Luminescence Properties and the Primary Process of Photochromism of 2-(2-Hydroxyphenyl)benzothiazole

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(Received November 12, 1977)

The luminescence behavior of 2-(2-hydroxyphenyl)benzothiazole at 77 K was studied in detail, special attention being paid to dual fluorescence at ≈500 and ≈370 nm and also to phosphorescence at ≈500 nm. From the dependence of these emission bands upon the hydrogen-bonding ability of solvents and the excitation spectra, it is concluded that the short- and long-wavelength fluorescence bands are due to the intermolecularly hydrogen-bonded enol imine and the keto amine produced from the intramolecularly hydrogen-bonded enol, respectively, and that the phosphorescence is due to the intermolecularly hydrogen-bonded enol imine. The estimated quantum yield of the enol fluorescence gives further support to the formation scheme of the photochromic colored species previously presented. The rate constants of the intramolecular hydrogen transfer at 77 and 293 K are evaluated to be larger than 4×10^{10} s^{-1} and 3×10^{12} s^{-1}, respectively.

Photochromism of *N*-salicylideneanilines has been interpreted to be an enol-keto phototautomerization, which involves not only hydrogen transfer but a geometrical change in the molecular framework.[1-4]

In a previous paper, the photochromism of *N*-salicylideneanilines, including 2-(2-hydrophenyl)benzothiazole (HBT), was studied at room temperature.[4] From the FT infrared absorption measurement, we presented the direct evidence of the keto amine form for the colored species of *N*-salicylideneanilines. Furthermore, with the aid of picosecond time-resolved spectroscopy, we found the transient precursor from which the colored species and the *cis*-keto amine were produced.

Cohen and Flavian observed anomalously red-shifted fluorescence for *N*-salicylideneanilines and suggested from the comparison with absorption spectra that it was attributed to the keto tautomer formed during the lifetime of the enol excited state. But they could not observe separately a long-lived component (phosphorescence) appearing in the same wavelength region.[5]

In the present work, we have studied in detail the fluorescence and phosphorescence spectra, lifetimes, and fluorescence quantum yields of HBT and related heterocyclic compounds in various solvents. The main aim of the present study is to investigate the effect of hydrogen bonding upon the luminescence properties in order to obtain further support for the mechanism of photochromism, and to estimate the rate constant of intramolecular hydrogen transfer.

Experimental

The compounds employed in the present work are 2-(2-hydroxyphenyl)bonzothiazole (HBT), 2-(2-methoxyphenyl)benzothiazole (MBT), and 2-(2-hydroxyphenyl)benzoxazole (HBO). Commercially available HBT and HBO were chromatographed from benzene on activated alumina. MBT was obtained by two methods; treatment of HBT with dimethyl sulfate and synthesis according to the method in literature.[6] Solvents used in the present study are: PM (1: 1 by volume of spectro-grade isopentane and spectro-grade methylcyclohexane), DCM (dichloromethane), AN (spectro-grade acetonitrile), AA (acetic acid), EPA (5: 5: 1 by volume of spectro-grade diethyl ether, isopentane, and ethanol), EM (1: 1 by volume of spectro-grade ethanol and methanol), and DMF (*N*,*N*-dimethylformamide).

Ultraviolet absorption spectra were measured with a Cary 14 RI recording spectrophotometer. Phosphorescence spectra and their decay times were measured with a conventional phosphoroscope by employing a 1 kW Hg arc as an exciting light source. Emission spectra were measured with a Spex 1700-II grating monochromator equipped with an EMI 6256S photomultiplier and a PAR 128 lock-in amplifier. Fluorescence and phosphorescence excitation spectra were measured by exciting samples with monochromatic light at various wavelengths obtained with a 1 kW Xe lamp and the Spex monochromator, and by detecting emission intensities by the combination of a Bausch and Lomb 0.5 m monochromator with the photomultiplier and the lock-in amplifier. The quantum yield ratio between the short- and long-wavelength fluorescences was obtained by comparing the integratedintensities of the corresponding bands in the corrected emission spectra.

