The Two n,π^* Transitions of Monohalogenoanthraquinones

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The n,π^* absorption and phosphorescence spectra of 1-fluoro-, 2-fluoro, 1-chloro-, 2-chloro-, 1-bromo-, and 2-bromoanthraquinones were studied in solutions, mainly at 77 K. These phosphorescence spectra and their lifetimes resemble those of anthraquinone (AQ), except for those of 1-F-AQ. The phosphorescence spectrum of 1-F-AQ is at longer wavelengths than that of AQ, and its lifetime is 0.8 ms in the methylcyclohexane solution, much shorter than that of AQ. All of the 1-halogenoanthraquinones showed two distinct n,π^* singlet-singlet absorption bands at 77 K, and 1-Br-AQ showed an additional band of the n,π^* singlet-triplet transition at 492 nm. The low-energy n,π^* singlet and triplet states of these compounds are discussed on the basis of these experimental results.

The lowest excited singlet and triplet states of carbonyl compounds including quinones are generally assigned to the n,π^* states. These n,π^* states are thought to be largely localized at the carbonyl groups, because of the strong Coulomb attraction between the excited electron and the remaining non-bonding positive hole. In quinones which have two carbonyl groups, each of the lowest excited singlet and triplet states is expected to consist of two n,π^* states close to each other in energy, as in the case of *p*-benzoquinone.[1] Previously, we have studied the n,π^* phosphorescence spectra of AQ in solutions at 77 K.[2] Recently, high-resolution n,π^* phosphorescence spectra of AQ in crystals and in solutions have been reported on by many authors.[3] In 1-halogenoanthraquinones, as the lone electron-pair of the oxygen and halogen atoms are close to each other, the interaction between them should be large. Therefore, it is very interesting how the n,π^* singlet and triplet levels would be affected by the halogen atom introduced to the 1-position of anthraquinone. Shcheglova *et al.*[4] have already discussed this problem on the basis of the emission spectra obtained by the photographic method, but some problems have remained to be clarified. For instance, no actual n,π^* absorption and emision spectra of monohalogenoanthraquinones have been reported. We have, therefore, studied the n,π^* absorption and emission spectra of monohalogenoanthraquinones at 77 K and discussed the above-mentioned problem.

Experimental

Measurements. The emission spectra and their lifetimes were measured in the methylcyclohexane solutions at 77 K by the way described in our previous paper.[2] A Cary Model 14 spectrophotometer was used to measure the absorption spectra. In the measurement of the absorption spectra at 77 K, the 1-cm cell and the Dewar vessel used in our previous work[5] were used again.

The absorption spectra were obtained in the heptane solutions at room temperature (R. T.) and at 77 K, in the benzene and heptane solutions, which were poly-crystalline at this temperature. Using these poly-crystalline solutions at 77 K, clear and about ten-times-intensified spectra were obtained in comparison with those at R. T., when the concentrations of solutes were regulated for their absorbances so as not to exceed 0.1 at R. T. This enhancement in absorbance is based on a mechanism similar to that which holds in the case of the diffuse-reflectance spectra. Both the benzene and heptane solutions gave almost the same spectra, but the spectra of the former were clearer than those of the latter.

Materials. 1-F-AQ and 2-F-AQ were synthesized from 1- and 2-aminoanthraquinones by diazotization and by the substitution of the diazo group by a fluorine atom[6] respectively. The other monohalogenoanthraquinones were commercially available. All of these quinones were refined by the two methods of vacuum sublimation and liquid column chromatography on alumina (the developer; toluene). The refined sample were melted within 1 °C of their melting points, as is shown in Table 1. The solvents—hexane, methylcyclohexane, benzene, and toluene—were all commercially available spectrograde reagents.

