Position Dependent Deuterium Effects on the Phosphorescence Lifetime of Phenanthrene

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Abstract: Phosphorescence lifetimes are reported for phenanthrene, the five monodeuteriophenanthrenes, and perdeuteriophenanthrene in EPA and 3-methylpentane at 76 K. A significant variation in lifetime with the position of deuteration is noted. The lifetimes in EPA are in the order $\tau_{d_0} < \tau_{2d_1} < \tau_{1d_1} < \tau_{3d_1} \simeq \tau_{4d_1} < \tau_{9d_1} < \tau_{d_{10}}$. Specifically, the lifetime lengthening upon deuteration at the 2 position is about 1%, at the 1, 3, and 4 positions are all about 6%, and at the 9 position is about 34%. Comparison with other published lifetimes indicates that the deuterium effects are additive. The significance of the results for current theories of radiationless transitions is briefly discussed.

Introduction

Since the first observations in 1960 that perdeuteration increases phosphorescence lifetimes,[1,2] deuterium effects have played an important role in the development of the theory of radiationless transitions. Early theoretical work by Robinson and others[3-5] pointed out that three factors were involved in the rate of intersystem crossing: a matrix element coupling the initial and final states, a vibrational overlap or Franck-Condon factor, and a density of vibrational levels of the final state in the vicinity of the initial state. In general these papers explained the deuterium effects in terms of a decrease in the Franck-Condon factors between the triplet state and the isoenergetic vibrational levels of the ground state.

Later observations of phosphorescence lifetimes of partially deuterated compounds revealed an additional type of isotope effect. Hirota and Hutchison[6] and Watts et al.[7,8] showed that α-deuterated naphthalene triplets decayed more slowly than the β-substituted counterparts. Similar position dependent deuterium effects have been noted in other aromatic hydrocarbons,[9-14] ketones,[15] and aldehydes.[16] It has quite generally been found that the rate of triplet decay depends on the positions of the deuterium atoms as well as on their number.

These results have led to the consideration of the effect of deuteration on the matrix elements coupling the two electronic states. Lin[17] was the first one to emphasize the importance of Born-Oppenheimer breakdown in radiationless transitions. Born-Oppenheimer breakdown should have an obvious dependence on nuclear mass, and Young used this to explain the position dependence in naphthalene.[18] Henry and Siebrand[19] emphasized the additional importance of spin-orbital coupling for intersystem crossing. They considered three mechanisms for the radiationless decay of the triplet state. The first is direct spin-orbital coupling between the electronic states involved. The second is vibronically induced spin-orbital coupling, also called the Herzberg-Teller mechanism. The third is spin-orbital coupling combined with Born-Oppenheimer breakdown. They chose the third mechanism as giving the best agreement with the position dependence in naphthalene. Henry and Charlton[10] also obtained good agreement for partially deuterated anthracenes using this theory. On the other hand, Metz et al. found good agreement with isotope effects in benzene, naphthalene, and anthracene using a Herzberg-Teller mechanism and including two-center integrals.[20]

One generalization which seems to hold for aromatic systems is that the deuterium effects on triplet decay rates are additive. That is, the change in decay rate for a polydeuterated molecule is the sum of the effects for the corresponding monodeuterated compounds. This has been shown to hold for benzene,[11] naphthalene,[7,8] anthracene,[10] and *trans*-stilbene,[12,13] but not as well as in the nonplanar *cis*-stilbene derivatives.[13] This additivity is inherent in the theory of Henry and Siebrand, which uses a one-center approximation. Metz has shown that the Herzberg-Teller approach including two-center terms also predicts additivity.[21]

The fact is that several different theoretical approaches have been able to rationalize the experimental position dependence of deuterium effects in naphthalene and some other molecules. Phenanthrene was chosen for the present study because it has five inequivalent sites for isotopic substitution, and it was felt that data on the relative effects at all five would provide a better test for theoretical approaches than the two sites in naphthalene or the three in anthracene. Charlton and Henry[14] have recently measured lifetimes of several partially deuterated phenanthrenes, but no monodeuterated derivatives were studied. It is hoped that the present study, coupled with that of Charlton and Henry, will provide a comprehensive set of data which will further illuminate the nature of the nonradiative process.

