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External Heavy-Atom Perturbed Intersystem Crossing from the Excited Singlet and Triplet States of Anthracene and 9,10-Dibromoanthracene in Fluid Solution[1]

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Abstract: The apparent bimolecular rate parameters $(k_{\mathrm{T\overline{MQ}}}, k_{\mathrm{G\overline{TQ}}})^2$ characteristic of the external heavy atom quenching of molecular singlet and triplet states in the system anthracene (A) [solvent = cyclohexane; quenchers = bromobenzene, ethyl iodide] and 9,10-dibromoanthracene (DBA) [solvent = ethanol, quencher = KI] have been determined and are used to describe the sensitivity of the external heavy-atom effect acting on the nonradiative singlet ↔ triplet intersystem crossing processes of A and DBA in fluid solution at 24 ± 2°. In addition triplet quantum yields determined by the method of Medinger and Wilkinson[3a] are reported for A in cyclohexane and DBA in ethanol.

That external heavy atoms, Q (meaning heavy atoms, molecules containing heavy-atoms, ions of heavy-atoms ..... present in the solvent), can enhance both radiative and nonradiative electronic relaxation probabilities in aromatic hydrocarbons, M, is a phenomenon that is now well documented in the photochemical literature.[4,5] The relevant photophysical relaxation processes of particular interest are

intersystem crossing from $^1\mathrm{M}^*$

$$^1\mathrm{M}^* \xrightarrow{k_{\mathrm{TM}}} {}^3\mathrm{M}^* \quad \text{process TM} \tag{i}$$

intersystem crossing from $^3\mathrm{M}^*$

$$^3\mathrm{M}^* \xrightarrow{k_{\mathrm{GT}}} {}^1\mathrm{M} \quad \text{process GT} \tag{ii}$$

phosphorescence

$$^3\mathrm{M}^* \xrightarrow{k_{\mathrm{PT}}} {}^1\mathrm{M} \quad \text{process PT} \tag{iii}$$

In searching for a better understanding of the mechanism[5-8] of the external heavy-atom effect it is important to establish the relative sensitivity of the above processes to this perturbation. Experimental investigations[6,9-11] directed toward this end have been carried out to some extent revealing quite consistently that a heavy-atom environment increases k_{PT} more than k_{GT}. Evidence assessing the relative sensitivity of k_{TM} *vs.* k_{GT}, k_{PT} is sparse, conflicting, and uncertain.[9b,10] Birks[12] has analyzed the data of ref 9b for the naphthalene-propyl halide system claiming rather generally that the influence of the external heavy-atom effect on k_{TM} is much greater than that on k_{PT} or k_{GT}.

The studies referenced above were commonly based on the phosphorescence properties of the $^3\mathrm{M}^*$ excitation and consequently were conducted in low-temperature solid solutions.[13] Little attention has been given to sensitivity studies (k_{TM} vs. k_{GT}) in room temperature fluid solution where the external heavy-atom effect can be utilized as a tool in mechanistic and synthetic photochemistry.[14,15] The observed heavy-atom effect is expected to differ under these two environmental constraints. At low temperature process i predominantly originates from the zero-point vibronic level of $^1\mathrm{M}^*$; thus the number of possible relaxation modes is limited to intermediate triplet state(s) ($^3\mathrm{M}^{**}$) with energies less than or equal to the $^1\mathrm{M}^*$ zero-point energy. Higher triplet state(s) sufficiently close in energy to $^1\mathrm{M}^*$ may influence the $^1\mathrm{M}^* \rightarrow {}^3\mathrm{M}^{**}$ intersystem crossing rate by thermal population of the vibrational states of $^1\mathrm{M}^*$, and these triplet state(s) could then provide different spin-orbit coupling schemes with the perturbing singlet states of the $^1\mathrm{M}^*$-Q interaction. Also, in low-temperature rigid solution molecular diffusion is considerably reduced and the bimolecular encounter dependence of the $^1\mathrm{M}^*$-Q, $^3\mathrm{M}^*$-Q interactions is correspondingly reduced. If orientation and distance requirements afford important contributions to the total heavy-atom interaction then these aspects are minimized in frozen solution due to the random M*-Q distributions and slow diffusion. Furthermore, the differing nature of solvent-solute interactions associated with the temperature and environmental.dependence of dispersion forces and/or collisions may have direct influence on the density of vibronic states and related Frank-Condon factors for the important interacting states involved in processes i and ii.

In this report we demonstrate that the overall process

$$^3\mathrm{M}^* + \mathrm{Q} \longrightarrow {}^1\mathrm{M} + \mathrm{Q}$$

contributes significantly to the molecular triplet state decay

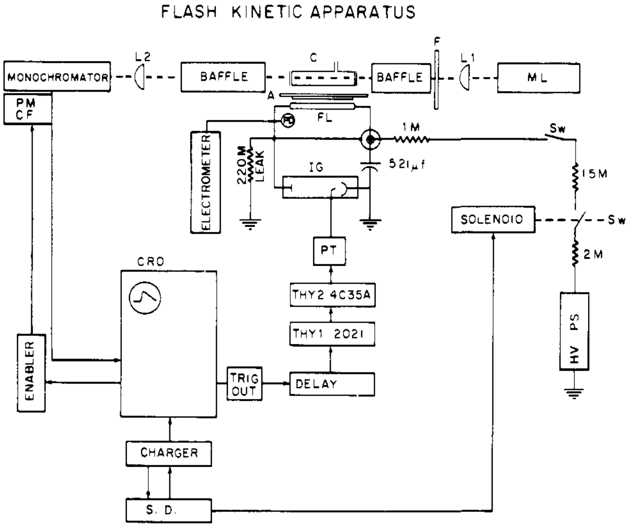

Figure 1. Flash kinetic apparatus: PM = 1P28 photomultiplier tube; CF = cathode follower; L1, L2 = lenses; C = sample cell; F = filter; A = flash slit and filter assembly; FL = flash lamp; IG = ignitron; SW = high-voltage switch; PT = pulse transformer; S.D. = solenoid drive panel; PD = photodiode.

of A (Q = bromobenzene, ethyl iodide) and DBA (Q = potassium iodide) in fluid solution at ambient temperature. We are therefore able to compare this result with the corresponding heavy-atom quenching process

$$^1M^* + Q \longrightarrow {}^3M^* + Q$$

competing with $^1M^*$ fluorescence. Combining this information with triplet quantum yield data provides a phenomenological measure of the external heavy-atom effect operating on the $^1M^*$ and $^3M^*$ excitations of A and DBA in the heavy-atom solvent systems employed. The essential measurements included in our experimental method are outlined here: (1) τ_M, molecular fluorescence lifetime of M; (2) q_{FM}, molecular fluorescence quantum efficiency of M (normalized fluorescence spectrum in dilute solution); (3) F and F^0, molecular fluorescence quantum intensity (spectrum) of M in the presence and absence of Q, respectively (fluorescence quenching); (4) $y_T(t)$ and $y_T{}^0(t)$, microsecond flash induced triplet response (as a function of time ≡ t) of M in the presence and absence of Q, respectively (these functions are analyzed to obtain corresponding values at $t = 0$ viz. $y_T(0)$, $y_T{}^0(0)$ and the respective pseudo-first-order rate components α and α^0 (triplet quenching)).