The fluorescence quantum yield of HBT excited at 354 nm was determined with use of a Shimadzu RF-502 spectrofluorometer. The standard material was 9,10-diphenylanthracene, the quantum yield of which was determined to be 0.93 in 3-methylpentane.[7] A flash-photolysis apparatus at room temperature and method for the determination of fluorescence lifetimes were described previously.[4] The flash photolysis experiments were carried out at 77 K with an apparatus at Institute of Applied Electricity, Hokkaido University.[8]

Results and Discussion

Fluorescence and Absorption Spectra of HBT, MBT, and HBO. The absorption and emission spectra of HBT, MBT, and HBO are given in Figs. 1, 2, and 3, respectively. HBT and MBT belong to 2-phenyl derivatives of benzothiazole and have similar molecular structures. Their emission properties, however, are quite different. In EPA at 77 K HBT shows dual fluorescence with peaks at 500 and 370 nm, while MBT exhibits single fluorescence as a mirror image of the absorption band.

The short-wavelength fluorescence of HBT shows vibrational structure pertinent to the 2-phenyl derivatives of benzothiazole like MBT,[9] and therefore is attributed to the lowest excited singlet state of the enol tautomer.

The Stokes shift amounts to 8500 cm^{-1} for the long-

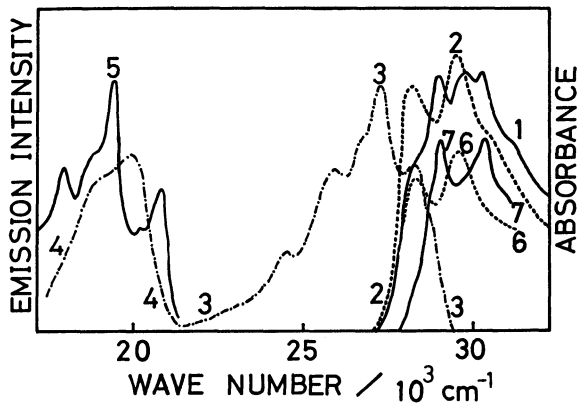

Fig. 1. The absorption, emission, and excitation spectra of HBT at 77 K: curve 1, absorption in EPA; curve 2, absorption in PM; curve 3, fluorescence of the enol imine in EPA; curve 6, fluorescence excitation spectrum of the keto amine in EPA; curve 7, fluorescence and phosphorescence excitation spectrum of the enol imine in EPA. Curves 3, 4, and 5 were measured under the excitation at 313 nm.

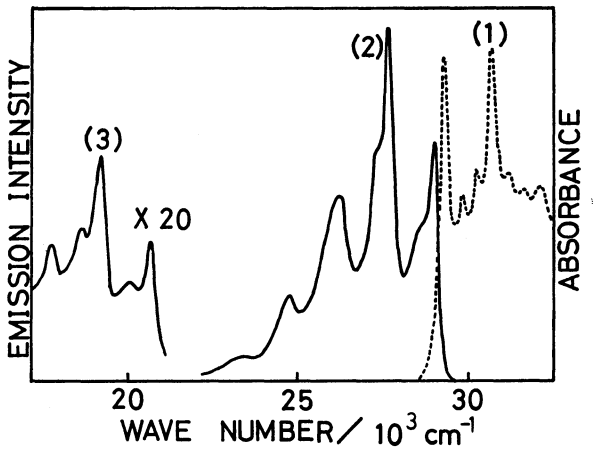

Fig. 2. The absorption (curve 1), fluorescence (curve 2), and phosphorescence (curve 3) spectra of MBT in EPA at 77 K. Curves 2 and 3 were measured under the excitation at 313 nm.

