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The Phosphorescence Spectra of 1,4-Naphthoquinone and Its Alkyl Derivatives in Solutions at 77 K

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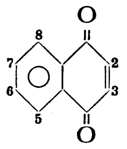
The phosphorescence spectra of 1,4-naphthoquinone (NQ), 2-methyl-, 2,6-dimethyl-, 2,6-diisopropyl-, and 2,6-di-*t*-butyl-NQ's in various kinds of solutions at 77 K were studied. The phosphorescence bands of NQ and 2,6-di-*t*-butyl-NQ in all the solutions and those of the other NQ's in saturated hydrocarbon solutions are assigned to the n,π* band. In the ethanol solution, 2-methyl-NQ shows a dual phosphorescence, the lifetimes of which are different and which depends on the excitation wavelength. In the Daifloil solutions, 2-methyl- and 2,6-dimethyl-NQ's also show a dual phosphorescence. In the toluene solutions, these two NQ's show remarkably broad phosphorescence bands. These facts are discussed on the basis of the electronic structures at the excited states of these NQ's.

Heretofore, we have studied the n,π* phosphorescence spectra of various kinds of quinones in solutions at 77 K.[1–3] In many organic solvents, 1,4-naphthoquinone (NQ) shows n,π* phosphorescence at 77 K, while 2,3-dimethyl-NQ shows no n,π* phosphorescence. In this connection, it is interesting to study the phosphorescence spectra of other NQ alkyl derivatives. However, few studies of the phosphorescence spectra of NQ alkyl derivatives have been reported.[4] In this work, we have studied the phosphorescence spectra of NQ, 2-methyl-, 2,6-dimethyl-, 2,6-diisopropyl-, and 2,6-di-*t*-butyl-NQ's in various kinds of solutions at 77 K.



(NQ)

Experimental

Measurements. The phosphorescence spectra and their lifetimes in solutions at 77 K have been measured using an Aminco-Bowman spectrofluorophotometer in the manner described in previous papers.[1–3] Hg 313 and 365 nm lines of a Hanovia 150W xenon-mercury lamp were used as the exciting light. Two photomultipliers, HTV R106 and R105UH, were used for the measurements of phosphorescence spectra and their lifetimes respectively. The spectral response of the photomultiplier tube and the spectral transmittance of the monochromator have not been taken into account. The concentrations of sample solutions ranged from 10^{-3} to 10^{-5} mol/dm^3. The solvents used were normal paraffins (hexane, heptane, and octane), methylcyclohexane, ethanol, Daifloil (polymers of trifluorochloroethylene), and toluene. Except for the case of normal paraffins, all the solutions formed the glass state at 77K.

Materials. Commercially-available NQ was purified by active-carbon treatment in cyclohexane (mp 124.3—125.3 °C). Commercially-available 2-methyl-NQ was purified by the zone-melting method (mp 106.8—107.4 °C). 2,6-Dimethyl-, 2,6-diisopropyl-, and 2,6-di-*t*-butyl-NQ's[5,6] were synthesized from 2,6-dimethyl, 2,6-diisopropyl, and 2,6-di-*t*-butylnaphthalenes respectively. 2,6-Dimethyl-NQ was purified by vacuum sublimation, and the others, by recrystallization from ethanol (mp 138.0—139.0 °C, 62.5—63.5 °C, and 84.0—85.0 °C respectively). Spectro-grade hexane, heptane, methylcyclohexane, and toluene of the Dozin Yakukagaku Co., spectro-grade octane of the Tokyo Kasei Kogyo Co., analytical-grade ethanol of the Wako Junyaku Kogyo Co., and Daifloil ♯1 (mean molecular weight 500) of the Daikin Kogyo Co. were used without further purification.

