

Absorption and Fluorescence Spectra of 10-Hydroxy-benzo[h]quinoline and 10-Methoxy-benzo[h]quinoline in various Solvents¹⁾

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(Received May 25, 1993)

The absorption, fluorescence, and fluorescence-excitation spectra of 10-hydroxy-benzo[h]quinoline (HBQ), and its methoxy derivative, 10-methoxy-benzo[h]quinoline (MBQ), have been observed in various solvents. HBQ shows two types of fluorescence spectra. The first is a broad and structureless fluorescence band with a peak at ca. 490 nm (FP band). The second is a broad and structureless fluorescence band with a peak at around 590 nm - 630 nm (FT band) owing to the solvent polarity. On the other hand, MBQ shows a sharp fluorescence band with a peak at 380 nm in cyclohexane (FN band) and broad and structureless band with a peak at 470 nm in aqueous solutions (FP band). Based on the experimental results, the FN, FP, and FT bands can be assigned to the fluorescences originated from neutral form, protonated form, and tautomer owing to excited state intramolecular proton transfer of HBQ and/or MBQ, respectively. The FN band from HBQ was not well resolved in the present experimental conditions. It has become apparent that HBQ is a new molecule showing excited state intramolecular proton transfer.

1. Introduction

The process of the excited-state intramolecular hydrogen-atom transfer is fundamental process in chemistry and biology²⁻⁶⁾. The process would also be a potential tool for application to photodevices using photochromism⁷⁾, photochemical hole burning⁸⁻¹⁰⁾, and making a proton-transfer laser¹¹⁻¹⁴⁾. The molecules which undergo the process have been known for various types of molecules. 10-hydroxy-benzo[h]quinoline (HBQ) has a possibility of this process. In this paper we have examined the photophysical process of HBQ and its methoxy substituted compound 10-methoxy-benzo[h]quinoline (MBQ). These molecular structures are shown in Fig. 1. Compared

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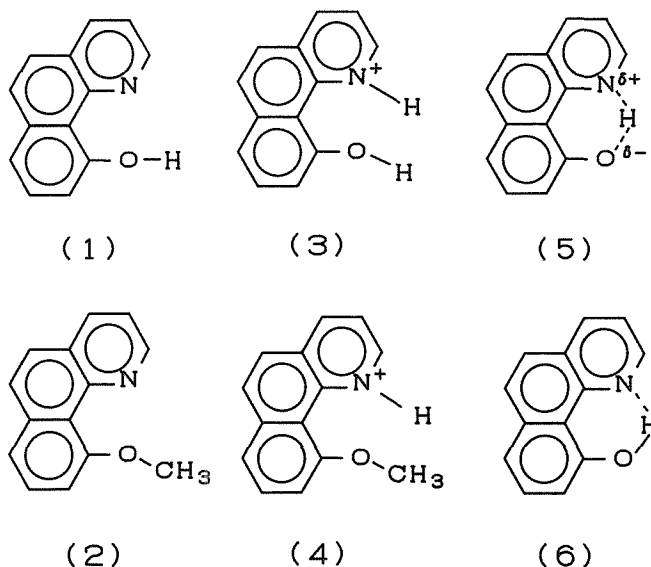


Fig. 1. The various molecular forms of 10-hydroxy-benzo[h]quinoline (HBQ) and 10-methoxy-benzo[h]quinoline (MBQ). (1) neutral form of HBQ, (2) neutral form of MBQ, (3) protonated form of HBQ, (4) protonated form of MBQ, (5) excited state intramolecular proton transfer form of HBQ, and (6) intramolecular interaction form of HBQ.

with the photophysical process of MBQ and HBQ, it has become apparent that HBQ is a new molecule indicating excited-state intramolecular proton transfer. Since there is little study on the chemistry of HBQ¹⁵⁾, we will report here IR- and UV-absorption spectra, ¹H- and ¹³C-NMR, and GC-MS for HBQ and MBQ.

