Comparative Study of Spin–Orbital Coupling for Halogenated Ethylbenzenes by a Study of Their Fluorescence

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The effects introduced by a change in the distance separating a chromophore from a non-conjugated perturber upon the fluorescence quantum yield have been investigated. Substitution of a chlorine or bromine atom at either the α- or β-position in ethylbenzene led to a substantial reduction in the quantum yield of fluorescence of the hydrocarbon. The results obtained have been interpreted as providing a quantitative measure of the degree of orbital mixing between chromophore and perturber. The mechanism for the quenching reaction involved spin–orbital coupling and results implicating the involvement of an intermediate, excited state, charge transfer complex (exciplex) have been explained. A quantitative comparison of the fluorescence quenching exhibited by internal and external halogen atoms has been made.

SPIN–ORBITAL coupling provides the mechanism which allows the otherwise 'forbidden' intercombinational transitions of singlet and triplet states of molecules.[1] The phenomenon arises from the magnetic interactions between the orbital motion of an electron and the electron's spin magnetic moment. The magnitude of spin–orbital coupling in most organic molecules is strongly dependent upon the atomic numbers of nuclei near the chromophore.[2] When a heavy atom is substituted into an aromatic molecule the following properties result:[3] (a) the fluorescence quantum yield (ϕ_F) is decreased due to enhancement of the intersystem-crossing rate constant; (b) the phosphorescence quantum yield (ϕ_P) may be increased; (c) the phosphorescence lifetime is decreased; and (d) the oscillator strength of the ($T_1 \longleftarrow S_0$) absorption transition is increased.

EXPERIMENTAL

Materials.—Benzene and ethylbenzene (Hopkin and Williams) were fractionally distilled and the middle fraction collected. The halogenated ethylbenzenes (Eastman) were distilled under reduced pressure and contained no detectable impurity upon g.l.c. analysis. 2-Chloro- and 2-bromobutane (Hopkin and Williams) were fractionally distilled and the middle fraction redistilled. Analysis by g.l.c. indicated that neither contained any impurity. Carbon tetrachloride and cyclohexane were spectroscopic grade (Hopkin and Williams) and showed no impurity upon absorption or fluorescence spectroscopy. Both compounds were distilled prior to use.

Procedure.—Fluorescence spectra were recorded at 270 nm using right-angle excitation geometry with a Perkin-Elmer fluorescence spectrophotometer MPF 2A. Cyclohexane solutions (10^{-3}M) of the fluorescent species were used for the fluorescence quantum yield determinations after purging for 10 min with oxygen-free nitrogen. Quantum yields were determined by comparison with toluene and biphenyl standards according to the procedures recommended by Berlman.[4] The shape and position of the fluorescence spectra were independent of the excitation wavelength which suggested the absence of self-absorption. The quantum yield of fluorescence was independent of concentration within the range 10^{-5}—10^{-2}M so that at a concentration of 10^{-3}M self-quenching *via* excimer formation was negligible. The efficiency of fluorescence quenching by external halogenated compounds was determined by measurement of the change in fluorescence quantum yield of cyclohexane solutions of ethylbenzene (10^{-3}M) in the presence of various concentrations of the quencher. The quencher concentration was always in at least forty-fold excess over that of ethylbenzene.

RESULTS

Halogen Substitution in the Ring.—Direct substitution of a halogen atom into the benzene nucleus resulted in a reduced fluorescence quantum yield (ϕ_{MF}) as indicated by the results in the Table (lines 1—3). These results showed that the efficiency of fluorescence quenching correlated with the spin–orbital coupling constant (ζ) of the halogen atom. Spin–orbital coupling depends not only upon ζ but also upon the excited state singlet–triplet energy gap and upon the degree of mixing between the excited state and the perturbing atom or group.[5] This latter parameter introduces the importance of the distance between the chromophore and a non-conjugated perturber.

Quantum yields for internal quenching of the molecular fluorescence of ethylbenzene [a]

Compound	ϕ_{MF}	$\lambda_{max.}$MF/nm	ϕ_{EF}	$\lambda_{max.}$EF/nm	ζ/cm^{-1}
PhH	0·0518				
PhCl	0·0042	288			587
PhBr	<0·0001	294	<0·0001	314	2,460
$PhCH_2CH_3$	0·1316	284			
$PhCH_2CH_2Cl$	0·0955	283			587
$PhCHClCH_3$	0·0419	308			587
$PhCH_2CH_2Br$	0·0032	303	0·0014	375	2,460
$PhCHBrCH_3$	<0·0001	307	<0·0001	376	2,460

[a] 10^{-3}M Solutions in cyclohexane, purged with nitrogen for 10 min.

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Halogen Substitution in the Side-chain.—The results shown in the Table (lines 4—8) list ϕ_{MF} values for a series of halogen-substituted ethylbenzenes. At the concentration used for this study (10^{-3}M) self-quenching was absent and the differences in the values of ϕ_{MF} obtained were attributed to intramolecular spin–orbital coupling since substitution of a halogen atom into the aromatic nucleus does not result in a significant change in the excited state singlet–triplet energy gap.[6] The absorption spectra of the halogenated compounds were identical with those of the parent hydrocarbons. Previous studies concerned with spin–orbital coupling in bromonaphthonorbornanes [7] failed to find a simple relationship between spin–orbital coupling and the distance between the chromophore and a non-conjugated perturbing atom.

