The Effect of Bromine Substitution on the Charge-Transfer Emission of the Complex of Phenanthrene and Tetracyanobenzene

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The absorption spectra of the charge-transfer complexes of sym-tetracyanobenzene (TCNB) with phenanthrene, 9-bromophenanthrene, and 9,10-dibromophenanthrene are measured in chloroform solutions at room temperature. The total emission and phosphorescence spectra of the donors and the complexes are measured at 77 K in rigid glasses. The phosphorescence decay lifetimes are determined for phenanthrene, TCNB, and for the phenanthrene-TCNB complex, and a decrease in the phenanthrene-TCNB complex lifetime relative to the lifetimes of the two components is observed. The luminescence spectra of the complexes exhibit both a red shift and a lack of structure as compared with the donor spectra. The results are interpreted, in agreement with the results of Iwata *et al.* for the phenanthrene-TCNB complex (1), as an indication that there is a considerable degree of charge-transfer character in the lowest triplet state (T_1) . Bromine substitution leads to a decrease in the energy of the phenanthrene triplet state. As a result, the energy gap between the donor molecule triplet state and the complex charge-transfer triplet state decreases from phenanthrene, to 9-bromophenanthrene, to 9.10-dibromophenanthrene. The results suggest that the proximity of these two triplet states in 9.10dibromophenanthrene and its charge-transfer complex leads to some local donor triplet state character in the emitting complex triplet state.

INTRODUCTION

Studies of the charge-transfer complexes of sym-tetracyanobenzene (TCNB) and a number of aromatic hydrocarbons have yielded new insights into the possible photophysical processes in such systems. Iwata *et al.* (1) found that some of these chargetransfer complexes showed phosphorescence characteristic of either the donor or the acceptor. However other complexes, such as those with mesitylene, durene, hexamethylbenzene, phenanthrene, and triphenylene, showed phosphorescence which was markedly different from that of either the donor or acceptor. They assigned this latter type of phosphorescence as occurring from a charge-transfer triplet state. This assignment was verified by later triplet-triplet absorption studies (2-4) and by ESR studies (5). These later studies (4, 5) also gave an estimate of the degree of charge-transfer character in the lowest triplet state from calculations (4) and from ESR (5). The results showed that, in many cases, there was considerable interaction between the pure charge-transfer state and the locally excited donor or acceptor triplet state.

TCNB has a number of characteristics which make it a suitable acceptor in the study of charge-transfer complexes, especially when the donors are compounds with relatively low energy excited states. Because it is an aromatic compound with four nitrile substituents, TCNB has a strongly electron-deficient π system with an electron affinity

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of 1.6 eV (6). It is moderately soluble in organic solvents. Finally, and most importantly for studies of the type in this paper, its lowest electronic states are relatively high in energy $[S_1 \simeq 32,000 \text{ cm}^{-1} (7)]$. This permits the study of charge-transfer and donor transitions without interference from acceptor transitions.

Although there have been some studies of the effect of heavy atom substitution on donor phosphorescence in charge-transfer complexes (&-10), there has been little attention paid to the effect of heavy atom substitution of the donor on phosphorescence which is largely of charge-transfer character. It was with this goal in mind that we began a study of the luminescence behavior of bromine substituted phenanthrenes and their charge-transfer complexes with TCNB.

EXPERIMENTAL

TCNB (Eastman-Kodak reagent grade) was purified by recrystallization from ethanol. Phenanthrene (Eastman-Kodak reagent grade) and 9-bromophenanthrene (Baker reagent grade) were purified by repeated recrystallization from ethanol and zonerefining. 9,10-dibromophenanthrene was synthesized from 9-bromophenanthrene according to Scheme 1. The intermediate and final products were checked by mass





spectroscopy, and no detectable impurity was found in the final product. The synthesized 9,10-dibromophenanthrene was recrystallized twice from ethanol.

