shows that the choice of partial charges can have a drastic effect on both the sign and magnitude of the calculated rotational strengths. Since the G values sometimes differ between the two cases by as much as an order of magnitude or more, it appears that refined partial charges are needed before anything more than a qualitative estimation of the measurability of the CD spectrum can be made within the fpc model.

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Heavy Atom Effects on the Triplet Lifetimes of Naphthalene and Phenanthrene

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Abstract: Heavy atom effects on triplet decay rates are reported for the eight monohalonaphthalenes and for ten monohalophenanthrenes. The decrease in the lifetime with substitution is shown to vary with the square of the atomic spin-orbit coupling factor for the attached halogen. The position dependence is qualitatively related to the unpaired spin density distribution in the molecule. Investigation of the lifetimes of several polyhalogenated naphthalenes and phenanthrenes indicate both positive and negative deviations from an additive model for heavy atom effects. Substituent-induced shifts of the 0-0 band of the phosphorescence spectra are also tabulated.

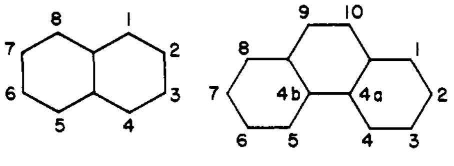
It was first noted by McClure[1] in 1949 that substitution of a halogen atom for a proton in aromatic molecules has a dramatic effect on the triplet state properties. The explanation involved an enhancement of spin-forbidden processes due to an increase in spin-orbit coupling induced by the halogen atom substituent. In aromatic hydrocarbons the so-called "internal heavy atom effects" include the following: (1) the phosphorescence lifetime decreases;[1-7] (2) the fluorescence lifetime usually decreases;[2,6-8] (3) the phosphorescence quantum yield may increase;[2,7,8] (4) the intersystem crossing rate increases;[2,7,8] (5) the oscillator strength of the $T_1 \leftarrow S_0$ absorption increases;[3,9,10] (6) S_1 and T_1 are lowered in energy, i.e., the emission spectra are red shifted;[2,9-15] (7) the vibronic substructure of the absorption and emission spectra changes.[9-13]

The magnitudes of these effects are related to the nuclear charge of the substituent, and increase through the series F, Cl, Br, I. They are also dependent, in general, on the position of substitution. The present work is concerned chiefly with the first effect noted above. Other of the effects will be noted or discussed briefly.

Previous studies of the heavy atom effect on phosphorescence lifetimes suffer from two inadequacies. First, although the nuclear charge dependence for naphthalene has been quite extensively studied, investigations of other aromatic hydrocarbons have been few and incomplete. Second, a position dependence of the heavy atom effect has not been characterized or discussed in detail. Naphthalene phosphorescence lifetimes,[1] within the precision of earlier measurements, show little or no position dependence, a presumably accidental situation. Furthermore, the scatter of experimental values from different research groups[1-3] obscures any possible small position effect in naphthalene. Position effects on triplet lifetimes of other molecules have been reported by Zanker[4] and Masetti et al.[6,7] but the data are incomplete.

It was, therefore, felt that a comprehensive position and mass dependence study on a molecule other than naphthalene was in order. Phenanthrene is ideal for several reasons. First, it is a relatively simple and well-characterized aromatic hydrocarbon. In addition, it has five inequivalent substitution sites while naphthalene has only two. Furthermore, many halogenated phenanthrenes were available from a previous study of position-dependent deuterium effects.[16] In the course of the phenanthrene studies, apparent steric effects in some dihalo compounds led to an examination of some dihalonaphthalenes and a reexamination of the lifetimes of the monohalonaphthalenes.

The numbering systems for naphthalene and phenanthrene are as follows:



Experimental Section

Phenanthrenes. The sources of the monobromophenanthrenes have been described previously.[16] The iodophenanthrenes were prepared by dissolving 0.1-0.2 g of the corresponding bromophenanthrene in anhydrous ether and adding a slight excess of butyllithium. Then slightly over 1 molar equiv of iodine was added and the mixture stirred until the iodine color persisted. The solution was then shaken with aqueous sodium thiosulfate and then with water and the ether layer evaporated to dryness.

