BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1433—1435 (1969)

Fluorescence Spectra of Some Benzimidazoles in Acid Media

Michio KONDO and Harumitsu KUWANO

Central Research Laboratories, Sankyo Co., Ltd., Shinagawa-ku, Tokyo

(Received June 20, 1968)

Few papers have been published on the fluorescence spectra of benzimidazole in the protonated state.[1,2] For benzimidazole perchlorate, two fluorescence bands were observed in an ethanol solution at a low temperature. The weak, broad, structureless band observed at about 29000 cm^{-1} was assigned to the emission from the excited singlet state, ^1L_a, on the basis of the results of fluorescence polarization experiments.[2] This indicates the reversal of the excited energy levels, ^1L_a and ^1L_b. The present note will report on the fluorescence of some benzimidazole derivatives in acid and neutral media.

The benzimidazoles studied have pK_a values ranging from 4.9 to 6.8. The absorption spectra of these compounds show two separated absorption bands, ^1L_a and ^1L_b, in neutral and acid solutions. The protonation causes slight blue shifts in the two absorption bands for each compound.

Neutral benzimidazole molecules show an emission band at about 34500 cm^{-1}, whereas the cations give rise to a broad, structureless emission band peaking at about 27800 cm^{-1}.

Neutral molecules of 2-methylbenzimidazole give an emission band at 34250 cm^{-1}. However, two emission bands are observed in acid media where the molecules are presumed to be completely protonated. This is in marked contrast to the fact that benzimidazole cations exhibit only one emission band. One of the two emission bands of the 2-methylbenzimidazole cations is located at 34840 cm^{-1} and it has unresolved structure, whereas the other is a broad, structureless band peaking at about 27800 cm^{-1}. The former emission bands shifts 590 cm^{-1} to higher frequencies relative to the emission band observed for neutral molecules and is observed to a considerable extent even in a 10 N sulfuric acid solution. These facts suggest that this fluorescence originates not from neutral but from cationic species.

It is possible to ascribe this emission band to the neutral species which could be present in the excited state if the pK_a^* value were assumed to be much smaller than pK_a. However, it is very difficult to imagine a large difference between the pK_a^* values of benzimidazole and 2-methylbenzimidazole in the excited state, for they are very similar in physical and chemical properties.

Another derivative of benzimidazole, 5-chlorobenzimidazole, behaves quite differently from the two compounds mentioned above. Neutral molecules show an emission band at 32890 cm^{-1}. An emission band from the cations is observed at 33900 cm^{-1} with no accompanying band at lower frequencies. In this case, the protonation causes a blue shift in both absorption and emission spectra. Even in a solution of 10N sulfuric acid, no emission band was observed at about 27800 cm^{-1}. This fact suggests that the normal emission band from the protonated species should not be far apart from the absorption band, and that the broad, structureless emission observed for benzimidazole and 2-methylbenzimidazole cations is abnormal.

From the large red shift of the broad, structureless emission band of the 2-methylbenzimidazole cations, one can suspect that the emission band is attributable to the formation of a kind of excimers.[3] However, this possibility can be ruled out for the following

TABLE 1. CLASSIFICATION OF FLUORESCENCE SPECTRA OF SOME BENZIMIDAZOLES

Cation	pK_a	Emission band ~34000 cm^{-1}	Emission band 27800 cm^{-1}	Class*
Benzimidazole cation	5.5	−	+	A
2-Methyl-BI cation**	6.1	+	+	B
2-Ethyl-BI cation	6.2	+	+	B
2-Benzyl-BI cation	5.7	+	+	B
5-Methyl-BI cation	5.7	−	+	A
2,5-Dimethyl-BI cation	6.7	+	+	B
5-Chloro-BI cation	4.9	+	−	C
2-Methyl-5-chloro-BI cation	5.7	+	−	C

* Symbol A means an emission spectrum at a lower frequency. B means a fluorescence spectrum consisting of two bands. C means an emission band at a higher frequency.

** BI stands for benzimidazole.

1) T. K. Adler, *Anal. Chem.*, **34**, 685 (1962).

2) H. U. Schütt and H. Zimmerman, *Ber. Bunsenges. Physik. Chem.*, **67**, 54 (1963).

3) Th. Förster and K. Kasper, *Z. Elektrochem.*, **59**, 976 (1955).

reasons: (i) the concentration change (10^{-4} mol/l to 10^{-6} mol/l) caused no variation in the relative intensity of the two bands or in the shape of the emission spectrum, (ii) the emission spectrum was independent of the viscosity of the media, as was seen from the fact that the emission spectrum obtained in an aqueous solution was essentially the same as that obtained in aqueous glycerol (60 vol%). Furthermore, in different acids, (0.1N sulfuric, hydrochloric, perchloric, and acetic acid), the emission spectra of the two bands were essentially the same in shape and in intensity ratio. These facts suggest that the appearance of the second emission band is not due to some bimolecular or multimolecular mechanism, but to unimolecular mechanism.

