(27) S. Arrhenius, *Z. Phys. Chem. (Leipzig)*, **4**, 226 (1889).
(28) (a) H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); (b) *Chem. Rev.*, **17**, 65 (1935).
(29) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, Mass., 1974, p 96.
(30) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions: a Study of Metal Complexes in Solution", Wiley, New York, 1967, p 129.
(31) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins *Inorg. Chem.*, **4**, 929 (1965); **5**, 622 (1966).
(32) R. W. Henkens and J. M. Sturtevant, *J. Am. Chem. Soc.*, **90**, 2669 (1968).
(33) A. Y. Romans, M. E. Graichen, C. H. Lochmuller, and R. W. Henkens, *Bioinorg. Chem.*, **9**, 217 (1978).
(34) J. A. Micelli and J. E. Stuehr, *Inorg. Chem.*, **11**, 2783 (1972).
(35) M. L. Ludwig and W. N. Libscomb in "Inorganic Biochemistry", Vol. I, G. E. Eichorn, Ed., American Elsevier, New York, 1973, p 438.
(36) J. E. Coleman in ref 35, p 488.

Solvent Effects on the Photophysics of Dibromoanthracene

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Abstract: The fluorescent lifetimes and relative fluorescent quantum yields of 9,10-dibromoanthracene solutions have been measured. It is found that the nonradiative transition rate of the lowest excited singlet of 9,10-dibromoanthracene is strongly dependent on the solvent and temperature, but is unaffected by the presence of heavy atoms in the solvent molecules. The temperature dependence is attributed to an endothermic transition from the lowest excited singlet state S_1 to an adjacent higher excited triplet level, T_q. The solvent dependence is due to the different extent to which S_1 and T_q are shifted by the solvent. The solvent effect on T_q is only about 30% of that on S_1. The absence of external heavy atom effect is explained on the basis that no new intersystem-crossing channel is made available by the introduction of external heavy atoms.

Introduction

It has been reported that solutions of 9,10-dibromoanthracene (DBA) in ethanol or cyclohexane exhibit increased fluorescence quantum yields when ethyl iodide, bromobenzene, or benzene are added.[1,2] The fluorescence yield of DBA in pure bromobenzene is greater than that of DBA in benzene, ethanol, or *n*-hexane.[3] These are interesting observations since normally ethyl iodide and bromobenzene are quenchers for the fluorescence of aromatic molecules. These two quenchers are believed to quench the fluorescence of organic molecules by the heavy-atom effect[4] through a route which gives exclusively the triplet state.[4-8] The presence of heavy atoms increases the overall rate of intersystem crossing from the lowest excited singlet state S_1 to the triplet manifold. This anomalous heavy-atom effect is also observed for 9-bromoanthracene.

There have been attempts to explain this anomalous heavy-atom effect. Measurements of the temperature dependence of DBA fluorescence yield in four solvents showed that the activation energies for intersystem crossing for DBA in benzene and bromobenzene were greater than that in *n*-hexane or ethanol.[3] This suggests the probable origin for the strong solvent effect on the emission yield of DBA solutions, but does not give an adequate explanation for the absence of heavy-atom quenching in the DBA solutions studied. In a more recent paper, the enhancement of fluorescent emission from DBA in cyclohexane solutions by ethyl iodide or benzene was attributed to the formation of an exciplex which had a higher emission efficiency.[2] This explanation should be examined more critically. The fluorescence spectra of DBA in cyclohexane, benzene, and ethyl iodide are very similar. They have the same vibrational structure and exhibit only a small solvent shift of 4–5 nm. The usual red-shifted, structureless emission from an exciplex is not observed for DBA in benzene or ethyl iodide solution. Since no exciplex formation can be detected in the fluorescence spectrum, it was considered advisable to investigate the fluorescence decay response from DBA solutions.

The kinetics of exciplex photophysics in solution are well known,[4,9-11] and measurement of the time profile of the DBA fluorescence would be expected to indicate whether an exciplex is responsible for the increase in the emission yield of DBA in ethyl iodide or benzene.