2. Experimental

HBQ (Tokyo Kasei Kogyo Co. Ltd.) was purified by repeated recrystallizations from petroleum ether. MBQ was prepared by adding 115 mg of sodium hydride (NaH 2.88 m mol purity 60 %) to a solution of 461 mg (2.36 m mol) of HBQ in 2 ml dimethyl formamide (DMF). The mixture was stirred for 25 min at 333 K, and cooled at room temperature. Then 0.20 ml (3.21 m mol) of methyl iodide (CH₃I) was added to it, and stirred for 60 min. The resulting mixture was poured into 200 ml of water to yield white and thin layered crystal. The crystal was washed by water and yield 246 mg (m. p. 413-415 K). The measurements of TG, DTA and DSC indicated that the prepared crystal was pure enough to be subjected to spectroscopic studies. Since the spectral data for HBQ and MBQ are restricted for ¹H- and ¹³C-NMR in reference¹⁵⁾, we give the IR, NMR, and GC-MS data for HBQ and MBQ.

HBQ. IR 3420(ν_{OH} this broad absorption band is characteristic of internal hydrogen bonding), 1230 cm^{-1} ; ^1H NMR δ 7.2-7.7(m. 6H aromatic), 7.9(d 1H $J=17.3$ Hz), 8.8(d 1H $J=2.7$ Hz), 14.5(brd S 1H indicates that the hydroxy group forms internal hydrogen bonding between $-\text{OH} \cdots \text{N}$); ^{13}C NMR δ 114.0, 120.2, 123.9, 126.0, 129.0, 129.6, and 135.6(CH aromatic), 117.6, 134.8, 142.9, and 148.4(C aromatic), 144.6($-\text{C}=\text{N}$ -), 159.3($-\text{C}-\text{OH}$); MS m/z (rel. intensity) 195(M^+ 100), 167(48), 139(18), 113(6); high-resolution MS m/z 195.0671($\text{C}_{13}\text{H}_9\text{NO}$ requires 195.0681).

MBQ. IR 2815($\text{O}-\text{CH}_3$), 1263($=\text{C}-\text{O}-\text{C}$), 1043($=\text{C}-\text{O}-\text{C}$) cm^{-1} ; ^1H NMR δ 4.1(S 3H $\text{O}-\text{CH}_3$), 7.2-8.2(m. 7H aromatic), 9.12(brd S 1H); ^{13}C NMR δ 56.5($\text{O}-\text{CH}_3$), 110.0, 120.1, 120.8, 125.8, and 127.9(CH aromatic), 126.5, 134.9, and 136.1(C aromatic), 148.0($=\text{C}=\text{N}$ -), 159.0($\equiv\text{C}-\text{O}$ -); MS m/z (rel. intensity) 209(M^+ 76), 180(100), 178(M^+-CH_3 92), 166(10), 152(15); high-resolution MS m/z 209.0828($\text{C}_{14}\text{H}_{11}\text{ON}$ requires 209.0837).

Cyclohexane and ethanol were purchased from Wako, HCl, NaOH, NaH, DMF, and CH_3I were purchased from Tokyo Kasei and used without further purification. Water was deionized and distilled.

IR spectra(KBr disks)were obtained with a Fuji FIRS-25 Spectrometer. NMR spectra were recorded on Nippondenshi JMN-FX-60 spectrometer at 60 MHz for ^1H and 15 MHz for ^{13}C . Chemical shift(δ) in CDCl_3 are reported in part per million (ppm) downfield from TMS. MS spectra were measured on Hitachi M80B double focus GC-MS spectrometer at an ionizing potential of 70 eV. The TG, DTA, and DSC were carried out using a SEIKO-220C thermal analyzer. The electronic absorption spectra were recorded on a Hitachi U-3210 recording spectrometer. The emission spectra were recorded on a Shimadzu RF-5000 fluorescence spectrometer.

3. Results and Discussion

3. 1. Absorption spectra of MBQ in various solutions.

Generally speaking, methylation of hydrogen in hydroxy group is an efficient method to elucidate the H transfer. The absorption spectrum of MBQ should not largely be effected by the methylation of hydrogen in hydroxy group. The absorption spectra of MBQ in various solutions are shown in Fig.2. The spectrum observed in cyclohexane is similar in whole spectral feature to benzo[h]quinoline¹⁶⁾ and shows a characteristic vibrational profile with peaks at 359, 352, 342, 336 and 327 nm, respectively and a shoulder at ca. 320 nm. The absorption spectrum of MBQ can be assigned to a transition from ground-state neutral molecular form of MBQ(Fig. 1-2), since interaction between MBQ and cyclohexane is expected to be small. The absorption spectrum of MBQ observed in ethanol also shows vibrational structure but less fine structure compared with that observed in cyclohexane. These peak positions agree well with positions in cyclohexane. The spectrum observed in ethanol can be attributable to a neutral form of MBQ in the ground state, though MBQ molecules interact with

surrounding ethanol molecules.