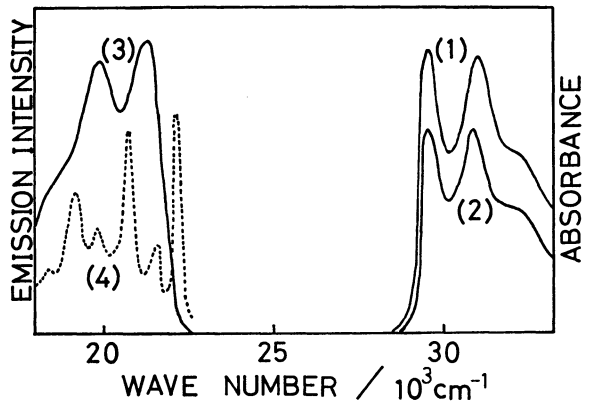

Fig. 3. The absorption and emission spectra of HBO at 77 K: curve 1, absorption in EPA; curve 2, absorption in PM curve 3, fluorescence of the keto amine in PM; curve 4, phosphorescence of the enol imine in PM. Curves 3 and 4 were measured under the excitation at 313 nm.

wavelength fluorescence of HBT. This suggests that the molecular framework changes in the excited state of the long-wavelength fluorescence. HBT can tautomerize from the enol imine to the keto amine, whereas MBT cannot. The excitation spectrum of the long-wavelength fluorescence of HBT in EPA at 77 K agrees well with the absorption spectrum of the HBT enol imine with the intramolecular hydrogen bond in PM at 77 K. This indicates that the long-wavelength fluorescence of HBT is due to the keto amine tautomer produced through hydrogen transfer in the excited state of the enol imine with the intermolecular hydrogen bond.

The relative intensities of the two fluorescence bands of HBT in solution are dependent on the solvent. The intensity of the short-wavelength fluorescence increases on going from the non-hydrogen-bonding or weakly hydrogen-bonding solvents (PM, DCM, and AN) to the strongly hydrogen-bonding solvents (AA, EPA, EM, and DMF). The fluorescence quantum yield ratios $\phi_f(E)/\phi_f(K)$ in various solvents are given in Table 1,

Table 1. $\phi_f(E)/\phi_f(K)$ in various solvents at 77K

	$\phi_f(E)/\phi_f(K)$
PM	$\leqslant 0.015$
DCM	$\leqslant 0.015$
AN	0.036 ± 0.002
AA	0.092 ± 0.005
EPA	1.6 ± 0.1
EM	3.0 ± 0.1
DMF	12 ± 1

where $\phi_f(E)$ and $\phi_f(K)$ are the fluorescence quantum yields for short- and long-wavelengths, respectively. When the short-wavelength fluorescence was too weak to be measured, an upper limit of $\phi_f(E)/\phi_f(K)$ was estimated from the limitation of detection. From these results and the discussion given above, it is concluded that the short-wavelength fluorescence of the dual emission is due to the enol imine with the intermolecular hydrogen bond, and the long-wavelength fluorescence to the keto amine produced by the hydrogen transfer in the excited state of the intramolecularly hydrogen-bonded enol imine. The absorption spectrum of HBT in EPA at 77 K is in good agreement with the superposition of the short- and long-wavelength fluorescence excitation spectra. In other words, the spectrum is interpreted as the superposition of the absorption spectra of the intramolecularly and intermolecularly hydrogen-bonded enol species of HBT.

Phosphorescence Spectra of HBT and MBT. HBT and MBT exhibit phosphorescence similar to that of 2-phenylbenzothiazole with respect to transition energy and vibrational structure.[9] The phosphorescence of HBT was observed only in the hydrogen-bonding solvents (AA, EPA, EM, and DMF). The $T_n \rightarrow T_1$ transition band of HBT was observed around 425 nm in EPA at 77 K, but not in the non-hydrogen-bonding solvent, PM at 77 K. In the HBT with the intramolecular hydrogen bond, hydrogen transfer through the bond occurs so fast that no triplet enol imine can be

formed. The excitation spectrum of HBT phosphorescence in EPA at 77 K is identical with that of the short-wavelength enol imine fluorescence. Thus the phosphorescence of HBT is assigned to the enol imine tautomer with the intermolecular hydrogen bond. The phosphorescence of the keto amine tautomer of HBT might appear above 600 nm from the position of the fluorescence band of the keto tautomer and the ordinary energy separation between π-π^* excited singlet and triplet states.