Experimental Section

Synthesis and Materials. Zone refined phenanthrene, labeled 99.999% pure, was obtained from James Hinton. Fluorescence spectra showed no trace of the usual anthracene impurity. Perdeuteriophenanthrene from Schwarz Bio Research, Inc. was quoted as 99.6% isotopic purity. Both were used as received.

The monodeuterated isomers were all prepared from the corresponding monobromophenanthrenes. 9-Bromophenanthrene was obtained from Aldrich Chemical Company and melted at 64-65 °C after recrystallization from ethanol. 4-Bromophenanthrene was the gift of Professor M. S. Newman[22] and was chromatographed over Fluorisil and recrystallized from ethanol before use. The 1- and 3-bromophenanthrenes were prepared from *o*- and *m*-bromobenzaldehyde (Aldrich), respectively. By means of a Wittig reaction these were converted to the corresponding stilbenes,[23,24] which were photocyclooxidized to the desired bromophenanthrenes.[25] 2-Bromophenanthrene was prepared by brominating dihydrophenanthrene in acetic acid. Evaporation of the solvent gave an oil from which 2-bromo-9,10-dihydrophenanthrene crystallized over a period of several weeks. Its melting point after recrystallization from ethanol was 53-57 °C. When the oil was refluxed with an equivalent amount of *N*-bromosuccinimide in CCl_4, 2-bromophenanthrene was obtained as an impure solid. This was codistilled with ethylene glycol. Recrystallization from ethanol raised the melting point to 94-96 °C.

Synthesis of the deuteriophenanthrenes proceeded as follows. Commercial anhydrous ether was further dried over sodium hydride or sodium-lead alloy and 10-15 ml distilled under nitrogen into a flask containing 250 mg of the bromophenanthrene. When the latter had dissolved, 1 ml of a 2.2 M solution of *n*-butyllithium (Ventron Corp.) was injected into the stirred solution. The solution usually boiled and turned yellow; in some cases a precipitate formed. Within 30 s, 1 ml of D_2O was injected into the flask. If this step was delayed for 5 min the deuterium content of the resulting phenanthrene was much lower, presumably because the lithiophenanthrene reacts slowly with the ether.

After the reaction with D_2O, the mixture was neutralized with dilute HCl. The ether solution was washed with water, dried with $MgSO_4$, and the ether evaporated. The residual solid corresponded to an almost theoretical yield of the deuteriophenanthrene. Traces of colored impurity were removed by dissolving in cyclohexane and passing the solution through an alumina column. The phenanthrene was purified by recrystallization from ethanol usually followed by vacuum sublimation.

Percentage deuteration was determined by low-voltage (16 eV) mass spectrometry; values used were averages of ten determinations and had standard deviations of less than 1%. The only detectable impurity in the monodeuteriophenanthrenes was the d_0 compound. The phenanthrene-d_{10} was about 91% d_{10}, 8% d_9, and less than 1% other partially deuterated species. High-resolution NMR spectra indicated that the protons of the d_9 compound were uniformly distributed among the five positions. The position of substitution in the monodeuterated compounds was confirmed by ^{13}C NMR using the assignment of Alger et al.,[26] and this also confirms those assignments of the ^{13}C spectrum.

Phillips 99% 3-methylpentane (3MP) was purified by washing with H_2SO_4 and water, refluxing over a drying agent, and distillation. It was then passed through columns of a silica gel and of alumina treated with $AgNO_3$. EPA is a mixed solvent composed of diethyl ether, isopentane, and ethanol in a 5:5:2 volume ratio. Anhydrous ether was refluxed over sodium-lead alloy and distilled. Absolute ethanol was slowly distilled for several days to remove aromatic impurities, chiefly benzene, until the impurities could not be detected spectroscopically. Spectroquality isopentane from MCB was used as received. Solutions were always made from freshly prepared EPA. No significant absorption or emission from the solvents could be detected under our experimental conditions.