Experimental Section

Chemicals. Anthracene and 9,10-dibromoanthracene were obtained from Eastman Kodak. Anthracene (scintillation grade) was vacuum sublimed ($<10^{-3}$ mm) twice. 9,10-Dibromoanthracene was chromatographed on alumina (activity grade 1), developed, and eluted with dry hexane. This procedure was again repeated with the reclaimed fraction and followed by a double vacuum sublimation. Cyclohexane (Eastman spectro ACS grade) was used without further purification. Potassium iodide (Fisher Scientific) was recrystallized from methanol-water. The reagent grade solvents bromobenzene, ethyl iodide, and 95% ethanol were carefully distilled on a 2 ft fractionating column packed with single-turn glass helicies.

Instrumentation. Fluorescence spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter. The spectral sensitivity distribution of the emission detector system of this instrument has been determined for the correction of emission spectra. Visible and ultraviolet absorption spectra were measured on a Cary Model 14 spectrophotometer. Fluorescence lifetimes were determined with a single photon counting fluorometer designed and constructed by Professor Brand and his research group at the Johns Hopkins University, Department of Biology.[16]

The flash photoelectric apparatus used in this research is of conventional design with some modification to facilitate reliable comparative measurements. Since this is our first report involving flash excitation methods a somewhat detailed description of the apparatus is presented. Figure 1 is a nonscale block diagram depicting the general arrangement of the optical system and its relation to the associated electronic equipment. We use an 8 cm linear Cajon flash lamp[17] filled with argon to a pressure of 30 Torr. The discharge from this lamp dissipates 125 J of electrical energy in a flash that develops its peak intensity in 7 μsec after excitation. The light level from the flash at 40 μsec after excitation is less than 1.0% of its peak value.

The sample housing (active area coated with Eastman White Reflectance Paint) was designed to provide reproducible location of cells (both cylindrical and rectangular cuvettes), flash filtering with planar glass filters, and a variable aperture to select desired incident flash intensity. Flash lamp intensity was monitored by viewing scattered light within the housing with an appropriately filtered EG&G SGD-100A photodiode. A convenient "sample and hold" intensity meter was obtained by integrating the current output of the photodiode with a Keithley Model 602 electrometer (ac coupled). Calibration of this system provided a means of correcting transient response to small variations in lamp intensity <2%. It also served as a check for spurious lamp behavior (this phenomenon occurs randomly and only with an old lamp >100 flashes) where the lamp discharge suffers an intensity variation of 5 to 10%. Data, to be used in replicate analyses, collected during this condition may be rigorously rejected and immediately remeasured.

Scattered light entering the detector (RCA IP28 P.M. tube) was minimal; this was due to a combination of a rather "slow" $f/8.7$ monochromator (Jarrell-Ash 78-460, 1 m focal length, Czerny-Turner) and an efficient light baffle assembly that was attached to sample housing. The steady-state monitoring source was a 200 W Mercury-Xenon Compact Arc lamp (Hanovia 901B-11) driven by a Hanovia No. 28-302 250 W power system. The mercury-xenon arc, in addition to providing a source of high brightness and relatively small size to penetrate the small effective aperature of the baffled optical system, normally operates in a diffuse mode where short time and long time signal instability is minimized. To further prevent long time instability from affecting the zero calibrations of a particular response the P.M. tube was pulsed on prior to flash lamp excitation. This sequence then generated the full-light dc level (transmittance = $T = I/I_0 = 1$) on a portion of the same oscilloscope sweep that was used to sample the transient response. The P.M. pulsing operation was performed in the enabler circuit of Figure 1 which has been described elsewhere.[18] Only the interior of the P.M. output pulse was sampled to avoid possible errors associated with the slightly distorted rise and fall sections of this pulse. The above timing sequence was secured through the interaction of the double time base feature of the Tektronix 535 A C.R.O. that was employed in a delayed sweep mode coupled to an external delay circuit.

The information transfer in the complete system is indicated with arrows in Figure 1. The apparatus as described in use with a "fresh" lamp will maintain lamp intensity variation to less than ±1%; errors due to independent full-light dc level sampling are virtually eliminated. The excellent timing stability developed in all control stages up to and including lamp excitation affords precise time zero location thus facilitating the collection of replicate data.

Degassing Procedures. The solutions used in the measurement of triplet response were degassed by repeated cycles of freezing, pumping, thawing, shaking, and refluxing for a 7-hr period on a high vacuum line. The initial freezing cycles were accomplished with a Dry Ice-acetone bath; for the final cycles liquid nitrogen was employed. The degassed solutions exhibited no solvent, solute, or heavy-atom component loss as evidenced by visible and uv absorption spectrophotometry. The sample cells (three optically matched 1 cm × 1 cm × 4.5 cm rectangular cuvettes and two optically matched 8.5 cm cylindrical cuvettes) were affixed with degassing bulbs and Ace No. 8194 stopcocks supplied with Viton A "O" rings that were conveniently baked out during the sample degassing period.

Solutions prepared for use in the fluorescence measurements (lifetime, quenching, and quantum yield) were degassed by purg-

Table I. Fluorescence Lifetimes and Quantum Efficiencies, Triplet Quantum Efficiencies

M	Solvent	τ_M, nsec	$q_{FM}{}^a$	$q_{TM}{}^b$	$q_{FM} + q_{TM}$
A	Cyclohexane	4.83	0.29 ± 0.015	0.74 ± 0.04	1.03 ± 0.04
DBA	95% ethanol	1.61	0.097 ± 0.008	0.79 ± 0.05	0.89 ± 0.05

[a] Error bars reflect precision of replicate determinations. [b] Error bars reflect estimated variance of least-squares fit to $r_F - 1 = (h - 1)q_{TM}$, Figures 3 and 4.

ing them with solvent saturated argon for 10 min. This procedure was compared with the more rigorous technique described above for both A and DBA solutions by monitoring the fluorescence spectra of identical samples degassed by both methods and no measurable difference was found.

Fluorescence Lifetime Determinations. The observed fluorescence response functions, $f_M(t)$, of A and DBA solutions corresponding to those used for determining fluorescence quantum yields were collected by the single photon sampling method. The functions $f_M(t)$, operationally expressed as the convolution of the fluorescence impulse response, $i_M(t)$, with the excitation profile, $e(t)$, were analyzed for multiexponential decay by the method of

$$f_M(t) = \int_0^t e(t - x) i_M(x) \, dx$$

moments. Convoluting the extracted functions, $i_M(t)$, with the excitation profiles and comparing these with the experimental fluorescence distributions clearly established that the impulse response for both A and DBA was characterized by a single exponential decay. The corresponding lifetimes are given in Table I.

Fluorescence Quantum Yields, Quenching. All fluorescence spectra were recorded in the right angle illumination mode, i.e., emission was detected at 90° to the excitation beam. Dark current compensation and ratio recording are internally provided with the Hitachi MPF-2A spectrofluorimeter. Solvent blanks were run with each spectrum.