The other benzimidazole derivatives studied can be classified into the three types described above on the basis of their fluorescence spectra. Table 1 presents this classification. From this table, it can be concluded definitely that there is no close relationship between the pK_a values and the appearance of the broad emission band at lower wave numbers. It is of interest to note, however, that 2-methylbenzimidazole gives an emission spectrum consisting of two components, whereas 5-methylbenzimidazole gives a single, broad, structureless fluorescence band at about 27800 cm^{-1}. This observation suggests that the introduction of a methyl group at the position 2 has a greater effect in producing the broad emission at lower frequencies than does the introduction of a methyl group at the position 5.

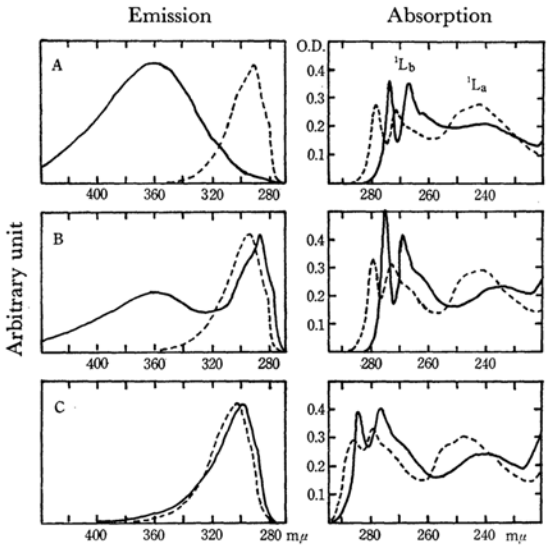

Fig. 1. Absorption and emission spectra of three benzimidazole derivatives in neutral (pH=9.3) —— and acid (0.1N H_2SO_4) —— media.
A: benzimidazole; B: 2-methylbenzimidazole; C: 5-chlorobenzimidazole.

The emission and absorption spectra are shown in Fig. 1 for the three benzimidazole derivatives in neutral and acid media. A correlation between the absorption and emission spectra in acid media can be obtained. In the case of the benzimidazole cation, the separation between the absorption bands is small and the emission is broad and is shifted to lower wave numbers. In contrast with this, two clearly-split absorption bands are observed for 5-chlorobenzimidazole cations, which show a single emission band with a small Stokes shift. For the compound with two emission bands, an intermediate splitting of the two absorption bands is observed. On the other hand, in neutral media, the two absorption bands are clearly split and only one emission band is observed for each compound. These observations suggest that the magnitude of the separation between the two excited singlet states, ^1L_a and ^1L_b, is an important factor in producing the broad emission band.

It is sure that the fluorescence originates from the equilibrium excited-state configuration, because the viscosity has no effect on the emission spectra. The relaxation process, through which the excited molecules in the Franck-Condon state change into the equilibrium-excited state, includes the reorientation of the polar solvent molecules to their equilibrium orientation in the field of the excited state of the polar solute molecules. For benzimidazole perchlorate, the emission from the ^1L_a state was observed at lower frequencies than that from the ^1L_b state.[2] This indicates that the ^1L_a state was much more stabilized than the ^1L_b state, perhaps due to the more polar character of the ^1L_a state. For the compounds, therefore, it may be possible to say that the ^1L_a states are more polar than the ^1L_b states. It is expected that the ^1L_a states are strongly stabilized by the interaction with polar solvent molecules, while the ^1L_b states are not, and that the reversal of the two excited energy levels can occur when the separation between them is small. In the case of the benzimidazole cation, the lowest vibration energy levels of the ^1L_a and ^1L_b states seem to be close to each other, and the reversal of the two energy levels could occur through the relaxation mentioned above. However, it may be difficult for the reversal to occur in the 5-chlorobenzimidazole cation because of its well-separated levels. The compounds with two excited levels intermediately split will give emission spectra consisting of two components as a result of a competitive emission from the two levels, ^1L_a and ^1L_b, which lie very close to each other after the stabilization mentioned above. Such a reversal of the two excited states has been reported for *p*-cyano-*N*,*N*-dimethylaniline,[4] for example.

4) E. Lippert, W. Lüder, F. Moll, W. Nägele, H. Boos, H. Prigge and I. Seibold-Blankenstein, *Angew. Chem.*, **73**, 695 (1961).

Experimental

Several benzimidazole derivatives were prepared by refluxing *o*-phenylenediamine and appropriate carboxylic acids in dilute hydrochloric acids.

The absorption spectra were measured with a Cary spectrophotometer Model 14. The fluorescence spectra were recorded on a Hitachi fluorescence spectrophotometer Model MPF-2.

In acid media, these compounds were stable, so the same absorption and emission spectra were obtained again on the next day. Prolonged irradiation did not cause any change in the absorption and emission spectra of benzimidazole. When the observing fluorescence was fixed at the higher-frequency band, the apparent excitation spectrum of 2-methylbenzimidazole cations was essentially the same as that obtained when the fluorescence was observed at the lower-frequency band. This is consistent with the fact that there only the protonated species are present in the solution.