BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3373—3376 (1970)

The Phosphorescence Bands of Anthraquinone in Crystalline Solvents at 77°K

Akira KUBOYAMA

Government Chemical Industrial Research Institute, Tokyo, Shibuya-ku, Tokyo

(Received May 23, 1970)

The phosphorescence bands of anthraquinone in the solvents used in this work are all safely assigned to the $\pi^*\rightarrow n$ bands on the basis of their short lifetimes. In *n*-paraffins (*n*-hexane, *n*-heptane, and *n*-octane), two phosphorescence bands which are close to each other are found. Considering the dependence of the relative intensities of these two phosphorescence bands on the carbon-numbers of the *n*-paraffins, it is assumed that the longer- and the shorter-wavelength bands are due to the anthraquinone molecules with the C–O bond axis parallel to and perpendicular to the longitudinal axis of the planar zig-zag form of the *n*-paraffin molecules in the *n*-paraffin crystals respectively. In chloroform and dioxane, a broad phosphorescence band shows a blue-shift relative to the corresponding band in the alkane solvents. In chloroform a sharp phosphorescence band was also observed for a solution which was rapidly cooled. This sharp band is assumed to be due to the anthraquinone molecules with a certain geometry relative to the surrounding chloroform molecules.

In a previous work,[1] we studied the phosphorescence bands of various *o*- and *p*-quinones and α-diketones in solutions and in fine crystals at 77°K. All the solutions studied there were glassy. However, valuable information on the properties of phosphorescence bands, on solute-solvent interactions, and on the arrangements of solutes in solvents is expected to be obtained from the study of the phosphorescence bands in crystalline solutions at low temperatures.[2,3] From this point of view, the phosphorescence bands of anthraquinone in solutions at 77°K have been studied by using various kinds of solvents, all of which form a crystalline state at 77°K.

Experimental

Measurements. The phosphorescence spectra and their lifetimes have been measured in the manner described in our previous paper.[1] The exciting light used was a mercury 313-mμ line emitted from a Hanovia xenon mercury lamp of 150 W. The solvents used were *n*-hexane, *n*-heptane, *n*-octane, 3-methylpentane, isooctane, methylcyclohexane, chloroform, and dioxane. The concentrations used ranged from 10^{-4}—10^{-5} M. The measurements were carried out at the liquid-nitrogen temperature (77°K) in air. Two kinds of cooling speeds, fast and slow, were used. For the rapid cooling, capillary quartz or Pyrex cells were plunged in liquid nitrogen. On the other hand, for the slow cooling the capillary cells were steeped in liquid nitrogen after having been hung immediately above the surface of liquid nitrogen for about 15 min. The solutions used were in polycrystalline states at 77°K except for methylcyclohexane and 3-methylpentane solutions, which were glassy at 77°K.

Materials. Commercially-available anthraquinone was purified by recrystallization. The melting point of the purified sample agreed with that reported in the literature. As for solvents, commercially-available spectro-grade *n*-hexane, *n*-heptane, *n*-octane, isooctane, methylcyclohexane, and chloroform were used without further purification. Aromatic impurities in commercially-available 3-methylpentane were removed with silica gel. After the treatment, the 3-methylpentane was distilled. Dioxane of a special grade was dried over sodium and distilled.

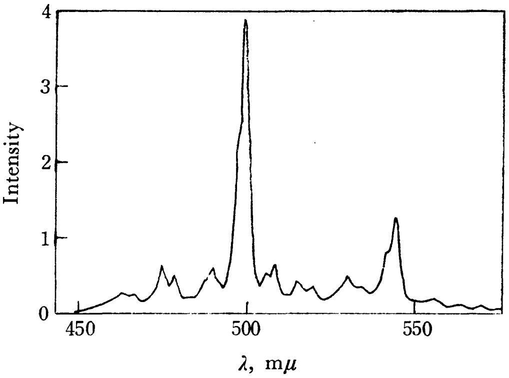

Fig. 1. Solvent: *n*-hexane, slow-cooling.

---

[1] A. Kuboyama and S. Yabe, This Bulletin, **40**, 2475 (1967); *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, **64**, 105 (1969).

[2] E. V. Shpol'skii, *Sov. Phys. Usp.*, **3**, 372 (1960); *ibid.*, **5**, 522 (1962).