The purpose of this work was twofold: the first was to examine more systematically the solvent dependence of the fluorescent yields of DBA solutions; the second was to investigate the anomalous heavy-atom effect in DBA solutions with the aim of advancing a reasonable explanation for the absence of quenching by heavy atoms.

Experimental Section

Fluorescence decay measurements were made with a time-correlated single photon counting instrument.[12] A nanosecond flash lamp manufactured by Photochemical Research Associates was used. The excitation monochromator was fixed at 385 nm while the analyzing monochromator was set at the second emission maximum of DBA, which was around 433 nm. Fluorescence spectra were taken with a Perkin-Elmer MPF-4 fluorescence spectrophotometer. For relative quantum yield determinations, no correction was made for the wavelength response of the photomultiplier. Absorption spectra were recorded with a Varian-Cary 219 spectrophotometer. All DBA solutions used for emission measurements were degassed by several freeze–thaw cycles. When not specified, the experiments were performed at room temperature (about 21 °C). At all other temperatures, the sample was held in a thermostated cell holder. The concentration of DBA in the fluorescence decay measurement was about 4×10^{-5} M, while for steady-state fluorescence spectral measurements it was about 8×10^{-6} M. DBA was recrystallized and then further purified by silica gel chromatography. All solvents were purified by at least one pass through an activated silica gel or alumina column.

Results

Over a range of more than two orders of magnitude, the fluorescence decay portion of all the DBA solutions studied here could be fitted with high precision to a single exponential decay function. The reduced χ^2 for fitting to the experimental data[13] was between 1.4 and 0.9. No improvement in χ^2 was

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Table I. S_1 Lifetime of 9,10-Dibromoanthracene in Various Solvents

	solvent	dielectric constant (ϵ)	lifetime τ, ns	$\bar{\nu}_{0,1}$, cm^{-1}
(a)	*n*-hexane	1.89	1.10	23 330
(b)	isooctane	1.94	1.17	23 310
(c)	diisopropyl ether	3.88	1.31	23 290
(d)	ethanol	24.3	1.41	23 280
(e)	cyclohexane	2.02	1.49	23 250
(f)	ethyl acetate	6.02	1.61	23 220
(g)	12% benzene[a]		1.67	23 200
(h)	24% benzene[a]		1.84	23 170
(i)	furan	2.95	1.90	23 120
(j)	41% benzene[a]		2.00	23 120
(k)	56% benzene[a]		2.23	23 080
(l)	71% benzene[a]		2.42	23 050
(m)	86% benzene[a]		2.61	23 030
(n)	toluene	2.38	2.64	23 020
(o)	*p*-xylene	2.27	2.74	23 000
(p)	carbon tetrachloride	2.24	2.81	23 000
(q)	benzene	2.28	2.80	22 990
(r)	chloroform	4.81	2.91	22 990
(s)	1,2-dichloroethane	10.7	3.08	22 990
(t)	ethyl iodide		2.94	22 890
(u)	bromobenzene	5.40	3.92	22 860
(v)	*o*-dichlorobenzene	9.93	4.17	22 860

[a] Percent of benzene in cyclohexane solution.

observed if the experimental data were fit to a double exponential function characteristic of exciplex photophysics.[10,11]

DBA in Cyclohexane, Ethyl Iodide, and Benzene. As noted previously,[2] the fluorescence yield of DBA increases when ethyl iodide or benzene are added to a cyclohexane solution. It is emphasized that single exponential decay kinetics of the DBA fluorescence response was observed for *all* the solutions studied here. The excited state lifetime of DBA, τ, obtained from the single exponential response was also found to increase upon the addition of ethyl iodide or benzene. Figure 1 shows the relationship between τ and the amount of ethyl iodide or benzene added to DBA in cyclohexane.

DBA in *o*-Dichlorobenzene, Toluene, Furan and Isooctane. The temperature dependence of τ of DBA in these four solvents was investigated. Typically for each solvent, four to five temperatures in the range 0-40 °C were studied. It was found that τ was strongly dependent on temperature. For each of the four solvents, the nonradiative transition rate, k_{nr}, of DBA was found to obey the Arrhenius equation

$$k_{nr} = A \exp(-W/kT)$$

The values of A and W in the four solvents will be given below.