Results

The phosphorescence spectra of all the NQ's in the saturated hydrocarbon solutions slowly cooled were too weak to be observed, while those in other solutions slowly cooled were almost the same in all respects as those in these solutions rapidly cooled. Therefore, in this paper the phosphorescence spectra of the sample solutions rapidly cooled are reported. The main phosphorescence spectra obtained are shown in Figs. 1—7. The wavelengths of the main peaks and the observed lifetimes of the phosphorescence spectra are shown in Tables 1 and 2 respectively. No phosphorescence spectrum can be observed for 2,6-di-*t*-butyl-NQ in the normal paraffin solutions. The spectrum of 2,6-dimethyl-NQ in the toluene solution is similar to that of 2-methyl-NQ in Fig. 7.

Discussion

First, the phosphorescence spectra of the saturated hydrocarbon solutions of the NQ's will be discussed. They may be assigned to the n,π* phosphorescence

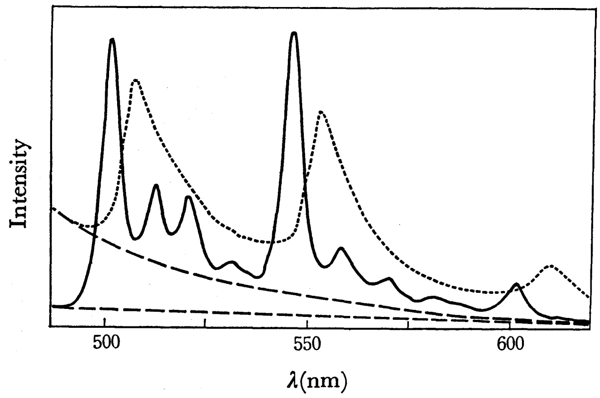


Fig. 1. Phosphorescence spectra of NQ and 2,6-(t-Bu)$_2$-NQ in solutions, 77 K.

——: NQ, hexane, ----: 2,6-(t-Bu)$_2$-NQ, methylcyclohexane.

Table 1. Main peak wavelengths in the phosphorescence spectra (nm)

	Methyl-cyclohexane	Hexane	Heptane	Octane	Ethanol	Daifloil	Toluene
NQ	501.5	501.5			498.5	495	493
	547	546.5			541.5	538	539
2-Me-NQ	497	496	496		498.5	497.5	≈521
	541.5	541	498.5		510.5	540.5	≈544.5
			540		541.5		
			544.5				
2,6-Me$_2$-NQ	496.5		498.5	493.5	513.5	498	≈521
	541		543.5	538	545.5	510	≈547.5
						540	
2,6-(*i*-Pr)$_2$-NQ	501	501	501		502	500	515
	546.5	545.5	545		546.5	543	547.5
2,6-(*t*-Bu)$_2$-NQ	507.5				506	504.5	509
	554				550.5	550	553

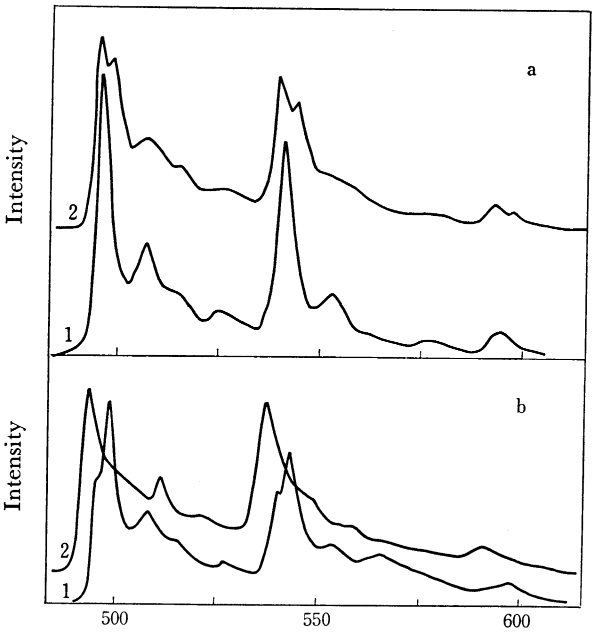


Fig. 2. Phosphorescence spectra of 2-Me- and 2,6-Me$_2$-NQ's in solutions, 77 K.
a: 2-Me-NQ, 1. hexane, 2. heptane, b: 2,6-Me$_2$-NQ, 1. heptane, 2. octane.

