The Intramolecular External Heavy Atom Effect in Bromo-, Benzo-, and Naphthonorbornenes

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Abstract: A theoretical analysis of the external heavy atom effect of a halogen atom on the radiative rate constant of phosphorescence is examined as a function of position of a bromine atom or atoms relative to a naphthalene or a benzene chromophore for a series of mono- and dibromo-, naphtho-, and benzonorbornenes. The theoretical results are then compared to experimental data and lead to the conclusion that the enhancement of the phosphorescence process takes place through the second-order mixing of the triplet states of the chromophore with the singlet charge transfer states arising primarily from an electron transfer from the orbitals of the heavy atom perturber to the unfilled π^* orbitals of the chromophore.

Introduction

Normally, an electronic transition from a singlet to a triplet state in a molecule is "spin forbidden" owing to the orthogonality of the spin functions.[2a] For transitions between states of different spin multiplicities to be observed, a spin–orbit perturbation is generally required.[2a] In aromatic hydrocarbons, the spin–orbit coupling is generally very small, but an introduction of heavy atoms into such molecules and/or into the surrounding medium has been found to create a dramatic increase in the rates of the various multiplicity-forbidden photophysical processes. The effect of a heavy atom bonded directly to the chromophore (internal heavy atom effect)[2b-d] or of a heavy atom not affixed but close to the chromophores (external heavy atom effect)[3] has been the focus of much theoretical[4] and experimental work.[5] The exact mechanism(s) of the heavy atom effect has not been clarified. The heavy atom could either enhance the singlet–triplet mixing already present in the molecule or introduce new perturbing states. In the case of the internal heavy atom effect, both mechanisms have been proposed.[5]

Murrell[6] and Tsubomura and Mulliken[7] presented evidence for the formation of a charge-transfer complex of aromatic hydrocarbon with oxygen as an external perturber and proposed that the enhancement of $T_1 \rightarrow S_0$ transition in aromatics is due to the intensity borrowing from the charge-transfer transition in the complex. Later, McGlynn and his co-workers[3] extensively studied the role of external heavy atom on the phosphorescence process and offered evidence for charge transfer complexes with alkyl halides as donors. However, the exact mechanism by which the external heavy atom increases the spin–orbit coupling has not been advanced. There are a number of experimental observations, notably those of Kearns et al.[8] and also of McGlynn et al.,[3] which indicate that an external heavy atom perturbation is purely electronic in nature and involves no vibronic coupling. Siegel and Judeikis[9] have shown, using the combined ESR and optical studies, that the phosphorescence process is more sensitive to the external heavy atom than either the intersystem crossing or the $T_1 \rightsquigarrow S_0$ radiationless process.

The object of the present investigation is to understand, more quantitatively, the role of an external heavy atom or atoms in the enhancement of phosphorescence. For this purpose, we have chosen to examine the spectroscopic data of a series of mono- and dibromonaphthonorbornenes[10,11] and a few monobromobenzonorbornenes (Figure 1) where the position of the halogen atom(s) is varied systematically on the rigid

bicyclic[2.2.1]heptane framework to allow us to precisely estimate the exact distance and orientation in space of the bromine atom relative to the naphthalene chromophore. Although there exist, in the literature,[8,12-14] some other reports where attempts were made to correlate the magnitude of perturbation with distances of the heavy atom, the systems studied are far from ideal because they lack a fixed and known geometry.

Theory

If the heavy atom is external to the chromophore but not too far from it, the heavy atom effect can operate through the overlap between the orbitals of the chromophore and the perturber containing the heavy atom. In other words, the enhancement of intensity of the $T_1 \rightarrow S_0$ radiative process may be assumed to be caused by a charge transfer either from the chromophore to the perturber or from the perturber to the chromophore. The bromo compounds of Figure 1 may therefore be treated as a composite system made up of either naphthalene or benzene as the chromophore and a C–Br bond as the perturber.