Lifetime of DBA in Various Organic Solvents at 21 °C. The DBA τ values in various pure and mixed organic solvents at 21 °C were determined. The relative energies of the lowest excited singlet state, S_1, of DBA in these solutions were also determined from the DBA fluorescence spectra. The second emission maximum, $\bar{\nu}(0,1)$, on the short-wavelength side (the $S_1(v = 0) \rightarrow S_0(v = 1)$ transition) was taken as the reference point for the S_1 energy. $\bar{\nu}(0,1)$ was used instead of the usual $\bar{\nu}(0,0)$ because $\bar{\nu}(0,1)$ could be determined more accurately. The experimental results are summarized in Table I, which is arranged in decreasing order of $\bar{\nu}(0,1)$. It should be noted that in Table I, with this arrangement of $\bar{\nu}(0,1)$, the τ values are approximately arranged in increasing order.

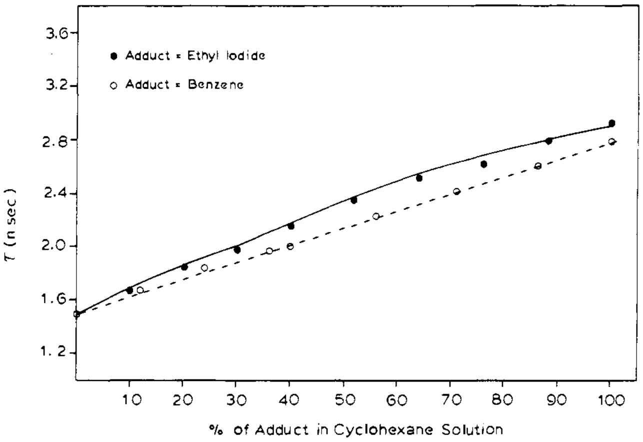

Figure 1. Effect of ethyl iodide and benzene on the lifetime of S_1 of 9,10-dibromoanthracene.

Table II. Relative Fluorescence Yields of 9,10-Dibromoanthracene

solution	$k_{FM}(s)/k_{FM}(0)$	$\tau(s)/\tau(0)$	$[\Phi(s)/\Phi(0)]_\tau$	$[\Phi(s)/\Phi(0)]_{ex}$
cyclohexane	1	1	1	1
12% benzene[a]	1.01	1.12	1.13	1.14
24% benzene[a]	1.02	1.23	1.25	1.26
36% benzene[a]	1.03	1.32	1.36	1.37
41% benzene[a]	1.04	1.34	1.39	1.39
56% benzene[a]	1.05	1.50	1.58	1.56
71% benzene[a]	1.06	1.62	1.72	1.72
86% benzene[a]	1.07	1.75	1.87	1.89
benzene	1.07	1.89	2.02	2.04

[a] Percent of benzene in cyclohexane solution.

Discussion

It is well known that for the reaction

$$A^* + Q \rightleftharpoons (AQ)^*$$

the decay kinetics of the excited monomer A* and the exciplex (AQ)* can be described by the sum and the difference of two exponential functions, respectively.[4,9-11] As described above, when benzene or ethyl iodide are added to cyclohexane solutions of DBA, the fluorescence response of DBA still follows simple first-order decay kinetics. Figure 1 also shows that the S_1 lifetime of DBA in cyclohexane increases monotonically upon addition of benzene or ethyl iodide. Hence, the attribution of enhancement of DBA fluorescence in cyclohexane by benzene or ethyl iodide to exciplex formation[2] is not required by the experimental results. No evidence whatsoever of exciplex formation is obtained either in the steady-state fluorescence spectra or the fluorescence decay kinetics.

The $S_1 \rightarrow S_0$ radiative transition rate k_{FM} can be calculated from the Strickler and Berg equation[14]

$$k_{FM} = 2.88 \times 10^{-9} n^2 \langle \nu_f^{-3} \rangle^{-1} \int \frac{\epsilon(\nu) d\nu}{\nu} \qquad (1)$$

where n is the refractive index of the solution, ϵ and ν are the molar extinction coefficient and wavenumber, respectively, and $\langle \nu_f^{-3} \rangle^{-1}$ is calculated from the emission spectrum by

$$\langle \nu_f^{-3} \rangle^{-1} = \frac{\int I(\nu) d\nu}{\int I(\nu) \nu^{-3} d\nu}$$

Once k_{FM} of DBA is calculated, then the fluorescence quantum yield of DBA, $\Phi(s)$, can be calculated by

$$\Phi(s) = k_{FM}(s)\tau(s) \qquad (2)$$

where $\tau(s)$ is the experimental S_1 lifetime in a given solution.