[3] E. J. Bowen and B. Brocklehurst, *J. Chem. Soc.*, **1955**, 4320; R. Shimada, *Spectrochim. Acta*, **17**, 14 (1961).

Results

The phosphorescence spectra obtained are shown in Figs. 1—6. All the spectra are uncorrected for the response of the photomultiplier, and the scales of the ordinates are arbitrary. In Table 1, the wavelengths of the strongest peaks near 500 $m\mu$ in the phosphorscence spectra in various solvents are given. The observed lifetimes of the phosphorescence bands were all close to that (3.3 msec) in methylcyclohexane and methanol-ethanol (1 : 4) mixture obtained in our previous work.[1)]

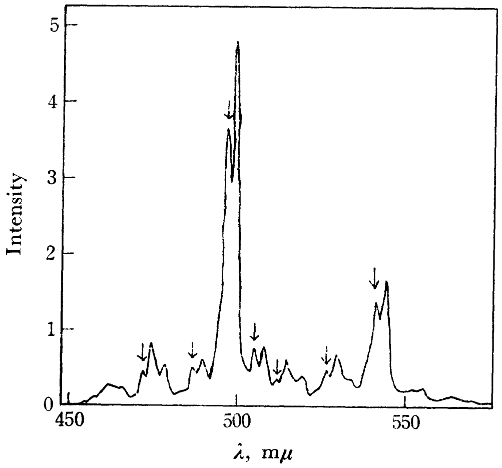

Fig. 2. Solvent: n-heptane, slow-cooling.

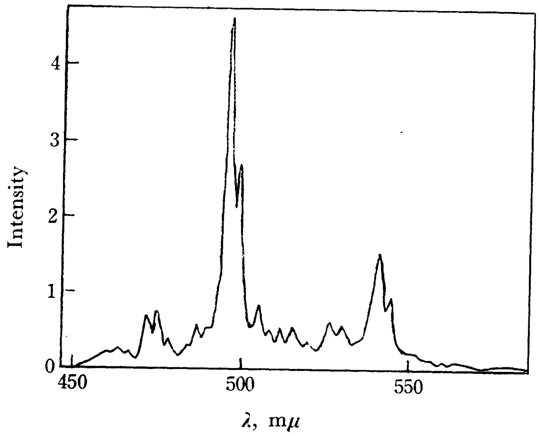

Fig. 3. Solvent: n-octane, slow-cooling.

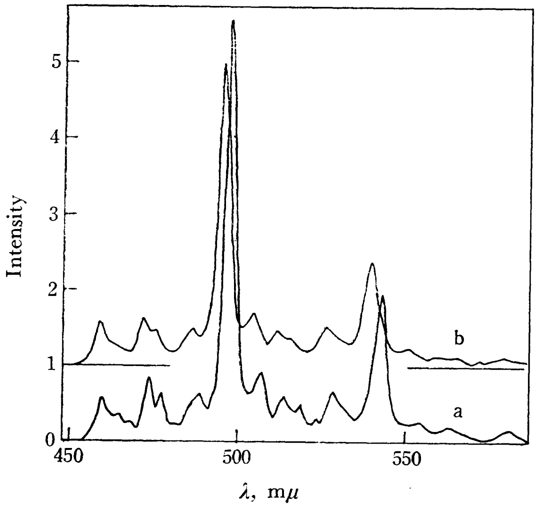

Fig. 4. Solvent: methylcyclohexane, slow-cooling.
a: crystalline state, b: rigid glass state

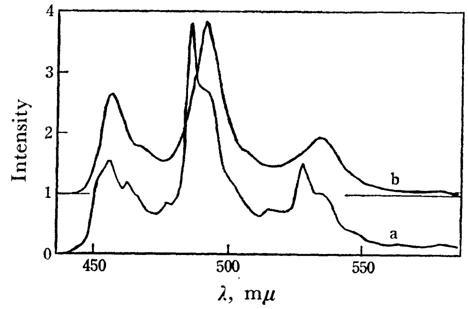

Fig. 5. Solvent: chloroform.
a : rapid-cooling, b : slow-cooling

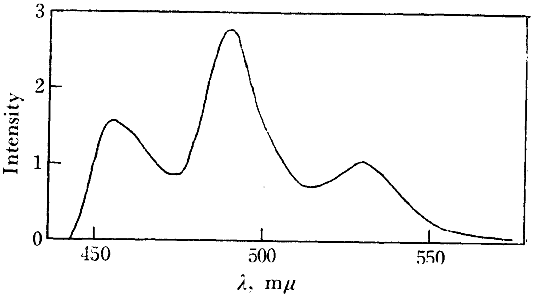

Fig. 6. Solvent: dioxane, slow-cooling.

