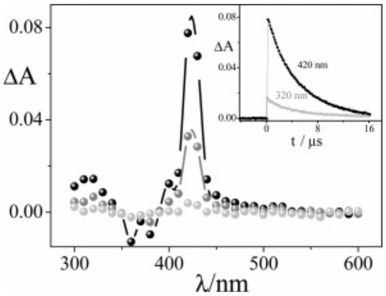

Figure 7. Room temperature T−T spectra of DBA exciting at 355 nm in 3MP at different delays (black, 0.3 μs; gray, 4.3 μs; light gray, 15 μs) and decay kinetics (inset).

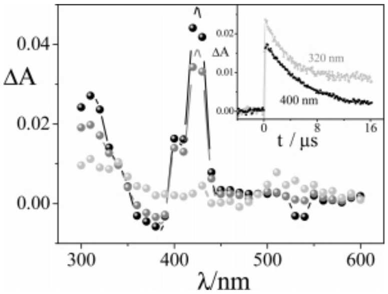

Figure 8. Room temperature T−T spectra of DBA exciting at 267 nm in 3MP at different delays (black, 0.2 μs; gray, 1.9 μs; light gray, 15 μs) and decay kinetics (inset).

dithienylketone, $E_T = 262$ kJ mol^{-1}, was used as the sensitizer because it does not extract hydrogen from the solvent).[17] However, no photochemistry was observed from the triplet state of MBA. This result allows us to conclude that photochemistry only occurs in an excited singlet state.

Discussion

There are several salient observations that are of particular significance regarding the presence of fluorescence and photochemistry in DBA and MBA.

First, no photochemistry was *observed* for either DBA or MBA when exciting into S_1 either at room temperature or at 80 K, whereas when exciting into S_2, photochemistry was present, with the quantum yield decreasing as the viscosity of the solvent increased. In a rigid matrix at 80 K, photochemistry was unobservable, however, see later discussion.

Second, for both DBA and MBA, the yield of fluorescence when exciting into S_1 at either room temperature or 80 K was independent of the wavelength of excitation and also, therefore, the vibrational level or mode that was excited. On the other hand, when exciting into S_2, the fluorescence yield decreased and varied with the wavelength of excitation, Table 3. A similar behavior was observed for A. In fact, at 80 K, the yield of fluorescence is reduced by ~50, 68, and 77%, for DBA, MBA, and A, respectively, by just exciting into the zero level of S_2 and decreased rapidly with excitation into higher vibrational levels. Our result for MBA regarding the fluorescence yield at 80 K agrees with others[10] when exciting into S_1 ($\Phi_F \sim 1$) but is in sharp disagreement when exciting into S_2 because they give the fluorescence yield value as 1.

The intersystem crossing to the triplet state should be negligible given that $\Phi_F \sim 1$ when exciting into S_1 at 80 K. Although we did not measure the Φ_T at 80 K for either DBA or MBA, others[10] have given the value as ~0.001 for both. Also, they have noted that, for DBA, no T−T absorption was observed when exciting into S_2 (261 nm) at 77 K, therefore, we can assume $\Phi_T \sim 0$. From the fluorescence yields in Table 3, 0.45 for DBA and 0.32 for MBA at 80 K, by using the relationship $\Phi_F(S_2) = \Phi_F(S_1) \times \Phi_{IC}\{S_2(0) \rightarrow S_1(0)\}$, the yield of internal conversion, Φ_{IC} of the process $S_2(0) \sim\!> S_1(0)$, is 0.49 for DBA and 0.32 for MBA. With $\Phi_T \sim 0$ when exciting into S_2 at 80 K, the photochemical yield from $S_2(0)$ would be ~0.51 for DBA and 0.68 for MBA even though no photochemistry was actually observed at 80 K. Further discussion of these seeming paradoxes is given below.

Our inability to observe photochemistry (C−Br bond breakage) at 80 K for both DBA and MBA does not infer that photochemistry did not, in fact, actually occur. Recall that earlier we showed the photochemical yield was highly sensitive to the viscosity of the solvent, see Tables 4 and 5 as well as Figure 6. Thus, as viscosity is increased, the true photochemical yield is masked. At the extremely high viscosity of 3MP at 80 K (9.4×10^9 cp),[19] the radicals produced by C−Br bond breakage cannot escape from the solvent cage and, moreover, quickly recombine within the cage, giving the *appearance* that no photochemistry occurred. It is worthwhile noting that the $\Phi_{PC} = 0.68$ for MBA estimated above has just the same value as found for the limit yield extrapolated from the graph of eq 1. Such a correspondence was not found for DBA, probably because the photoreaction, giving MBA and then A, is not as clean as for MBA.