Table II lists the fluorescence quantum yields of DBA in solutions containing different proportions of benzene and cyclohexane and relative to that of DBA in pure cyclohexane. $[\Phi(s)/\Phi(0)]_{ex}$ is obtained experimentally by direct measure-

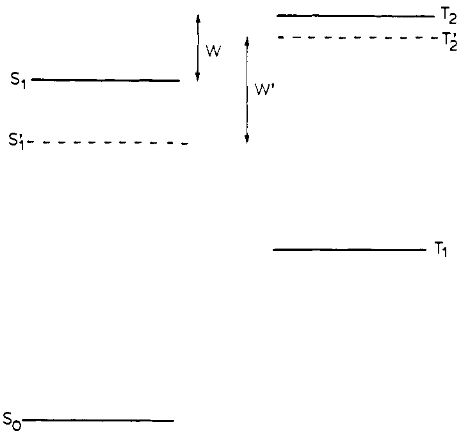

Figure 2. Energy levels of DBA.

Table III

solvent	$\bar{\nu}(0,1)$, cm^{-1}	W, cm^{-1}	ln $A/10^8$	k_{FM}, 10^7 s^{-1}
o-dichloro-benzene	22 860 ± 10	1820 ± 30	9.3 ± 0.2	9.6
toluene	23 010 ± 10	1740 ± 40	9.5 ± 0.2	10.0
furan	23 120 ± 10	1690 ± 50	9.7 ± 0.2	9.5
isooctane	23 310 ± 10	1550 ± 90	9.5 ± 0.5	8.9

ment while $[\Phi(s)/\Phi(0)]_\tau$ is calculated from eq 2. The agreement between the two columns in Table II is very good. This suggests that the enhancement of the fluorescence yield of DBA in cyclohexane can be explained simply and adequately as a general solvent effect. The enhancement is due mainly to a much smaller S_1 nonradiative transition rate, k_{nr}, for DBA in the presence of benzene.

Generally, k_{nr} can be expressed as[15]

$$k_{nr} = k^0_{nr} + A \exp(-W/kT) \qquad (3)$$

where k^0_{nr} is a temperature-independent term. For anthracene and its meso derivatives, k_{nr} involves mainly intersystem crossing from S_1 to the triplet state.[6] For meso-substituted[3,16] anthracenes, $k^0_{nr} \approx 0$. Hence, for DBA molecule

$$k_{isc} = k_{nr} = 1/\tau - k_{FM} = A \exp(-W/kT) \qquad (4)$$

where k_{isc} is the intersystem crossing rate from S_1 to the triplet state. The temperature-dependent term in eq 3 derives from the transition from S_1 to T_q (usually T_2) which is close to S_1. W is then the separation between T_q and S_1.[3,17] Table III gives the values of W and A of DBA in the solvents o-dichlorobenzene, toluene, furan, and isooctane obtained by plotting ln k_{nr} vs. $1/T$. The activation energies W obtained by this method are in the same range as the W values reported previously which were obtained by fluorescence quantum yield measurement.[3] It should be noted in Table III that the ln A values are relatively constant compared to the corresponding variations in W. Hence, for DBA, the marked solvent dependence of k_{nr} may be viewed as having its origin in the variation of W with solvent.

It is also clear from Table III that there exists a correlation between W and $\bar{\nu}(0,1)$. As $\bar{\nu}(0,1)$ increases monotonically from o-dichlorobenzene to isooctane, W decreases monotonically in the same order. The observed correlation between $\bar{\nu}(0,1)$ and W for DBA can be explained by the energy diagram presented in Figure 2. T_q is tentatively labeled as the T_2 state of DBA.[3] The solvent effect on S_1 is greater than that of T_2. Hence, when S_1 is stabilized to S_1' by a solvent, T_2 is stabilized by a smaller amount to T_2'. Hence, the separation between T_2 and S_1 increases as S_1 is lowered in energy.