Relaxation Processes of Excited HBT in Hydrogen-bonding and Non-hydrogen-bonding Solvents. The relaxation processes after photoexciation of the HBT enol imine for HBT in non-hydrogen-bonding or weakly hydrogen-bonding solvents and in strongly hydrogen-bonding solvents are summarized in Figs. 4(a) and 4(b), respectively. In the former case in which HBT with the intramolecular hydrogen bond exists, the hydrogen transfer through the bond proceeds very fast in the excited state and the intermediate, X, is detected by picosecond time-resolved spectroscopy.[4] The photochromic state P and the *cis*-keto amine were formed from X competitively. In the latter case in which both intramolecular and intermolecular hydrogen bonded species coexist in equilibrium in the ground state, besides the processes mentioned above, the formation and decay processes of the triplet enol imine occur. "Sol" in Fig. 4(b) refers to a solvent molecule.

Electronic Spectra of HBO and HBT. The absorption spectrum of HBO in EPA at 77 K is essentially the same as that in PM (Fig. 3), showing that the dominant species in EPA at 77 K is the enol imine with the intramolecular hydrogen bond. The intramolecular hydrogen bond of HBO is more stable than that of HBT,[10] as Durmis *et al.* showed in their study of the dissociation constants.[11]

The emission spectra of HBO in PM are shown in Fig. 3. The emission properties of HBO in EPA at 77 K are very similar to those in PM at 77 K. The intensity of the keto amine fluorescence is much larger than that of the enol imine fluorescence or phosphorescence. The ratio $\phi_f(E)/\phi_f(K)$ was estimated to be less than 0.01 both in EPA and in PM at 77 K. The excitation spectra of the keto amine fluorescence and the enol imine phosphorescence agree with the absorption spectrum in PM at 77 K.

A difference between HBT and HBO is seen with respect to the yield of enol triplet formation. In PM at room temperature, the $T_n \leftarrow T_1$ transition was observed with HBO but not with HBT, while the photochromic transient absorption was observed with HBT but not with HBO. The phosphorescence of the enol imine with the internal hydrogen bond was observed with HBO but not with HBT at 77 K. These facts indicate that the intersystem crossing yield of the enol tautomer is larger for HBO than for HBT. The relaxation processes after photoexcitation of the HBO enol tautomer in EPA and in PM at 77 K are summarized in Fig. 5.