Photoelectron spectroscopic measurements[15] show that in alkyl bromides the two lone-pair orbitals of the halogen atom are doubly degenerate and their energies are greater than the ionization potentials of the aromatic hydrocarbons. Nuclear quadrupole measurements[16] have shown only 9% s character of the halogen orbital in the C–Br bond of alkyl bromides. We may, therefore, presume that the doubly degenerate lone pair orbitals of the halogen atom on the norbornene moiety are most likely to be two mutually perpendicular 4p orbitals. Since the low-energy bands in benzene and naphthalene arise from a transition from a filled π orbital to an unfilled π^* orbital, the relevant molecular orbitals, for the present purpose, are an occupied π and an unoccupied π^* molecular orbitals of the chromophore, the two lone pair orbitals of the halogen, n_0 and n_0', and the bonding and antibonding orbitals σ and σ^* of the C–Br bond. Their relative energetic positions are shown schematically in Figure 2. Using these orbitals one can construct several zero-order electronic states of different multiplicities. These states are shown in Figure 3, where the orbitals shown within the parentheses make up the configurations for the various states. It is seen that except for the S_1^0 and T_1^0 states, which are locally excited states of the chromophore, all other states in Figure 3 are the charge-transfer states. The relative positions of S_3^0 and S_4^0 and that of T_3^0 and T_4^0 shown in this figure may or may not be correct but this knowledge is not crucial for the conclusions derived from the present investigation.

The interaction between the chromophore and the perturber can take place either through the lone-pair orbitals of the
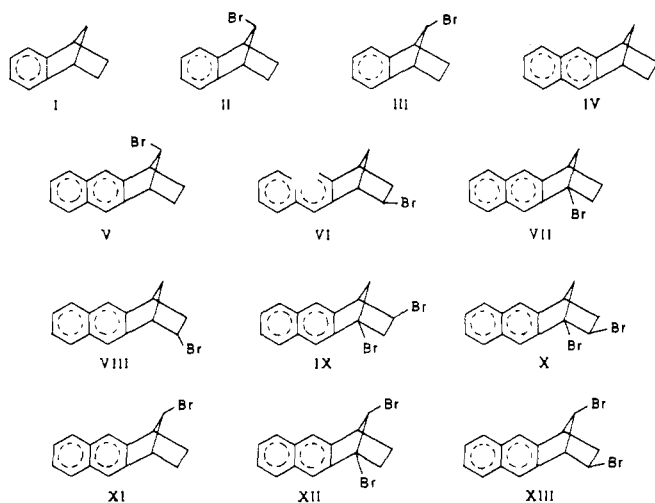
Figure 1. The position of the bromine atom(s) on the bicyclic [2.2.1]heptane framework in the benzo- and naphthonorbornenes pertinent to this study.

halogen and/or through the σ and σ^* orbitals of the C–Br bond, depending on the stereochemical disposition of the C–Br bond with respect to the π systems. The perturbation Hamiltonian is given by

$$H' = V + H_{SO} \tag{1}$$

where V represents the interaction perturbation between the chromophore and the perturber and H_{SO} is the usual one-electron spin–orbit interaction operator which has its origin at the Br nucleus. This operator is defined as[5]

$$H_{SO} = \sum_i \frac{Ze^2}{4m^2c^2} \frac{1}{r_i{}^3} \mathbf{l}_i \mathbf{s}_i \tag{2}$$

Equation 2 shows that the spin–orbit term is a short-range function of distance from the Br nucleus and should be extremely small everywhere except near the nucleus. We, therefore, neglect, in the following, any two-center spin–orbit terms. The perturbation V is assumed to be an effective one-electron operator and cannot therefore be defined explicitly. However, the matrix elements of V over the orbitals of the chromophore and the perturber can be assumed to be proportional to the intramolecular orbital overlap while those over the orbitals that are localized either on the chromophore or on the perturber vanish. Employing the second-order perturbation theory and remembering that in aromatic molecules the spin–orbit mixing between the lowest triplet and the ground state is vanishingly small,[2a] one may write the wave function of the emitting triplet state T_1, corrected to the second order, as

$$|T_1\rangle = |T_1{}^0\rangle + \sum_i \left\{ \frac{\langle T_1{}^0|H'|S_i{}^0\rangle}{E_{T_1{}^0} - E_{S_i{}^0}} \right. $$
$$- \frac{\langle T_1{}^0|H'|S_i{}^0\rangle\langle T_1{}^0|H'|T_1{}^0\rangle}{(E_{T_1{}^0} - E_{S_i{}^0})^2} \right\} |S_i{}^0\rangle$$
$$+ \sum_{i \neq 1} \frac{\langle T_1{}^0|H'|T_i{}^0\rangle\langle T_i{}^0|H'|S_i{}^0\rangle}{(E_{T_1{}^0} - E_{T_i{}^0})(E_{T_1{}^0} - E_{S_i{}^0})} |S_i{}^0\rangle \tag{3}$$

