Uno and Machida on imide conformers. A reanalysis of the 3500–500-cm^{-1} spectrum (Table VII) is completely consistent with formimide being cis-trans in the liquid state, in agreement with the gas-phase microwave data.

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Position-Dependent Deuterium Effects on Radiationless Transitions in Anthracene[1]

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Abstract: The triplet lifetimes of several specifically deuterated anthracenes are measured in glassy solution at 77°K by monitoring the decay of triplet–triplet absorption after flash excitation. The derivatives studied comprise the *9,10-*d_2, *1,4-*d_2, *2,3-*d_2, *1,4,5,8-*d_4, *2,3,6,7-*d_4, *1,2,3,4-*d_4, and d_{10} compounds. Their triplet lifetimes show a significant dependence on the position of substitution. This dependence is interpreted theoretically, and the ratio of triplet deactivation rates for isomers containing the same number of deuterium substituents is calculated and compared to the experimental lifetime ratios. It is pointed out how this comparison might be used to further elucidate the theoretical interpretation of radiationless transitions.

The observation of a deuterium effect on the triplet state lifetimes of aromatic hydrocarbons has provided an important stimulus for the development of theories of radiationless processes.[2,3] The first effects were observed by Hutchison and Mangum[4] for naphthalene and by Wright, Frosch, and Robinson[5] for benzene. In each case a large increase of the triplet state lifetime was observed (2.1 to 16.9 sec for naphthalene and 16 to 26 sec for benzene). These results were explained by the Robinson and Frosch theory of radiationless transitions[6] in terms of the Franck–Condon factor associated with the rate k of a radiationless transition according to the simple Golden Rule formula of time-dependent perturbation theory.

$$k = (2\pi/\hbar)\rho J F(\mathrm{E}) \qquad (1)$$

Here ρ is the density of final vibrationally excited states and J is an electronic integral coupling the two states. The Franck–Condon factor $F(\mathrm{E})$ is the well-known sum of products of vibrational overlap integrals. Deuterating aromatic hydrocarbons increases their triplet lifetimes due to an increase in Franck–Condon factors. This can be understood on the basis of the decreased overlap of the lower frequency CD modes relative to CH modes for the same energy gap. This effect is now well established experimentally[7] and the involvement of Franck–Condon factors has received extensive theoretical verification from the calculations of Siebrand.[7,8]

More recently a different type of deuterium effect on triplet lifetimes was observed by Hirota and Hutchison[9] and by Watts and Strickler[10] for naphthalene and by Simpson, *et al.*, for biphenyl.[11] In both molecules the triplet lifetime showed a dependence not only on the number of deuterium substituents but also on the position of substitution. In the naphthalene experiments, the authors compared the triplet lifetimes of derivatives having numerically the same but positionally different deuterium substituents. If the deuterium effect was due solely to an effect on the Franck–Condon factor associated with the vibrational modes, which have an equal *a priori* probability for accepting the electronic energy, then two such isomers would show essentially the same triplet decay rate. However, in the extensive series of naphthalene isomers investigated by Watts, *et al.*,[10] the differences were substantial and consistently demonstrated that deuterium substitution in an α position had a greater lifetime increasing effect than deuterium substitution in a β position. The possibility that the observed effect is due to an effect on the radiative decay probability is remote because of the minor contribution of this channel to triplet deactivation.[12]

The roughly additive nature of the effect observed by Watts, *et al.*, implies that it must be local in character. An explanation of the results based on this observation has been given by Henry and Siebrand.[13,14] Starting

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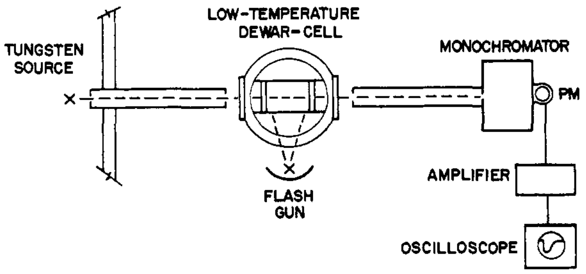

Figure 1. Flash apparatus.