The absorption spectra of MBQ in 5 M HCl and aqueous solutions show a broad and structureless spectra with a peak at 387 nm. This broad absorption band should be attributed to the protonated form at N atom of MBQ in the ground state. This protonated form of MBQ is shown in Fig. 1. It is noted that the absorption spectrum of MBQ in water has shoulders around at 363 and 344 nm. These positions agree with the vibrational peaks of MBQ observed in ethanol. Therefore, the results in water show that the ground-state species of MBQ in water exist in both the neutral and protonated forms.

3.2. Fluorescence spectra of MBQ in various solutions.

The fluorescence spectra of MBQ in various solutions is shown in Fig. 3. There is no excitation wavelength dependence in the spectrum except in water. The fluorescence spectrum in cyclohexane shows a vibrational structure with peaks at 367, 380, and 397 nm. The spectrum observed in ethanol also showed a sharp band with a peak

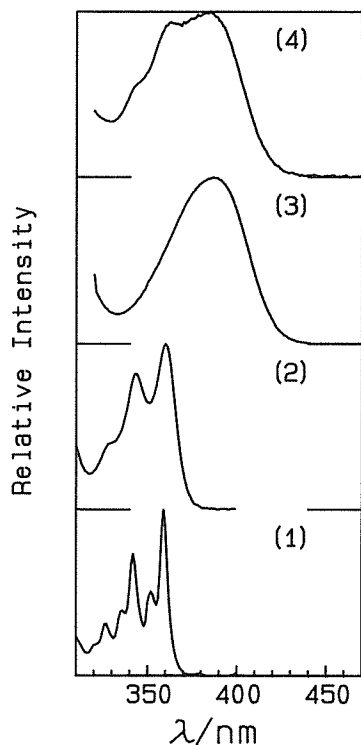


Fig. 2. The absorption spectra of MBQ in (1) cyclohexane, (2) ethanol, (3) 5 M HCl, and (4) water.

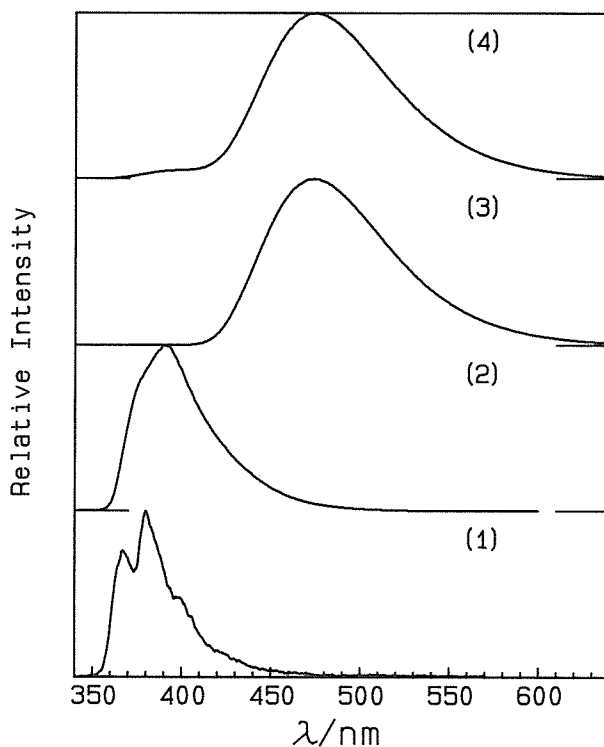


Fig. 3. The fluorescence spectra of MBQ in (1) cyclohexane, (2) ethanol, (3) 5 M HCl, and (4) water.

at 388nm and no excitation wavelength dependence. Since there are probably no specific interaction between MBQ and cyclohexane in its excited state, the fluorescence band observed in cyclohexane can be assigned to a fluorescence of excited neutral form of MBQ. Because of interaction between MBQ and ethanol, the spectrum in ethanol is broader than the spectrum in cyclohexane. The spectrum in 5 M HCl shows a broad and structureless band with a peak at 473 nm. Although it is not shown here, the fluorescence spectrum of MBQ in 0.2 M HCl gave us the same spectrum that observed in 5 M HCl. These results indicate that the excited-state species of MBQ in 5 M HCl is the protonated form of MBQ.