In eq 3 the second and third terms involve respectively the two-center and the one-center spin–orbit coupling terms. Although the energy denominator in the third term may be an order of magnitude larger than that in the second term, it is believed that this could be made up for many times over by having the one-center terms in the numerator of the third term. Hence the second term of eq 3 is ignored. We shall, therefore, deal with the third term as follows:
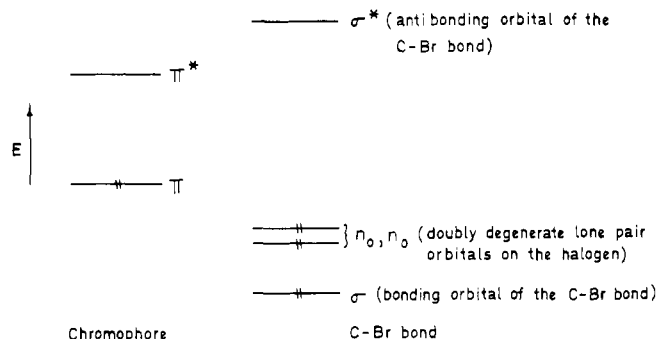
Figure 2. Relative energies of the relevant MOs in (di)bromonaphthonorbornenes.
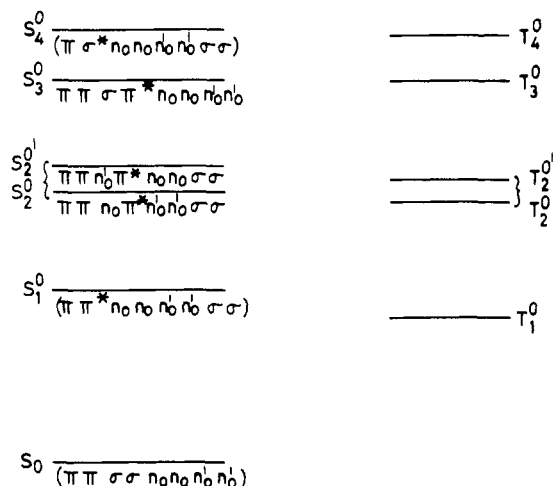
Figure 3. Relative position of the various zero-order electronic states of different multiplicities; S and T refer to the singlet and triplet states.

$$\langle T_1{}^0|H'|T_2{}^0\rangle\langle T_2{}^0|H'|S_2{}^{0\prime}\rangle$$
$$= \langle T_1{}^0|V|T_2{}^0\rangle\langle T_2{}^0|H_{SO}|S_2{}^{0\prime}\rangle$$
$$= \langle n_0|V|\pi\rangle\langle n_0|H_{SO}|n_0'\rangle \tag{4}$$

The matrix element of V in eq 4 is proportional to the intramolecular orbital overlap $S_{n_0\pi}$ between a lone-pair orbital n_0 and the π orbital of the chromophore. The integral $\langle n_0|H_{SO}|n_0'\rangle$ is a one-center spin–orbit term involving the two mutually perpendicular 4p orbitals on the bromine nucleus. We may, therefore, write

$$\frac{\langle T_1{}^0|H'|T_2{}^0\rangle\langle T_2{}^0|H'|S_2{}^{0\prime}\rangle}{(E_{T_1{}^0} - E_{T_2{}^0})(E_{T_1{}^0} - E_{S_2{}^0{}'})}$$
$$= K_1 S_{n_0\pi}\langle n_0|H_{SO}|n_0'\rangle = K_1' S_{n_0\pi} \tag{5}$$

Similarly

$$\frac{\langle T_1{}^0|H'|T_3{}^0\rangle\langle T_3{}^0|H'|S_2{}^0\rangle}{(E_{T_1{}^0} - E_{T_3{}^0})(E_{T_1{}^0} - E_{S_2{}^0})}$$
$$= K_2 S_{\sigma\pi}\langle \sigma|H_{SO}|n_0\rangle = K_2' S_{\sigma\pi} \tag{6}$$

$$\frac{\langle T_1{}^0|H'|T_2{}^0\rangle\langle T_2{}^0|H'|S_3{}^0\rangle}{(E_{T_1{}^0} - E_{T_2{}^0})(E_{T_1{}^0} - E_{S_3{}^0})}$$
$$= K_3 S_{n_0\pi}\langle \sigma|H_{SO}|n_0\rangle = K_3' S_{n_0\pi} \tag{7}$$