An important question is what is the source of the excitation wavelength dependence of the fluorescence yields in the S_2 excited state at 80 K. Based on our previous experience with other photochemically active molecules[1−5] under similar conditions of solvent and temperature, we suspected that, for DBA and MBA, the "vibronic effect" was operative. That is, photochemistry and vibrational relaxation were in competition at any vibrational level of any mode. However, there is a potential problem with considering photochemistry alone as the explanation of the excitation wavelength dependence of the fluorescence for DBA and MBA when exciting into S_2, because in that case, photochemistry should also be excitation wavelength dependent. This was not found. Note that anthracene also appears to show an excitation wavelength dependence for its fluorescence at 80 K when exciting into S_2, Table 3. However, we do not believe that A would show photochemistry under the conditions of our experiments. Therefore, our observation for A, as well as for MBA and DBA, would seemingly have to include competition between photophysical processes as vibrational relaxation within the singlet manifold and intersystem crossing $S_2 \rightarrow T_x$. Interestingly, it has been found that the fluorescence yield of A seeded in a supersonic jet showed basically smooth regional excitation wavelength dependences in the first excited state (S_1) at energies above the 0 level. These were believed to be related to intrastate intramolecular vibrational energy redistribution.[20] There was *no* data obtained in the S_2 where we *do* see a vibronic level dependence of the yield of fluorescence. On the other hand, for both MBA and DBA, they[20] saw significant dependence of the fluorescence yield upon the vibronic level excited within S_1. This was more marked in DBA than MBA. These findings were believed to be the result of direct coupling [$S_1 \rightarrow T_1$] and a mediated coupling [$S_1 \rightarrow T_x \rightarrow T_1$]. The mediated coupling was believed to be dominant in MBA, while the direct mechanism was believed to be dominant in DBA. Recall we do *not* see any excitation wavelength dependence of fluorescence, nor do we see photochemistry, in the *first* excited-state of these two molecules in a solvent at 80 K. However, others[20] have noted that Ar complexed DBA suppressed the oscillatory change(s) in the fluorescence of DBA because of modification of the near resonant interaction of a particular level of S_1 with one of T_x. Again, *no* data was obtained in S_2, where we *do* see notable dependence of the fluorescence yield on the wavelength/level excited. Despite all of the foregoing considerations, based on the parallel behavior of the fluorescence yield of A compared with DBA and MBA, we can ascribe the presence of some degree of competitive photophysical process(es) for the dependence of the fluorescence yield of DBA and MBA upon exciting wavelength within S_2.

Regarding the question of why photochemistry occurs in S_2 but not S_1, recall that the S_2 state is a $\pi \rightarrow \pi^*$ state with some $\pi \rightarrow \sigma^*$ character for the C−Br bond, while the S_1 is a pure $\pi \rightarrow \pi^*$ state. This should result in C−Br bond breakage photochemistry, as is observed in the experimental results.

Furthermore, from ZINDO/S calculations, a third electronic nonoptically active state with a $\pi \rightarrow \sigma^*$ character is predicted at energies comparable with the second observed transition of DBA and MBA. This state is shifted to much higher energy for A. Based on the foregoing, an alternative interpretation for the vibronic effect observed on fluorescence but not on photochemistry could be that the optically silent $\pi \rightarrow \sigma^*$ state is responsible for the photocleavage of DBA and MBA, while the fluorescence emissions in DBA, MBA, and A comes from the same type $\pi \rightarrow \pi^*$ state with a mixed $\pi \rightarrow \sigma^*$ character.[21]

Summary and Conclusions

Neither DBA nor MBA display any photochemistry when excited into the S_1 state at room temperature (293 K) or 80 K. Also, the fluorescence quantum yields are very high when exciting into S_1 (0.9 to ∼1) at 80 K, but very low when exciting into S_1 at room temperature (0.006 to 0.07). Furthermore, the fluorescence yields are independent of the wavelengths of excitation into S_1 either at room temperature or 80 K.

In contrast to the above, when exciting into S_2, the fluorescence yields are highly dependent on the excitation wavelength and the vibrational level excited within a given mode at both room temperature and 80 K. A parallel behavior was found for anthracene. The photochemistry yield at room temperature for both DBA and MBA, excited in S_2, are independent of the excitation wavelength but are dependent on the viscosity of the solvent; the higher the viscosity, the lower the observed yield of photochemistry. In fact, if the viscosity of the solvent becomes high enough, no photochemistry is observed. The reason for this is that the radicals produced by C−Br bond breakage cannot escape from the solvent cage and, moreover, quickly recombine within the cage giving the *appearance* that no photochemistry occurred.

Even though we know photochemistry occurs when exciting S_2 for both DBA and MBA, we cannot assign the wavelength dependence of the yield of fluorescence to the potential presence of a “vibronic effect” in photochemistry. The reason for this is anthracene shows a parallel dependence of fluorescence upon excitation into S_2, yet we believe no photochemistry occurs. Thus, there is contribution of a “vibronic effect” involving photophysical competition (vibrational relaxation within the singlet manifold and intersystem crossing).

The presence of photochemistry in S_2 and its absence in S_1 is principally due to the fact that the S_2 state has a π,σ^* character in the C−Br bond. On the other hand, the S_1 state has its origin from a π,π^* delocalized configuration. Furthermore, no photochemistry occurs in the lowest triplet state of either DBA or MBA.

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