Fluorescence quantum yields were determined relative to quinine bisulfate in 1.0 N sulfuric acid by use of the relation

$$q_{FM} = q_{FS} \frac{A_M}{A_S} \frac{f_S}{f_M} \frac{n_M{}^2}{n_S{}^2} \quad (1)$$

where the subscripts M and S refer to the sample and quantum standard, respectively. $A_{M(S)}$ is the integrated area under the corrected fluorescence spectrum, $f_{M(S)}$ is the fraction of light absorbed at the exciting wavelength, and $n_{M(S)}$ is the refractive index of the solvent. The precision of this method was tested by repeating determinations at different excitation wavelengths. When the sample and quantum standard were both excited at a common wavelength, variation among the final q_{FM} values was less than 5%. A correction for the relative spectral distribution of the excitation source-monochromator combination was applied when the sample and standard did not have an acceptable common excitation region. Yields determined in this condition were within 8% of the above values. In these quantum yield determinations all concentrations were adjusted to keep the absorbance of the solutions less than 0.02 in a 1 cm path length at each exciting wavelength. The molecular fluorescence quantum yields (averaged) for A in cyclohexane and DBA in ethanol are reported in Table I.

The fluorescence quenching functions F^0/F ($\equiv \phi_{FM}{}^0/\phi_{FM}$) were also determined with the aid of eq 1 where the identifications ϕ_{FM} with q_{FM} and $\phi_{FM}{}^0$ with q_{FS} are now operative. The fluorescence spectra corresponding to $\phi_{FM}{}^0$ (relative fluorescence yield of M in the absence of Q) and to ϕ_{FM} (relative fluorescence yield of M in the presence of Q) were all measured in one experiment under identical excitation-emission conditions with the same solutions that were used in the flash photolysis experiments. The excitation wavelengths were chosen to maximize fluorescence intensity to ensure a narrow excitation bandpass compatible with stable detector sensitivity. Optical densities at the excitation wavelengths utilized were of the order of 0.1 and we therefore determined the arbitrary unperturbed yields, $\phi_{FM}{}^0$, relative to quinine bisulfate. The values of $\phi_{FM}{}^0$ agreed with those measured in dilute solution (q_{FM}) by better than 10% implying that any self absorption errors associated with the quenching measurements were small. The refractive index of each solution used in a given quenching run was measured with an Abbé refractometer. The slight solvent perturbation on the $^1M^* \leftarrow {}^1M$ absorption spectrum evidenced in the A-bromobenzene system was accounted for at the fluorescence excitation wavelength in the term f_S/f_M of eq 1.

Flash Measurements. The transient response of the flash induced $^3M^*$ excitation (triplet response) is conveniently expressed in terms of the absorbance log $I_0/I(t) \equiv y_T(t) = \epsilon_T(\lambda_a)[^3M^*(t)]l$ for the biphotonic transition $^3M^{**} \leftarrow {}^3M^*$ ($h\nu_a$) that is selected to monitor the $^3M^*$ concentration as a function of time. $\epsilon_T(\lambda_a)$ is the $^3M^*$ extinction coefficient at the analysis wavelength, λ_a, and l is the optical path length of the sample. Under the experimental conditions of this work triplet response for all systems investigated was controlled by concurrent first- and second-order relaxation. Dynamically this behavior is expressed in the nonlinear equation

$$-\frac{dy_T(t)}{dt} = \alpha y_T(t) + \beta y_T{}^2(t)$$

resulting in

$$y_T(t) = [(1/y_T(0) + \beta/\alpha)e^{\alpha t} - \beta/\alpha]^{-1} \quad (2)$$

where α and β represent the first- and second-order contributions to the $^3M^*$ depopulation, respectively. More specifically α is a sum of first- and pseudo-first-order rate parameters and β is a sum of

$$\alpha = \Sigma k^{(1)} \quad (3)$$

$$\beta = \Sigma k^{(2)}/\epsilon_T l \quad (4)$$

second- and pseudo-second-order rate parameters divided by the product of ϵ_T and l. Zero time corresponding to the maximum in the $[^1M^*(t)]$ temporal distribution is taken as the centroid of the lamp profile. To analyze triplet decay curves in terms of eq 2 a statistical scheme which utilizes the techniques of nonlinear regression analysis has been assembled. Basically, the method directs a guided search for the parameters α, β, and $y_T(0)$ and when the minimization conditions defining the "principle of least squares" are approached the search is refined with an appropriate analytical solution until the "best" parameter estimates consistent with the raw data $[t, y_T]$ are found. The method has been fully tested and evaluated in this laboratory and was found to provide a sensitive and reliable analysis package for the data we have encountered.[19]

To justify the use of eq 2 in describing the triplet decay data presented in this report the following experimental testimony is furnished. (1) The data when analyzed in terms of pure first-order or pure second-order response functions were ill-fitted. In contrast, well-behaved function fitting and statistical confidence were secured with eq 2. (2) The reality of the parameter β as derived from eq 2 was established in two ways. (a) From eq 4 we observe that $\beta = \beta(\lambda)$, in fact $1/\beta = l\epsilon_T/\Sigma k^{(2)}$ is proportional to the $^3M^{**} \leftarrow {}^3M^*$ absorption spectrum. A comparison of the spectra derived from $1/\beta$ and y_T is given in Figure 2 for A in cyclohexane. (b) Equation 4 also implies that $\beta = \beta(l)$. We had available 1 and 8.5 cm path lengths. The condition $\beta(1\text{ cm})/\beta(8.5\text{ cm}) = 8.5$ at a given analysis wavelength was satisfied by the data within experimental error.

It was found that in order to reproducibly characterize a given response function replicate decay sampling was essential, i.e., the resultant triplet response function $y_T(t)$ for a given specimen was derived from an average of three to eight separate measurements (appropriately weighted in the fit to eq 2) depending on the quality of the data. Under the excitation conditions employed no detectable decomposition of any sample or heavy-atom quencher was observed upon exposure to 20 or fewer flashes. For a typical "heavy-atom run" proper incident flash intensity was selected by adjusting the slit assembly inside the lamp housing and holding it fixed; appropriate filters were chosen to ensure that the heavy atom component did not absorb any exciting or monitoring light. All optical adjustments were maintained constant during an entire run.