TABLE 1. MELTING POINTS OF MONOHALOGENOANTHRAQUINONES (°C)

1-F-AQ	232.0—233.0 (226—227[5])
1-Cl-AQ	160.5—161.5 (162[7])
1-Br-AQ	190.0—191.0 (188[7])
2-F-AQ	199.0—200.0 (203—204[5])
2-Cl-AQ	208.5—209.5 (208—209[7])
2-Br-AQ	208.4—209.1 (204—205[7])

Results

The observed n,π^* absorption spectra of monohalogenoanthraquinones are shown in Figs. 1 and 2. The spectra of 2-F-AQ and 2-Cl-AQ, which are not shown in these figures, quite resemble that of 2-Br-AQ. The wavelengths of the peaks and shoulders in these absorption spectra are listed in Table 2. The emission spectra of 1- and 2-halogenoanthraquinones in solutions at 77 K are shown in Figs. 3, 4, and 5, while the wave-

TABLE 2. WAVELENGTHS (nm) OF THE ABSORPTION PEAKS AND SHOULDERS

A) Heptane solutions at R.T. (the values in parentheses are molar absorption coefficients)					
1-F-AQ	376,		392.5,		419 (67)
1-Cl-AQ	377,		397.5,		419 (76)
1-Br-AQ	377,		396.5,		419(110[a])
2-F-AQ	374,	376.5,	396.5,	402,	421
2-Cl-AQ	376,	378,	397.7,	405,	424.5
2-Br-AQ	376.5,	379,	398,	405.5,	424 (70[a])
B) Benzene solutions at 77K					
1-F-AQ	400,	410,	413.5,	421.5,	436
1-Cl-AQ	416,	450,			
1-Br-AQ	416.5,	435,	460,	492	
2-Br-AQ	406,	416.5			

a) Values in the toluene solutions.

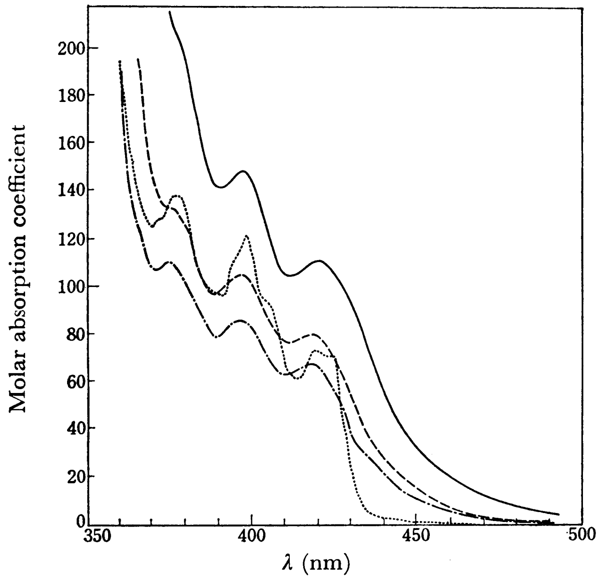

Fig. 1. Absorption spectra in the heptane solutions at R.T.
——: 1-Br-AQ, - - - -: 1-Cl-AQ, -·-·-: 1–F–AQ, and ····: 2-Br-AQ. The scale of the ordinate for 1-Br- and 2-Br-AQ's is arbitrary.

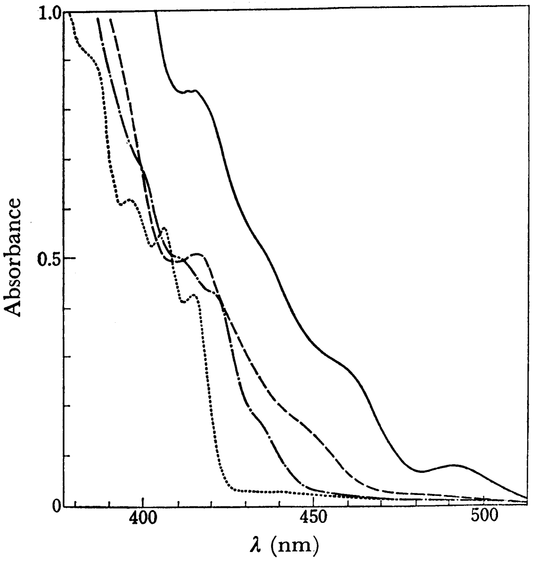

Fig. 2. Absorption spectra in the benzene solutions at 77 K.
——: 1-Br-AQ, - - - -: 1-Cl-AQ, -·-·-: 1-F-AQ, and ····: 2-Br-AQ. The scale of the ordinate is arbitrary.