Table 1. Strongest-peak wavelengths in various solvents

Solvent	Wavelengths ($m\mu$)
n-Hexane	499
n-Heptane	499
n-Octane	496
Methylcyclohexane (Crystalline state)	497
Methylcyclohexane	495
3-Methylpentane	495
Isooctane	495
Chloroform	492
Chloroform (Rapid-cooling)	486
Dioxane	490

Discussion

The phosphorescence bands in the solvents used in this work can all saelfy be assigned to the $\pi^* \rightarrow n$ band on the basis of their short lifetimes.

As is shown in Figs. 1—3, the phosphorescence spectra in the n-paraffins show sharp, fine structures. Previously, Shpol'skii[2] found that, when the longitudinal dimention of the planar zig-zag form of an *n*-paraffin molecule used as a solvent is close to the molecular dimension of a solute aromatic hydrocarbon, for example, anthracene (7.5 Å) in *n*-heptane (7.6 Å),[4] the fluorescence spectrum of the solution shows a very sharp, fine structure. This Shpol'skii effect has been generally observed for the electronic absorption and emission spectra of various aromatic compounds which have a rigid molecular structure. Anthraquinone has a rigid molecular structure, and the dimension (7.4 Å) of its long axis (perpendicular to the C–O bond axis) is close to that of *n*-heptane, while that (5.3 Å) of its short axis (parallel to the C–O bond axis) is relatively close to that (6.3 Å) of *n*-hexane. That of *n*-octane is 8.9 Å.[4] Therefore, it may be surmised that the sharp phosphorescence band in the *n*-paraffins mentioned above are due to the Shpol'skii effect. In *n*-heptane (Fig. 2), the peaks corresponding to the two main peaks near 500 and 540 mμ in methylcyclohexane (Fig. 4) have doublet structures. Similar doublet structures are also found in *n*-hexane and *n*-octane (Figs. 1, 3). In *n*-hexane the intensity of the shorter wavelength peak relative to that of the longer wavelength one in each doublet structure is considerably weaker than that in *n*-heptane. On the other hand, in *n*-octane the intensity of the longer-wavelength in each doublet structure is considerably weaker than that of the corresponding shorter-wavelength peak, contrary to the cases of *n*-heptane and *n*-hexane.

The effect of the cooling speed on the doublet structures is as follows. The relative intensity of the weaker peak (shorter-wavelength peak) to that of the stronger peak in each doublet structure increases in the case of *n*-hexane (Fig. 1), and decreases in the case of *n*-heptane (Fig. 2), for solutions which are rapidly cooled. On the other hand, in the case of *n*-octane (Fig. 3), the intensity of the weaker peak (longer-wavelength peak) relative to that of the stronger peak in each doublet structure becomes considerably stronger for solutions which are rapidly cooled. In these paraffins the wavelengths of peaks in the phosphorescence band are all the same, irrespective of the cooling speed. Though the reproducibility of the doublet structures in each case is not very good, the difference in the relative intensity of the two peaks of the doublet structure among the three paraffins is always definite.

From these facts it may be concluded that, in these paraffins, two phosphorescence bands closely overlap,[5] and that, in *n*-hexane, the longer-wavelength phosphorescence band and, in *n*-octane, the shorter-wavelength band appear more intensely. The energy difference between these two phosphorescence badns is *ca.* 100 cm^{-1}. On the basis of a comparison of the phosphorescence spectra in these paraffins, the peaks identifiable with the shorter-wavelength band are denoted with an arrow in Fig. 2. These two phosphorescence bands in these paraffins are assumed to be due to the anthraquinone molecules incorporated in two different ways in the paraffin crystals.