Table II. Quenching Data

M/Q/solvent	[M], mol l.$^{-1}$	[Q], mol l.$^{-1}$	$r_F - 1$	$h - 1$	$\alpha - \alpha^0 \times 10^{-3}$, sec^{-1}
A/bromobenzene/cyclohexane	5.03×10^{-5}	0.0	0.0	0.0	0.0
	5.03×10^{-5}	0.573	1.128	1.365	0.215
	5.03×10^{-5}	1.15	2.138	2.890	0.504
	5.03×10^{-5}	1.56	2.940	4.198	0.525
	5.03×10^{-5}	1.91	3.560	4.822	0.762
	5.03×10^{-5}	2.68	5.009	6.781	1.122
A/ethyl iodide/cyclohexane	8.04×10^{-5}	0.0	0.0	0.0	0.0
	8.04×10^{-5}	0.025	0.435	0.507	1.45
	8.04×10^{-5}	0.050	0.973	1.229	2.83
	8.04×10^{-5}	0.090	1.754	2.415	6.62
	8.04×10^{-5}	0.125	2.368	3.244	9.42
DBA/KI/95% ethanol	3.18×10^{-5}	0.0	0.0	0.0	0.0
	3.18×10^{-5}	0.0210	0.1937	0.216	0.7
	3.18×10^{-5}	0.0419	0.3680	0.477	2.0
	3.18×10^{-5}	0.0587	0.5281	0.660	3.7
	3.18×10^{-5}	0.0797	0.6938	0.899	4.1
	3.18×10^{-5}	0.0965	0.8688	1.069	4.7

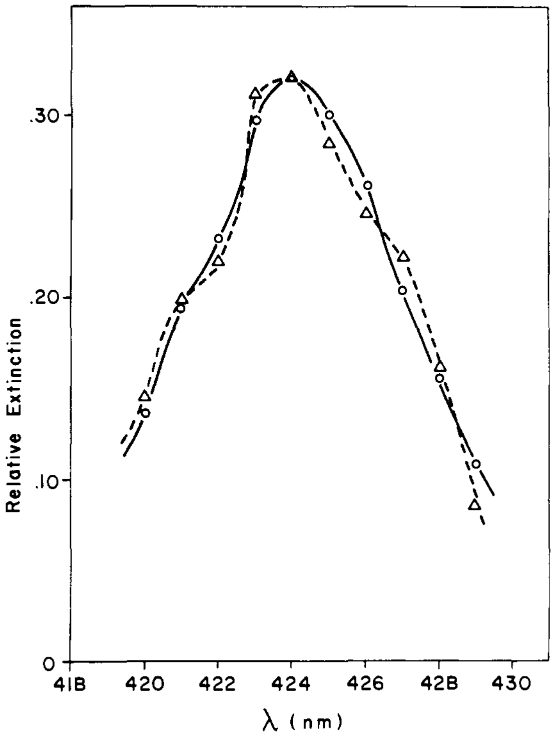

Figure 2. Triplet-triplet absorption spectrum of A in cyclohexane solution derived from (○) y_T and (△) $1/\beta$.

To check for direct $^3M^* \leftarrow {}^1M$ absorption as a possible contributor to the $^3M^*$ excitation in the DBA-KI system a Corning CS 3-69 cut-off filter was placed in the flash assembly. With this filter excitation intensity at 18,500 cm^{-1} (well above E_T = 14,060 cm^{-1} for DBA)[20] was approximately equivalent to that available in the argon discharge at the $^1M^* \leftarrow {}^1M$ excitation energy. No triplet absorption was observed with this filter in place.

Results and Discussion

To provide reference for the relevant photophysics encountered in this study, a mechanistic scheme (Scheme I) is presented which is consistent with the experimental observations.

Triplet Quantum Yields. Medinger and Wilkinson[3a] have developed a method for determining triplet quantum yields ($q_{TM} = k_{TM}\tau_M$) by combining the measurements F, F^0, $y_T(0)$, $y_T{}^0(0)$ for a range of solutions with constant [^{1}M] and different concentrations of Q. The expression

$$r_F - 1 = (h - 1)q_{TM};\ r_F = F^0/F \text{ and } h = \frac{y_T(0)F^0}{y_T{}^0(0)F} \tag{5}$$

predicted by Scheme I is linear in $h - 1$, thus q_{TM} is obtained as the slope of the plot ($h - 1$, $r_F - 1$). Equation 5 is based on the assumption that the overall process depicted in step 5 of Scheme I accounts for the total quenching of the $^1M^*$ excitation by Q. Wilkinson and coworkers[3] have used eq 5 to determine q_{TM} for a representative sample of aromatic systems. The values of q_{TM} were found to be independent of the nature of the heavy-atom quencher. Employing this technique we have obtained triplet quantum yields for A in cyclohexane and DBA in ethanol; the data and results (consistent with eq 5) are summarized in Tables I and II and Figures 3 and 4.

It is observed that the sum $q_{FM} + q_{TM}$ for A in cyclohexane is unity within the experimental precision as controlled by the estimated variance in a least-squares analysis of the q_{TM} data. This condition is not satisfied by DBA in ethanol solution. If the "real" error bars associated with these q_{TM} determinations approach ±10%[3a] then $q_{FM} + q_{TM} = 1$ could be realized for the DBA results at the extreme error limit. We conclude that our findings do not rule out the possibility of a small but measurable internal quenching component corresponding to internal conversion from $^1M^*$ in the DBA-ethanol system.

An examination of the quantum yield results (Table I) reveals that dibromination of A in the 9,10 positions reduces the fluorescence quantum efficiency (by a factor of 3) from 0.29 to 0.097 but maintains the triplet quantum efficiency essentially constant: $q_{TM} = 0.74$ for A and $q_{TM} = 0.79$ for DBA.[21] However, the lifetime of the fluorescent state of DBA is considerably decreased from that of A and upon examining the molecular rate parameters derived from this quantum yield data (Table III) it is discovered that k_{FM} is not altered by dibromination and that the intersystem crossing rate parameter increases in DBA ($k_{TM} = 49.1 \times 10^7$ sec^{-1}) relative to A ($k_{TM} = 15.3 \times 10^7$ sec^{-1}) revealing the presence of a moderately induced internal heavy-atom perturbation for DBA.

This comparison, however, is not entirely satisfactory in showing the extent of internal heavy-atom perturbation induced in A by dihalogenation of the 9 and 10 positions. For example, the molecular parameters[23] $q_{FM} = 0.56$, $q_{TM} = 0.48$, and $\tau_M = 7.2$ nsec for 9,10-dichloroanthracene in ethanol determine $k_{TM} = 6.67 \times 10^7$ sec^{-1} which is significantly less than the value of k_{TM} that was found for A.

Scheme I

Process			Rate parameter	
$^1M + h\nu \longrightarrow {}^1M^*$			Light absorption	(1)
$^1M^* \longrightarrow {}^1M + h\nu_{FM}$	k_{FM}	k_M	Fluorescence	(2)
$^1M^* \longrightarrow {}^1M$	k_{GM}		Internal conversion	(3)
$^1M^* \longrightarrow {}^3M^*$	k_{TM}		Intersystem crossing	(4)
$^1M^* + Q \longrightarrow {}^3M^* + Q$	$k_{T\overline{MQ}}$		Heavy-atom quenching	(5)
$^3M^* \longrightarrow {}^1M + h\nu_{PT}$	k_{PT}	k_T	Phosphorescence	(6)
$^3M^* \longrightarrow {}^1M$	k_{GT}		Internal quenching	(7)
$^3M^* + A \longrightarrow {}^1M + A$	$k_{G\overline{TA}}$		Adventitious quenching	(8)
$^3M^* + {}^1M \longrightarrow 2\,{}^1M$	$k_{G\overline{TG}}$		Concentration quenching	(9)
$^3M^* + Q \longrightarrow {}^1M + Q$	$k_{G\overline{TQ}}$		Heavy-atom quenching	(10)
$^3M^* + {}^3M^* \longrightarrow {}^{1,3,5}D^{**}(?)$	k_{TT}		Triplet–triplet interaction	(11)