Sample Preparation. As the deuterium effects were expected to be small, special effort was directed toward effects of small magnitude often overlooked. Samples were made up at 1×10^{-3} M in 10-mm o.d. Pyrex tubes. Solutions were degassed by 10-12 freeze-pump-thaw cycles and sealed under vacuum. Degassing was found to increase the phosphorescence lifetime by about 1%. Annealing effects of the type described by Martin and Kalantar[27] were also investigated. In 3MP the lifetimes of slowly cooled samples (lowered into liquid nitrogen at about 5 mm/min) were longer than those of rapidly cooled samples by 3-5% and somewhat more reproducible. No similar effects were found in EPA. All measurements were made on samples cooled slowly and allowed to remain frozen for at least 30 min before lifetime determinations.

Apparatus. Lifetime measurements were made with the expected small effects in mind. The decay of phosphorescence intensity was measured using photon counting detection and a multichannel analyzer in the multiscaling mode. This method is inherently linear over a wide dynamic range, limited only by the pulse pair resolution (100-200 ns) at high count rates and by the dark current (<1 count/s for a cooled EMI 6256S photomultiplier) at low count rates. The highest count rate was never allowed to exceed 5×10^4 counts/s which is less than 1% of the maximum count rate. A run consisted of 20-50 individual decays added together and gave several decades of good exponential decay. An average dark current was subtracted from each point, and the decay curve was corrected for the decay of the isotopic impurities. The results were analyzed using a weighted least-square program and gave correlation coefficient ranging from 0.99980 to 0.99998, indicating near perfect exponential decays.

The sample was immersed in liquid nitrogen in a Becquerel type phosphoroscope acting as a shutter for the excitation and emission. The excitation was by a short arc mercury lamp through a Bausch and Lomb monochromator using a wavelength of 3070 Å, and emission was detected through a Jarrell-Ash 0.75-m spectrograph set at 4900 Å.

Five to ten runs were made on each sample. The samples were thawed and refrozen between runs to average out some apparent nonreproducibility in the local glass environment. The lifetime of phenanthrene-d_0 was measured after every four-six runs as a standard to check the procedure. The lifetimes were averaged over the several runs, and the standard deviation among the runs was calculated. Further details of the experimental apparatus and the analysis of results will be found in a thesis by one of us.[28]

Results

Table I. Isotopic Purities and Lifetime of Deuteriophenanthrenes

Isomer	Isotopic purity percent	3MP		EPA	
		τ, s[a]	Std dev[b]	τ, s[a]	Std dev[b]
d_0	100	3.80	0.05	3.89	0.03
$1\text{-}d_1$	93.7	4.04	0.02	4.10	0.01
$2\text{-}d_1$	90.1	3.84	0.04	3.92	0.04
$3\text{-}d_1$	93.8	4.06	0.02	4.14	0.01
$4\text{-}d_1$	94.5	4.03	0.04	4.15	0.02
$9\text{-}d_1$	96.6	5.20	0.07	5.20	0.01
d_{10}	91	14.68	0.16	16.14	0.02

[a] The lifetimes are corrected for isotopic impurities. [b] These are standard deviations among five to ten runs. The expected standard error of the mean would be smaller.

Table I gives the isotopic purities and lifetimes of the deuteriophenanthrenes in 3MP and EPA. Most lifetimes are slightly longer in EPA than in 3MP, but the difference is hardly significant except in the case of phenanthrene-d_{10}. However, the standard deviations are significantly smaller in EPA so a comparison of values is more meaningful.