External Halogen Quenching.—A comparison of the magnitude of aromatic hydrocarbon fluorescence quenching by external and internal halogen atoms was made. Linear Stern–Volmer [8] quenching plots were obtained for the quenching of ethylbenzene fluorescence by 2-chloro- and 2-bromo-butane and carbon tetrachloride in cyclohexane solution. Values for the fluorescence quenching rate constant (k_q) for each of these halogenated alkanes were determined from the slope of the Stern–Volmer plot (C_4H_9Cl, $4{\cdot}27 \times 10^7$; C_4H_9Br, $6{\cdot}55 \times 10^7$; CCl_4, $5{\cdot}21 \times 10^9$ l mol^{-1} s^{-1}).

DISCUSSION

The results listed in the Table (lines 4—6) indicated that the ϕ_{MF} value in the presence of a chlorine substituent decreased as the distance between the site of fluorescence and the chlorine atom was reduced although the effect of a β-substituent was still appreciable. The β-chloro-group was more efficient in quenching fluorescence than either hydroxy- or amino-groups attached directly to phenyl.[9] Previous studies [10] have shown bromine to be more efficient than chlorine in fluorescence quenching and the values in the Table (lines 4—8) confirmed this observation. Both an α-bromine atom and a bromine attached directly to the benzene ring gave ϕ_{MF} values $<0{\cdot}0001$ and the difference between these compounds has been determined by relative fluorescence intensity measurements ($PhCHBrCH_3 = 5{\cdot}78$; $PhBr = 1{\cdot}00$). These intensity measurements were made for solutions with identical optical densities at the excitation wavelength. The results for induced fluorescence quenching efficiency for both chlorine- and bromine-substituted compounds paralleled the change in the degree of mixing between the excited singlet state and the halogen atom perturber as the distance between these two species was varied.

Weak, intramolecular, excited state, charge transfer complex (exciplex) fluorescence was observed for the bromine-substituted compounds (Table; lines 3, 7, and 8). Since the quantum yield for exciplex fluorescence (ϕ_{EF}) for both bromobenzene and 1-phenylethyl bromide was $<0{\cdot}0001$, relative fluorescence intensity measurements were again made to compare the fluorescence of these two compounds ($PhBr = 1{\cdot}41$; $PhCHBrCH_3 = 1{\cdot}00$). The ratio of molecular to exciplex fluorescence for phenethyl bromide was 2 whilst the ratio for bromobenzene was $<0{\cdot}1$. These results indicated that exciplex formation was probably an important feature of the fluorescence quenching mechanism.

It has been suggested by Kasha [11] that, with heavy atom quenchers, exciplex formation followed by enhanced inter-system crossing to the exciplex triplet state is the dominant mechanism for impurity quenching. The value of ϕ_{EF} for phenethyl bromide was high when compared with values previously obtained for exciplex fluorescence [12] and this suggests appreciable stabilization of the singlet exciplex state (^1E) in this case. The absence of exciplex fluorescence for internal chlorine substituents may be rationalized in terms of the efficiency of bromine as an electron donor, the stability of charge transfer complexes involving bromine and specific interaction in phenethyl bromide. The stereochemical requirements for the formation of an intramolecular exciplex by bromine–benzene interaction where the bromine atom acts as the donor and the electron deficient $^1S^*$ excited state of the benzene nucleus acts as the acceptor, are fulfilled easily by formation of a five-membered ring (1). A previous investigation [13] reported intramolecular exciplex fluorescence for *NN*-diethyl-1-naphthylalkylamines and *NN*-diethyl-9-anthrylalkylamines in which the alkyl chain length was varied between one and three carbon atoms. For this study,[13] exciplex fluorescence was most intense when the alkyl chain consisted of two or three carbon atoms. The addition of a halogenated solvent to a cyclohexane solution of ethylbenzene did not effect a change in the absorption spectrum but ϕ_{MF} decreased with increasing concentration of halogenated compound. No exciplex fluorescence was observed for the three halides used for external quenching. Carbon tetrachloride showed greatly enhanced quenching efficiency over 2-chlorobutane with a hundred-fold increase in the Stern–Volmer rate constant. Quenching of benzene fluorescence by

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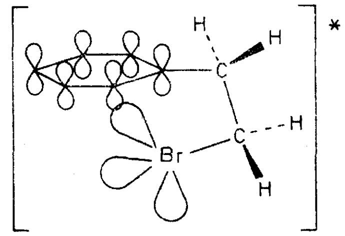

(1)

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halogenated compounds in the vapour phase[14] has also confirmed carbon tetrachloride as a much more efficient fluorescence quencher than monohalogenated alkanes. Concentrations of 7·5M- and 0·05M-2-chlorobutane and -carbon tetrachloride respectively were required to give efficiencies comparable with internal quenching by a β-chloro-substituent.

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