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Fluorescence and Phosphorescence Spectra of α-Naphthol in Relation to Hydrogen Bonding and Proton Transfer

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Formation of a hydrogen bond between α-naphthol and a suitable proton-accepting substance may result in a change of the fluorescent state (or the lowest excited singlet state S_1) of α-naphthol from ${}^1L_b$ to ${}^1L_a$ state. It is possible that the proton may be transferred from the naphthol to the proton acceptor in the fluorescent state.[1] These problems were discussed in a previous paper by Suzuki and Baba using ether and triethylamine as proton acceptors.[2] The present note reports the results of further investigations on the same problems and also on the possibility of proton transfer in the phosphorescent state (or the lowest triplet state T_1). In this study we have employed dimethylformamide as a proton acceptor in addition to ether and triethylamine.

Figure 1 shows fluorescence and phosphorescence spectra of α-naphthol at 77°K in a mixture of isopentane and methylcyclohexane containing ether, dimethylformamide, or triethylamine.

From the behavior of the excitation-polarization spectra related to fluorescence, it has been demonstrated that the naphthol-ether system forms a simple hydrogen-bonded complex in S_1 state of ${}^1L_b$ type, while in the naphthol-triethylamine system the proton transfer takes place to yield an ion pair within the lifetime of the excited singlet state, and the fluorescence originates in the ion pair from its S_1 state which can be assigned to ${}^1L_a$ state[2].

It is seen from Fig. 1 that on changing the proton acceptor from ether to dimethylformamide the fluorescence spectrum is displaced to the red, as expected from the greater proton-accepting power of the amide as compared to ether.[3,4] In the case of dimethylformamide as acceptor, however, the fluorescence spectrum is located at a considerable distance from the spectrum of the ion pair of naphthol-triethylamine system. Thus the former is regarded as due to the α-naphthol molecule which forms a simple hydrogen bond with the amide. On the other hand, the spectrum of the naphthol-amide system is structureless, suggesting the S_1 state to be ${}^1L_a$. The excitation-polarization spectrum related to the fluorescence of this system was measured and found to be very similar to the corresponding polarization spectrum obtained for the ion pair of naphthol-amine system.[2] We thus conclude that the fluorescent state of the hydrogen-bonded complex between the naphthol

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[1] N. Mataga and Y. Kaifu, *J. Chem. Phys.*, **36**, 2804 (1962); H. Baba, *ibid.*, **49**, 1763 (1968) and papers cited therein.

[2] S. Suzuki and H. Baba, This Bulletin, **40**, 2199 (1967).

[3] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco, Calif. (1960), Appendices.

[4] When dimethylformamide was used as proton acceptor, a small amount of ether (0.2 mol/l) was added to get a better rigid glass. However, owing to the greater proton-accepting power of the amide, α-naphthol is considered to form the hydrogen bond only with the amide molecule.

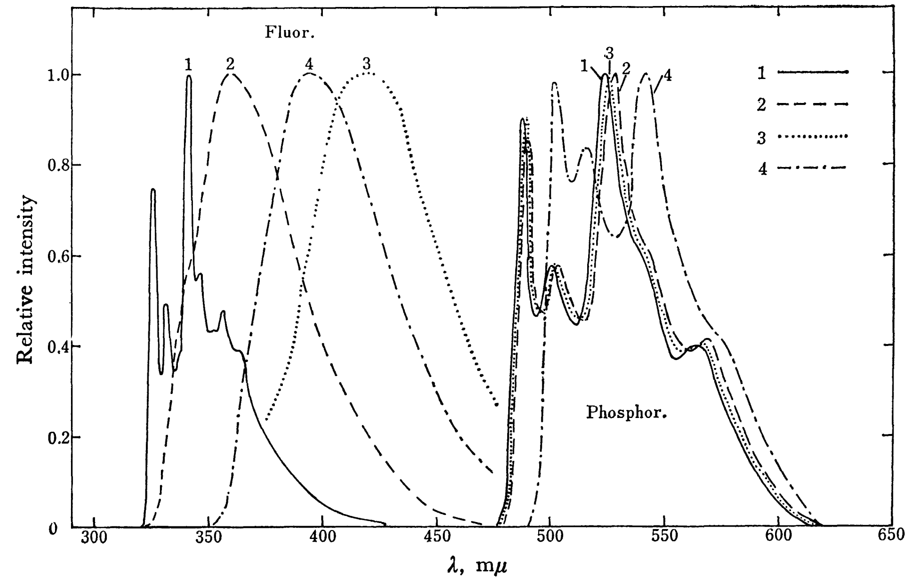

Fig. 1. Fluorescence and phosphorescence spectra of α-naphthol at 77°K: 1, 2, and 3, in isopentane-methylcyclohexane (volume ratio, 1:1) containing ether (1.0 mol/*l*), dimethylformamide (0.015 mol/*l*), and triethylamine (0.2 mol/*l*), respectively; 4, in ethanol-methanol (5:1) containing potassium hydroxide (5×10^{-3} mol/*l*).