Since no complete single-crystal X-ray-analysis has been made for these paraffin crystals, precise structural details are unknown. However, considering the crystal data[6] for other *n*-paraffins, it may be assumed that, in the paraffin crystals used in this work, the paraffin molecules with the planar zig-zag form are arranged in parallel rows.[2] As for the anthracene in *n*-heptane crystals, mentioned before, it may be assumed that the anthracene molecules are arranged with their long axis parallel to the longitudinal axis of *n*-heptane molecules in *n*-heptane crystals.[2] It may analogically be assumed that, in the three paraffin crystals, anthraquinone molecules are incorporated in two different ways, namely, with their C–O bond axis parallel to and perpendicular to the longitudinal axis of the paraffine molecules, and that the above two phosphorescence bands are due to the anthraquinone molecules arranged in these two ways. If so, the difference in the relative intensities of the two phosphorescence bands between *n*-hexane and *n*-octane, mentioned before, can be explained on the reasonable presumption that, in *n*-hexane, most anthraquinone molecules are situated with their C–O bond axis parallel to the longitudinal axis of *n*-hexane molecules, while in *n*-octane most quinone molecules direct the C–O bond axis perpendicular to the longitudinal axis of *n*-octane molecules, and that the longer- and the shorter-wavelength phosphorescence bands are due to the anthraquinone molecules with the C–O bond axis parallel to and perpendicular to the longitudinal axis of the paraffin molecules. The situation in *n*-heptane can be assumed to be intermediate between those in *n*-hexane and *n*-octane. It can also be assumed that, in *n*-heptane, a majority of the anthraquinone molecules direct the C–O bond axis (short axis) parallel to the longitudinal axis of the *n*-heptane molecules, unlike as in the case of anthracene. This situation may be mainly due to the dipole-induced dipole interaction between the polar carbonyl groups of the quinone molecules and the *n*-heptane molecules, which may be stronger in the case of the anthraquinone molecules directing the C–O bond axis parallel to the

---

[4] In obtaining these data, hydrogen atoms are neglected. The value for anthracene is that of the long axis.

[5] The similar conclusion was obtained by D. N. Shygorin *et al.* ("Advances in Spectroscopy," Vol. 1 (1957), p. 672).

[6] J. M. Robertson, "Organic Crystals and Molecules," Cornell Univ. Press. Ithaca (1953), p. 165.

longitudinal axis of the *n*-heptane molecules than in the other case because of the anisotropy of the polarizability of the *n*-heptane molecules.

Methylcyclohexane solutions at 77°K usually form glassy states and show the same phosphorescence band, irrespective of the cooling speed. When the solution is cooled slowly, it occasionally becomes polycrystalline, and the phosphorescence band in the crystalline solution is different from that in the glassy solution. The phosphorescence band in the crystalline solution shifts toward wavelengths longer by *ca.* 80 cm^{-1} and becomes sharper than that in the glassy solutions (Fig. 4). Both in polycrystalline isooctane and in glassy 3-methylpentane the phosphorescence band is unaffected by the cooling speed and is very similar to that in the methylcyclohexane glass.

In chloroform (Fig. 5), a broad phosphorescence band appears for the slowly-cooled solutions. On the other hand, the rapidly-cooled solutions exhibit a sharp phosphorescence band, accompanied by a weak, broad band on its longer wavelength side. The weaker band situated at the same position as the broad band observed for the slowly-cooled solutions. It may be assumed that the sharp band is due to the anthraquinone molecules incorporated in the crystalline part of the chloroform matrix and that the broad band is associated with the anthraquinone molecules in the amorphous part of chloroform.

Generally speaking, the solvent effects on the energies of an absorption band and the corresponding emission band of solutions at 77°K are expected to be similar, since both the solute and solvent molecules can hardly move at 77°K. As a result, the solvent effects on the energies of the $\pi^*\rightarrow n$ phosphorescence band at 77°K and the corresponding $n\rightarrow\pi^*$ absorption band at room temperature can also be expected to be similar to some extent. Therefore, the blue shift of the phosphorescence bands in chloroform relative to those in the saturated hydrocarbons may be attributed to the hydrogen-bond formation between anthraquinone and chloroform.

In dioxane (Fig. 6), the same broad phosphorescence band is found for both the slowly- and rapidly-cooled solutions. This broad band may also be due to the anthraquinoe molecules in the disordered crystals of dioxane. A blue shift of the phosphorescence band in dioxane relative to those in the saturated hydrocarbons may be due to the π-n-type charge-transfer interaction between anthraquinone and dioxane molecules.[7]

---

[7] A. Kuboyama, This Bulletin, **33**, 1027 (1960); *Gov. Chem. Ind. Res. Inst., Tokyo*, **57**, 1 (1962).