where $S_{\sigma\pi}$ is the overlap between the back lobe of the σ orbital of the C–Br bond and the π orbital of the chromophore, wherever possible (see Table I). The integral $\langle \sigma|H_{SO}|n_0\rangle$ also involves a one-center spin–orbit term involving the two perpendicular 4p orbitals of the bromine atom. In eq 5–7 K_1', K_2', and K_3' are treated as constants but cannot be equal to each other because not only the different kinds of orbitals are in-
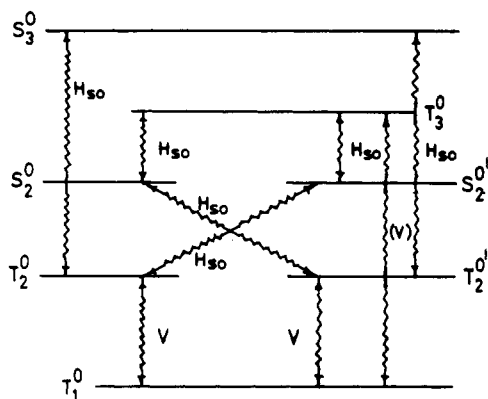
Figure 4. A state diagram showing the coupling mechanism. V and H_{SO} are defined in the text.

Table I. Observed Values of K_p in EPA at 77 K, Length of the Dipole Vectors **R** and **R'**, the Angle between Two Vectors θ, and the Values of η^2

molecule	K_p, s^{-1}	$S_{\sigma\pi}$**R**, Å	$S_{n_0\pi}$**R'**, Å	θ, deg	η^2
I	0.15				
II	3.54		0.041		0.082
III	16.7	0.900			0.810
IV	0.026				
V	0.63		0.033		0.053
VI	0.82	0.25			0.063
VII	0.95		0.038		0.071
VIII	1.9		0.054		0.140
IX	2.9	0.25	0.038	77	0.167
X	3.3	0.25	0.038	50	0.220
XI	5.1	0.66			0.431
XII	7.7	0.66	0.038	60	0.69
XIII	9.4	0.66, 0.25		46	0.72

volved but also the energy denominators are different. Thus, the T_1^0 state of the chromophore can contaminate the S_2^0, $S_2^{0'}$, and S_3^0 states either through an interaction with the two lone-pair orbitals of the halogen or through the back lobe of the C–Br bond or through both pathways. The contamination of the S_4^0 state is neglected because it involves the two-center spin-orbit terms. The mixing mechanism of the important charge-transfer states with the T_1^0 state of the chromophore is shown schematically in Figure 4. Equation 3 can, therefore, be written as

$$|T_1\rangle = |T_1^0\rangle + (K_1'S_{n_0\pi} + K_2'S_{\sigma\pi})|S_2^{0'}\rangle$$
$$+ (K_1'S_{n_0'\pi} + K_2'S_{\sigma\pi})|S_2^0\rangle + K_3'(S_{n_0\pi} + S_{n_0'\pi})|S_3^0\rangle \quad (8)$$

Equation 8 shows that the triplet state of the chromophore can borrow its intensity primarily from those charge-transfer states which arise from an electron transfer from the perturber to the chromophore. The intensity of the charge-transfer transition is fairly high and according to Mulliken's theory[17] the transition dipole moments are given by

$$\langle S_2^0|e\bar{r}|S_0\rangle = ea\mathbf{R} + ebS_{n_0\pi^*}\mathbf{R}/2 \quad (9)$$

$$\langle S_2^{0'}|e\bar{r}|S_0\rangle = ea\mathbf{R} + ebS_{n_0'\pi^*}\mathbf{R}/2 \quad (10)$$

and

$$\langle S_3^0|e\bar{r}|S_0\rangle = ea'\mathbf{R}_1 + eb'S_{\sigma\pi^*}\mathbf{R}_1/2 \quad (11)$$

where a, b, a', and b' are related to the mixing coefficients of the corresponding charge-transfer states with the ground state wave functions, and **R** and **R$_1$** are the distances from the nearest carbon atom of the chromophore to the bromine nucleus and to the center of the C–Br bond in the perturber, re-

spectively. Mulliken[17] has shown that in the benzene–iodine complex the first term in the transition moment integral is larger than the second term because of the smallness of the overlap.