band, based on their main progressions of the C–O stretching vibration and their short lifetimes, as may be seen in Figs. 1—3 and Tables 1 and 2.[7] In the methylcyclohexane solutions, as may be seen in Table 1, the phosphorescence bands of 2-methyl- and 2,6-dimethyl-NQ's show a blue shift, in comparison with that of NQ, while that of 2,6-diisopropyl-NQ shows no shift and that of 2,6-di-*t*-butyl-NQ shows a considerable red shift. The blue shift in the cases of 2-methyl- and 2,6-dimethyl-NQ's is characteristic of the n,π* transition.[8] The red shift in the case of 2,6-di-*t*-butyl-NQ may be due to the interaction between the *t*-butyl group and the lone-electron-pair of the carbonyl group located close to it. The shorter lifetime of the phosphorescence band of 2,6-di-*t*-butyl-NQ than those of the other NQ's, as may be seen in Table 2, may also be due to the same reason.

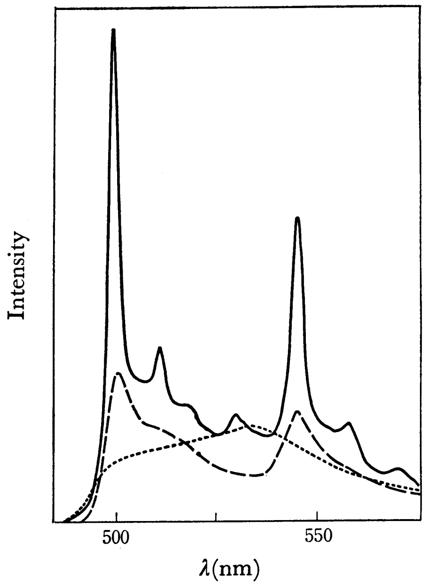


Fig. 3. Phosphorescence spectra of 2,6-(*i*-Pr)$_2$-NQ in solutions, 77 K.
——: Hexane, ——: heptane, ······: octane.

As for the Shpol'skii effect,[9] sharp spectra are observed in the normal paraffin solutions, as may be seen in Figs. 1—3. In the heptane solutions of 2-methyl- and 2,6-dimethyl-NQ's, two closely located phosphorescence bands are observed, as in the case of anthraquinone[2] previously reported. It is noticeable that, in 2,6-diisopropyl-NQ, the heptane solution alone shows a sharp band.

Let us turn to the phosphorescence spectra of the

Table 2. Observed lifetimes of the phosphorescence bands (ms)

	Heptane	Ethanol	Daifloil	Toluene
NQ	≲0.5	≲0.5	1.2	1.3
2-Me-NQ	0.65	1.5	1.6	2.0
2,6-Me$_2$-NQ	0.75	1.6	1.8	2.1
2,6-(*i*-pr)$_2$-NQ	0.9	1.6	1.8	2.1
2,6-(*t*-Bu)$_2$-NQ	≪0.5[a)]	≪0.5	≪0.5	≪0.5

a) The datum in the methylcyclohexane solution.