Primary Process of Photochromism. The yield $\phi_f(K)$

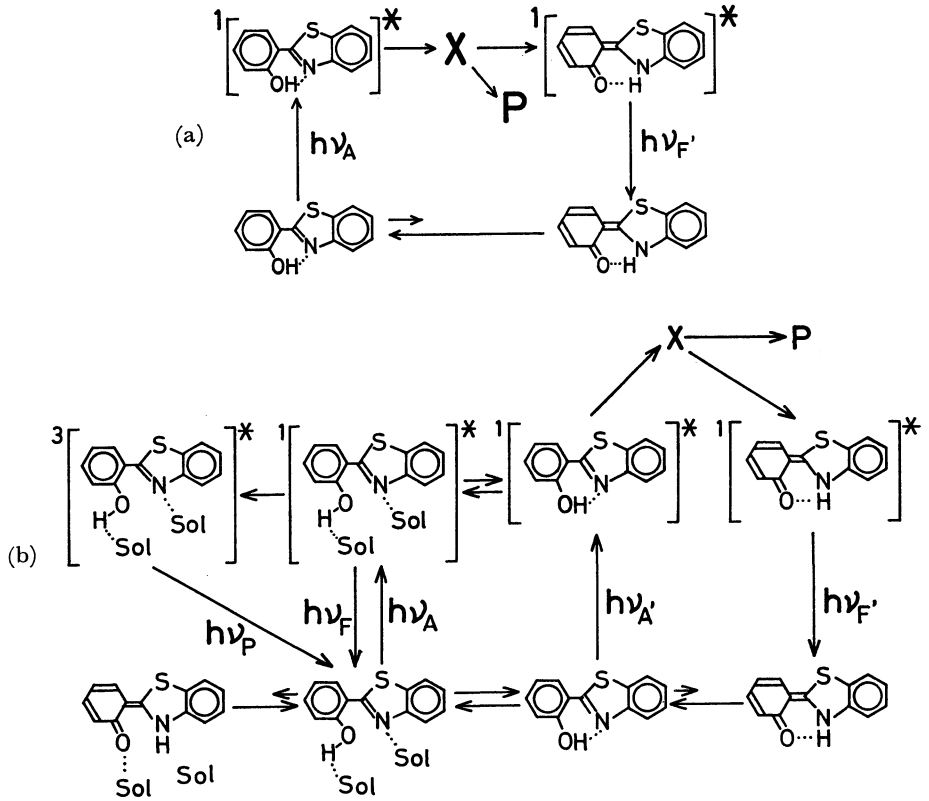

Fig. 4. Schematic diagrams representing the ground state equilibrium and relaxation processes in the excited state of HBT.
(a) In the weakly hydrogen-bonding or non-hydrogen bonding solvents.
(b) In the strongly hydrogen-bonding solvents.

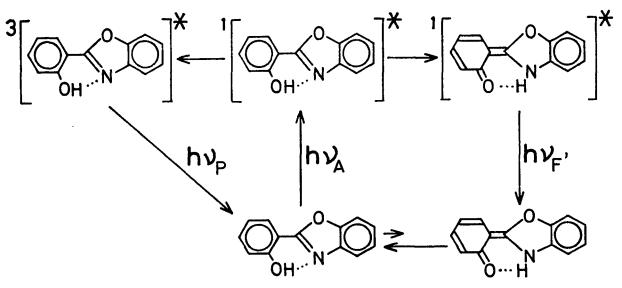

Fig. 5. Schematic diagram representing the ground state equilibrium and relaxation processes in the excited state of HBO.

of HBT in PM at 77 K was determined to be 0.36, and the ratio $\phi_f(E)/\phi_f(K)$ was estimated to be less than 0.015 (Table 1). From these values $\phi_f(E)$ at 77 K was evaluated to be less than 5.4×10^{-3}. For HBT in PM at 293 K, the yield $\phi_f(K)$ was determined to be 0.006, and the ratio $\phi_f(E)/\phi_f(K)$ was estimated to be less than 0.012. Thus the yield $\phi_f(E)$ at 293 K was evaluated to be less than 7.2×10^{-5}.

The enol fluorescence radiative rate constant k_f^e was estimated to be 2.3×10^8 s^{-1}.[12] From this value and the yield $\phi_f(E)$, the lifetime of the enol imine fluorescent state was estimated to be shorter than 3.1×10^{-13} s. This is much shorter than the lifetime of the precursor, X, of the photochromic species (53 ps) determined in previous study.[4] This means that the enol imine fluorescent state is not the precursor. Thus we obtain an additional support for the scheme in which P is not formed directly from the enol excited state.

