The Phosphorescence Spectra of Methyl-substituted 9,10-Anthraquinones in Solutions at 77 K

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The phosphorescence spectra and their lifetimes of 9,10-anthraquinone and its 2-methyl and 2,3-dimethyl derivatives in various kinds of glassy solutions at 77 K have been obtained. In the non-hydrocarbon solutions, 2-methylanthraquinone shows, in most cases, a dual phosphorescence, consisting of a $n\pi^*$ phosphorescence and a $\pi\pi^*$ phosphorescence with different lifetimes, while 2,3-dimethylanthraquinone shows a very broad $\pi\pi^*$ phosphorescence spectrum. The quinone-solvent interactions and the relative positions of the close-lying $^3n\pi^*$ and $^3\pi\pi^*$ levels of these quinones are discussed on the basis of the experimental results.

Previously, we have studied the phosphorescence spectra of 9,10-anthraquinone[1,2] (AQ) in various solutions at 77 K. All the phosphorescence spectra observed have been of the $n\pi^*$ type, having a distinct progression of the C–O stretching vibration and a short lifetime around 3 ms. Recently, we have observed the $\pi\pi^*$ phosphorescence spectra of alkylsubstituted 1,4-naphthoquinones[3] in glassy solutions at 77 K, while in 1,4-naphthoquinone only the $n\pi^*$ phosphorescence spectra have been observed in all the solutions. This is thought to be due to the rise of the phosphorescent $n\pi^*$ level and the fall of the low-lying $^3\pi\pi^*$ level of 1,4-naphthoquinone in the alkyl derivatives, resulting from the alkyl-group substitutions and the specific (hydrogen-bond and charge-transfer) and dispersion-force[4] interactions between the quinones and solvents. In this work, the phosphorescence spectra of the methyl-substituted anthraquinones, 2-methyl- and 2,3-dimethyl-AQ's, in various kinds of glassy solutions at 77 K have been studied from this point of view. The phosphorescence spectra of AQ in those solutions have also been studied for the purpose of comparison.

Experimental

Measurements. The phosphorescence spectra and their lifetimes in solutions at 77 K were measured using a phosphoroscope in the manner described in previous papers.[1-3] The solvents used were methylcyclohexane, toluene, ethanol, methanol, and 1-chloro- and 1-bromobutanes. All the solutions were glassy at 77 K. In the toluene solutions, the crystalline state was also formed by slow-cooling.[2] The concentrations of the solutions used always less than 10^{-3} mol dm^{-3}.

Materials. The AQ and the methyl-substituted anthraquinones used were commercially available. The AQ and 2-methyl-AQ were zone-refined (mp 286.6—287.2 °C and 176.6—177.5 °C). The 2,3-dimethyl-AQ was twice recrystallized, from a toluene–cyclohexane (1 : 2) mixture and from acetic acid (mp 207.5—208.8 °C). Spectrograde methylcyclohexane, methanol, and toluene of the Dozin Yakukagaku Co., analytical-grade ethanol of Wako Pure Chemical Industries, and G.R.-grade 1-choro- and 1-bromobutanes of the Tokyo Kasei Kogyo Co. were used.

Results. The phosphorescence spectra obtained are shown in Figs. 1—6, while their observed lifetimes are shown in Table 1.[5] In the methyl-substituted anthraquinones, the phosphorescence spectra depend on the turning-rate of the sector and the excitation-wavelength in some cases, but show no concentration dependence. In AQ, the phosphorescence spectra show none of these dependences. In the captions of Figs. 3—5, the words in parentheses, "slow" and "fast", denote that the turning-rates of the sector are slow and fast respectively. In the captions of Figs. 5 and 6, the wavelengths in parentheses denote the excitation-wavelengths. When the phosphorescence spectra showed sector-turning-rate dependences, two kinds of lifetimes were obtained, the shorter ones of which were obtained with the sector turning relatively fast, and the longer ones of which, with the sector turning as slow as possible.