Table 3. Wavelengths (nm) of the emission peaks in the methylcyclohexane solutions at 77 K

1-F-AQ	476.6	517.2	565.5	622.5
1-Cl-AQ	456.5	493.7	537.5	589.3 (515, 560)[a]
1-Br-AQ	456.8	493.7	538.0	589.4
2-F-AQ	454.4	492.1	535.5	587.1
2-Cl-AQ	458.2	495.4	539.7	592.7
2-Br-AQ	458.4	496.0	540.5	593.2

a) Those of the shorter-lifetime component.

Table 4. Lifetimes (ms) of the phosphorescence bands in the methylcyclohexane solutions at 77 K

1-F-AQ	0.8
1-Cl-AQ	3.5, $\lesssim 0.1$
1-Br-AQ	3.5
2-F-AQ	3.2
2-Cl-AQ	3.3
2-Br-AQ	2.5

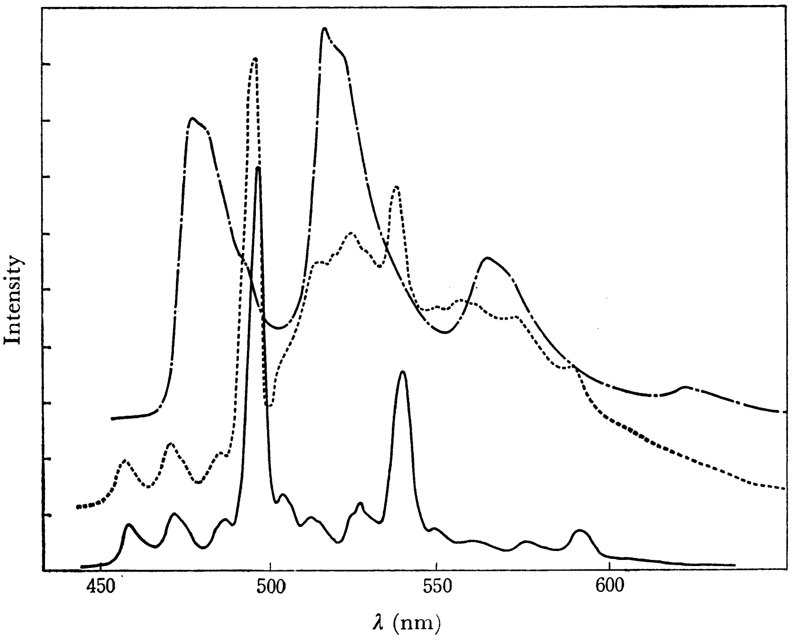

Fig. 3. Phosphorescence spectra of 1-halogeno AQ's in the methylcyclohexane solutions at 77 K, ——: 1-Br-AQ, - - - -: 1-Cl-AQ, and -·-·-: 1-F-AQ.

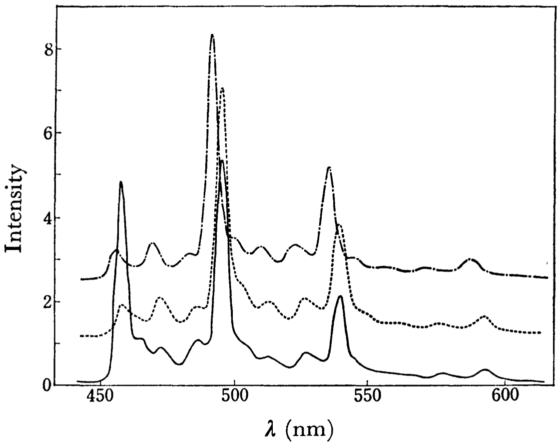

Fig. 4. Phosphorescence spectra of 2-halogeno AQ in the methylcyclohexane solutions at 77 K, ——: 2-Br-AQ, ----: 2-Cl-AQ, and -·-·-: 2-F-AQ.