Estimation of the Rate Constant of the Intramolecular Hydrogen Transfer. The rate constants of the intramolecular hydrogen transfer at 77 and 293 K were estimated from the enol imine fluorescence quantum yield, which is given by

$$\phi_f(E) = \frac{k_f^e}{k_f^e + k_{fq}^e + k_{HT}}, \quad (1)$$

where k_{fq}^e and k_{HT} represent the rate constants of the radiationless transition other than hydrogen transfer and of the intramolecular hydrogen transfer in the excited singlet state of the enol imine, respectively. From the decay times of the enol imine fluorescent state in the hydrogen bonding media, $(k_f^e + k_{fq}^e)$ in PM was estimated to be about 1×10^9 s^{-1} at 77 K. By putting the numerical values into Eq. 1, k_{HT} was evaluated to be larger than 4×10^{10} s^{-1} at 77 K. At room temperature, $(k_f^e + k_{fq}^e)$ is at most of the order of 10^{11} s^{-1}; k_{HT} was estimated from the values mentioned above to be larger than 3×10^{12} s^{-1} in PM at 293 K.[13] By assuming an Arrhenius equation with a frequency factor of 10^{13} s^{-1} for k_{HT}, an upper limit of 0.9 kcal/mol was estimated for the barrier to the hydrogen transfer.[14] The value of k_{HT} at 77 K is greater than that for the 1,7-diazaindene hydrogen bonded dimer in 3-methylpentane at 77 K (5×10^8 s^{-1}) by a factor of at least 80,[15] and at 293 K it is greater than the value for 2,4-bis(dimethylamino)-6-(2-hydroxy-5-methylphenyl)-1,3,5-triazine in cyclohexane at 298 K (1.1×10^{10} s^{-1}) by a factor of at least 270.[16] These large k_{HT} values can be explained as follows.

(1) A strong intramolecular hydrogen bond is formed in the HBT ground state, as shown by the pK_a value, NMR and IR spectroscopy and X-ray crystal analysis.[11,5,17] The O–N distances in the six-membered chelate ring are 2.605 Å for HBT, 2.584 Å for *N*-(5-chlorosalicylidene)aniline, and 2.609 Å for 2-chloro-*N*-salicylideneaniline.[18] These are examples of the shortest O–N distance in the OH···N hydrogen bond systems, the average O–N distance of which is 2.80 Å.[19] This strong intramolecular hydrogen bond favors the rapid hydrogen transfer in the excited state.

(2) Upon photoexcitation the phenolic hydroxyl group becomes more acidic and the imino nitrogen more basic than in the ground state. A similar situation has been reported for intramolecularly hydrogen-bonded salicylic acid derivatives.[20]

We are greatly indebted to Prof. Katsumi Kimura and Dr. Yohji Achiba, Hokkaido University, for their kindness in performing flash photolysis experiments at 77 K. We wish to thank Dr. Kazuo Shibata and Dr. Yorinao Inoue, the Institute of Physical and Chemical Research, for their kindness in putting the spectrofluorometer (Shimadzu RF-502) at our disposal.

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10) On treatment with dimethyl sulfate under the usual conditions, HBT is easily methylated but HBO is hardly converted into the corresponding methoxy derivative. This reflects the difference in stability of the intramolecular hydrogen bond between HBT and HBO.

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12) The fluorescence radiative rate constant k_f^e was calculated by Förster's formula:

$$k_f^e = 2.88\times10^{-9}n^2\int\frac{(2\nu_0-\nu)^3}{\nu}\varepsilon(\nu)d\nu.$$

13) This value of k_{HT} is of the same order or a little larger than the usual values of the rate constants of vibrational relaxation in condensed media. This suggests that the intramolecular hydrogen transfer occurs from not only the thermalized

state in the lowest excited singlet state (S_1) but levels of S_1, and gives a plausible explanation for dependence on the excitation wavelength of the quantum yield of the photochromic colored species reported by Rosenfeld *et al.*[2c]

14) The hydrogen transfer in the enol excited state is a cooperative phenomenon, in which such particular vibrations as the stretching vibrations of the phenolic hydroxyl group and the aromatic nucleus of the salicylaldehyde moiety, participate. Consequently, it is reasonable to assume that the rate constant of phototautomerization follows the Arrhenius equation with a frequency factor of 10^{13} s^{-1}, which is commonly observed for the order of the stretching vibration frequency in the excited state.

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