The spectrum in water shows a little wavelength dependence. When it is excited at 340 nm, there are two broad and structureless fluorescence peaks ; one has a peak at around 390 nm, and the other has a peak at 474 nm. The position of the former is substantially the same region as that in the position observed in cyclohexane and in ethanol. When it is excited at 384 nm, there is only one peak at 474 nm. These results indicate that there are two excite-state species in water, one is the neutral form of MBQ (peak at 390 nm) and the other is the protonated form of MBQ (peak at 474 nm). Though they are not shown here, the fluorescence-excitation spectra of MBQ are substantially the same of its absorption spectra in each solvents.

3. 3. Absorption spectra of HBQ in various solutions.

The absorption spectra of HBQ in various solutions are shown in Fig. 4. The spectral feature of HBQ observed in cyclohexane is distinct from that the results shown Fig. 2 for the absorption spectra of MBQ, although methylation should not be expected to largely effect in their electronic structure. The spectra are broad and have two peaks at 381 and 367 nm in cyclohexane and a peak at 371 nm and a shoulder at ca. 359 nm in ethanol. It is noted that the spectra shift to the blue in the order of cyclohexane and ethanol. On the other hand, the absorption spectrum of HBQ in 5 M HCl shows a broad and structureless spectrum with a peak at 389 nm and its spectral feature resembles to the absorption spectrum on MBQ in 5 M HCl solution. This indicates that HBQ in 5 M HCl originates from protonated form of the ground state, while the absorption spectra in cyclohexane and ethanol show that they originate from neutral form of HBQ, though HBQ molecules interact with surrounding solvent molecules by hydrogen bonding. The blue shift observed in ethanol compared with that in cyclohexane support a specific intramolecular hydrogen bonding. These molecular structure (protonated form and intramolecular interaction form of HBQ) are illustrated in Fig. 1.

3. 4. Fluorescence spectrum of HBQ in various solutions.

Figure 5 show the fluorescence spectra of HBQ in various solutions. The most marked aspect of fluorescence spectrum in cyclohexane is that the spectrum shows large red shift, and broad and structureless band with peak at 630 nm (abbreviated to

the FT band). There is no excitation wavelength dependence in the spectra. The spectrum is quite different compare with the results obtained for MBQ in cyclohexane. The fluorescence spectrum observed in ethanol also show a broad and structureless band with peak at 604 nm. Although this spectrum shows a little blue shift compared with that observed in cyclohexane, it is substantially the same to that observed in cyclohexane and quite different to that for MBQ in the same solvent. On the other hand, the spectrum in 5 M HCl shows broad and structureless band with peak at 496 nm (abbreviated to the FP band) and shows no excitation wavelength dependence. It has become obvious that there are two fluorescent bands for HBQ ; the FT band and the FP band. In addition to this, there is fluorescence spectra of MBQ presented in short wavelength region with peaks at 367, 380, and 397 nm in cyclohexane. We abbreviated to this structured fluorescence band to the FN band.

It has been become obvious that the FT band is only observed for HBQ and not observed for MBQ in various solvents. The FN band is only observed for MBQ and not observed for HBQ in various solvents. The FP band is observed for both MBQ and HBQ. The intramolecular hydrogen-bonding between N atom and hydrogen atom of methoxy group is improbable for MBQ, but it is actual between N atom and the hydrogen atom in hydroxyl group for HBQ. Therefore, we can concluded that the intramolecular hydrogen-bonding formation between N atom and hydrogen atom in hydroxyl group for HBQ is responsible for the appearance of the FT band. The FT band is originated from the excited-state intramolecular proton transfer form of HBQ.

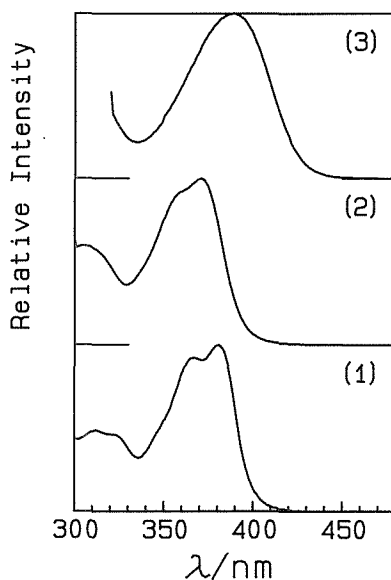


Fig. 4. The absorption spectra of HBQ in (1) cyclohexane, (2) ethanol, and (3) 5 M HCl.