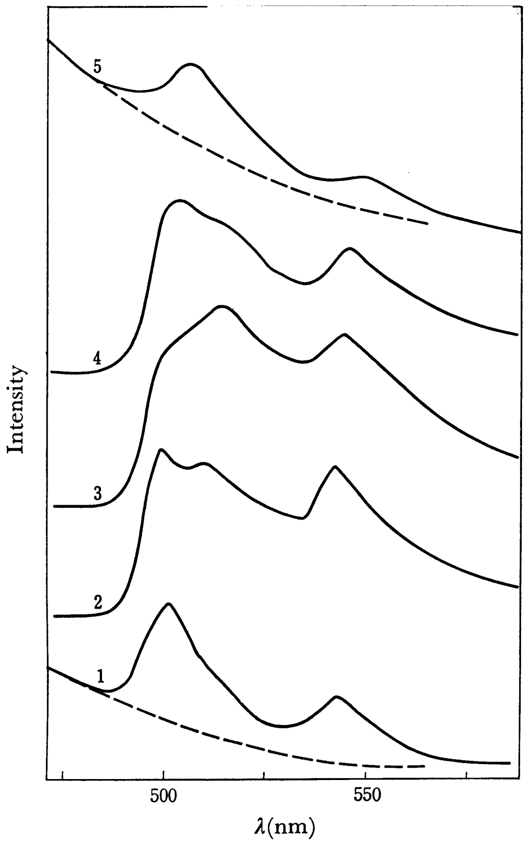


Fig. 4. Phosphorescence spectra of the NQ's in the ethanol solutions, 77 K.
1: NQ, 2: 2-Me-NQ, 3: 2,6-Me_2-NQ, 4: 2,6-(*i*-$Pr)_2$-NQ, 5: 2,6-(*t*-$Bu)_2$-NQ.

NQ's in the ethanol solutions. The phosphorescence bands of the NQ's except for 2,6-dimethyl-NQ are assigned to the n,π^* band in the ethanol solutions, since they show clear vibrational structures of the C–O stretching mode and have short lifetimes (Fig. 4 and Tables 1 and 2). The phosphorescence spectrum of 2,6-dimethyl-NQ shows no vibrational structure of the C–O stretching mode and may be assigned to the π,π^* band. From the comparison between Curves 2 and 3 in Fig. 5, we can see that the intensity of the shortest wavelength peak decreases for 2-methyl-NQ with a decrease in the turning-rate of the sector. This means that 2-methyl-NQ shows two closely located phosphorescence bands (the so-called dual phosphorescence[10]) with different lifetimes. The one containing the shortest wavelength sharp peak has a shorter lifetime than the other and may be assigned to the n,π^* band. The other band, which is broad and which shows no C–O stretching vibrational structure, may be assigned to the π,π^* band. In Table 2, the lifetime for 2-methyl-NQ in the ethanol solution is that of the broad band.

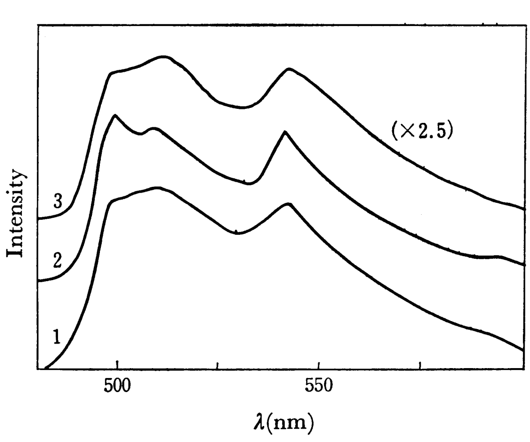


Fig. 5. Phosphorescence spectra of 2-Me-NQ in the ethanol solution, 77 K.
1: 313 nm line ex., sector fast, 2: 365 nm line ex., sector fast, 3: 365 nm line ex., sector slow.

It is considered that the lowest $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ levels are higher and lower respectively for 2-methyl-NQ than for NQ[11] as a result of the methyl-group substitution, and that in each quinone these levels are higher and lower respectively in the ethanol solution than in the saturated hydrocarbon solutions, as a result of the hydrogen-bond formation[1] between ethanol and the quinone. Consequently, in the ethanol solution of 2-methyl-NQ, the lowest $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ levels may reasonably be assumed to be very close. The abovementioned dual phosphorescence may result from this closeness of the lowest $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ levels of 2-methyl-NQ in the ethanol solution. It is uncertain at this stage whether the two phosphorescences have their origin in like molecules or in differently solvated species. In 2,6-dimethyl-NQ, considering the case of 2-methyl-NQ, the lowest $^3(\pi,\pi^*)$ level may be somewhat lower than the lowest $^3(n,\pi^*)$ level in the ethanol solution because of the two methyl-group substitution, so only the π,π^* phosphorescence band is observed. The short lifetimes of the phosphorescence bands assigned to the π,π^* band in Table 2 may result from the mixing of the phosphorescent $^3(\pi,\pi^*)$ states with the nearby $^3(n,\pi^*)$ states.