A Quantitative Relation between k_p, the Intramolecular Orbital Overlap, and the Distance of the Heavy Atom. Since the phosphorescence process is more sensitive to the external heavy atom than any other photophysical process,[9] from eq 8–11 a relationship between K_p, the rate constant for the phosphorescence process, the overlap, and the distance of the heavy atom from the chromophore is anticipated. The radiative lifetime is related to the transition moment D and the frequency $\bar{\nu}$ as

$$\tau^0 = \frac{4.146 \times 10^{11}}{D^2\bar{\nu}^3} \quad (12)$$

If τ^0 is the radiative lifetime of the phosphorescent state, one obtains for K_p the equation

$$K_p = \frac{D^2\bar{\nu}^3}{4.146 \times 10^{11}} = K'D^2 \quad (13)$$

where

$$K' = \bar{\nu}^3/4.146 \times 10^{11} \quad (14)$$

$$\mathbf{D} = \langle T_1|e\bar{r}|S_0\rangle \quad (15)$$

Substituting for T_1 eq 8 in eq 15 one obtains

$$\mathbf{D} = \bar{\mathbf{D}}_0 + (K_1'S_{n_0\pi} + K_2'S_{\sigma\pi})\langle S_2^{0'}|e\bar{r}|S_0\rangle$$
$$+ (K_1'S_{n_0'\pi} + K_2'S_{\sigma\pi})\langle S_2^0|e\bar{r}|S_0\rangle$$
$$+ K_3'(S_{n_0\pi} + S_{n_0'\pi})\langle S_3^0|e\bar{r}|S_0\rangle \quad (16)$$

where $\mathbf{D}_0$ may be treated as the transition moment vector for the $T_1^0 \rightarrow S_0$ process in the chromophore. Since K_p^0, the rate constant for the phosphorescence process in the chromophore, is very small compared to K_p for the bromo compounds, $\mathbf{D}_0$ may be neglected in eq 16. Entering eq 9–11 in eq 16 and ignoring the second-order terms in the overlap, one obtains

$$\mathbf{D} = \{K_1'(S_{n_0\pi} + S_{n_0'\pi}) + 2K_2'S_{\sigma\pi}\}a\mathbf{R} + K_3'(S_{n_0\pi} + S_{n_0'\pi})a'\mathbf{R}_1 \quad (17)$$

There are two degenerate mutually perpendicular lone-pair orbitals, n_0 and n_0', on the bromine nucleus. The orientation of these two lone-pair orbitals can be so chosen that one of them overlaps with the π orbital of the chromophore to a maximum extent while the overlap with the other component is negligibly small. Let us assume that the maximum overlap is accomplished with the n_0 component; then equation 17 takes the form

$$\mathbf{D} = X_1S_{n_0\pi}\mathbf{R}' + X_2S_{\sigma\pi}\mathbf{R} \quad (18)$$

where

$$X_1 = K_1'a + K_3'a' \quad (19)$$

$$X_2 = 2K_2'a \quad (20)$$

and **R'** is the average of **R** and **R$_1$**. Since $K_p = K'D^2$, for most monobromo compounds of Table I, the enhancement of K_p is due to the interaction of the chromophore orbital with either the lone-pair orbital or the σ orbital of the C–Br bond in the perturber. The magnitude of such interaction depends on the overlap. The method of estimation of the overlap integrals $S_{n_0\pi}$ and $S_{\sigma\pi}$, the structural parameters chosen in such calculations, and the magnitude of the overlap in bromobenzo- and bromonaphthonorbornene systems are given in the Appendix. For dibromo compounds, **D** of eq 18 should be given by the resultant of the two dipoles, which depends on the angle between the two dipole vectors **R'** and **R**. The plot of K_p vs. $S_{n_0\pi}^2R'^2$ for compounds V, VII, and VIII of Table I and a similar plot of