Discussion

AQ shows only the $n\pi^*$ phosphorescence spectra in the solvents used in this work at 77 K; they show a distinct progression of the C–O stretching vibration and short lifetimes (Figs. 1 and 2 and Table 1).[6] Therefore, AQ may have the T_1 $n\pi^*$ state in these cases.[7] The phosphorescence spectrum of AQ in a toluene crystal is at wavelengths longer by *ca.* 250 cm^{-1} than that in toluene glass, and is situated very close to that in methylcyclohexane. Therefore, the charge-transfer interaction between AQ and toluene in a toluene crystal may be very small. Similar phenomena are also observed in the cases of the methyl-substituted anthraquinones, as will be mentioned later.

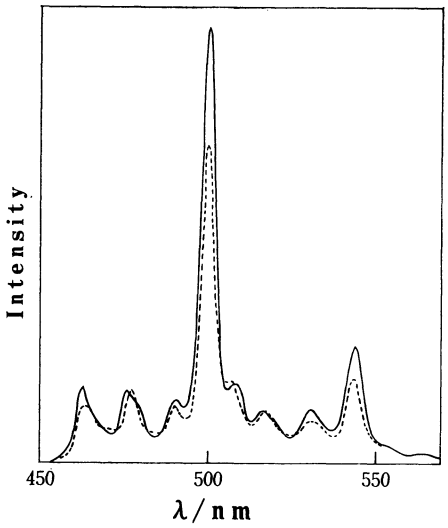

Fig. 1. Phosphorescence spectra of AQ and 2,3-dimethyl-AQ in methylcyclohexane at 77 K.
——: AQ, ------: 2,3-dimethyl-AQ.

TABLE 1. OBSERVED LIFETIMES, τ, OF THE PHOSPHORESCENCE SPECTRA

	τ/ms					
Solvent	Methylcyclohexane	Toluene	Ethanol	Methanol	1-Chlorobutane	1-Bromobutane
AQ	3.3	3.6 (3.4)[a]	3.3	3		3.1
2-Methyl-AQ	4.6	17 86 (4.7)	5	13 47	7 64	7 29
2,3-Dimethyl-AQ	5.1	100 (7.6)	92	150	73	19

a) The values in parentheses are the ones in toluene crystals.

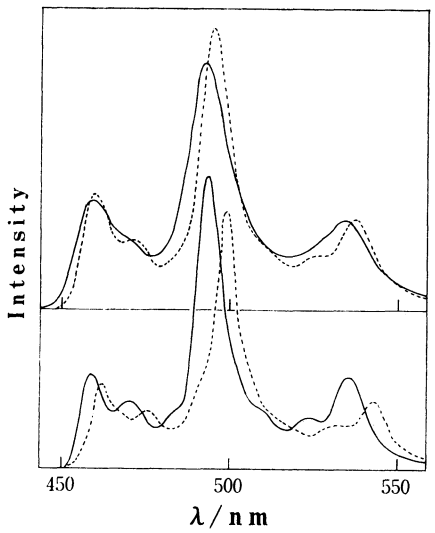

Fig. 2. Phosphorescence spectra of AQ in solutions at 77 K.
(1) Lower curves, ——: toluene glass, ------: toluene crystals, (2) Upper curves, ——: methanol, ------: 1-bromobutane.

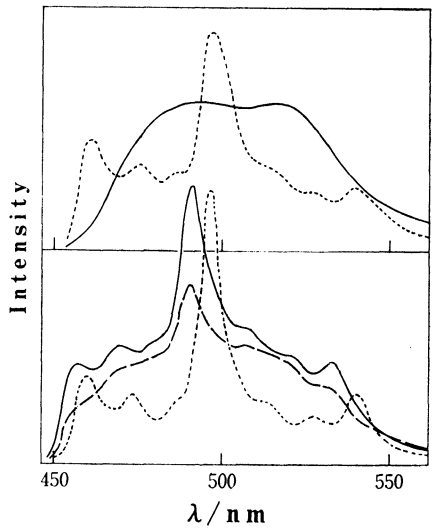

Fig. 3. Phosphorescence spectra of 2-methyl- and 2,3-dimethyl-AQ's in toluene at 77 K.
(1) Lower curves, 2-methyl-AQ, ——: glass (fast), — —: glass (slow),------: crystals, (2) upper curves, 2,3-dimethyl-AQ, ——: glass, ------: crystals.