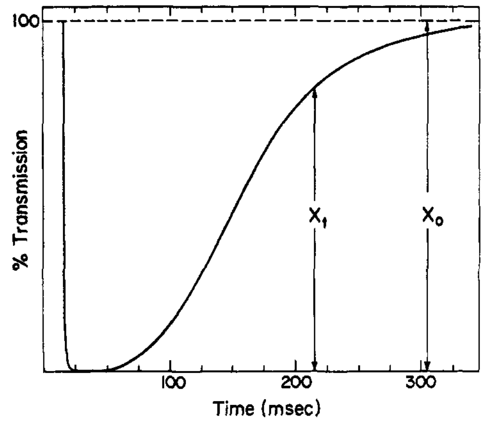

Figure 2. Reproduction of the oscilloscope display recorded during flash excitation of a sample of anthracene-*9,10-d_2* in EPA at 77°K.

from pure spin Born–Oppenheimer functions as zero order states, they predict three principal mechanisms for intersystem crossing. The third of these mechanisms, which is expected to predominate for the $T_1 \rightarrow S_0$ transition in naphthalene, is governed by a matrix element $H_{10}{}^{(3)}$ of the form[14]

$$|H_{10}{}^{(3)}|^2 = F(\mathrm{E})\{\sum_k(\hbar^3\omega_k{}^{(0)}/2\mu_k)^{1/2} \times \sum_i(E_i - E_0)^{-1}[\langle \mathrm{S}_0|H_{\mathrm{s0}}|\mathrm{T}_i\rangle\langle \mathrm{T}_i|\partial/\partial Q_k|\mathrm{T}_1\rangle + \langle \mathrm{S}_0|\partial/\partial Q_k|\mathrm{S}_i\rangle\langle \mathrm{S}_i|H_{\mathrm{s0}}|\mathrm{T}_1\rangle]\}^2 \quad (2)$$

Here ω_k and μ_k are the frequency and the reduced mass of the inducing vibrational mode k. The dominant contributions to $H_{10}{}^{(3)}$ are made by intermediate states T_i and S_i of mixed $\sigma\pi$ character.[14,15] Thus, since both S_0 and T_1 are $\pi\pi$ states, the inducing vibrational modes k will be out-of-plane bending modes and it is these modes that lead to the position dependent isotope effect. Both the spin–orbit and vibronic matrix elements in $H_{10}{}^{(3)}$ are dominated by one-center terms and are proportional to the local π electron density and to the out-of-plane bending amplitude, respectively. Substitution of H by D will lead to a reduction in the CH out-of-plane bending amplitude and thus will reduce the rate of the radiationless transition. The effect will be largest for those positions where the π electron coefficient has the largest absolute value. This is in agreement with the results observed in naphthalene where the π electron coefficient at α carbons is greater than at β carbons. Moreover, calculations based on this approach have accounted quite accurately for the magnitude of the effect.[13,14]

It is of interest to extend both experimental observations and theoretical calculations of the partial deuterium effect to other molecules. Hopefully, it will serve as a continuing catalyst for the development of the theory of radiationless transitions. To this end, we have performed experiments and calculations on the partially deuterated derivatives of anthracene. A preliminary report containing the results of two of the seven deuterated derivatives studied has been published elsewhere.[16]

Anthracene has some advantages for a study of this type. Unlike biphenyl, its planar structure makes it amenable to calculations. Its long radiative lifetime (180 sec)[12] and low triplet energy ensure that even for the totally deuterated molecule the triplet decay is almost exclusively nonradiative. Thus, the effect we are observing is most certainly an effect on the radiationless decay rate. Since it has three distinct CH sites compared to two for naphthalene, the number of possible isomers containing the same number of deuterium substituents is increased and comparison with theory is facilitated.

Experimental Section

Materials. All but the 9,10- and perdeuterioanthracenes were synthesized by preparing Diels–Alder adducts of the appropriately deuterated butadiene and either *p*-benzoquinone or 1,4-naphthoquinone. These adducts were subsequently converted to the anthracenes by successive oxidation and reduction. The *9,10-d_2* derivative was prepared by acid-catalyzed hydrogen–deuterium exchange. All of the synthesized derivatives were purified by column chromatography (Woelm alumina) and/or recrystallization from chloroform. A detailed description of the syntheses will appear elsewhere.[17] Perdeuterioanthracene was obtained from Dr. D. F. Williams of the National Research Council of Canada and used as received.

