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Effect of Hydrogen Bonding on the Phosphorescence of Benzo[*c*]cinnoline in Polyhydric Solvents

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Synopsis. Phosphorescence of benzo[*c*]cinnoline has been found to be enhanced in polyhydric solvents, such as ethylene glycol, glycerol, and aqueous ethanol. Enhancement of the phosphorescence emission can be attributed to the formation of the hydrogen bond in the triplet state of benzo[*c*]cinnoline with the solvent molecules.

Emission characteristics of ortho-diazines, such as pyridazine and benzo[*c*]cinnoline (9,10-diazaphenanthrene, abbreviated hereafter as BCC), have often been discussed.1) BCC shows intense fluorescence, but its phosphorescence emission efficiency is very low.2) Recently, Lin and Stikeleather3) observed enhanced phosphorescence of BCC in the fluorinated alcohols. The alcohols act as a proton-donor in hydrogen bonding with BCC, thus inducing the phosphorescence of the substrate. They suggested that the lack of phosphorescence in hydrocarbon solvents was not due to a nonpopulated triplet state, but rather due to the $T_1 \rightarrow S_0$ radiationless rate being much faster than the radiative rate.

In general, the hydrogen bond between solute and solvent has some influence on the emission properties of the solute. As for cinnoline, for example, it is known that the formation of a hydrogen bond induces phosphorescence, although it is a poor phosphorescer in non proton-donating solvents.4)

The formation of the hydrogen bond in the ground state BCC with proton-donating solvents was proved from a blue shift of the $n\pi^*$ absorption spectrum.5) In the lowest excited singlet state of BCC, the hydrogen bond is formed at low temperature, but it is broken at room temperature.6,7)

In this paper, we will report the enhanced phosphorescence emission of BCC in polyhydric alcohols and aqueous monohydric alcohols, and will discuss the hydrogen bonding in the lowest triplet state of BCC with those solvents.

Experimental

BCC was obtained from Aldrich Chem. Co. and was purified by recrystallization from ethanol. Emission spectra were recorded on a Shimadzu RF-500 spectrofluorimeter at 77 K. Excitation spectra were corrected for the intensity of incident light using a rhodamine B solution.

Results and Discussion

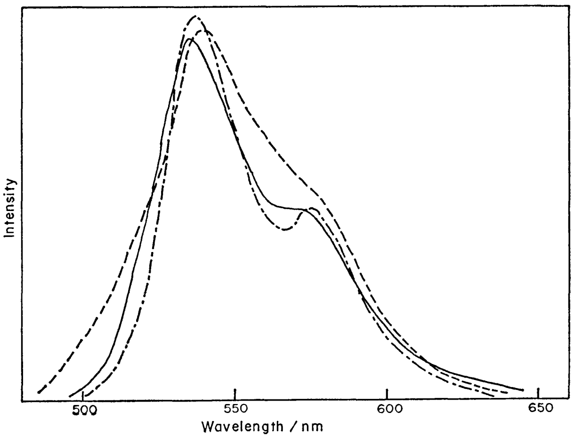
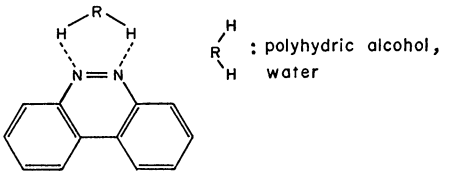


Fig. 1. Phosphorescence spectra of BCC.
—: In a mixture of ethanol and water (1:1), ----: in glycerol, ---: in ethylene glycol.

In monohydric alcohols, such as ethanol and 2-propanol, BCC shows no appreciable phosphorescence under our experimental conditions. However, it was found that in mixture of the monohydric alcohols and water (1:1 vol) the phosphorescence emission could be observed around 540 nm with a significant yield. In addition, ethylene glycol and glycerol were also found to be suitable solvents for the appearance of the phosphorescence of BCC. The observed phosphorescence spectra are presented in Fig. 1. None of the emission arises from the solvents used here. Moreover, the possible photochemical change of the sample was not detected.8) The formation of a dimer of BCC at low temperature as reported by Hoytink *et al.*9) can be ruled out as an origin of the observed phosphorescence, because polar solvents are used in this study. Hochstrasser and Marzzacco10) reported the crystalline $T_1 \leftarrow S_0$ absorption spectrum and they assigned the lowest triplet at 5384.6 A (0—0 band) as the $\pi\pi^*$ type. The 0—0 band of $T_1 \leftarrow S_0$ absorption spectrum corresponds in position to that of the phosphorescence observed in this study.