2,7-Dibromophenanthrene was prepared by brominating 9,10-dihydrophenanthrene in acetic acid and then dehydrogenating with *N*-bromosuccinimide in carbon tetrachloride. From 9 g of the dihydrophenanthrene 4.82 g of the 9,10-dihydro-2,7-dibromophenanthrene, mp 166–168 °C, was obtained. From 3.38 g of this material and 1.78 g of NBS in 40 mL of carbon tetrachloride, 3.2 g of 2,7-dibromophenanthrene, mp 197–199 °C, was obtained. Recrystallization from toluene gave 2.72 g of shining rods, mp 197–201 °C.

9,10-Dichlorophenanthrene was prepared by passing chlorine into a solution of phenanthrene in carbon disulfide.

The 9,10-dibromophenanthrene was a gift of Professor Wittig.

The halogenated phenanthrenes were purified as needed by one or more of the following: codistillation with ethylene glycol, chromatography over Florisil, or recrystallization from methyl or ethyl alcohol.

Naphthalenes. 1,2-Dibromonaphthalene was prepared from 2-naphthol by first brominating in acetic acid to give 1-bromo-2-naphthol.[17] This was then heated with phosphorus tribromide.[18]

1,3-Dibromonaphthalene was synthesized by brominating 1-aminonaphthalene in acetic acid[19] to give 1-amino-2,4-dibromonaphthalene and then removing the amino group through diazotization.[20]

1,2,4-Tribromonaphthalene was prepared by diazotizing 1-amino-2,4-dibromonaphthalene and precipitating the diazonium tribromide.[21] This was then decomposed by melting to give the tribromonaphthalene.

1,8-Dichloronaphthalene was prepared from 1,8-diaminonaphthalene.[22]

All other halogenated compounds studied were commercially available. Preparation and purification of the solvents have been detailed previously.[16]

Apparatus and Methods. The measurements of the lifetimes and spectra were basically the same as previously described.[16] In general, the shorter the lifetime to be measured, the faster the phosphoroscope blades were rotated, the shorter the dwell time selected on the multichannel analyzer, and the more individual decay traces added together to constitute a run. The dwell time was always chosen so that the decay was monitored over at least five mean lifetimes. The number of decay traces constituting a run ranged from 15 to 20 for the fluoronaphthalenes to 6000 for 2-iodonaphthalene. An equal number of scans with a solvent blank were made and any contributions to the decay due to dark current, scattered light, or solvent impurity were subtracted from the raw data before analysis was performed. At least five runs were made and the results averaged for each sample. As before, the samples were made up at a concentration of 1×10^{-3} M, degassed to 5×10^{-4} Torr, and slowly cooled to 76 K in liquid nitrogen.

In making measurements on such a large number of compounds, it was not feasible to go through extensive purification routinely in each case. Consequently, several criteria of purity were used to determine whether or not further purification was necessary. These were: (1) visual inspection of the compound; (2) melting point measurements and comparison with the literature values when possible; (3) inspection of the phosphorescence spectrum and comparisons with published spectra[10-13] when possible; (4) inspection of the linearity of the phosphorescence decay curve (a correlation coefficient of at least 0.9990 when the decay was monitored over five to eight mean lifetimes was considered a minimum value to indicate single exponential decays); (5) low-voltage mass spectrometry. These criteria generally were applied in the order given and failure to meet any one was considered grounds for further purification. Purification generally involved either vacuum sublimation or recrystallization.

One impurity problem is of special note as it was not fully resolved. For 2-bromonaphthalene and perfluoronaphthalene it was noted that, upon degassing, the normal green phosphorescence was replaced by an intense long-lived blue emission. The blue emission appears to be emission from an impurity in the ethanol of the EPA solvent. As the solvent emission is ordinarily at least an order of magnitude weaker than the sample emission, some sort of energy transfer mechanism is implicated. Repeated purification of the samples and solvents gave no change. As oxygen appeared to prevent the energy transfer, lifetimes of oxygenated samples of 2-bromonaphthalene and perfluoronaphthalene were measured. Although the sample emission is also slightly oxygen quenched (between 5 and 10%), this will not change any conclusions drawn here.

Results and Discussion

The triplet lifetimes of the monohalonaphthalenes in EPA are given in Table I, along with their standard deviations, the rate constants for triplet decay ($k = 1/\tau$), and some corresponding data for solutions in 3-methylpentane (3 MP). The actual spectra are given elsewhere,[23] but the shifts relative to phenanthrene of the phosphorescence 0-0 bands in EPA are included in the table when they could be measured. Table II gives the corresponding data for monohalonaphthalenes, and, for comparison, values obtained by other workers. In general, the agreement with literature values is fair and indicates the degree of reproducibility from one laboratory to another. The measurements reported in this work have the advantage of all being measured on the same apparatus and so should be internally consistent. The lifetime of 2-fluoronaphthalene has not been reported before.