The isotope ratios of the final products were determined by low voltage mass spectrometry (Finnigan 1015, 8 eV) and were accurate to approximately ±2%.

EPA (5:5:2 ether, isopentane, ethanol) was obtained as an especially purified glass-forming solvent from the American Instrument Co. Isopentane and methylcyclohexane were purified by the method of Potts.[18]

Lifetime Measurements. The rates of triplet deactivation were measured by monitoring the decay of triplet–triplet (T–T) absorption. The technique has been described by Porter[19] and the present experimental arrangement is a modification of his original design (see Figure 1). The light source consisted of a source lamp (General Electric CPR 18A, 6 V) powered by a 6-V battery. The collimated beam passed through an 8-cm quartz sample cell built into a quartz dewar (Kontes/Martin M203908). The sample was prepared as a 10^{-4}–10^{-5} M solution in EPA or IM_4 (1:4 isopentane, methylcyclohexane) and cooled to a glass at 77°K. The transmitted beam was monitored with a 0.25-m Jarrell-Ash grating monochromator set to the anthracene T–T absorption maximum at 425 mμ and by a phototube (Hamamtsu R106) whose amplified signal was fed to an oscilloscope (Fairchild 766 H/F). The sample was flashed with an electronic flash gun (Honeywell Model 65C) with the polystyrene filter removed, and attenuation of the transmitted light was recorded photographically from the oscilloscope trace. A typical trace is reproduced in Figure 2.

Treatment of Data. The relative concentrations of triplet molecules are given by log (X_0/X_t) where X_0 is the 100% transmission signal and X_t is the transmission at time t. Thus, since the decay should be first order, a plot of ln log (X_0/X_t) *vs.* t was fitted to a straight line using a least mean squares analysis. The nega-

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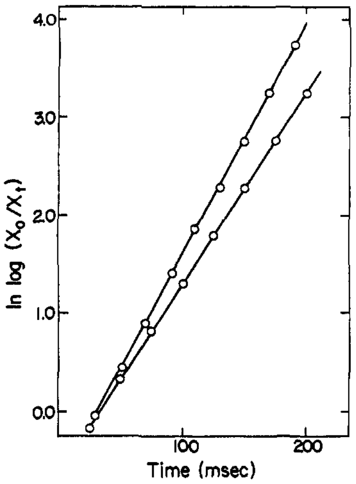

Figure 3. A first-order analysis of the transmission data recorded during triplet decay of anthracene-$2,3$-d_2 and anthracene-$9,10$-d_2.

tive reciprocal of the slope yielded the lifetime. Three samples of each deuterated molecule and four samples of anthracene were prepared, and ten measurements were made on each sample. There were no significant variations in lifetime from sample to sample nor was there any discernible trend in the measured lifetime for a given sample. All lifetimes were averaged for each molecule and the standard deviation determined. We also calculated the correlation coefficient r which is a measure of the fit of the data to a straight line.[20] $r = -1$ corresponds to a perfect correlation and $r = 0$ to no correlation. The average value of r for each of the isomers fell in the range -0.9996 to -0.9998 which indicated an almost perfect first-order fit.

Results

The triplet lifetimes are given in Table I along with the measured isotopic purities and the standard deviations obtained from the averaging of 30 lifetime measurements (40 for anthracene d_0). The mean lifetimes for anthracene-d_0 and anthracene-*1,4,5,8*-d_4 measured in IM_4 were 37.8 and 54.0 msec, respectively. Two values of the triplet lifetime of the *2,3,6,7*-d_4 isomer are given in Table I. Some difficulty was encountered in the synthesis of this compound[17] and thus the isotopic purity of these samples is substantially lower than in the other cases. The two samples whose lifetimes are reported in Table I were obtained in two different attempts at its synthesis. The compound with the 43.8-msec lifetime (A) had as its principal impurities d_3($\simeq$17%) and d_2($\simeq$8%) isomers with partial substitution occurring in the 2,3,6,7 positions. The compound with the 45.7-msec lifetime (B) had as its principal impurities d_5($\simeq$15%) and d_3($\simeq$8%). In the d_5 contaminant, the extra deuterium is most probably in the 1 position. Thus, compound A, because it contains less deuterium than the desired isomer, forms a lower bound for the triplet lifetime of the pure *2,3,6,7*-d_4 isomer. Similarly, the B compound forms an upper bound. Therefore, we take τ for this isomer to be 45.0 msec.