Chloroform (Matheson Coleman and Bell, spectroscopic grade) was used for the absorption spectra. Two glasses were used for the emission spectra: EPA (American Instrument Company; diethyl ether: isopentane: ethanol, 5:5:2), and EP (diethyl ether (Fisher microanalysis grade): isopentane (Phillips pure grade), 1:1). The glasses showed no detectable luminescence at 77 K. The EP and EPA glasses were used interchangeably and no difference between the luminescence characteristics of either the donors or the complexes could be detected between the two glasses.

The absorption spectra were measured on a Cary 14 spectrophotometer in a 1 cm quartz cell. The chloroform solutions of the donor and acceptor were separately prepared and mixed immediately before measuring the absorption spectrum of the complex.

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The total emission and the phosphorescence spectra were measured at 77 K using the emission spectrometer described previously (11). The excitation source was a high pressure Mercury-Xenon lamp (200 watt Hanovia 901-B). The phosphorescence spectra were isolated using a rotating can phosphoroscope. The three donor molecules were excited at 315 nm while the complexes were excited at or near the charge-transfer absorption bands at 400 nm, 445 nm, and 425 nm for the phenanthrene, 9-bromophenanthrene complexes respectively. For both the phenanthrene and the 9-bromophenanthrene complexes, no detectable emission could be observed by exciting the donor molecule alone under the same conditions.

The phosphorescence decay times of phenanthrene, TCNB, and the phenanthrene-TCNB complex were measured with the lifetime apparatus described by Charlton and Henry (12). In the measurement of the lifetime of the complex, a Corning glass filter, CSO-52, was placed between the sample and the excitation flash to cut off exciting light below 340 nm.

RESULTS

The absorption spectra for $\lambda > 360$ nm of the donor and its TCNB complex in chloroform solution at room temperature for 9-bromophenanthrene and 9,10-dibromophenanthrene are shown in Figs. 1 and 2. The spectra obtained for phenanthrene and its TCNB complex were the same as were published previously by Iwata *et al.* (1). Since TCNB does not absorb above 350 nm, the change in the absorption spectrum is due to the formation of a charge-transfer complex. The charge-transfer maximum is resolved in the case of the phenanthrene complex, but in the 9-bromosubstituted complex it appears only as a shoulder on the donor absorption. In the 9,10-dibromo-substituted complex, the charge-transfer absorption is completely buried under the donor absorption and is detectable only through the overall enhanced intensity throughout the chargetransfer region.

The total emission spectra of 9-bromophenanthrene and 9,10-dibromophenanthrene are shown in Figs. 3 and 4. The phosphorescence of 9-bromophenanthrene has been



FIG. 1. Absorption spectra of 9-bromophenanthrene and the 9-bromophenanthrene-TCNB complex in CHCl_a at room temperature. Concentration: TCNB = $2 \times 10^{-3} M$, 9-bromophenanthrene = $2 \times 10^{-2} M$.



FIG. 2. Absorption spectra of 9,10-dibromophenanthrene and 9,10-dibromophenanthrene-TCNB complex in CHCl₃ at room temperature. Concentration: TCNB = $2 \times 10^{-3} M$, 9,10-dibromophenanthrene = $1 \times 10^{-2} M$.

observed previously by Goodman and Roy (13) and the phosphorescence portion of Fig. 3 is similar to their spectrum. The total emission and phosphorescence spectra for the TCNB complexes of the three phenanthrene related donors at 77 K are given in



FIG. 3. Total emission spectrum of 9-bromophenanthrene in EPA glass at 77 K. Excitation wavelength = 315 nm. Concentration = $2 \times 10^{-2} M$.



FIG. 4. Total emission spectrum of 9,10-dibromophenanthrene in EPA glass at 77 K. Excitation wavelength = 315 nm. Concentration = $1 \times 10^{-2} M$.