The phosphorescence bands of the methyl-substituted anthraquinones in methylcyclohexane (Fig. 1)[13] may reasonably be assigned to the $n\pi^*$ spectrum because of their similarity to that of AQ and their short lifetimes (Table 1). Since the positions of the phosphorescence spectra of the methylsubstituted anthraquinones are very close to that of AQ, the rise in the T_1 $n\pi^*$ levels of the methyl-substituted anthraquinones relative to that of AQ may be very small. As may be seen in Table 1, the lifetime of 2-methyl-AQ is a little longer and a little shorter respectively than those of AQ and 2,3-dimethyl-AQ. This may be due to increases in the mixing[14-16] of the close-lying $^3\pi\pi^*$ state into the T_1 $n\pi^*$ state in these methyl-substituted anthraquinones, accompanied by decreases in the energy separation between these two states resulting from the methyl-group substitutions.

The phosphorescence spectrum of 2-methyl-AQ in toluene glass, obtained with the sector turning fast (Fig. 3), is considerably broader than that of AQ in toluene glass, while the one obtained with the sector turning slow is still broader. In this case, two considerably different lifetimes (17 and 86 ms) are obtained (Table 1). In these spectra, two kinds of phosphorescence spectra, the relatively sharp $n\pi^*$ spectrum and the broad $\pi\pi^*$ spectrum, seem to overlap. The above facts may be explained as follows. As the shorter lifetime (17 ms) is too long as that of the $n\pi^*$ spectrum, it is thought that 2-methyl-AQ in toluene glass has the T_1 $\pi\pi^*$ state and that the energy separation between the T_1 $\pi\pi^*$ state and the close-lying T_2 $n\pi^*$ state is distributed according to the degree of solvation of the quinone molecules.[17] Consequently, the degree of mixing of the T_2 $n\pi^*$ state into the T_1 $\pi\pi^*$ state and the rate of thermal population to the T_2 $n\pi^*$ state in the excited states[18] may take various values. Hence, dual phosphorescences, consisting of the $n\pi^*$ and $\pi\pi^*$ spectra, appear with various figures and lifetimes.

In the toluene glassy solution of 2,3-dimethyl-AQ, the very broad phosphorescence spectrum may be assigned to the $\pi\pi^*$ spectrum because of the absence of the C–O stretching vibrational structure and its long lifetime (100 ms). Previously, in the toluene glassy solution of 2-methyl-1,4-naphthoquinone, a similar, very broad phosphorescence spectrum with a short lifetime (2.0 ms) was observed. The difference in the lifetime between these two quinones is remarkable. Since the intensity of the latter phosphorescence spectrum is considerably weaker than that of the former, the short lifetime of the latter may be mainly due to the existence of some efficient non-radiative dissipative route from the

phosphorescence state.

The above differences in the phosphorescence spectra of 2-methyl- and 2,3-dimethyl-AQ's between the methylcyclohexane and toluene glass solutions may be partly due to the rise in the $^3n\pi^*$ levels resulting from the π-π type charge-transfer interaction between the quinones and toluene, and partly due to the fall in the $^3\pi\pi^*$ levels resulting from the relatively strong dispersion-force interaction between the quinones and toluene.[19] The phosphorescence spectra of the methylsubstituted anthraquinones in toluene crystal may be assigned to the $n\pi^*$ spectra because of their similarity to that of AQ and their short lifetimes, close to those in the methylcyclohexane solution.

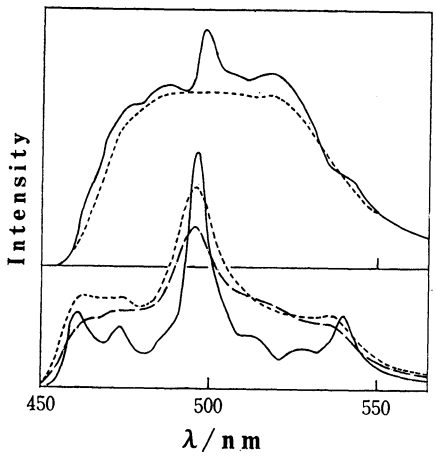

Fig. 4. Phosphorescence spectra of 2-methyl- and 2,3-dimethyl-AQ's in alcohols at 77 K.
(1) Lower curves, 2-methyl-AQ, ——: ethanol, ------: methanol (fast), — —: methanol (slow), (2) Upper curves, 2,3-dimethyl-AQ, ——: ethanol, ------: methanol.