It can be shown from Figure 2 that

$$(\alpha - 1)[\bar{\nu}(0,1) - \bar{\nu}_0(0,1)] = W - W_0 \qquad (5)$$

where $\bar{\nu}_0(0,1)$ and W_0 refer to a reference solution and α is the ratio of the solvent stabilization energies of the T_2 state to that of the S_1 state. We have pointed out previously that, compared to W, A is relatively independent of solvent. If α in eq 5 is a constant independent of the nature of the solvent, then combining eq 4 and 5 we get

$$k_{nr} = M \exp[(1 - \alpha)\bar{\nu}(0,1)/kT]$$

where $M = A \exp\{-[(1 - \alpha)\bar{\nu}_0(0,1) + W_0]/kT\}$ and is independent of solvent. Figure 3 plots ln k_{nr} vs. $\bar{\nu}(0,1)$ of DBA for the solvents listed in Table I. k_{nr} is calculated from eq 4 using a mean k_{FM} value of 9.5×10^7 s^{-1}, which is the average of the k_{FM} values of DBA obtained in o-dichlorobenzene, toluene, furan, and isooctane. The fluorescence quantum yield of DBA in ethanol at 21 °C is found to be 0.13 using this value of $k_{FM} = 9.5 \times 10^7$ s^{-1} and $\tau = 1.41$ ns. This calculated quantum yield compares favorably with an earlier reported value of 0.12 of DBA in ethanol at 21 °C.[3] It is obvious from Figure 3 that, except for DBA in ethyl iodide (point t), all the other experimental points lie reasonably close to a straight line. Neglecting the ethyl iodide point, least-squares, fit analysis of the data gives a linear correlation coefficient = 0.995[13] and a value of $\alpha = 0.31 \pm 0.02$. In other words, the stabilization energy of T_2 of DBA by solvents is only about 30% that of S_1 stabilization.

We have demonstrated that the marked solvent dependence of the fluorescence quantum yield of DBA solutions is a consequence of the variation of k_{nr} of DBA with solvent. k_{nr} varies greatly with solvent because the S_1 and T_2 states of DBA are stabilized to a different extent.

Now, let us examine the anomalous heavy atom effect in the DBA molecule. On comparison with their expected k_{nr}, it is obvious from Figure 3 that the S_1 intersystem crossing rate of DBA is not increased by bromobenzene and is only slightly increased by ethyl iodide. This apparent absence of external heavy atom effect can be explained reasonably well using the known facts of heavy atom quenching and the relative energy levels of DBA. In DBA, the temperature-independent term k^0_{nr} in eq 3 is close to zero.[3,16] This indicates that the intersystem crossing from S_1 to T_1 is very slow.[17] The inefficiency of this process may be due to the fact that in meso-substituted anthracenes the S_1–T_1 separation is very large; e.g., for DBA the energies of S_1 and T_1 are about 25 000 and 14 000 cm^{-1}, respectively.[4,18] Thus, the isoenergetic transition from S_1 to b presented in Figure 4 is very small because a very large amount of electronic energy has to be converted to vibrational energy. The presence of external heavy atoms will not eliminate the cause of this inefficiency and hence k^0_{nr} remains small.

We have shown that the S_1 intersystem crossing rate of DBA consists mainly of the transition from S_1 to T_2 having an energy W above that of S_1. The transition from S_1 to T_2 will be rapid whenever the energy requirement is satisfied because little excess electronic to vibrational energy conversion is necessary and the presence of the two bromine atoms in DBA ensures a large spin-orbit coupling between the wave functions of the singlet and triplet states.[4,19] Hence, the rate of transition k_a from the state a or above in Figure 4 to T_2 is very fast. The overall rate of transition from S_1 to T_2 will depend on (a) k_a, (b) W, and (c) the thermal population of the S_1 vibrational states. The general effect of solvent on the magnitude of W has been discussed previously. The thermal population is not expected to change with solvent. In the presence of external heavy atoms, for a typical aromatic molecule, k_a is increased markedly and hence the fluorescent emission is quenched.[20] But, in

