Studies on the Phosphorescence Spectra. I. Phosphorescence Spectra of 1-Naphthol and 2-Naphthol

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The phosphorescence spectra of aromatic compounds have been studied rather extensively. Lewis and Kasha1) showed that the phosphorescent state of a molecule is equivalent to the lowest triplet state. McClure2) measured the lifetime of the phosphorescence of various aromatic compounds and interpreted his results from the standpoint of spin-orbit interaction3). The symmetry consideration of the spin-orbit interaction operator has been made by McClure4), Weissman5), and Mizushima and Koide6). A quantitative calculation of the spin-orbit interaction has been given by Pople and Sidman7,8) and by Hameka and Oosterhoff9). Research into the triplet states in relation to the molecular compounds has been done by Reid10,11), Platt et al.12), Czekalla et al.13) and McGlynn et al.14-16). Moreover, the triplet states of aromatic compounds have been considered to play an important role in various phenomena, for example, in the energy transfer between molecules14-17) and in photoelectric coductivity18).

The analyses of the triplet states of simple molecules themselves, however, are as yet incomplete. Before dealing with the application of the triplet states a more thorough examination of the phosphorescence spectra is necessary.

In this paper, as a first step toward this goal, the phosphorescence spectra of 1- and 2-naphthols are presented.

Only a little research into the phosphorescence spectra of naphthols has been undertaken so far. In 1944 Lewis and Kasha1) observed the phosphorescence spectra of 1- and 2-naphthols and reported the 0, 0-band positions in EPA solvent (5 parts diethyl ether, 5 isopentane, and 2 ethanol) at 20500 cm^{-1} and 21100 cm^{-1} respectively. McClure2) measured the lifetimes of the phosphorescence and gave 1.9±1 sec. for 1-naphthol and 1.3±1 sec. for 2-naphthol.

Experimental

Apparatus. — The apparatus used is similar in principle to that devised by Heckman19), and is shown schematically in Fig. 1. A xenon short arc lamp (1 kW) (A) provides an exciting light, which is, after passing through slits (B) and a lens (C), reflected from a front surface aluminum mirror (D) and enters a cell through a quartz window. The cell is cooled by liquid nitrogen and has been evacuated to prevent adverse effects from oxygen molecules and from condensation of air. Phosphorescent light emitted from the surface of the rigid sample is reflected by another mirror and is collimated to a Shimadzu quartz spectrograph (G) with a dispersion of 100 cm^{-1}/mm. around, 25000 cm^{-1}. The exciting light and the phosphorescent light are separated by a Bequellel type phosphoroscope (E)20). The exposure times ranged from a few minutes to several hours on Neopan SSS film. Spectrograms were calibrated

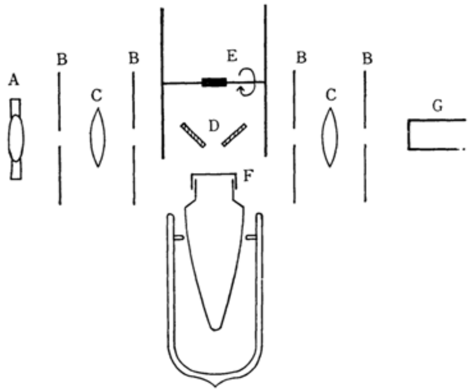

Fig. 1. Apparatus.

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with an iron spectrum and were measured with a Riken B-type microphotometer. The maximum precision is believed to be $\pm 5\,\mathrm{cm}^{-1}$ for the sharp bands.

Materials. — The solvents used were ethanol, diethyl ether, *n*-hexane, petroleum ether, and carbon tetrachloride. These were purified in the following ways. Ethanol was distilled with sulfuric acid, heated under reflux with potassium hydroxide and silver nitrate, and then distilled. The distillate was dried with activated aluminum amalgam, filtered and distilled. The distillate was further passed through a silica gel-column and was finally distilled. Diethyl ether was shaken with a solution of sodium carbonate, washed with a saturated sodium chloride solution, dried over calcium chloride, distilled over sodium, passed through a silica gel column, and distilled again. *n*-Hexane and petroleum ether were both treated with concentrated sulfuric acid and fuming sulfuric acid, washed with water containing potassium hydroxide, and distilled. Carbon tetrachloride was heated under reflux with potassium hydroxide and distilled. The distillate was again heated with mercury and distilled. The solvents thus purified had no or practically no phosphorescence.

Both 1- and 2-naphthols were recrystallized from ligroin three times. Further purification was made by sublimation under reduced pressure just before measurement.

Results and Discussion

Naphthol exhibits phosphorescence in ethanol and in diethyl ether. The phosphorescence of naphthol in ethanol is more intense than that in ether. In the other solvents used, namely, in *n*-hexane, petroleum ether, and carbon tetrachloride, there is no detectable phosphorescence. When a very small quantity of ethanol, 1% of the total, is added to any of the above solvents, intense phosphorescence can be observed in each case.

The solvent effect upon the intensity of the phosphorescence seems quite complex. The above result resembles that reported by Fernandes and Becker[21], but the same explanation is not possible. Lewis, Lipkin and Magel[22] and Yamamoto[23] have considered that the solvent for the measurement of phosphorescence must have a hydrogen bonding capacity. The above result, however, is not accounted for by their theories. Discussion will be postponed until further experiments have been carried out.