In the methanol solution of 2-methyl-AQ (Fig. 4), a dual phosphorescence similar to that in the toluene solution is observed. As the shorter lifetime (13 ms) is close to that in the toluene solution, the T_1 state of 2-methyl-AQ in methanol is thought to be the $\pi\pi^*$ state, as in the toluene solution. On the other hand, in the ethanol solution of 2-methyl-AQ, the T_1 state may be the $n\pi^*$ state, as its phosphorescence spectrum show a distinct C–O stretching vibrational structure and its lifetime is short.

2,3-Dimethyl-AQ in methanol may have the T_1 $\pi\pi^*$ state because of the similarities of the phosphorescence spectrum and its lifetime to those in the toluene glassy solution. In the phosphorescence spectrum of 2,3-dimethyl-AQ in ethanol, the sharp $n\pi^*$ and broad $\pi\pi^*$ spectra seem to overlap, but the relative weight of the former seems to be far smaller than that of the latter. In view of the above relative weights of the two spectra and the sector-turning-rate independence of the phosphorescence spectrum, it is thought that the $^3\pi\pi^*$ level is lower than the $^3n\pi^*$ level, and that the $n\pi^*$ spectrum appears weakly because of the thermal population in the excited states. The above results indicate that the hydrogen-bond between ethanol and the quinones is,

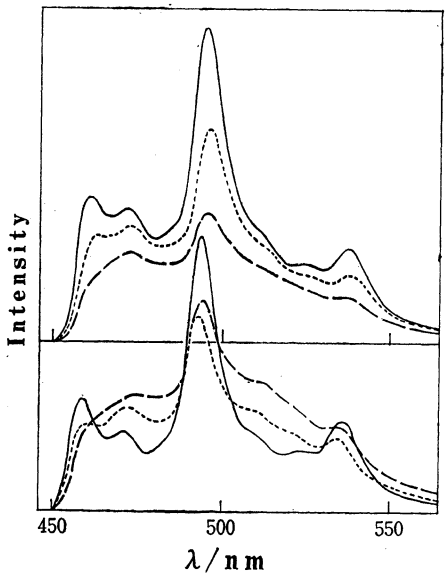

Fig. 5. Phosphorescence spectra of 2-methyl-AQ in 1-chloro and 1-bromobutanes at 77 K.
(1) Lower curves, 1-chlorobutane, ——: (fast, 313 nm), ------: (fast, 365 nm), — —: (slow, 313 nm), (2) upper curves, 1-bromobutane, ——: (fast, 313 nm), ------: (fast, 365 nm), — —: (slow 313 nm).

to some extent, weaker than that between methanol and the quinones.

In the 1-chloro- and 1-bromobutanes solutions of 2-methyl-AQ, dual phosphorescences similar to those in the toluene and methanol solutions are observed (Fig. 5). In these 1-halogenobutane solutions, however, as the shorter lifetimes (7 ms in both solutions) are considerably shorter than those in the toluene and methanol solutions, and are rather close to those in the methylcyclohexane and ethanol solutions, it is thought that differently solvated species which have either the T_1 $n\pi^*$ or the T_1 $\pi\pi^*$ state coexist and that the shorter

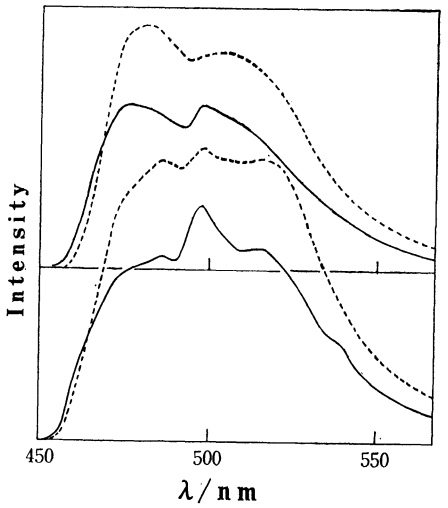

Fig. 6. Phosphorescence spectra of 2,3-dimethyl-AQ in 1-chloro and 1-bromobutanes at 77 K.
(1) Lower curves, 1-chlorobutane, ——: (313 nm), ------: (365 nm), (2) upper curves, 1-bromobutane, ——: (313 nm), ------: (365 nm).