Nuclear Charge Dependence. The data presented in Tables I and II show a clear dependence of the triplet state lifetime on the identity of the substituent. In general, for a given position of substitution, the phosphorescence lifetime decreases by about one order of magnitude in each step in the F, Cl, Br, I substituent series. This decrease in lifetime can be accounted for by the increase in spin-orbit coupling in the series. The observed decay rate is a sum of the radiative and nonradiative rates for the molecule, but both processes should be proportional to the magnitude of spin-orbit coupling between singlet and triplet states. Thus we feel free to consider the total decay rate in terms of spin-orbit coupling.

McGlynn, Azumi, and Kinoshita[27] have discussed spin-orbit coupling in aromatic molecules in terms of a simple molecular orbital approach. Because ab initio calculations are impractical, they discuss the semiempirical relationships between decay rates and atomic spin-orbit constants, ζ, obtained from atomic spectra. The values of ζ for F, Cl, Br, and I are 272, 587, 2460, and 5700 cm^{-1}, respectively.[27,28] The effective spin-orbit coupling should be related to the sum over all atoms of ζ^2 multiplied by some measure of the effectiveness of that atom, but since ζ for carbon is only 32 cm^{-1} and for hydrogen much smaller, it should be a good approximation to assume that all spin-orbit coupling comes from the halogen atoms in aromatic halides. The net result of this analysis is that, for substitution at a particular site, the total decay rate should be proportional to the square of the spin-orbit coupling factor for the halogen substituent.

This proportionality can be demonstrated by a plot of the logarithm of the triplet decay rate constant against log ζ^2 for the halogen.[27] Plots of this type for monohalogenated naphthalenes and phenanthrenes are shown in Figure 1. The linearity over several orders of magnitude is remarkable, and the slopes are all close to unity as expected. This serves to justify the somewhat drastic assumptions made in the analysis.

Position Dependence. The effect of the position of substitution on triplet decay rates of haloaromatics is not as familiar as the nuclear charge dependence. Naphthalenes show little position dependence, and data on other aromatics have been much less complete, so there has been little discussion of the importance of the position of substitution.

The position dependence for halonaphthalenes is small but consistent. As shown in Table II and Figure 1, the lifetimes of 2-halonaphthalenes are longer than those of the corresponding

Table I. Triplet Lifetimes of Monohalophenanthrenes in EPA and 3MP at 76 K[e]

	EPA				3MP		
	τ, s	σ, s	k, s^{-1}	ΔE_{00}, cm^{-1} [a]	τ, s	σ, s	k, s^{-1}
2-Cl-	2.47	0.02	0.404	−20			
3-Cl-	1.03[b]		0.971				
9-Cl-	0.32	0.01	3.12	−550			
1-Br-	0.0641	0.0006	15.6		0.0543	0.0004	18.4
2-Br-	0.197	0.004	5.08	−90	0.117	0.0035	5.65
3-Br-[c]	0.0491	0.0006	20.4	−460	0.0428	0.0003	23.4
4-Br-	0.0260	0.0004	38.5		0.0235	0.0002	42.6
9-Br[d]	0.0108	0.0001	92.6	−550	0.0113	0.0002	88.5
2-I-	0.0271	0.0003	36.9	−90			
3-I-	0.00684	0.00008	146	−460			
9-I	0.00173	0.00002	578	−660			

[a] Energy shift of phosphorescence 0–0 band relative to phenanthrene. In some cases the 0–0 band is not resolved. [b] Reference 6. [c] Reported as 0.050 s in ref 6. [d] Reported as 0.013 s in ref 6 and 0.010 s in ref 24. [e] For comparison the lifetime of phenanthrene is 3.89 s in EPA and 3.80 s in 3MP (ref 16).