In 2-methyl-NQ, as may be seen from a comparison between Curves 1 and 2 in Fig. 5, the phosphorescence spectra observed by the two kinds of excitations, the 313 and 365 nm line excitations, where the former corresponds to the excitation to the $^3(\pi,\pi^*)$ state, and the latter to the excitations to both the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states,[16,17] are different. From this fact it may be concluded that a part of the quinone molecules excited to the $^3(\pi,\pi^*)$ state at the 313 nm line excitation directly transfer to a high-energy triplet state through the intersystem crossing.

Since all the phosphoresence bands of the NQ's in the Daifloil solutions show clear progressions of the C–O stretching vibration and short lifetimes (Tables 1 and 2), these bands may be assigned to the n,π^* band. The phosphorescence band of NQ in the Daifloil solution shows a more considerable blue shift than do those in the saturated hydrocarbon solutions (Table 1). This blue shift may be mainly due to the n-σ type charge-transfer interaction between the lone-pair orbitals of the carbonyl groups of NQ and the σ^*-orbitals of the C–Cl bonds of Daifloil.[3]

The phosphorescence spectrum of 2,6-dimethyl-NQ in the Daifloil solution depends on the turning-rate of the sector (Fig. 6). A similar situation is also observed

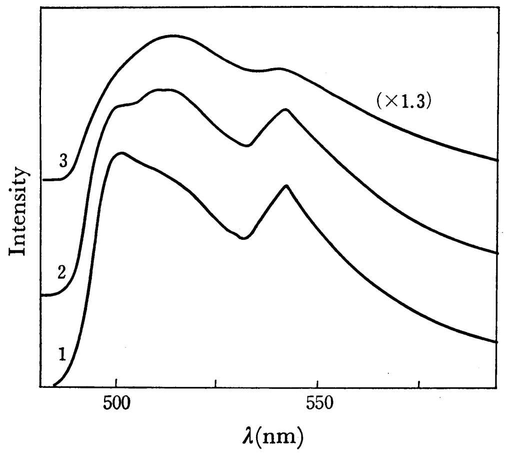


Fig. 6. Phosphorescence spectra of 2,6-Me$_2$-NQ in the Daifloil solution, 77 K.
1: No sector, 2: sector fast, 3: sector slow.

for 2-methyl-NQ. Therefore, as may be seen in Fig. 6, a dual phosphorescence which consists of a sharp band and a broad band appears in these two NQ's in the Daifloil solutions, as in the case of 2-methyl-NQ in the ethanol solution. The lifetimes for these two NQ's in the Daifloil solutions in Table 2 are those of the broad bands. In this case, the phosphorescence spectra do not depend on the exciting wavelength.

As for the phosphorescence spectra of the NQ's in the toluene solutions, as may be seen in Fig. 7 and Tables 1 and 2, their lifetimes are all short; those of NQ and 2,6-di-*t*-butyl-NQ show a clear vibrational structure of the C–O stretching mode, while those of the other NQ's do not show it. Especially those of 2-methyl- and 2,6-dimethyl-NQ's show almost no structure. The former may reasonably be assigned to the n,π^* band, but the latter may be assigned to the π,π^* band, which has the n,π^* character to some extent, in view of their short lifetimes.