Figs. 5-7. The intensities of the two curves are not comparable since a phosphoroscope was used to isolate the phosphorescence. The phenanthrene-TCNB complex emission has been observed previously by Iwata *et al.* (1). They obtained a value of 19.2×10^3 cm⁻¹ (521 nm) for the charge-transfer phosphorescence maximum in EP glass at 77 K as compared to our result of 19.4×10^3 cm⁻¹ (515 nm). Table I compares the highest wavenumber phosphorescence maxima of the donor molecules to the total emission and



FIG. 5. Total emission and phosphorescence spectra of phenanthrene-TCNB complex at 77 K in EP and EPA glasses, respectively. Excitation wavelength = 440 nm. Concentration: Phenanthrene = $2 \times 10^{-2} M$, TCNB = $1 \times 10^{-3} M$. Intensity of total emission and phosphorescence are not directly comparable.



FIG. 6. Total emission and phosphorescence spectra of 9-bromophenanthrene-TCNB complex at 77 K in EP glass. Excitation wavelength = 445 nm. Concentration: 9-bromophenanthrene = $1 \times 10^{-2} M$, TCNB = $1 \times 10^{-3} M$. Intensities of total emission and phosphorescence are not directly comparable.

phosphorescence maxima for the complexes in EP and EPA glasses. For the broad charge-transfer complex band, the errors given are estimated from a comparison of three measurements.

Finally, Table II gives the phosphorescence decay times of the phenanthrene-TCNB complex and its components in EPA glass at 77 K. The results represent an average obtained from a least-mean-squares analysis of a plot of the logarithm of intensity versus



FIG. 7. Total emission and phosphorescence spectra of 9,10-dibromophenanthrene-TCNB complex at 77 K in EPA glass. Excitation wavelength = 425 nm. Concentration: 9,10-dibromophenanthrene = $1 \times 10^{-2} M$, TCNB = $1 \times 10^{-3} M$. Intensities of total emission and phosphorescence are not directly comparable.

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TABLE 1.

Position of the Emission Maxima of Phenanthrene and its Brownhatd Derivatives, and their (CNB Complexes $(\propto 10^{-4}~{\rm cm}^{-1})$

Molecule	a plans	enterion ^(Complex)	"phos ⁻ (deeplex)
·····	••••		
Phenanthrene	22.0	$(1,6,\pm)0,1^{\mathrm{b}}$	$16.2\pm0.01_{\rm p}$
9-Bromophenanthrene	20.8	19.5 ± 0.1^{b}	$19.5 \pm 0.1^{\mathrm{b}}$
9,10-Dibromophenanthrene	20.3	20.0 + 0.35	$19.7 \pm 0.1^{\circ}$

^aHighest wavenumber phosphorescence maximum in EPA at 77°K.

^bIn EP at 77°K.

^Cin EPA at 77°K.

time for five decay curves. The error quoted is the standard deviation of these measurements. The measured lifetime for phenanthrene agrees with the value of 3.8 sec determined in EPA at 77 K by other workers (14, 15). The lifetime for TCNB is in good agreement with the value of 3.6 sec obtained in ethanol at 77 K by Hayashi *et al.* (5).

DISCUSSION

As has been noted by Iwata *et al.* (1), the emission of the phenanthrene-TCNB complex is primarily charge-transfer in nature. Both the total emission spectrum and the phosphorescence have lost the characteristic structure present in the emission of the component molecules. The phosphorescence is substantially red shifted in the complex relative to phenanthrene. Furthermore the position of the total emission of the complex indicates that the fluorescence component of this emission is also red shifted from the value for phenanthrene.¹ Moreover the phosphorescence decay time of the complex is significantly shorter than the phosphorescence lifetime of either the donor or the acceptor.

Similar results are shown for the 9-bromophenanthrene-TCNB complex. Once again the structured emission spectra of the components are replaced by the broad red shifted

¹ As noted earlier, the higher energies of the excited states of TCNB means that they can be neglected in such comparisons.