Figures 2 and 3 show the phosphorescence spectra of 1- and 2-naphthols in ethanol, where the ordinates are the plate blackness in arbitrary units. The spectra in ether are almost the same as those in ethanol, except that the latter are less intense.

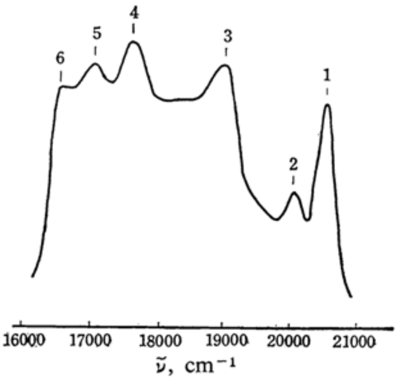

Fig. 2. Phosphorescence spectrum of 1-naphthol.

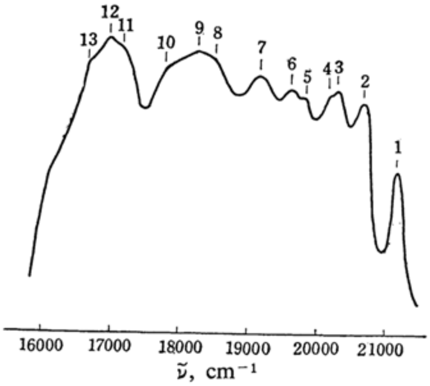

Fig. 3. Phosphorescence spectrum of 2-naphthol.

Vibrational analyses are given in Tables I and II. The infrared and the Raman spectra data determined by the present author are used as a basis of analysis.

A comparison of the spectra of naphthols with the spectrum of naphthalene is of interest. The phosphorescence spectrum of naphthalene was reported by Czekalla et al.[13] As can be seen in Fig. 3, the phosphorescence spectrum of 2-naphthol resembles that of naphthalene in its spectral shape. The spectrum of naphthalene has more vibrational bands than that of 2-naphthol, and every band in the latter, except band 3, has its corresponding band in the former. Both spectra have almost the same progressions. Band 3 at $20325\,\mathrm{cm}^{-1}$ in the spectrum of 2-naphthol is quite puzzling. This band is separated by $830\,\mathrm{cm}^{-1}$ from the 0, 0-band. Although there is a rather strong band at $842\,\mathrm{cm}^{-1}$ in the infrared spectrum, no reasonably matched band is found in the Raman spectrum. Further, there is no corresponding

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TABLE I. PHOSPHORESCENCE SPECTRUM OF 1-NAPHTHOL

Band No.*	Wave number	$\Delta\tilde{\nu}$	Analysis
1	20550		0, 0
2	20060	490	0, 512
3	19075	1475	0, $\left.\begin{matrix}1390\\1584\end{matrix}\right\}=1487$
4	17630	2920	0, 1390+1584=2974
5	17055	3475	0, 512+1390+1584=3486
6	16370	4180	0, 1390×3=4170

* Number as given in Fig. 2.

TABLE II. PHOSPHORESCENCE SPECTRUM OF 2-NAPHTHOL

Band No.*	Wave number	$\Delta\tilde{\nu}$	Analysis
1	21155		0, 0
2	20655	500	0, 519
3	20325	830	
4	20150	1005	0, 519×2=1038
5	19775	1380	0, 1380
6	19590	1565	0, 1587
7	19070	2085	0, 519+1587=2106
8	18400	2755	0, 1380×2=2760
9	18220	2935	0, 1380+1587=2967
10	17710	3445	0, 519+1380+1587=3467
11	17055	4100	0, 1380×3=4140
12	16875	4280	0, 1380+1470×2=4320
13	16640	4515	0, 1470×2+1587=4527

* Number as given in Fig. 3.

band in the phosphorescence spectrum of naphthalene. Therefore, in this paper, this band remains unexplained.

The phosphorescence spectrum of 1-naphthol has even fewer vibrational bands than that of 2-naphthol. Bands 4, 5 and 6 are very wide, and their centers could only with difficulty be determined exactly. Every band except band 3 has its counterpart in the spectrum of 2-naphthol and also in that of naphthalene. Band 3 is separated by 1475 cm^{-1} from the 0, 0-band. There is a strong infrared band at 1460 cm^{-1} and a Raman band at 1458 cm^{-1}. Therefore, band 3 may be ascribed to this vibration. However, through comparison of the spectrum of 2-naphthol with the spectra of 1-naphthol and naphthalene, this band is tentatively ascribed to a superposition of 1390 and 1584 cm^{-1}.

As has been stated above, the spectra of 1- and 2-naphthols resemble the spectrum of naphthalene. Accordingly, the lowest triplet state of naphthol may be considered to be like a perturbed triplet state of naphthalene, not a new type of state, such as a charge-transfer state.

Next, the direction of a transition moment will be discussed. Naphthol has no symmetry, apart from its symmetry with respect to the molecular plane. However, on the basis of what has been mentioned above, consideration of a transition moment may be made by analogy with the case of naphthalene.

The 0, 0-band of naphthalene is shifted toward blue by the introduction of a hydroxyl group, as is seen in an ordinary π-π transition. The amount of blue shift is 750 cm^{-1} for 1-naphthol and 145 cm^{-1} for 2-naphthol. That 1-substitution gives rise to a large shift and 2-substitution, to only a small shift shows that the phosphorescence of naphthol, as well as that of naphthalene, has a moment of a short-axis direction. Williams[24] reached the same conclusion by observing the polarization of the phosphorescence of naphthalene.

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