It should be noted that the phosphorescence of protonated BCC in 4 mol/dm^3 HCl aqueous 2-propanol, which was reported earlier,11) was quite similar in shape to the spectra in Fig. 1, though the former has a maximum at somewhat longer wavelength.12) In the present case, therefore, enhancement of the phosphorescence can reasonably be explained in terms of the hydrogen bonding between the solute and the solvents. In the aqueous alcohols, water seems to act as a proton-donor. It is worth noting that the solvent molecule which is suitable for the emission has at least two hydrogen atoms which can take part in the hydrogen bonding with the aza nitrogen atoms of BCC. Accordingly, the following hydrogen bonds are though to be formed. In fact, ethylene glycol monoethyl ether, which could not form such hydrogen bonds, did not induce the phosphorescence. Therefore, there is a distinct difference in the hydrogen bonding with the triplet state BCC between the mono- and polyhydric alcohols.



In order to see the difference in hydrogen bonding with the ground (S_0) and the lowest excited singlet (S_1) BCC between mono- and polyhydric alcohols, the absorption and fluorescence spectra were determined at room temperature. Owing to the hydrogen bonding, the nπ^* absorption band exhibits a large blue shift, thus appearing as a shoulder at the long wavelength of the first $\pi\pi^*$ band in both the mono- and polyhydric alcohols. The shape of the shoulder is the same in both solvents. The wavelengths of the fluorescence maxima in the polyhyric alcohols and the aqueous alcohols are almost the same as those in the monohydric alcohols, *e.g.*, 485 nm in ethylene glycol and 488 nm in ethanol. Therefore, we could not find any differences in hydrogen bonding properties of BCC in the S_0 and S_1 states between the mono- and polyhydric alcohols at room temperature.

Figure 2 shows the excitation spectra of the fluorescence at room temperature and of the phosphorescence at 77 K in glycerol. The phosphorescence excitation spectrum is shifted to somewhat longer wavelengths compared with the fluorescence excitation spectrum which corresponds to the absorption spectrum. This shift suggests that in polyhydric alcohols the hydrogen bonds are strengthened at low temperature, that is, the formation of the hydrogen bonds occurs as illustrated above.

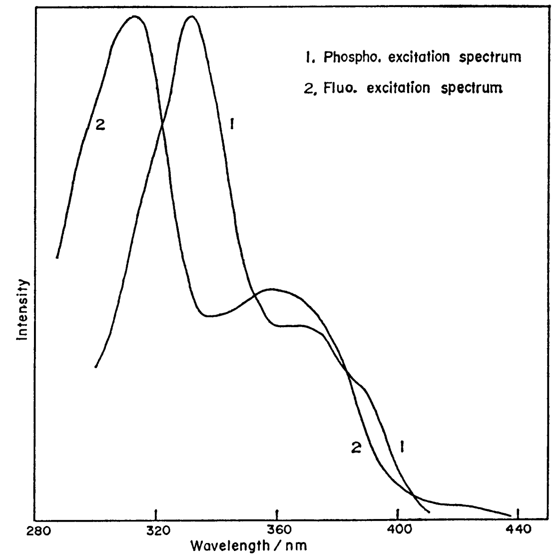


Fig. 2. Excitation spectra of phosphorescence at 77 K (1) and of fluorescence at room temperature (2) in glycerol (5×10^{-5} mol/dm^3).

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8) BCC has been found to be photoreduced to give 5,6-dihydro BCC in ethylene glycol and glycerol to be published.

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12) In glycerol and the acidic medium the phosphorescence band has two peaks. The separations of these peaks in both media are similar to each other (1200 cm^{-1}).