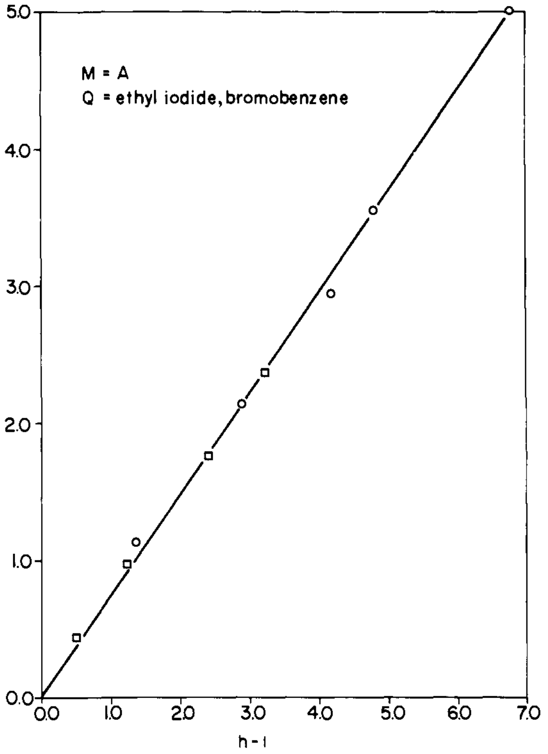

Figure 3. Triplet yield plot for A in cyclohexane solution: (○) Q = bromobenzene; (□) Q = ethyl iodide.

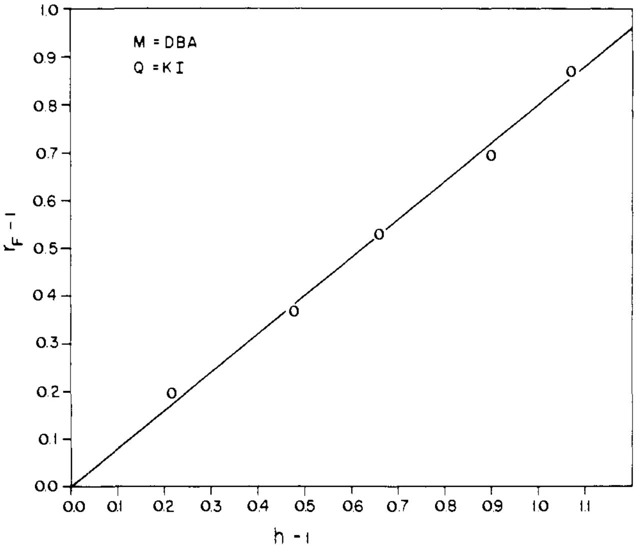

Figure 4. Triplet yield plot for DBA in 95% ethanol, Q = KI.

The fluorescence quantum yield of the A nucleus is very sensitive to the position of substitution and exhibits a considerable temperature dependence for substitution in the meso positions.[23,26-28] Lim and coworkers[28] have found a converse temperature dependence of the fluorescence and relative triplet production for a series of 9- and 9,10-halo- and alkyl-substituted anthracenes (DBA included); at 77°K the fluorescence quantum yield was determined to be 1.00 ± 0.05 for all these compounds when excited with 365-nm radiation. This temperature dependence is partially explained by a mechanism that invokes activated intersystem crossing from $^1M^*$ to a nearly isoenergetic triplet state $^3M^{**}$ (believed to be the second triplet state)[29] where substitution in the meso positions of A is expected to lower the transversely polarized $^1L_a(={}^1M^*)$ singlet state relative to $^3M^{**}$. Other considerations such as Frank-Condon factors, vibronic interaction, and the possibility of parallel relaxation to other neighboring triplet states may contribute to the observed activation energy; however, the location of $^3M^{**}$ relative to $^1M^*$ does appear to be primarily responsible for the varying degree of temperature dependence of q_{FM} and q_{TM} for derivatives of A.[30]

Since dialkyl and dihalo substituents in the 9 and 10 positions of A give fluorescence maxima in almost the same region (considerably lower in energy than $^1M^*$ for A), it seems more appropriate to compare the induced internal heavy-atom effect for DBA relative to other 9,10 derivatives where a common energy basis (at least for $^1M^*$) is

Table III. Derived Rate Parameters

M/Q/solvent	$k_M \times 10^{-7}$, sec^{-1}	$k_{FM} \times 10^{-7}$, sec^{-1}	$k_{TM} \times 10^{-7}$, sec^{-1}	$k_{GM} \times 10^{-7}$, sec^{-1}	$k_{T\overline{MQ}} \times 10^{-7}$, l. mol^{-1} sec^{-1}	$k_{G\overline{TQ}} \times 10^{-2}$, l. mol^{-1} sec^{-1}	k_{GT}, sec^{-1}	$\alpha^0 \times 10^{-2}$, sec^{-1} [c]
A/bromobenzene/ cyclohexane	20.7	6.00	15.3		39.4	4.16	22[a]	2.55
A/ethyl iodide/ cyclohexane	20.7	6.00	15.3		396	695	22[a]	2.55
DBA/KI/95% ethanol	62.1	6.02	49.1	<7.0	551	514	<100[b]	373

[a] From ref 12. [b] See ref 32. [c] Averaged among the M–Q quenching runs.

Table IV. Molecular Parameters for Several Disubstituted Meso Anthracene Compounds

Compd	q_{FM}	q_{TM}	$q_{FM} + q_{TM}$	τ_M, nsec	$k_{TM} \times 10^{-7}$, sec^{-1}	Singlet[e] energy, 10^2 cm^{-1}	Solvent
Anthracene[a]	0.29	0.74	1.03	4.83	15.3	265	Cyclohexane
Anthracene[b]	0.30	0.72	1.02	5.2[g]	13.8	265	Ethanol
9,10-Dimethylanthracene[c]	0.89	0.03	0.92	11[f]	0.273	248	Ethanol
9,10-Diphenylanthracene[c]	0.89	0.02	0.91	6.8[f]	0.294	248	Ethanol
9,10-Dichloroanthracene[d]	0.56	0.48	1.04	7.2[f]	6.67	248	Ethanol
9,10-Dibromoanthracene[a]	0.097	0.79	0.89	1.61	49.1	247	Ethanol

[a] This work. [b] From ref 3e. [c] From ref 22. [d] From ref 23. [e] Estimated from short-wavelength peaks of fluorescence spectrum. [f] From ref 24. [g] From ref 25.

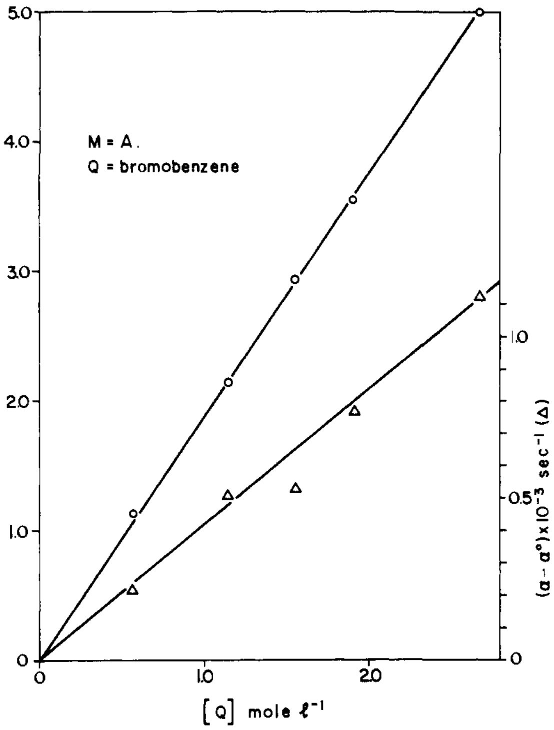

Figure 5. Fluorescence quenching (○) and triplet quenching (△) plots, A-bromobenzene in cyclohexane.