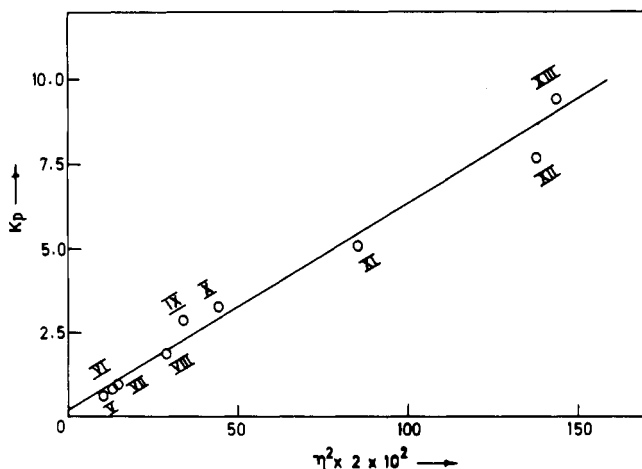**Figure 5.** The plot of K_p vs. η^2 for the various mono- and dibromonaphthonorbornenes of Table I.

Figure 6. A norbornene system with labeled hydrogen atoms.

K_p vs. $S_{\sigma\pi}^2 R^2$ for compounds VI, IX, and XIII gave approximate straight lines. From their slopes we obtain

$$X_1/X_2 \simeq 7 \tag{21}$$

Hence we may write now from eq 13, 18, and 21

$$K_p = K'X_2^2\eta^2 \tag{22}$$

where

$$\bar{\eta} = [7S_{n_0\pi}\mathbf{R}' + S_{\sigma\pi}\mathbf{R}] \tag{23}$$

In Table I are given the observed values of K_p, the magnitude of the vectors $S_{n_0\pi}\mathbf{R}'$ and $S_{\sigma\pi}\mathbf{R}$, the angles between them for the dibromo compounds, and η^2. The results show that there is a correlation between K_p and η^2 for a series of (di)bromonaphthonorbornenes. In Figure 5 is also shown an approximate linear plot of K_p vs. η^2 for various bromonaphthonorbornenes.

Discussion

The above results suggest that the enhancement of the phosphorescence process in the bromo compounds of Figure 1 is due to charge transfer followed by spin–orbit coupling. The charge transfer takes place either from the lone-pair orbitals or from the back lobe of the σ orbital of the C–Br bond to the chromophore or via both pathways in some dibromo compounds. Although the extent of contamination of the chromophore triplet state with the singlet charge-transfer state depends primarily on the overlap of the donor and acceptor orbitals, the enhancement of the phosphorescence depends on the product of the overlap and the charge-transfer distance. One therefore should not expect any straightforward distance dependence of the external heavy atom effect. The results of Table I further show that the enhancement of the phosphorescence process should not necessarily increase as the number of heavy atoms affixed to the norbornene frame is increased. The orientation of the heavy atom orbitals relative to the chromophore orbital is important in the mechanism of the enhancement process. These conclusions are in general agreement with other previous results[3,8] that an external heavy atom perturbation is electronic in nature and involves no vibronic coupling.

Some results of Table I, especially for molecules III, VI, XI, and XIII, seem to suggest that the heavy atom effect parallels the trends seen for the NMR and ESR coupling phenomena in systems of similar structure. The norbornene system[18] (Figure 6) exhibits a long-range NMR coupling between syn proton H_a and the endo protons H_i and H_j and between the anti
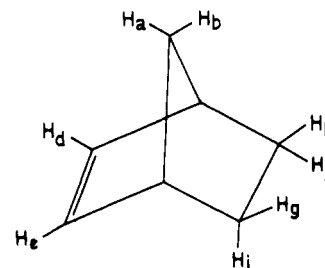
proton H_b and the olefinic protons H_d and H_e. Lemaire et al.[19] observed the positive sign of the long-range coupling of the same nature in the NMR spectrum of bicyclic nitroxide, which seems to indicate that the coupling is due to delocalization. Similar results are known for the hyperfine splitting seen in the ESR spectra of bicyclic semidiones,[20] semiquinones,[21] semifuraquinones,[22] and 7-norbornenyl-type radicals.[23] It was proposed for norbornene[24,25] that the spin density at the anti proton H_b (Figure 6) resulted from the back lobe overlap of the carbon–hydrogen sp³ orbital with the p_π orbital of the olefin. In general, the back lobe overlap is frequently invoked to explain the coupling and subsequent splittings seen in the magnetic resonance spectra of bicyclic systems.[20–25]

Our results also reveal that the heavy atom effect of halogens situated at the anti-7 position in molecules III and XI and at the exo-2 position in molecule VI is transmitted to the chromophore through the overlap of the back lobe of the σ orbital of the C–Br bond with the π molecular orbitals of the chromophore, as they conform to a W arrangement.