TABLE 2. ASSIGNED T_1 STATES OF THE QUINONES[a)]

Solvent	Methylcyclohexane	Toluene	Ethanol	Methanol	1-Chlorobutane	1-Bromobutane
AQ	$n\pi^*$	$n\pi^*$ ($n\pi^*$)	$n\pi^*$	$n\pi^*$	$n\pi^*$	$n\pi^*$
2-Methyl-AQ	$n\pi^*$	$\pi\pi^*$ ($n\pi^*$)	$n\pi^*$	$\pi\pi^*$	$n\pi^*$, $\pi\pi^*$	$n\pi^*$, $\pi\pi^*$
2,3-Dimethyl-AQ	$n\pi^*$	$\pi\pi^*$ ($n\pi^*$)	$\pi\pi^*$	$\pi\pi^*$	$\pi\pi^*$	$\pi\pi^*$

a) The states in parentheses are the ones in toluene crystals.

lifetimes are due to the species which have the T_1 $n\pi^*$ state. In the 1-halogenobutane solutions of 2,3-dimethyl-AQ, in view of their phosphorescence spectra (Fig. 6), it is thought that the $^3\pi\pi^*$ level is lower than the $^3n\pi^*$ level, and that the weak appearances of the sharp $n\pi^*$ spectrum are due to the thermal population in the excited states, as in the ethanol solution.

As may be seen in Fig. 5, with the same turning-rate of the sector the weights of the sharp $n\pi^*$ spectrum relative to the broad $\pi\pi^*$ spectrum are considerably larger in the 313 nm excitation than in the 365 nm excitation. Similar excitation-wavelength dependences are seen in the case of 2,3-dimethyl-AQ in Fig. 6. In a previous work,[3)] a similar phenomenon was also observed in the phosphorescence spectrum of 2-methyl-1,4-naphthoquinone in ethanol at 77 K, where the weight of the sharp $n\pi^*$ spectrum relative to the broad $\pi\pi^*$ spectrum was larger in the 365 nm excitation than in the 313 nm excitation. No definitive explanation of these facts can be obtained at this stage.

In Table 1, the lifetimes corresponding to those of the $\pi\pi^*$ phosphorescence spectra of the methyl-substituted anthraquinones in 1-bromobutane are quite short in comparison with those in the 1-chlorobutane solutions. This may be due to the intermolecular heavy-atom effect[20)] brought about by the bromine atom in 1-bromobutane.

The T_1 states of these quinones in the solutions assigned in this work are shown in Table 2. When the quinone molecules with the T_1 $n\pi^*$ and $\pi\pi^*$ states are thought to coexist, both of the two states are described in Table 2. The results obtained in this work may be useful in studying the photochemistry of these quinones.

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4) In general, the dispersion-force interaction between solutes and solvents brings about far larger red-shifts for $\pi\pi^*$ spectra than for $n\pi^*$ spectra, and so under this interaction the $\pi\pi^*$ levels become much lower than the $n\pi^*$ levels.

5) In a previous paper,[1)] the observed lifetime of the phosphorescence spectrum of AQ in a methylcyclohexane–toluene (4 : 1) mixture at 77 K (6.3 ms) is erroneous; the correct value is 3.8 ms.

6) The phosphorescence spectra of AQ in ethanol and 1-chlorobutane are similar to those of 2-methyl-AQ in ethanol (Fig. 4) and of AQ in 1-bromobutane (Fig. 2) respectively.

7) AQ is thought to have two low-energy triplet levels, $n\pi_+^*$ and $n\pi_-^*$, like *p*-benzoquinone.[8,9)] In the text, the $n\pi^*$ triplet level corresponds to the lower one of them, while the higher one is neglected in order to simplify the discussion. According to the CNDO/S-Cl[10)] calculations,[11)] in *p*-quinones the triplet $n\pi_-^*$ level (the $^3B_{1g}$ level in AQ) is lower than the $n\pi_+^*$ level (the ^3A_u level in AQ).[12)]

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19) The refractive index of toluene ($n_D^{20}=1.497$) is considerably larger than that of methylcyclohexane ($n_D^{20}=1.423$). Therefore, the dispersion-force interaction between quinones and toluene is thought to be considerably larger than that between quinones and methylcyclohexane.

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