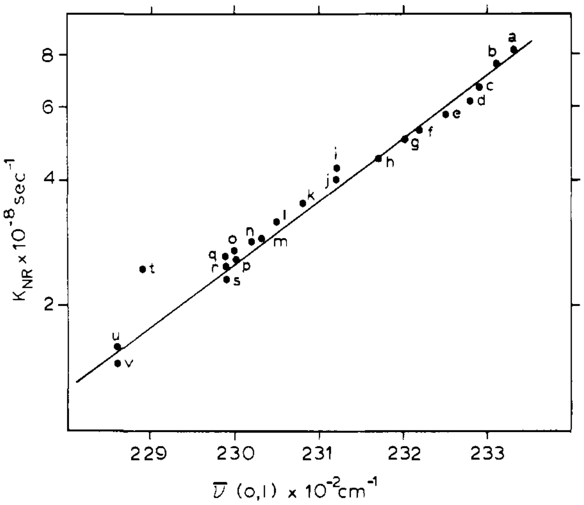

Figure 3. Plot of ln k_{nr} vs. $\bar{\nu}(0.1)$. Points refer to Table I.

DBA, k_a is already very large because of the internal heavy atom effect. Then the effect on k_a by external heavy atom perturbation will be relatively insignificant. Hence, the overall intersystem crossing rate of DBA is unaffected by an external bromine atom (in bromobenzene) and is only very slightly increased by an iodine atom (in ethyl iodide).

The effect of bromobenzene on hexane solutions of 9-phenylanthracene can also be explained by following this line of reasoning. It was observed that the fluorescence yield of 9-phenylanthracene was decreased at first by addition of bromobenzene. But on addition of more bromobenzene ($\geq$3 M) the yield began to increase.[1] Bromobenzene affects the S_1–T_2 separation of 9-phenylanthracene the same way as in DBA. The difference between DBA and 9-phenylanthracene is that the k_a in 9-phenylanthracene is probably much smaller than that in DBA because of the absence of internal heavy atoms. On initial addition of bromobenzene to hexane solutions of 9-phenylanthracene, k_a is increased markedly. At first, this increase in k_a is more important than the increase in W and hence the overall intersystem crossing rate increases. After the addition of a sufficient amount of bromobenzene, the relative change of k_a with addition of more bromobenzene becomes less important than the increase in W, as in the case of DBA. Thus, after the addition of more than 3 M bromobenzene, k_{nr} decreases and hence the fluorescence yield of 9-phenylanthracene increases with the further addition of bromobenzene.

The experimental result can also be analyzed according to the following scheme:

$$\begin{array}{ll} S_1 \rightarrow S_0 + h\nu & k_{FM} \\ S_1 \rightarrow T_2 & k_{nr} \\ T_2 \rightarrow S_1 & k_1 \\ T_2 \rightarrow T_1, \text{etc.} & k_2 \end{array}$$

Normally for other fluorescent molecules $k_1 \ll k_2$, but the presence of the two bromine atoms in DBA may render this condition not applicable.[21] In the limit $(k_1 + k_2) \gg k_{FM}$ and k_{nr}, it can be shown that $1/\tau = k_{FM} + k_{nr}k_2/(k_1 + k_2)$ and that eq 2, $\Phi(s) = k_{FM}(s)\tau(s)$, is still valid. k_2 is a very fast process involving no activation energy and one expects $k_1 \leq k_2$, even in DBA. If $k_1 \ll k_2$, $1/\tau$ is simply equal to the sum of k_{FM} and k_{nr}. On the other hand, for $k_1 \approx k_2$, k_1 must also be very fast and hence involving no activation energy. Under this condition, the measured nonradiative transition rate k_{nr}(measured) is given by $k_{nr}(\text{measured}) = k_{nr}k_2/(k_1 + k_2)$. Since both k_1 and k_2 then involve no activation energy, the difference between k_{nr}(measured) and k_{nr} is in their preexponential terms. There is insufficient data in the literature for us to estimate the value of $k_2/(k_2 + k_1)$.[21] Hence, we neglect the $T_2 \rightarrow S_1$ transition in our previous discussion since the only modification required for including the $T_2 \rightarrow S_1$ transition is to alter the value of the preexponential factor A in k_{nr} which is shown experimentally to be not too dependent on the solvent.