We therefore conclude as follows. The external heavy atom effect is electronic in nature. The heavy atom perturber introduces a number of singlet charge-transfer states with which the triplet states of the chromophore mix through a second-order mechanism involving one-center spin–orbit coupling terms. The magnitude of such mixing and that of the enhancement of the phosphorescence process depends crucially on the orientation of the heavy atom relative to the chromophore.

Appendix

Estimation of $S_{n_0\pi}$. Nowhere in the literature has the formalism of the overlap integral involving the 4p and 2p orbitals (Slater type) been reported. Following the standard procedure we have obtained the general mathematical expressions for the σ and π types of the overlap integrals. They are as follows:

$$\langle 4p_\sigma | 2p_\sigma \rangle = \frac{3}{2}\alpha^{7/2}\beta^{3/2}\frac{1}{\sqrt{6!2!}}\{B_2(A_0 - A_4)$$
$$- 2A_3B_3 - A_2(B_4 - B_0) + 2A_1B_1\} \tag{A.1}$$

$$\langle 4p_\pi | 2p_\pi \rangle = \frac{3}{4}\alpha^{7/2}\beta^{3/2}\frac{1}{\sqrt{6!2!}}\{A_4(B_0 - B_2)$$
$$+ 2A_3(B_1 - B_3) + B_4(A_0 - A_2) + A_2(2B_2 - B_0)$$
$$+ 2A_1(B_3 - B_1) - A_0B_2\} \tag{A.2}$$

Table II

molecules	distance of the Br atom from the nearest C atom/atoms of the chromophore, Å	distance of the Br atom from the next nearest C atom/atoms of the chromophore, Å	distance of the C atom of the C–Br bond from the nearest C atom of the chromophore, Å
II	3.00	3.93	2.24
III	4.13	>5	2.24
VII	2.92	3.44	1.54
VIII	2.68	3.20	2.24
VI	4.25	4.58	2.24

Table III. Overlap Data

molecule	$S_{\sigma\pi}$	$S_{n_0\pi}$
II		0.015
III	0.201	
V		0.012
VI	0.059	
VII		0.015
VIII		0.021
XI	0.160	

where

$$A_K(a) = \int_1^\infty \exp(-au)u^k du \qquad (A.3)$$

$$B_K(b) = \int_{-1}^{+1} \exp(-bv)v^k dv \qquad (A.4)$$

$$a = \frac{1}{2}(\alpha + \beta) \qquad b = \frac{1}{2}(\alpha - \beta) \qquad (A.5)$$

$$\alpha = K_1 R \qquad \beta = K_2 R \qquad (A.6)$$

K_1 and K_2 are the orbital exponents of the 4p and 2p Slater-type orbitals and R is the internuclear distance in atomic unit. The functions A_K and B_K are obtained from the tables of molecular integrals.[26]

Estimation of $S_{\sigma\pi}$. $S_{\sigma\pi}$ involves the overlap between the $2p_\pi$ orbital of the chromophore and the $2p_\sigma$ and 2s orbitals of the carbon atom of the C–Br bond. These data are obtained from the published tables of the overlap integrals.[27]

The structural parameters chosen for the norbornene system are as follows: all bond angles, 109° 28′; C–C bond length, 1.54 Å; C–Br bond length, 1.94 Å. In Table II are given the various distances between the chromophore and the perturber used in the calculations of the overlap.

Besides the above, for the estimation of the overlap the atomic orbital coefficients on each carbon atom of benzene and naphthalene are needed. In most aromatic hydrocarbons,[28] particularly anthracene and higher polyacenes, the intense low-energy band arises primarily from a transition between the highest occupied and the lowest unoccupied π molecular orbitals. This band is polarized along the short axis of the molecule and known as the L_a band. In naphthalene and benzene[28] the lowest energy band known as the L_b band is, on the other hand, the long axis polarized. In view of the strong vibronic coupling between the L_a and L_b states in naphthalene,[29,30] the highest filled π orbital is mixed considerably with the subjacent π orbital. Therefore, for the calculations of the overlap the atomic orbital coefficients on each carbon atom of benzene and naphthalene are chosen respectively as 0.4 and 0.32, which are obtained from the normalization condition. In Table III are given the approximate magnitudes of the important overlap terms.

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