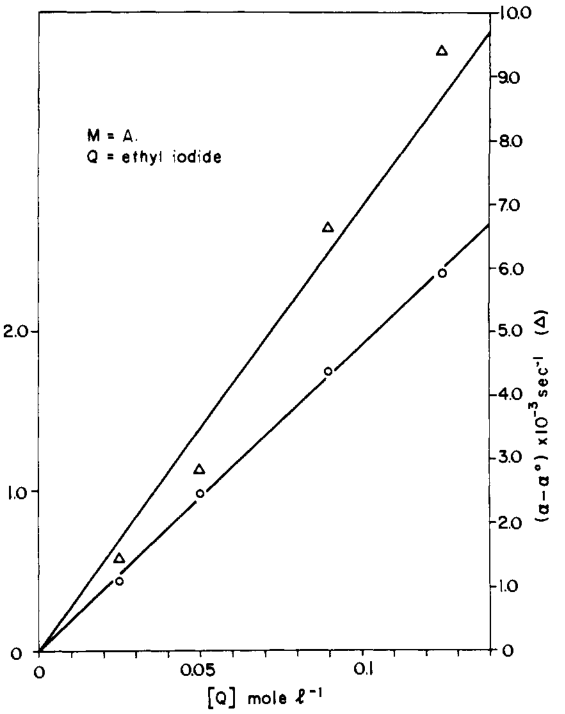

Figure 6. Fluorescence quenching (○) and triplet quenching (△) plots, A-ethyl iodide in cyclohexane.

realized. In Table IV we have collected fluorescence and triplet quantum yield data from the literature for several 9,10-anthracene derivatives. Although the available data are limited, it is observed that the trends in q_{FM}, q_{TM}, and the 200-fold increase in k_{TM} in going from 9,10-dimethylanthracene to DBA vividly display a sensible comparison for the induced internal heavy-atom effect operating in these meso anthracene derivatives.

Heavy-Atom Quenching. The fluorescence quenching plots (Figures 5-7) for the A-bromobenzene, A-ethyl iodide, DBA-KI systems are linear in [Q], hence the rate parameters $k_{T\overline{MQ}}$ characteristic of the $^1M^*$ quenching process

$$r_F - 1 = \tau_M k_{T\overline{MQ}}[Q] \quad (6)$$

were extracted. They are given in Table III.

We were able to observe triplet quenching in these systems consistent with the overall process described in step 10 of Scheme I. Analysis of the triplet decay curves including the common triplet state deactivation processes of Scheme I (steps 6-10) will give for the pseudo-first-order decay parameters

$$\alpha = \alpha^0 + k_{G\overline{TQ}}[Q]$$

in the presence of Q and

$$\alpha^0 = k_T + k_{G\overline{TG}}[^1M]_0 + \sum_A k_{G\overline{TA}}[A]$$

in the absence of Q, where $[^1M]_0 = [^1M]$ at $t \leq 0$. The rationale here was to examine $\alpha = \alpha([Q])$ for the same data samples that were used in the determination of q_{TM}. Since the component $k_{G\overline{TQ}}[Q]$ was found to be comparable to α^0 in these systems and since α^0 is predominantly controlled in room temperature fluid solution by the pseudo-first-order contributions[31] $k_{G\overline{TG}}[^1M]_0 + k_{G\overline{TA}}[A \equiv O_2]$ quantitative correlation could only be realized by maintaining $\alpha = \alpha([A])$ constant for each sample of a given quenching run. In order to keep α^0 constant each sample in the run would have to be identically degassed, since the outgassing technique employed in this investigation did not reduce the $[O_2]$ level below measurable significance. This task was not feasible under our experimental conditions inasmuch as the samples had to be degassed at different times and the standardized degassing procedure that was adopted could not be exactly reproduced from sample to sample. To circumvent this difficulty a "lifetime blank" was used to monitor α^0 with each M-Q sample. The "lifetime blank" solution (identical to the M-Q = 0 reference) was simultaneously degassed with the corresponding M-Q samples. This technique made possible the generation of triplet quenching parameters essentially independent of oxygen contamination.

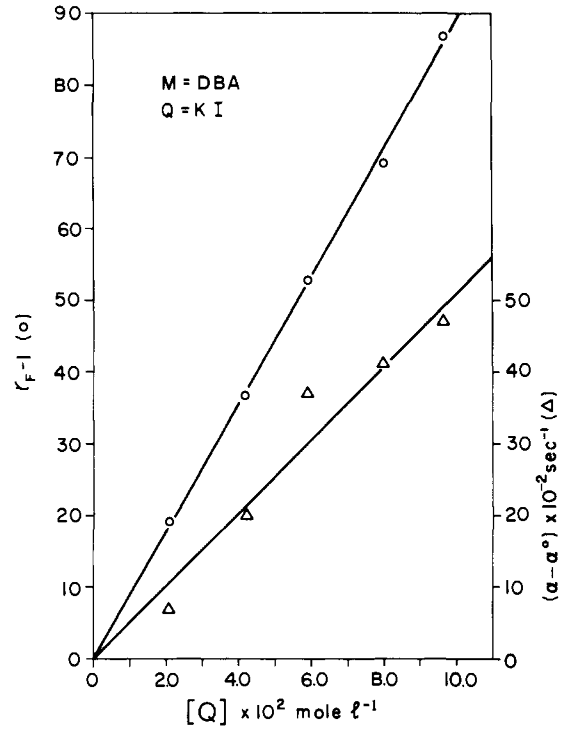

Figure 7. Fluorescence quenching (O) and triplet quenching (Δ) plots, DBA-KI in 95% ethanol.

It was assumed that no significant impurity was introduced with the heavy-atom quenching component Q. The triplet quenching functions (eq 7) are plotted in Figures

$$\alpha - \alpha^0 = k_{G\overline{TQ}}[Q] \tag{7}$$

5-7; Tables II and III contain respectively the quenching data and derived parameters $k_{G\overline{TQ}}$.

The fate of the $^3M^*$-$^3M^*$ interaction, step 11 in Scheme I, is unknown in this work; however, we have verified that it is little influenced by Q as revealed in the constancy of the β parameters that were determined in the triplet quenching experiments. Also, it was not possible to quantitatively describe the $^3M^*$-^1M interaction, step 9, yet the experiments of Langelaar et al.[31c] and the observed decay parameter $\alpha^0 = 3.73 \times 10^4$ sec^{-1} (large relative to A; $\alpha^0 = 255$ sec^{-1}) for the DBA-ethanol system (with $k_{GT} < 100$ sec^{-1})[32] which was degassed under similar conditions with A suggest the importance of this contribution. We suspect that the difficulty associated with the quantitative observation of concentration quenching via the flash technique results from different [$^3M^*$] distributions in the specimen solutions caused by varying the ^1M concentration.