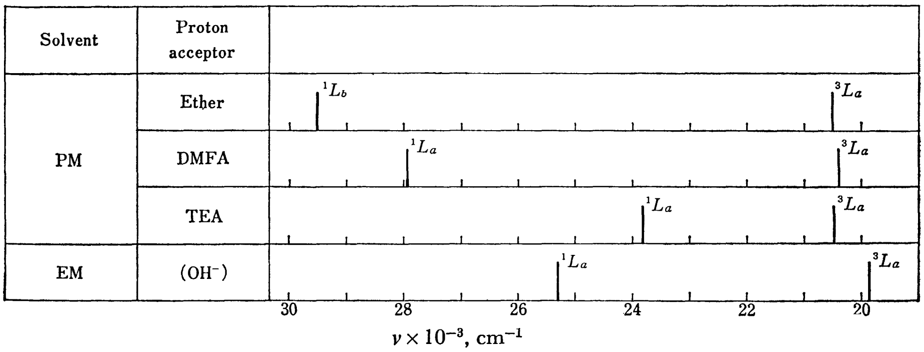

Fig. 2. Location of fluorescence maxima and phosphorescence 0–0 bands at 77°K for α-naphthol hydrogen-bonded with proton acceptors of different strengths and for α-naphtholate ion. PM, isopentane-methylcyclohexane (1 : 1); EM, ethanol-methanol (5 : 1); DMFA, dimethylformamide; TEA, triethylamine.

and dimethylformamide is of ^1L_a type.

In Fig. 1 are also shown the fluorescence and phosphorescence spectra of α-naphthol in an alkaline ethanol - methanol mixture in which the naphthol is converted to the naphtholate ion. Figure 2 shows the positions of the fluorescence and phosphorescence spectra of α-naphthol coupled with different proton acceptors, together with the positions of spectra of naphtholate ion. The emitting states are given in the Platt notation; the phosphorescent states are assigned to ^3L_a, as is generally accepted.[5] It should be noted that S_1 and T_1 states have the same electron configuration L_a in all cases except for the case of ether as proton acceptor.

The phosphorescence spectrum of α-naphthol - triethylamine system closely resembles the corresponding spectra of the naphthol - ether and naphthol - dimethylformamide systems both in position and in shape. The phosphorescence spectra of the naphthol associated with any of the proton-accepting substances are quite different from the spectrum of the α-naphtholate ion. Consequently, it is reasonable to attribute the former spectra to the respective hydrogen - bonded complexes in which no proton transfer occurs. Thus, phosphorescence is emitted solely from the simple hydrogen - bonded species even when triethylamine is used as the proton acceptor. Since in the naphthol - triethylamine system the ion pair is responsible for the fluorescence, proton transfer must occur in the reverse direction within the lifetime of T_1 state.

The results of the present investigations on the fluorescence and phosphorescence spectra of α-naphthol in relation to hydrogen bonding and proton transfer are consistent with the view that the acidity of a phenolic compound is in general much weaker in the triplet state than in the excited singlet state.[6]

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[5] S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J. (1969).

[6] G. Jackson and G. Porter, *Proc. Roy. Soc. Ser., A*, **260**, 13 (1961).

Experimetal

α-Naphthol was recrystallized from ligroin and was sublimed *in vacuo*. Methylcyclohexane of spectroscopic quality was used without further purification. Isopentane was passed through a silica-gel column. Ethyl ether was distilled over metallic sodium. Dimethylformamide was shaken with potassium hydroxide and calcium oxide and was then distilled. Triethylamine was fractionally distilled over phosphorus pentoxide. Absorption and emission spectra and excitation-polarization spectra were measured at 77°K in the same way as described previously.7)

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7) T. Takemura and H. Baba, This Bulletin, **42**, 2756 (1969).