Table I. Measured Triplet Lifetimes for Anthracene and Its Partially Deuterated Isomers

Anthracene	Purity, %	τ, msec	Std dev, msec
d_0		36.3	0.9
2,3-d_2	86	40.5	0.4
1,4-d_2	91	42.5	0.8
2,3,6,7-d_4	74	43.8	0.9
	77	45.7	0.7
1,2,3,4-d_4	88	47.3	0.9
9,10-d_2	86	51.8	0.8
1,4,5,8-d_4	95	53.0	0.9
d_{10}		117.8	1.8

The standard deviations given in the table are typically less than 2%.

In Figure 3 we have plotted $-\ln \log (X_0/X_t)$ *vs.* time for single runs of the *2,3*- and *9,10*-d_2 isomers. Both the excellent linearity of the data and the change of slope for the two isomers are readily apparent.

Calculations

As with naphthalene,[13,14] we will attempt to account for the results on the basis of triplet deactivation in anthracene being governed by mechanism 3, *i.e.*, by matrix elements of the type given in eq 2. This contention is supported by spin-polarization studies in anthracene,[21,22] which show that 97% of the triplet decay occurs *via* the in-plane triplet sublevels τ_x and τ_y as is predicted by a mechanism 3 type deactivation.[14] The main possible competing mechanism, which involves $\pi\pi^*$ states as intermediate states,[14] would lead to deactivation *via* the out-of-plane τ_z sublevel.

As mentioned in the introductory section, the mechanism described by eq 2 gives rise to an isotope effect through the factors involving the reduced mass and frequency of the inducing vibrational mode. If we take the ratio of these factors for C–D and C–H oscillators and use the harmonic approximation to replace the ratio of reduced masses by a frequency ratio, we obtain an isotope factor of the form

$$s = (\omega_{ki}/\omega_k)^{3/2} \qquad (3)$$

where i labels the heavier isotope. In anthracene the CH bending modes that induce deactivation from the x triplet sublevel have b_{1u} symmetry. These modes have an average frequency of 857 and 693 cm^{-1} for the normal and deuterated isomers, respectively.[23] These values yield

$$s = (693/857)^{3/2} = 0.73 \qquad (4)$$

Since these frequencies are close to those observed for the modes which induce deactivation from the y triplet component and since on the basis of spin polarization measurements[21,22] decay from τ_x is twice as important as decay from τ_y, we use only this single value of s.

The evaluation of the matrix elements in $|H_{10}^{(3)}|$ leads to a spin–orbit, vibronic product of the form[14,16] $fc_1^2 + gc_2^2 + hc_9^2$, where c_1, c_2, and c_9 are π-electron MO coefficients and f, g, and h are constants effectively determined by the geometry of the system for both the x and the y triplet components. For anthracene $f_x = -2g_x$ and $h_x = -2g_x$, while $f_y = h_y = 0$ and $g_y = -(3^{1/2})g_x$. Thus, if we consider two isomers of anthracene containing the same number of deuterium substituents N and take the number of 1,4,5,8 or α deuterium substituents to be N_α and N_α', respectively, the number of 2,3,6,7 or β deuterium substituents to be N_β

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$$\frac{k}{k'} = \frac{\sum_n \{[4 + (s - 1)N_\alpha]f_n c_1^2 + [4 + (s - 1)N_\beta]g_n c_2^2 + [2 + (s - 1)(N - N_\alpha - N_\beta)]h_n c_9^2\}^2}{\sum_n \{[4 + (s - 1)N_\alpha']f_n c_1^2 + [4 + (s - 1)N_\beta']g_n c_2^2 + [2 + (s - 1)(N - N_\alpha' - N_\beta')]h_n c_9^2\}^2} \quad (5)$$

$$\frac{k}{k'} = \frac{t^2 c_1^4 + u^2 c_2^4 + v^2 c_9^4 - tuc_1^2 c_2^2 - uvc_2^2 c_9^2 + 2tvc_1^2 c_9^2}{(t')^2 c_1^4 + (u')^2 c_2^4 + (v')^2 c_9^4 - t'u'c_1^2 c_2^2 - u'v'c_2^2 c_9^2 + 2t'v'c_1^2 c_9^2} \quad (6)$$

and N_β', respectively, and thus the number of 9,10 or γ deuterium substituents to be $N - N_\alpha - N_\beta$ and $N - N_\alpha' - N_\beta'$, respectively, we obtain, for the relative ratios of triplet deactivation in the two isomers, eq 5 where $n = x, y$. Substitution for f, g, and h as given above yields eq 6 where $t = 4 - 0.27N_\alpha$, $u = 4 - 0.27N_\beta$, and $v = 2 - 0.27(N - N_\alpha - N_\beta)$.