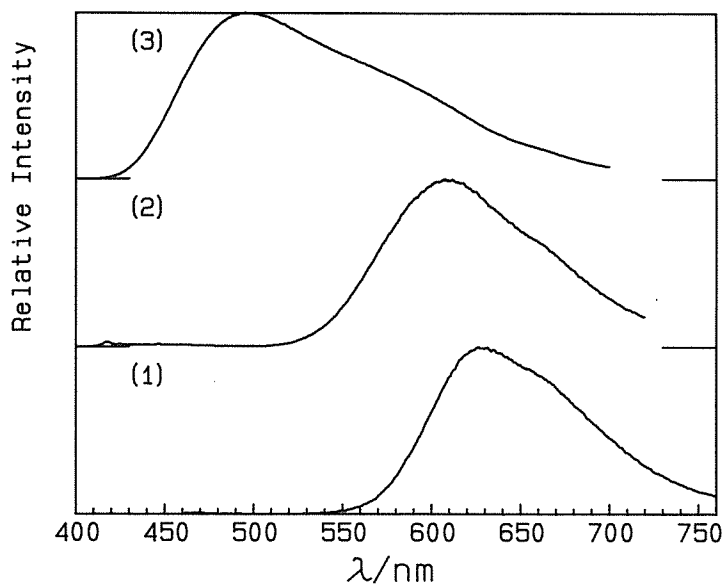


Fig. 5. The fluorescence spectra of HBQ in (1) cyclohexane, (2) ethanol, and (3) 5 M HCl.

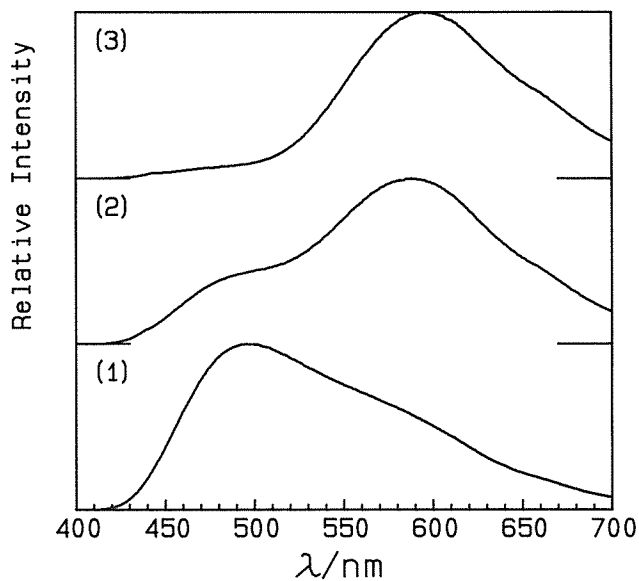


Fig. 6. The fluorescence spectra of HBQ in (1) 5 M HCl, (2) 1.3 M HCl, and (3) 0.5 M HCl solutions.

Figure 6 shows the fluorescence spectra of HBQ in 5 M, 1.3 M, and 0.5 M HCl solutions. There are two fluorescence bands around at 495 nm (the FP band) and around at 590 nm (the FT band). The main fluorescence band in 0.5 M HCl is the FT band. The intensity of the FP band became strong in the order of increasing the acid strength and the FP band became the main band in 0.2 and 5 M HCl solutions. The fluorescence spectra showed no excitation-wavelength dependence. Therefore the FP band is belonged to the protonated form of HBQ. Though they are not shown here, the fluorescence-excitation spectrum of HBQ are substantially the same of its absorption spectrum in each solvents.

4. Conclusion

HBQ shows two types of fluorescence spectra. The first is a broad and structureless fluorescence band with a peak at ca. 490 nm (the FP band). The second is a broad and structureless fluorescence band with a peak at around 590-630 nm (the FT band) owing to the solvent polarity. On the other hand, MBQ shows a sharp structured fluorescence band with a peak at around 380 nm in cyclohexane and a broad structureless band with a peak 480 nm in acidic solvents. The FN, FP, FT bands can be assigned to fluorescences originated from neutral form, protonated form, and tautomer of HBQ and/or MBQ, respectively. It has become apparent that HBQ is a new molecule showing excited-state intramolecular proton transfer.

[Note added in proof] After making our measurement, we found a similar study was reported for HBQ (M. L. Martinez, W. C. Cooper, and Pi-Tai Chou, *Chem. Phys. Lett.*, **193**, 151(1992)).

5. Acknowledgment

The authors thank Professor K. Koyama for his encouragement.

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