Table II. Triplet Lifetimes of Monohalonaphthalenes in EPA at 76 K[i]

Compd	τ, s	σ, s	k, s^{-1}	ΔE_{00}, cm^{-1} [a]	τ_{lit}, s
1-F-	1.85	0.02	0.54	−160	1.4,[b] 1.5[d]
2-F-	1.80	0.02	0.56	0	
1-Cl-	0.330	0.002	3.03	−600	0.23,[b] 0.30,[c] 0.29[d]
2-Cl-	0.377	0.001	2.65	−110	0.47,[c] 0.48[f]
1-Br-	0.0158	0.0002	63.3	−640	0.014,[b] 0.018,[c] 0.020,[d] 0.0154[e]
2-Br-[h]	0.176	0.0001	56.8	−110	0.021,[c] 0.02[g]
1-I-	0.00243	0.00002	412	−640	0.0023,[b] 0.0025,[c] 0.002,[d] 0.00259[e]
2-I-	0.00262	0.00005	382	−420	0.0025[c]

[a] Energy shift of phosphorescence 0–0 band relative to naphthalene. [b] Reference 3. [c] Reference 1. [d] Reference 2. [e] Reference 24. [f] Reference 25. [g] Reference 26. [h] Not degassed. [i] For comparison the lifetime of naphthalene is 2.60 s in alcohol (ref 39).

1-halonaphthalenes by amounts ranging from 4 to 14%. In halophenanthrenes, however, the position dependence is very striking. The lifetimes of 9-halophenanthrenes are very close to those of the corresponding naphthalenes, but the life times of the 2-halophenanthrenes are an order of magnitude longer. The lifetimes of the other halophenanthrenes fall in between these two extremes. In particular, for the brominated compounds, the lifetimes fall in the order 2-Br > 1-Br > 3-Br > 4-Br > 9-Br. Lifetimes of the available chloro- and iodophenanthrenes fall in the same order.

In a treatment of phosphorescence lifetimes by perturbation theory, the effect of a heavy atom is to mix singlet and triplet states, thus making intercombination processes allowed. The position dependence of the substituent effects arises from a variation in how effectively the substituent can mix the appropriate states. The nature of the particular states being mixed and the mechanism of the mixing are topics of considerable interest. The position dependence may provide a test of various possibilities.

Ideally, one should consider the radiative and nonradiative rates separately, as there is no reason to expect the position dependence to be identical. However, separation of the two rates requires accurate quantum yield measurements. For example, Masetti et al.[6] have made such measurements on 3- and 9-bromophenanthrene. Their lifetimes are similar to ours. They showed that the radiative rates for the two compounds differed by a factor of 3.0 and the nonradiative rates by a factor of 4.2. Unfortunately, we do not yet have good enough quantum yield data to permit a similar analysis for all the compounds. However, there seems to be at least a qualitative similarity between the position effects on the two processes, so our data on the lifetimes should still be useful.

A considerable amount of work has been done on heavy atom effects on the radiative process in substituted aromatics.[13,28,29] Studies of substituent effects on the vibrational structure and polarization of the emission have been especially useful. Heavy atoms seem both to enhance the mixing of σ and π states which is important in unsubstituted aromatics and to induce an additional mixing of π states by some vibronic mechanism. It has been suggested[29] that the mixing may involve charge transfer states. Much less is known about the nonradiative processes as these can only be studied indirectly. They involve a coupling between the triplet and ground states. Direct coupling is symmetry allowed in the C_s point group of most substituted aromatics, but it may occur through a vibronic

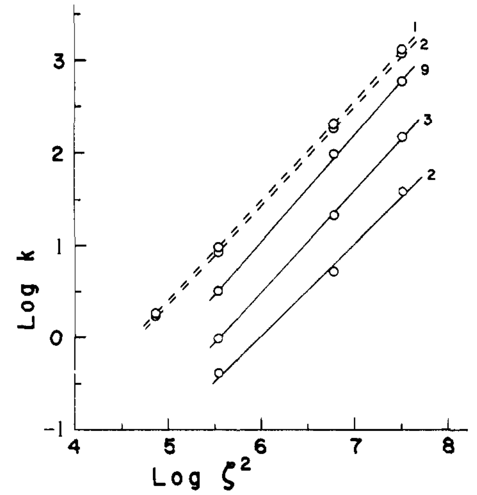


Figure 1. Variation of the triplet decay rate of monohaloaromatics with atomic spin–orbit factor. The solid lines are phenanthrenes substituted in the indicated positions. The dashed lines show the values for halonaphthalenes, but are displaced upwards by 0.5 log unit to avoid confusion with the 9-halophenanthrenes.