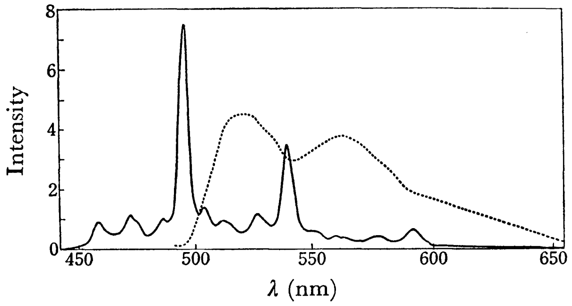

Fig. 5. The two components of the phosphorescence of 1-Cl-AQ in the methylcyclohexane solution at 77 K, ——: the phosphorescence with longer lifetime, and ····: that with shorter lifetime.

lengths of their peaks and their lifetimes are listed in Tables 3 and 4 respectively. The shoulder at 493 nm in the emission spectrum of 1-F-AQ became smaller and smaller as the sample was refined repeatedly, and its position was the same as those of the highest peaks of 1-Cl-AQ and AQ (see Fig. 3). Therefore, it may be considered to be due to some impurities.

The total emission of 1-Cl-AQ consists of two components which are different in lifetime. The emission spectrum with the longer lifetime of 3.5 ms could be observed separately with a sector, while that with the shorter lifetime was obtained as the difference between the total spectrum and the spectrum obtained with the sector. This shorter lifetime was too short to be measured. The intensity ratio of the longer-lifetime spectrum to the shorter-one was about 1: 2. These two spectra are shown in Fig. 5.

Discussion

In 1-halogenoanthraquinones, one of the two carbonyl groups is adjacent to the halogen atom, and the lone electron-pair orbital of its oxygen atom is thought to overlap considerably with that of the halogen atom. 1-Halogenoanthraquinones may be destabilized by this overlapping in the ground state, and stabilized by the charge-transfer interaction between the vacant n-orbital of the carbonyl group and the occupied n-orbital of the halogen atom in the n,π^* excited state. Therefore, one of these two lowest-energy n,π^* states, which is mainly localized at the carbonyl group adjacent to the halogen atom, may be considerably lower in energy than the other, which is mainly localized at the other carbonyl group. The order of the magnitudes of the separations between these two n,π^* levels is thought to be equal to the order of the van der Waals radii of the halogen atoms; Br>Cl>F.

As may be seen in Fig. 1, the n,π^* absorption spectra of the 1-halogenoanthraquinones at R.T. are similar to that of 2-Br-AQ, which in form is very similar to that of AQ, except for the long tails in the region of 430—500 nm. These tails and the shorter-wavelength absorption bands are considered to be due to the transition from the ground state to the above-mentioned lower and higher n,π^* singlet excited states respectively. As for the n,π^* absorption spectra at 77 K, which are shown in Fig. 2, the spectra of the 1-halogenoanthraquinones show structures up to 500 nm; the spectrum of 1-Br-AQ, for example, has three shoulders, at 416.5, 435, and 460 nm, and one peak, at 492 nm. The shoulder at 416.5 nm may be assigned to the shorter-wavelength n,π^* band, and the shoulders at 435 and 460 nm, to the longer-wavelength n,π^* bands. The absorption peak at 492 nm may be assigned to the n,π^* singlet-triplet absorption band intensified by the internal heavy-atom effect of the bromine atom, since the corresponding absorption in 1-Cl-AQ and 1-F-AQ cannot be found. This absorption peak may not be assigned to the π,π^* singlet-triplet absorption band, because a corresponding absorption cannot be observed in 2-Br-AQ. Since the n,π^* bands and the tails of the lowest π,π^* band of monohalogenoanthraquinones shift toward blue and red to a considerable extent at 77 K compared with those at R.T. (see Figs. 1 and 2), the spectra at 77 K are thought to be those of aggregates. In general, the n,π^* states in aggregates may be considered to be similar to those in solutions because of their localizing character. In this discussion, the electronic structures of the n,π^* states in these aggregates were assumed to be similar to those in isolated molecules, except for small energy shifts.