Using Hückel coefficients for the c's, we obtained the four independent ratios given in Table II, where we have also listed, for comparison, the observed rate constant ratios.

Table II. Calculated and Observed Rate Constant Ratios for Triplet Decay in Partially Deuterated Anthracene Isomers

Rate ratios	Obsd	Calcd
$k(9,10)/k(2,3)$	0.78	0.72
$k(1,4)/k(2,3)$	0.95	0.84
$k(1,4,5,8)/k(2,3,6,7)$	0.85	0.70
$k(1,2,3,4)/k(2,3,6,7)$	0.95	0.84

Discussion

The data of Table I clearly indicate that a position-dependent isotope effect is present. This is most dramatically indicated for the *9,10-d*$_2$ isomer whose lifetime is longer than two of the three d_4 isomers. The other striking observation about the lifetimes in Table I is that they correlate with the qualitative concept given in the introduction. The π electron coefficients in anthracene lie in the order $c_9 > c_1 > c_2$, and the measurements indicate a similar trend for the magnitude of lifetime lengthening upon deuterium substitution.

The calculated relative rate constants given in Table II show semiquantitative agreement with the observed rate ratios. However, the calculations do seem to overestimate the effect. We repeated them using π-electron coefficients generated by a CNDO program.[24] However, these calculated ratios are virtually identical with those obtained with Hückel coefficients, the largest difference being 0.01.

Most probably the overestimation in the calculations which also occurred in the naphthalene case[13,14] is mainly due to two causes. In the theory, a very simple symmetry adapted form is adopted for the CH and CC σ orbitals used in the formation of $\sigma\pi^*$ and $\pi\sigma^*$ intermediate states. A more detailed knowledge of these σ coefficients is possible through MO calculations such as INDO.[24] However, inclusion of these coefficients renders the theory much more numerically complex and does not appear to change its qualitative predictions but only affects the quantitative details.[25] It was our hope that by calculating ratios of the type given in Table II such errors would largely cancel. It would appear from the approximate agreement that this is so; however, this effect still probably contributes to the lack of quantitative agreement.

The second reason follows from the fact that in our earlier work[14] we maintained that in mechanism 2 coupling existed solely between $\pi\pi^*$ states and that matrix elements between $\pi\pi^*$ and mixed $\sigma\pi$ states cancelled. This is based on a one-center approximation but it is also possible that two-center terms in these matrix elements could lead to nonnegligible contributions. Since mechanism 2 is inherently stronger,[14] these higher order terms could be significant here whereas the same terms would be negligible in mechanism 3. These terms would dilute the local character of the calculated isotope effect and would generally cause calculations neglecting them to overestimate it. The partial deuterium effect could be used in this regard as a means of comparing the relative contributions of two-center terms in mechanism 2 to mechanism 3. Although the experimental data for any one series of derivatives might not be sufficient to give a meaningful answer, studies of the partial deuterium effect in a series of aromatic hydrocarbons could give valuable insight into this theoretical problem.

As pointed out by the referee, anharmonic coupling and Fermi resonance involving the anthracene vibrational modes have been neglected in our calculations. These effects will lead to an error in the s factor of eq 3 and 4 and, to a lesser extent, in the relations between the f, g, and h coefficients. We would expect such effects, although significant, not to be as important as the two causes of error mentioned above.

The measurements in IM$_4$ indicated, as expected, that only small changes in lifetime are encountered in going from a polar to a nonpolar medium.

Finally, we note the possible extension of theories of radiationless transitions into the much more complicated areas of photochemical reactions. Studies of the partial deuterium effect lead to an elucidation of the role played by the inducing vibrational mode and thus improve our presently held conceptions of the manner in which electronic excitation is distributed in molecules.[26]

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