Table III. Triplet Lifetimes of Polyhalogenated Naphthalenes and Phenanthrenes in EPA at 76 K

Compd	ΔE_{00}, cm^{-1} [a]	τ, s	σ, s	k_{exp}, s^{-1}	k_{calcd}, s^{-1} [b]	Percent deviation
		Naphthalene				
OctaF- [c]	−850	0.271	0.002	3.69	4.40	−16.1
1,2-DiCl-	−850	0.272	0.001	3.65	5.68	−35.7
1,4-DiCl-	−1120	0.128	0.001	7.81	6.06	+28.9
1,8-DiCl-		0.112	0.001	8.77	6.06	+44.7
1,2,3,4-TetraCl-	−1120	0.107	0.001	9.35	11.36	−17.7
1,2-DiBr-	−640	0.0134	0.0003	74.6	120	−37.8
1,3-DiBr-		0.00664	0.0001	151	120	+25.8
1,4-DiBr-	−1140	0.00586	0.0001	171	127	+34.6
2,3-DiBr-	−640	0.00794	0.0001	126	114	+10.5
1,2,4-TriBr-		0.00496	0.0001	202	183	+10.4
		Phenanthrene				
9,10-DiCl-	−1030	0.31	0.02	3.22	6.24	−48.4
9,10-DiBr-	−1030	0.0123	0.0001	81.3	185.	−56.1
2,7-DiBr-	−190	0.0914	0.0013	10.9	10.2	+6.9

[a] Energy shift of phosphorescence 0–0 band relative to that of the parent hydrocarbon. [b] $k_{calcd} = \Sigma_i k_i$ where i indicates a position of substitution in the molecule and k_i is the total decay rate constant for the corresponding monohalogenated compound. [c] Not degassed. Reported as 0.25 s in ref 2.

mechanism or through Born–Oppenheimer breakdown formally involving other states.[30]

The fact that halogen substitution produces only small shifts in the absorption and phosphorescence spectra suggests that a useful starting point for discussion is the assumption that the effects can be treated in terms of wave functions and properties of the parent hydrocarbon. The lowest triplet state can be visualized as arising from the promotion of an electron from the highest filled to the lowest unfilled π orbital of the molecule. In a very simple view, a perturbation mixing the ground and lowest triplet states may reduce to one-electron terms involving the electron which has changed orbitals. If the perturbation is localized at a particular carbon atom, then its effect should be related to the probability of finding this electron at that position, i.e., to the electron density at that center in these two π orbitals.

One obvious comparison is with the coefficients of the atomic orbitals at the various atoms in a Hückel calculation of these π orbitals.[31] For naphthalene the magnitudes of the Hückel coefficients at the 1 and 2 positions are 0.425 and 0.263, respectively. These would suggest that the lifetimes of the 1-halonaphthalenes should be shorter than those of the 2-halo compounds. This is qualitatively true, but the lifetimes are much closer than one might expect from the Hückel coefficients. In the case of phenanthrene the magnitudes of the Hückel coefficients at the 1, 2, 3, 4, and 9 positions are respectively 0.340, 0.042, 0.315, 0.233, and 0.415. Neglecting the 4 position for steric reasons discussed below, we see that the Hückel coefficients increase in the order $2 < 3 < 1 < 9$. The observed lifetimes of the bromophenanthrenes decrease in the order $2 > 1 > 3 > 9$. There is a general trend for shorter lifetimes of compounds substituted at positions of higher density, but the details of the ordering of the compounds are not explained. Thus Hückel coefficients are not adequate to explain the position effects.

A related measure of electron distribution in the appropriate π orbitals is the spin density at each center in the triplet state as determined from ESR spectra of the hydrocarbons. Hutchison and co-workers have measured spin densities in naphthalene[32] and phenanthrene.[33] For naphthalene the values at the 1 and 2 positions are 0.219 and 0.062, in agreement with the Hückel coefficients but in only very rough qualitative agreement with the lifetimes. In phenanthrene the spin densities are 0.131, −0.024, 0.158, −0.014, and 0.210 in the 1, 2, 3, 4, and 9 positions. These values increase in the order $2 < 1 < 3 < 9$ which differs from the order of Hückel coefficients but is in agreement with the order of decreasing lifetimes of bromophenanthrenes. There is a clear qualitative relationship between the position dependence of the substituent effect on lifetimes and these measures of electron distribution, but a quantitative treatment of lifetimes will need additional considerations. This is analogous to the situation found for the position dependence of the deuterium isotope effect on triplet lifetimes.[16]

The exclusion of 4-bromophenthrene from the previous arguments remains to be discussed. The 4 position is on the inside of the "v" formed by the three fused rings, and any substituent there larger than a hydrogen atom subjects the molecule to severe steric strain. This strain could be relieved by a displacement of the substituent out of the plane of the molecule or in plane but away from the other ring, or by a distortion and loss of planarity of the whole phenanthrene framework. Some combination of all three effects is probable.