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TABLES ()			
Phospherescence Decay Times for Phenanthrene, TCNB, and their Complex in EPA at $77^{\circ}\mathrm{K}_{*}$			
Moleculo	pines (sec)		
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Phenanthrene	1,80 + 0.02		
TENB	3, N2 (+ 10, 04		
Phenanthrene-TCNB	1.09 + 0.03		

emission of the complex. The maxima corresponding to the total emission and the phosphorescence are almost the same which indicates the predominance of phosphorescence over fluorescence as expected from the internal heavy atom effect. This effect is clearly operative in the emission spectra of the donor molecules themselves. Figures 3 and 4 show predominantly phosphorescence (480–580 nm) as compared to the weaker fluorescence at 360 nm and 360–440 nm, respectively. For the phenanthrene complex, the total emission and phosphorescence maxima differ by more than 2000 cm⁻¹. For the bromine substituted complexes (Figs. 6 and 7) however, the principal difference in the total emission and phosphorescence curves is the reduction in intensity in the latter due to the use of a phosphoroscope.

It would appear that both the fluorescence and phosphorescence of the 9,10-dibromophenanthrene-TCNB complex have some charge-transfer character as is evidenced by the loss of structure in emission and the red shift of the phosphorescence. In the case of the phenanthrene and 9-bromophenanthrene complexes, it was possible to excite directly into the charge-transfer state without exciting the pure donor molecule states because the charge-transfer absorption was at a sufficiently lower energy than the donor absorption. However, in the case of 9,10-dibromophenanthrene, the charge-transfer band is coincident with the donor absorption. Still, under many different conditions of excitation, the relative degree of structure and the nature and position of the phosphorescence remained unchanged. Energy criteria also support the contention that the lowest triplet state of the complex has charge-transfer character. The phosphorescence energy of the complex is essentially unchanged for the three complexes, which suggests that they share similar characteristics. On the other hand, the donor triplet energy decreases from phenanthrene, to 9-bromophenanthrene, to 9,10-dibromophenanthrene. As a result, the donor triplet state in this latter molecule is very close in energy to the chargetransfer triplet state. The proximity of the two states increases the probability of their interaction. Such an interaction is suggested in the phosphorescence of the complex (Fig. 7) which does show traces of donor phosphorescence structure.

Christodouleas and McGlynn (8) have studied the internal heavy atom effect on complexes which exhibit phosphorescence of the donor by examining the charge-transfer complexes of naphthalene with trinitrobenzene, tetrachlorophthalic anhydride, tetrabromo-phthalic anhydride, and tetraiodo-phthalic anhydride, in EP glass at 77 K. They found an increase in Φ_P/Φ_F , the ratio of the phosphorescence to the fluorescence yield, due to both charge-transfer complex formation and the heavy atom effect. Both effects led to an increase in intersystem crossing, ${}^{1}(DA)^{*} \longrightarrow {}^{3}(D^{*}A)$ (8). As we have mentioned, qualitatively this corresponds to our results for the heavy atom effect on the charge-transfer fluorescence and phosphorescence of the phenanthrene and the 9-bromophenanthrene complexes. However, here one does not know a priori whether the inductive or electron withdrawing effect of the bromine substituent is dominant over the resonance effect. If the inductive effect were dominant, it would be expected to increase the ionization potential of the phenanthrene donor molecule and thus to weaken the charge-transfer interaction. In this case, the increase in Φ_P/Φ_F in the 9-bromophenanthrene complex, relative to phenanthrene, due to the heavy atom effect would be partly offset by a decrease in $\Phi_{\mathbf{P}}/\Phi_{\mathbf{F}}$ because of decreased charge-transfer interaction. An investigation of such an effect is obviously of some interest but it must await the determination of reasonably accurate fluorescence yields which have proved extremely difficult to obtain for these very weak complexes (16).

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