In almost every case where comparison with the literature is possible, the lifetimes from the present study are slightly longer. Li and Lim[30] quote values of 3.7 and 15.2 s for phenanthrene-d_0 and -d_{10}. Charlton and Henry[14] also report 3.7 s for phenanthrene. Values of 3.80, 4.90, and 15.38 s are given by Heinrich et al.[12] for the d_0, $9\text{-}d_1$, and d_{10} compounds. However, Masetti et al.[31] give a lifetime of 3.90 s for phenanthrene, in good agreement with our 3.89 s. The differences may arise in several ways. The most probable reasons are the degassing, slow cooling, and correction for isotopic impurities in our work. Omission of any of these steps tends to make the lifetime shorter. Recent work by Johnson and Levin suggests that there might also be a slight dependence of lifetime on excitation wavelength.[32]

The data indicate a distinct position dependence of the deuterium effect. The smallest effect on the lifetime is for deuterium substitution in the 2 position. The lengthening of the lifetime is only about 1%. This may appear to be within the experimental uncertainty, but, in fact, in every set of runs when the ordinary phenanthrene and the phenanthrene-*2-d* were run at the same time, the latter invariably had a slightly longer lifetime, so the 1% lengthening of the lifetime appears to be real. The largest effect, about a 34% change in lifetime, is found for substitution at the 9 position. Substitution at the 1, 3, and 4 positions has very nearly the same effect, all around 6%. In 3MP the lifetimes are indistinguishable in our experiments. In ethanol the 1-deuteriophenanthrene is significantly shorter, but the 3- and 4-deuteriophenanthrenes are indistinguishable in lifetime.

In summary, the experimental facts are the following: Deuterium substitution at the 1, 3, and 4 positions has nearly the same effect—about a 6% lengthening of the triplet lifetime—with the 1-substitution being slightly less effective than the other two. Substitution at the 2 position has much less effect—about 1%—and at the 9 position a much larger effect—about 34%.

Discussion

Decay of the triplet state proceeds by two processes, radiative and nonradiative, whose rate constants can be designated by k_r and k_{nr}, respectively. The observed lifetime τ is related to these by

$$\tau^{-1} = k = k_r + k_{nr} \tag{1}$$

It has generally been assumed that deuteration changes only k_{nr} and not k_r. Experimental verification of this involves difficult determinations of small changes in quantum yields, and recent reports in the literature are somewhat conflicting. Lim and co-workers[30,33] report changes in k_r upon deuteration for several molecules in EPA at 77 K. In particular, for phenanthrene they report a 20% decrease in k_r and a fivefold decrease in k_{nr} upon perdeuteration. In contrast, however, Heinrich et al.[12,34] report little or no change in k_r for naphthalene or phenanthrene. Also Johnson and Studer[35] find little or no change for toluene and naphthalene in argon matrices at 20 K. In any even, the major change is in k_{nr}, and an explanation of the deuterium effects must be sought in the theory of radiationless transitions.

As mentioned above, effects of deuterium substitution on triplet decay rates have been found to be additive in other aromatic molecules. It is possible to check on the additivity in phenanthrene by comparing changes in decay rate when one deuterium is substituted for a hydrogen in the *i*th position. The values of Δk_i in s^{-1} for EPA are 0.0132 ± 0.0026, 0.0020 ± 0.0010, 0.0156 ± 0.0026, 0.0161 ± 0.0032, and 0.0648 ± 0.0024 for substitution in the 1, 2, 3, 4, and 9 positions, respectively. If the effects are additive, the decay rate of any species should be given by

$$k = k_H - \sum_i N_i \Delta k_i \qquad (2)$$

where k_H is the decay rate of the nondeuterated compound and N_i is the number of deuterium atoms in the *i* positions.