The spectrum of 4,5-dimethylphenanthrene has been interpreted in terms of a nonplanarity due to twisting about the 4a–4b bond,[34] and Newman and Hussey have actually separated the resulting optical isomers.[35] In fact the x-ray structure of phenanthrene itself[36] shows a slight twisting about this bond, and the effect must be exaggerated in the 4-substituted compounds. The absorption spectrum of 4-bromophenanthrene is qualitatively different from that of the other bromo derivatives, and Ginsburg and Goodman[13] have suggested that the unusual phosphorescence spectrum of this compound is explained by the loss of planarity. Beringer et al.[37] have interpreted the NMR deshielding of the 5 protons in 4-substituted phenanthrenes as being due to nonplanar distortions. Nonplanarity must increase the mixing of σ and π states of the molecule. Because of a vanishing of important spin–orbit coupling matrix elements between π states in planar systems, such a mixing of σ and π states should lead to enhanced spin–orbit interactions and, therefore, shorter triplet lifetimes. A similar effect has been noted in the triplet lifetimes of helicenes which get shorter as the deviations from planarity increase.[38] Thus we should not try to compare the lifetime of the 4-bromophenanthrene with the other compounds expected to be nearly planar.

Lifetimes of Polyhalogenated Compounds. Lifetimes of a number of polyhalonaphthalenes and phenanthrenes are listed in Table III. Thus far, the approximation concerning the one-center nature of the heavy atom effect has been implicit in the discussion of both nuclear charge effects and position effects. It is desirable to test this approximation by checking the additivity of heavy atom effects in polyhalogenated compounds. As the spin-orbit coupling of the entire molecule is assumed to be completely dominated by the spin-orbit coupling at the halogen, one might write

$$k_{\text{tot}} = \sum_{i} k_i$$

where the total rate constant, k_{tot}, for a polyhalogenated molecule is the sum of the rate constants for the corresponding monohalogenated molecules. Values of rate constants calculated in this way are listed in Table III where they may be compared with the experimental rate constants. The last column gives the percent deviation of the experimental value from the calculated value.

It is immediately obvious that the additivity relationship is *not* good for polyhalogenated compounds. The only compound for which the calculated and observed rate constants agree within experimental error is the 2,7-dibromophenanthrene, where the two substituents are on different rings and far apart.

The other compounds seem to be divided into two groups. Most compounds which have halogen atoms in adjacent positions have decay rates smaller than expected from additivity. The 2,3-dibromonaphthalene is an exception to this. 9,10-Dibromophenanthrene is the extreme example—it actually has a smaller decay rate than the monosubstituted 9-bromophenanthrene. On the other hand, most compounds having substituents on nonadjacent positions decay more rapidly than expected from additivity.

The deviations from additivity are in direct contrast to the excellent additivity relationship observed in the deuterium isotope effects.[16,39,40] It is clear that, in spite of the qualitative similarity, additional factors are involved in the heavy atom effects. The data are not sufficiently complete to prove any particular mechanism, but we can make some suggestions.

We believe that the smaller than additive rates when halogens are substituted in adjacent positions are an indication of some sort of steric effects, perhaps a distortion of the C–X bond such as to decrease the interaction between the heavy atom and the π system. The effect tends to be largest when the bond joining the two positions in the parent hydrocarbon is shortest. For example, the C_9–C_{10} bond in phenanthrene is 1.34 Å long,[36] and the C_1–C_2 and C_2–C_3 bonds in naphthalene are 1.36 and 1.42 Å, respectively.[41] Also, the deviations seem to be larger for the larger halogen substituents, and this is consistent with a steric effect.

We have fewer data on compounds with nonadjacent substituents, but they seem to have decay rates higher than expected from additivity. This probably means that an interpretation of the substituent effects will have to consider terms other than the one-center properties of the parent hydrocarbon. For example, the states may have some halogen-to-ring charge transfer character,[26] and resonance interactions between various such states may provide a synergistic effect. It should be noted that the shifts of the 0–0 bands are actually close to additive, even when the rate constants are far from additive. It is clear that more examples of lifetimes of polyhalogenated compounds would be helpful in understanding the effects.

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