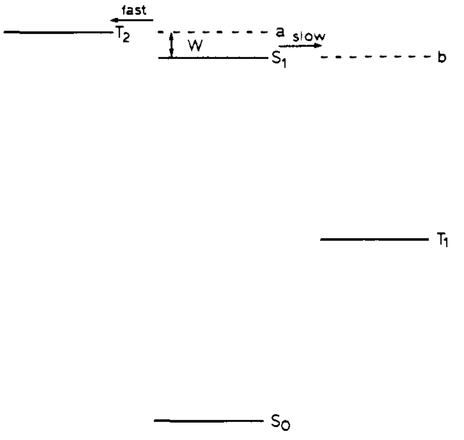

Figure 4. Intersystem crossing from S_1 to T_1 and T_2 in DBA.

From the above discussion, it can be deduced that the most favorable conditions to observe the anomalous heavy atom effect consist of (a) a very slow $S_1 \rightarrow T_1$ transition rate which is not due to the small mixing of the singlet and triplet state wave functions, (b) the ability of the heavy atom containing molecule to increase W, the activation energy of nonradiative transition, and (c) a fast k_a for $S_1 \rightarrow T_q$ (usually T_2) even before the introduction of the external heavy atoms. If a fluorescing molecule satisfies these requirements, e.g., DBA or 9-bromoanthracene, one expects to observe the anomalous heavy atom effect.[22]

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References and Notes

(1) A. Kearvell and F. Wilkinson, *Mol. Cryst.*, **4**, 69 (1968).
(2) R. P. Detoma and D. O. Cowan, *J. Am. Chem. Soc.*, **97**, 3291 (1975).
(3) A. Kearvell and F. Wilkinson, *Transitions Non Radiat. Mol., Reun. Soc. Chim. Phys.*, **20**, 125 (1969).
(4) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, 1970.
(5) H. Leonardt and A. Weller, "Luminescence of Organic and Inorganic Materials", H. Kallmann and G. M. Spruch, Eds., Wiley, New York, 1962.
(6) T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).
(7) A. R. Horrocks and F. Wilkinson, *Proc. R. Soc. London, Ser. A*, **306**, 257 (1968).
(8) A. Kearvell and F. Wilkinson, *Chem. Phys. Lett.*, **11**, 472 (1971).
(9) A. Weller, "The Exciplex", M. Gordon and W. R. Ware, Eds., Academic Press, New York, 1975.
(10) W. R. Ware, *Pure Appl. Chem.*, **41**, 635 (1975).
(11) W. R. Ware, D. Watt, and J. D. Holmes, *J. Am. Chem. Soc.*, **96**, 7853 (1974).
(12) W. R. Ware, "Creation and Detection of the Excited State", Vol. 1, A. A. Lamola, Ed., Marcel Dekker, New York, 1971.
(13) P. A. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, 1969.
(14) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).
(15) J. B. Birks, C. L. Braga, and M. D. Lumb, *Proc. R. Soc. London, Ser. A*, **283**, 83 (1965).
(16) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectrosc.*, **49**, 412 (1966).
(17) R. G. Bennett and P. J. McCartin, *J. Chem. Phys.*, **44**, 1969 (1966).
(18) M. R. Padge, S. P. McGlynn, and M. Kasha, *J. Chem. Phys.*, **24**, 588 (1956).
(19) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).
(20) M, Kasha, *J. Chem. Phys.*, **20**, 71 (1952).
(21) R. Schmidt, H. D. Brauer, and H. Kelm, *J. Photochem.*, **8**, 217 (1978).
(22) After this work was completed and submitted for publication, a paper by Dreeskamp and Pabst (*Chem. Phys. Lett.*, **61**, 262 (1979)) appeared which also emphasizes the role of the $S_1 \rightarrow T_q$ gap in the behavior of meso-substituted anthracene derivatives.