Several polydeuterated species were studied by Charlton and Henry.[14] It is not possible to compare our decay rates directly with theirs because under our conditions the lifetimes are slightly longer than theirs. However, we can assume that changes in rate can be obtained from eq 2 making use of our Δk_i and we can calculate the decay rate of their polydeuterated species based on their value for ordinary phenanthrene. Table II shows a comparison of results calculated in this way with those reported by Charlton and Henry. The errors in the calculated values are relatively large because they involve extrapolation of the small differences between the decay rates of ordinary and monodeuterated phenanthrenes. The agreement is within the given uncertainties except for the *9,10*-d_2 compound. It is not completely clear how the difference between our conditions and those of Charlton and Henry would affect the smallest decay rates, so we do not regard discrepancy for the *9,10*-d_2 compound as serious. We conclude that deuterium effects in phenanthrene are at least close to additive.

Table II. Observed and Calculated Rate of Triplet Decay of Polydeuteriophenanthrenes

Phenanthrene	Obsd[a] k, s^{-1}	Calcd[b] k, s^{-1}
d_0	0.270 ± 0.004	
2,4-d_2	0.257 ± 0.001	0.252 ± 0.009
1,3-d_2	0.240 ± 0.001	0.242 ± 0.010
2,4,5,7-d_4	0.239 ± 0.001	0.234 ± 0.013
1,2,3,4-d_4	0.225 ± 0.002	0.223 ± 0.014
1,3,6,8-d_4	0.200 ± 0.001	0.213 ± 0.015
9,10-d_2	0.162 ± 0.001	0.141 ± 0.009
d_{10}	0.065 ± 0.001	0.047 ± 0.028

[a] Calculated from the lifetimes reported by Charlton and Henry (ref 14). [b] Calculated from the observed k for phenanthrene-d_0 of ref 14 and the Δk_i from the present study.

The above values of Δk_i have also been used with our lifetime for phenanthrene-d_{10} to calculate the lifetimes of the d_9 compounds. These caculated lifetimes were then used to correct the lifetime of phenanthrene-d_{10} for the isotopic impurities in a self-consistent manner. This procedure lengthens the lifetime by about 1% compared with that observed for the impure compound.

Any theoretical calculation of the relative effects of deuteration at the different positions may be subject to question at three points—the nature of the perturbing Hamiltonian chosen, the quality of the electronic wave functions used, and any approximations used in evaluating matrix elements. Henry and Siebrand's theory[10,14,19] has considered spin-orbital coupling and Born-Oppenheimer breakdown as dual perturbations. They conclude that terms involving both effects and induced by out-of-plane vibrations are likely to be the most important. Calculations of matrix elements require both π and σ wave functions. For the former they use Hückel orbitals. Very little is known about the σ orbitals, so they use simple symmetry functions; since these are not treated in detail, the relative rate constants for molecules deuterated at different positions depend mainly on the magnitudes of the Hückel coefficients at those positions. This approach works quite well for naphthalene. In phenanthrene the Hückel coefficients for the 1, 2, 3, 4, and 9 positions are respectively[36] 0.340, 0.042, 0.315, 0.233, and 0.415. This theory would predict the smallest effect for substitution at the 2 position and the largest effect for the 9 position, in qualitative agreement with experiment. However, it would predict the effects of substitution at the other three positions to be spread out in between, in the order 4 < 3 < 1, with separations a reasonable fraction of the difference between 2-substitution and 9-substitution. This is not in agreement with experiment.

It is quite likely that Hückel wave functions and simple symmetry σ wave functions are inadequate for such a calculation, and it may be that the same theory applied to better wave functions would give good results. Another sort of test for the π wave functions is to compare them with spin densities observed by ESR techniques for the triplet state.[37] For the 1, 2, 3, 4, and 9 positions of phenanthrene these are respectively 0.131, −0.024, 0.158, −0.014, and 0.210. Qualitatively the 2 position has the lowest spin density and the 9 position the highest, in accord with the Hückel coefficients. Again the other three positions are spread out in between, but not in agreement with either Hückel coefficients or the deuterium effects. This suggests that Hückel wave functions are not good enough to treat the triplet state and further that a theory based on one-center terms and concentrating on only the highest filled and lowest unfilled orbitals is also likely to be inadequate.