Heavy-Atom Sensitivity. Two immediate conclusions follow from the heavy-atom quenching results for the systems encountered in this study.

(i) External heavy-atoms quench excited singlet states much more efficiently than triplet states. In fact the bimolecular rate parameters $k_{T\overline{MQ}}$ descriptive of singlet quenching are close (within an order of magnitude for bromobenzene quenching) to being diffusion controlled whereas the triplet quenching constants $k_{G\overline{TQ}}$ are well below this limit. This conclusion is implicit in the nature of the experimental method employed here, for if $k_{G\overline{TQ}} \approx 10^8$-$10^{10}$ l. mol^{-1} sec^{-1} conventional μsec flash photolysis resolution could not monitor the $^3M^*$ excitation with the heavy-atom concentrations that are necessary to quench the $^1M^*$ fluorescence.

(ii) A nonradiative process characteristic of external heavy-atom involvement is competing with triplet relaxation, GT, in fluid solution. That a similar competition is acting in the TM relaxation process was shown to be somewhat representative in the experiments of Wilkinson et al.[3] and is supported by the results of this study for the systems that were examined. Presumably these effects are associated with spin-orbit enhancement resulting from the $^{1,3}M^*$-Q interactions as they both involve singlet ↔ triplet intercombinations. It seems apparent that the external heavy-atom effect operating in fluid solution can appropriately be described by a quenching mechanism.

The fact that $k_{T\overline{MQ}}/k_{G\overline{TQ}} \gg 1$ (conclusion i) relates to the absolute magnitude of the observed heavy-atom quenching effect. An explanation of this result would require more detailed information concerning the nature of the $^{1,3}M^*$-Q interactions than is available in these experiments. It is clear that this explanation would focus attention on elucidating why the values of $k_{G\overline{TQ}}$ are small since the rate components $k_{T\overline{MQ}}[Q]$ must be competitive with intramolecular $^1M^*$ relaxation, k_M (and therefore large), in order to be observed.

Since the object of this investigation was to attempt to establish the sensitivity of the observed external heavy-atom effect acting upon the TM, GT intersystem crossing processes in room-temperature fluid solution, conclusion ii holds the most significance for our interpretation. The term sensitivity is used in a conventional sense to express the total heavy-atom effect on the already present rates k_{TM}, $k_{GT}(\alpha^0)$ that are being perturbed; i.e., we compare the total heavy-atom effect on k_{TM} with the total heavy-atom effect on $k_{GT}(\alpha^0)$. This comparison then must reflect the relative competition between the heavy-atom assisted and natural relaxation processes involved. In these experiments the extent of the heavy-atom perturbation is derived from the amount of heavy-atom present as expressed in the concentration of a single heavy-atom component. In this way it is possible to study heavy-atom sensitivity specific to a particular heavy-atom type.

To formalize the comparison we must examine the total rate parameters that describe the relevant TM, GT relaxations under heavy-atom influence. For the TM process

$$k_{TMQ} = k_{TM} + k_{T\overline{MQ}}[Q] = k_{TM}(1 + f_{TM})$$

where the heavy-atom enhancement coefficient, f_{TM}, is defined by

$$f_{TM} = (k_{T\overline{MQ}}/k_{TM})[Q]$$

A similar consideration of the GT process

$$\alpha = \alpha^0 + k_{G\overline{TQ}}[Q]$$

generates the corresponding coefficient

$$f_{\alpha^0} = (k_{G\overline{TQ}}/\alpha^0)[Q]$$

The enhancement coefficients f_{TM}, f_{α^0} represent the relative increase in the respective heavy-atom induced rates, thus their ratio

$$\frac{f_{TM}}{f_{\alpha^0}} = \frac{k_{T\overline{MQ}}/k_{TM}}{k_{G\overline{TQ}}/\alpha^0} \tag{8}$$

provides the desired sensitivity measure.

In this form, however, the comparison is not unique because of the parasitic composition of α^0 which is primarily due to external quenching and therefore f_{TM}/f_{α^0} only represents an upper limit to the *pure* sensitivity ratio viz. f_{TM}/f_{GT}. In principle

$$f_{GT} = f_{\alpha}{}^0\Big|_{[A],[^1M]=0} = \frac{k_{G\overline{TQ}}}{k_{GT}}[Q]$$

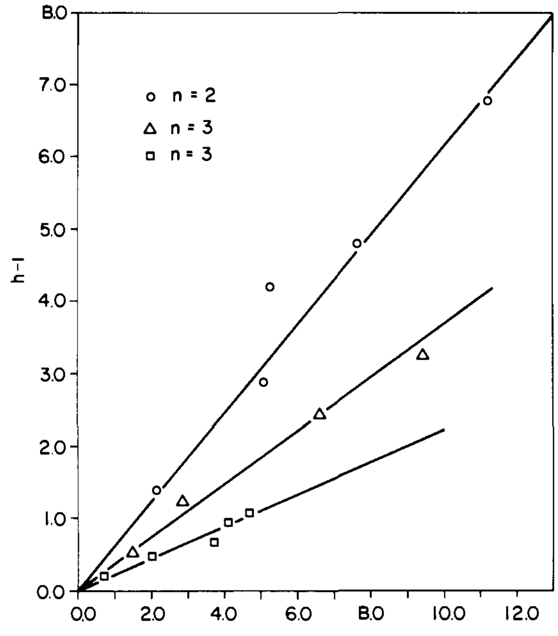

Figure 8. Heavy-atom sensitivity ratio plots for (○) A-bromobenzene-cyclohexane, (△) A-ethyl ioide-cyclohexane, (□) DBA-KI-95% ethanol.

could be approached experimentally in room temperature fluid solution if exhaustive degassing techniques and very dilute solutions were employed. The conditions $[A],[^1M] \rightarrow 0$ relate to minimizing the contributions $k_{G\overline{TA}}[A] + k_{G\overline{TG}}[^1M]_0$ in α^0 which presumably account for the observed temperature dependence of triplet decay in fluid solution.[33,31] It is assumed that $k_{GT} \approx k_T > k_{PT}$, an apparently valid condition for both A and DBA[12,34] (or that k_{GT} can be separated in an independent phosphorescence experiment if this inequality was not satisfied). In view of these considerations a more realistic sensitivity comparison can be obtained by making the substitution $k_{GT} \rightarrow \alpha^0$ in eq 8 where k_{GT} can be taken from lifetime measurements in rigid media. The competition of $k_{G\overline{TQ}}[Q]$ is now reduced to a single internal quenching contribution, k_{GT}, analogous to the competition in k_{TMQ} that was experimentally possible to resolve. Realize that eq 8 in its original form is still useful for assessing relative sensitivity under specific experimental conditions. The quantity $f_{TM}/k_{G\overline{TQ}}$ may be synthesized from the individual quenching and q_{TM} analyses or it can be conveniently extracted from the function

$$h - 1 = (f_{TM}/k_{G\overline{TQ}})(\alpha - \alpha^0)$$

(see Figure 8 and Tables II and V).