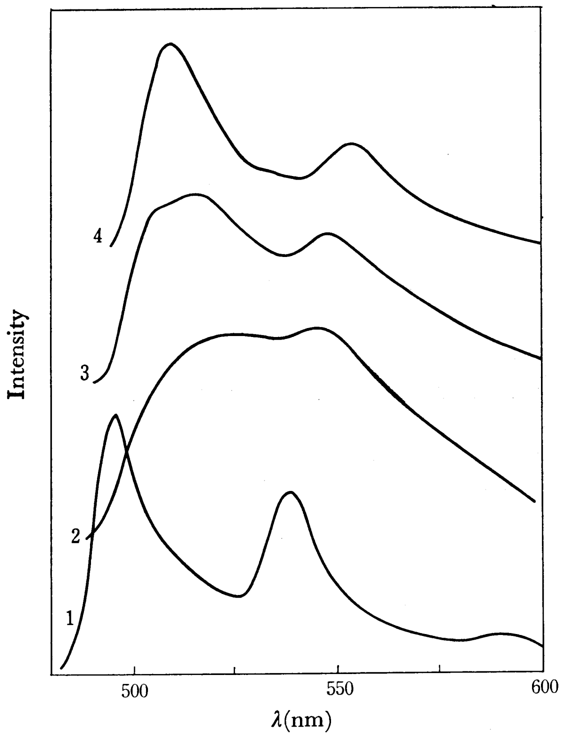


Fig. 7. Phosphorescence spectra of the NQ's in the toluene solutions, 77 K.
1: NQ, 2: 2-Me-NQ, 3: 2,6-(*i*-Pr)$_2$-NQ, 4: 2,6-(*t*-Bu)$_2$-NQ.

The phosphorescence band of NQ in the toluene solution shows a larger blue shift than those in the ethanol and Daifloil solutions (Table 1) as a result of the π-π type charge-transfer interaction between toluene and NQ.[1] As for the above-mentioned phosphorescence bands of 2-methyl- and 2,6-dimethyl-NQ's in the toluene solutions, the phosphorescent π,π^* states may mix with the triplet charge-transfer states also, for they are remarkably broad. On the other hand, the phosphorescence band of NQ in the toluene solution does not show such a broadening. The reason for this may be that, in NQ, it is difficult for the phosphorescent n,π^* state to mix with the triplet charge-transfer state because of the small overlapping between the donor π-orbital of toluene and the n-orbital of the carbonyl oxygen atoms of NQ.

As for the observed lifetimes of the phosphorescence bands of the NQ's in Table 2, those for all the NQ alkyl derivatives except for 2,6-di-*t*-butyl-NQ are, in each kind of solution, a little longer than that for NQ. The short lifetimes in the case of 2,6-di-*t*-butyl-NQ have been discussed before. It is noticeable that the observed lifetimes are, in each quinone, regularly in the following order of solvents: toluene>Daifloil>ethanol>heptane.

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7) In the heptane solution of NQ, a broad n,π^*-type phosphorescence band is observed besides a sharp n,π^*-type band; the former is far stronger and at wavelengths longer by *ca.* 750 cm^{-1} than the latter. Since the relative intensity of the former to the latter decreases with the lowering of concentration of the sample solutions, the former may be due to the aggregates.

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11) NQ is thought to have two low-energy $^3(\mathrm{n}, \pi^*)$ levels, the energy difference between which is several hundreds cm^{-1}, as in the case of *p*-benzoquinone.[2] In the text, the $^3(\mathrm{n}, \pi^*)$ 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+CI calculations,[13,14] the lowest $^1(\mathrm{n}, \pi^*)$ state of NQ is the $^1\mathrm{A}_2$ state, so the lowest $^3(\mathrm{n}, \pi^*)$ state may also be the $^3\mathrm{A}_2$ state, considering the case of *p*-benzoquinone.[12] On the other hand, the lowest $^3(\pi, \pi^*)$ state is the $^3\mathrm{B}_2$ state, according to both the CNDO/S+CI[13,14] and P-P-P[15,16] calculations.

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