The emission spectra of the monohalogenoanthraquinones in solutions at 77 K can all safely be assigned to the n,π^* phosphorescence, since they have, as may be seen in Figs. 3, 4, and 5, the principal vibrational structure of the carbonyl stretching frequency (*ca.* 1640 cm^{-1}) and the short lifetime of the order of a millisecond (see Table 4). These phosphorescence spectra quite resemble that of AQ in position, shape, and lifetime, except for that of 1-F-AQ and the shorter lifetime spectrum of 1-Cl-AQ.

As for the phosphorescence spectrum of 1-F-AQ, it lies at longer wavelengths (the energy difference is *ca.* 900 cm^{-1}) and has a shorter lifetime, than the spectra of the other monohalogenoanthraquinones. The phosphorescence quantum yields of 1-F-AQ, 1-Cl-AQ (total), and 1-Br-AQ were roughly estimated to be in the ratio of 3: 1: 1 by considering the relative absorbances at 420 nm of the n,π^* S_1-S_0 bands in nearly saturated methylcyclohexane solutions at R.T. and the relative intensities of the phosphorescences with excitations at 420 nm in the same solutions. According to this estimation, the phosphorescence of 1-F-AQ would have a much shorter natural lifetime than the others. The shorter-lifetime spectrum of 1-Cl-AQ, which has the vibrational structure of the C–O stretching and which lies at an energy lower by *ca.* 1000 cm^{-1} than that of 1-F-AQ is too broad to discuss in detail, but it may be assigned to the same kind of emission as that of 1-F-AQ.

On the basis of these facts, it may be concluded that the phosphorescence of 1-F-AQ and the shorter-lifetime emission of 1-Cl-AQ correspond to the emission from the above-mentioned lower n,π* triplet state, and that the phosphorescence of 1-Br-AQ and the longer-lifetime emission of 1-Cl-AQ correspond to that from the upper n,π* triplet state. In 1-Br-AQ and 1-Cl-AQ, the internal conversion between the two n,π* triplet states may be slow, since these states are considered, as has been mentioned before, to be mainly localized on the two carbonyl groups separately, far from each other and with a large energy difference between them. Therefore, the phosphorescence from the upper state can be observed in these molecules. However, this internal conversion may be faster in 1-F-AQ because of the small energy difference between these two states, so the emission from the upper state cannot be observed.

As for the phosphorescence of 1-F-AQ and the shorter-lifetime emission of 1-Cl-AQ, their lifetimes may be shortened by the relatively fast, radiationless process from the phosphorescent lower n,π* triplet state, which is due to the before-mentioned interaction between lone-pair orbitals of the oxygen atom and the adjacent halogen atom. In the case of 1-Br-AQ, the emission from the lower state may not be observed because of the slow internal conversion between the two n,π* states and the fast radiationless process from the lower n,π* state to the ground state, mainly due to the heavy atom effect of the bromine atom.

The n,π* singlet and triplet levels of 1-halogeno-anthraquinones and the phosphorescent processes, considered on the basis of the above discussion, are shown in Fig. 6.

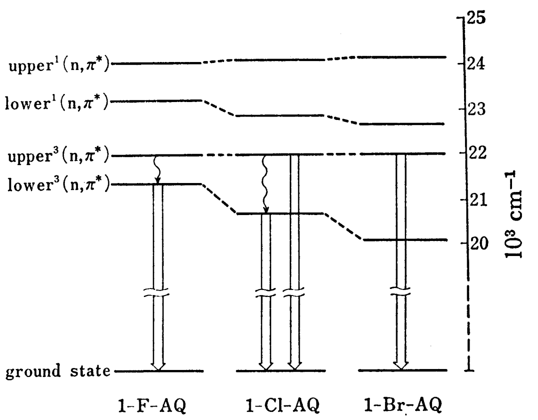

Fig. 6. Energy levels and phosphorescent processes of 1-halogeno AQ's, ⟹; phosphorescence, ⇝; internal conversion.

Shcheglova *et al.* have given a similar discussion of the two n,π* triplet states of the 1-halogenoanthraquinones based on their experimental results, and they have claimed that lower n,π* states of 1-Cl-AQ and 1-Br-AQ are not discrete but continuous states. This explanation may be rejected on the basis of this work.

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