The sensitivity ratios, f_{TM}/f_{GT}, thus obtained (Table V) demonstrate that in room-temperature fluid solution the external heavy-atom effect on k_{TM} is considerably less than the corresponding effect on k_{GT} for the considered M-Q systems. And for anthracene, ethyl iodide ($f_{TM}/f_{GT} = 0.0081$) influences this direction more than bromobenzene ($f_{TM}/f_{GT} = 0.14$) does. The possibility that $k_{T\overline{MQ}}$ for the A-ethyl iodide and DBA-KI systems may be diffusion limited (within the experimental error) does not alter the interpretation of f_{TM}/f_{GT} as representing the TM, GT heavy-atom sensitivity standard; if $k_{T\overline{MQ}}$ is diffusion limited then it is concluded that the external heavy-atom effect acting on process TM is diffusion limited. With A and bromobenzene this possibility does not arise and the ratio f_{TM}/f_{GT} (=0.14) is clearly less than unity.

One observes (Table V) that the ratios f_{TM}/f_{α^0} reflect the variable composition of α^0; only the A-ethyl iodide combination ($f_{TM}/f_{\alpha^0} = 0.093$) exhibits sufficient $^3M^*$-Q interaction to compete with the external quenching modes characteristic of the experimental conditions. These conditions maintain $f_{TM} > f_{\alpha^0}$ for the A-bromobenzene and DBA-KI systems.

Table V. Sensitivity Ratios

M/Q/solvent	$f_{TM}/k_{G\overline{TQ}} \times 10^4$, sec	f_{TM}/f_{GT}	f_{TM}/f_{α^0}
A/bromobenzene/ cyclohexane	61.5	0.14	1.6
A/ethyl iodide/ cyclohexane	3.66	0.0081	0.093
DBA/KI/95% ethanol	2.15	0.022	8.0

In conclusion, it is important to stress that the description of heavy-atom sensitivity as presented reflects the *total* interaction of the $^{1,3}M^*$-Q entities. The mechanism depicted in Scheme I furnishes little information concerning the detailed structure of the heavy-atom quenching events described in steps 5 and 10. This detail would expose the nature and extent of any photoassociation between $^{1,3}M^*$ and Q, the encounter dependence and stability of this association, and finally the interaction contribution leading to spin-orbit enhancement in $^{1,3}M^*$ whether it be of an exchange or charge transfer nature. The concept of external heavy-atom effect (sensitivity) in terms of such mechanistic detail is complex and the description would be very specific to the molecular systems involved since it would depend on resolving the individual interaction components responsible for the observed total effect. A description of external heavy-atom sensitivity that is based on total interaction, however, does provide an experimentally useful comparison.

Summary

Triplet quantum yields have been determined for A in cyclohexane ($q_{TM} = 0.74$) and DBA in 95% ethanol ($q_{TM} = 0.79$). For DBA this value and the derived intersystem crossing rate parameter, k_{TM}, reveals a sensible internal heavy-atom effect when compared with the corresponding parameters of other 9,10-meso anthracene derivatives.

External quenching of the excited singlet and triplet states of A and DBA by heavy-atoms (bromobenzene, ethyl iodide for A, and potassium iodide for DBA) in fluid solution has been observed. Bimolecular rate parameters characteristic of these processes, $k_{T\overline{MQ}}$ and $k_{G\overline{TQ}}$, respectively, were derived; the rate components $k_{T\overline{MQ}}[Q]$ and $k_{G\overline{TQ}}[Q]$ account for the observed external heavy-atom perturbation in these systems.

External heavy-atom sensitivity ratios f_{TM}/f_{GT} have been constructed from the rate parameters k_{TM}, $k_{T\overline{MQ}}$, $k_{G\overline{TQ}}$, and k_{GT}. These ratios compare the relative increase in the rate of intersystem crossing from $^1M^*$(TM) due to the presence of external heavy atoms to the relative rate increase of intersystem crossing from $^3M^*$(GT). The large values of $k_{G\overline{TQ}}[Q]$ observed (relative to k_{GT}) were such to maintain $f_{TM} < f_{GT}$ for the three M-Q systems studied indicating that intersystem crossing from $^3M^*$ is more enhanced than intersystem crossing from $^1M^*$ when these excitations are exposed to an external heavy-atom environment in room-temperature fluid solution.

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(33) Langelaar et al.[31c] have determined $k_{GTG} = 3 \times 10^6$ l. mol^{-1} sec^{-1} for A in ethanol at 298°K. We have estimated $k_{GTG} \approx 10^7$–5×10^8 for DBA in 95% ethanol. Assuming these values the concentration quenching contributions to α^0 at room temperature could be as large as 240 sec^{-1} and 1.6×10^4 sec^{-1} for A and DBA, respectively.

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9,10-Dibromoanthracene Excited State Interactions with Ethyl Iodide and Benzene in Fluid Solution[1]

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Abstract: The increase in the apparent molecular fluorescence of 9,10-dibromoanthracene (DBA) in fluid solution that results from the addition of ethyl iodide or benzene can be explained in terms of a collision-induced fluorescence process. Quantitative relative measurements of the fluorescence yield, triplet yield, and triplet quenching of DBA in cyclohexane solution as a function of ethyl iodide (and benzene) concentration have revealed a complex excited state relaxation distribution for the DBA–ethyl iodide interaction, while excited DBA interacts with benzene only to produce enhanced fluorescence. Bimolecular rate parameters appropriate to the mechanistic schemes invoked are given.

Ethanolic solutions of 9,10-dibromoanthracene (DBA) increase their fluorescence in the presence of added ethyl iodide, bromobenzene, and benzene.[2]

For the heavy-atom components, ethyl iodide and bromobenzene, this behavior is in disharmony with that expected since these molecules are well known for quenching the fluorescence of aromatic hydrocarbons via a route which leads exclusively to the population of the molecular triplet state (normal heavy-atom quenching).[1,3,4] Normal heavy-atom quenching can therefore be described by the overall process

$$^1M^* + Q \longrightarrow {}^3M^* + Q \qquad \text{(i)}$$

(where $^1M^*$ and $^3M^*$ are respectively the first singlet and triplet excited states of the aromatic, M, and Q is the quencher) and has been shown not to involve any interaction that does not lead to enhanced intersystem crossing of the $^1M^*$ excitation

$$^1M^* + Q \not\longrightarrow {}^1M + Q \qquad \text{(ii)}$$

In fact the seemingly universal nature of the heavy-atom interaction i has established its role in an accurate method for determining triplet quantum yields which uses relative measurements of triplet absorbance (as determined by flash absorption spectroscopy) and fluorescence intensities in the presence and absence of heavy-atom quenchers.[3a,5]

The unusual fluorescence enhancement noted above cannot be solely attributed to the aromatic constituent, DBA, in that this molecule exhibits normal fluorescence quenching with potassium iodide in 95% ethanol.[2] Also, increased fluorescence in these systems is little influenced by solvent polarity since we have observed qualitatively similar behavior in cyclohexane solution.

To better assess the excitation–relaxation distribution resulting from the interaction of DBA with benzene and ethyl