Metz has reported some calculations on deuterium effects in phenanthrene,[29] but has given few details. His calculation is based on vibronically induced spin-orbital coupling and includes two-center terms. His calculation, like the others, predicts the smallest effect for the 2-substitution and the largest for the 9-substitution. But it predicts the 1- and 3-substitution to have close to the same effect as 2-substitution and 4-substitution to have an effect intermediate between those and 9-substitution.

We conclude that none of these theories in the present form do a very good job on the triplet lifetimes of partially deuterated phenanthrenes, although they all explain some of the gross features. Phenanthrene is a more complicated molecule than naphthalene or anthracene and thus provides a better test of theoretical approaches. It is hoped that the present data will eventually lead to an improved understanding of radiationless processes in aromatic molecules.

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Effect of Pressure on the Fluorescence of 9-Carbonyl Substituted Anthracenes

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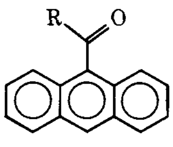
Abstract: The pressure dependence of the fluorescence intensity of 9-anthraldehyde, acetylanthracene, and 9-benzoylanthracene was investigated. It was observed that for each of these compounds the intensity of fluorescence increased remarkably as the external pressure was raised. In each case the energy of the fluorescent transition decreased with increasing pressure, leading to a large red shift in the emission spectrum. These data are interpreted to indicate that a change in the energy separating the lowest excited singlet and upper triplet energy levels occurs when these compounds are subjected to high pressure.

The fate of an electronically excited molecule is determined by the relative rates of the various paths available for its eventual return to the ground state. Thus, the net result of electronic excitation (fluorescence, phosphorescence, chemical reaction, radiationless decay, etc.) depends upon those factors that control the rates of the decay paths. External variables have proved useful in directing the decay of an excited molecule toward a particular path. For example, the external heavy atom effect has been used to enhance the rate of intersystem crossing and hence to increase the quantum efficiency for triplet formation.[1] We have investigated the effect of external pressure on the competition among various decay paths for a series of 9-carbonyl substituted anthracenes (**1**).



1a, R = H
1b, R = CH_3
1c, R = Ph

Aldehyde **1a** is reported to fluoresce only weakly in nonpolar solution at room temperature and atmospheric pressure.[2] Ketones **1b** and **1c** are totally nonfluorescent under these conditions. As the temperature is lowered the fluorescence efficiency of **1a** and **1b** increases but benzoylanthracene **1c** is nonfluorescent even at 77 K.[3] It has been suggested that the dominant decay path for the excited singlet of these 9-carbonyl substituted anthracenes is an intersystem crossing to an upper triplet. The temperature dependence of fluorescence is therefore a result of a thermal barrier to this intersystem crossing.[4] The height of the barrier is dependent upon the particular substituent, which accounts for the different thermal behavior of anthracenes **1b** and **1c**.

External pressure has been observed to affect the energy levels of excited states in a predictable and regular fashion. It has been shown that increased pressure causes singlet–singlet transitions to decrease in energy relative to singlet–triplet transitions.[5] This effectively raises the energy of the triplet relative to the excited singlet. Johnson and Offen[6] have exemplified this effect by showing that the fluorescence lifetime of anthracene in polymethylmethacrylate (PMMA) increases by a factor of three when the external pressure is varied from 1 atm to 30 kbars. Shaw and Nicol[7] confirmed that this was the result of the inhibition of intersystem crossing due to displacement of the excited singlet and upper triplet levels.

In this paper we report our results which show that the external pressure may be used to control the selection of decay modes by the electronically excited singlet state of the 9-carbonyl substituted anthracenes. By varying the applied pressure we have succeeded in converting the nonfluorescent anthracene derivatives **1a**, **1b**, and even **1c** to efficiently emitting molecules at room temperature.

Experimental Section

9-Anthraldehyde (**1a**) and 9-acetylanthracene (**1b**) were purchased from Aldrich Chemical Co. and purified by column chromatography,

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