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Complex Formation and Ionization in 3,5-Dialkyl-4-hydroxybenzylidenemalononitrile in the Ground State, and Non-radiative Relaxation in the Excited State

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The interaction of 3,5-dialkyl-4-hydroxybenzylidenemalononitrile (HO-BMN) with ethanol, pyridine, and triethylamine in hexane gives rise to a hydrogen bonding complex formation in a low concentration of ethanol (pyridine and triethylamine) at room temperature. For ethanol concentration >5 mol dm^{-3}, the H-bonded complex exhibits further interaction with another ethanol (pyridine and triethylamine) molecule leading to the formation of anion form of this compound. However, no excited-state proton transfer was observed in several solvents. HO-BMN is fairly fluorescent in a solid solution of boric acid glass at room temperature, as well as in the rigid organic solution at 77 K, but almost non-fluorescent in fluid media at room temperature ($\phi \approx 10^{-4}$). The non-radiative process of HO-BMN in fluid media is discussed in terms of torsional relaxation of the excited state.

It was reported that 3,5-di-*t*-butyl-4-hydroxybenzylidenemalononitrile (*t*-Bu$_2$-HO-BMN) is the most potential uncoupler of oxidative phospholylation.[1,2] This is attributed to the properties of the proton transfer and conduction in phospholipid bilayer.[3] Yamaguchi *et al.* reported that the *t*-Bu$_2$-HO-BMN shows a ternary complex formation with valinomycin and potassium ion. On the other hand, this compound exhibits the dimer formation in 3-methylpentane at low temperature and the excited-state proton transfer in the dimer.[4] The unusual property of this compound seems to be attributable to the strong electron acceptor group (malononitrile) as a substituent of phenol.

This paper describes unusual spectroscopic properties of various 3,5-dialkyl-4-hydroxybenzylidenemalononitrile (HO-BMN) both in the ground and excited states. HO-BMN exhibits hydrogen bonded complex formation with ethanol (pyridine and triethylamine) in a dilute ethanol solution (*ca.* 1 mol dm^{-3}) in hexane. The ground-state ion-pair formation occurs by the further interaction between the H-bonded complex and another ethanol molecule in ethanol concentration greater than 5 mol dm^{-3}. However, no proton transfer was observed in the excited state of these compounds. Although HO-BMN shows fairly strong fluorescence in boric acid glass at room temperature and in several glassy or rigid solutions at low temperature, the compounds are almost non-fluorescent in the fluid solution at room temperature. Remarkable temperature dependence of fluorescence intensity and lifetime of the compounds dependent on rigidity of the solution was interpreted in terms of torsional relaxation of the excited state.

Experimental

The purification of materials and solvents was described.[4] Ethanol (Nakarai, 99.5%) was purified by distillation after refluxing over magnesium metal. Pyridine (Nakarai GR) and triethylamine (Nakarai GR) were distilled twice after refluxing over potassium metal for 3—5 h. Solid solution of boric acid glass was prepared as follows. Boric acid was heated and melted in a porcelain dish at 150—180 °C, transparent liquid being obtained. The samples were then dissolved into liquid glass at this temperature (the samples were stable in this process). Solid-glass solution was obtained after the temperature had fallen to room temperature.

Since materials are insoluble in aqueous solution, determination of pK_a was performed in aqueous ethanol solution (50, 40, and 30 w/v %). The pK_a in 100% aqueous solution (Table 1) was obtained by an extrapolation from values in the mixed solution.[5]

Measurement of fluorescence and absorption spectra was made as described previously.[4] Fluorescence quantum yield was determined using quinine sulfate (2.1×10^{-5} mol dm^{-3} in 0.5 mol dm^{-3} H_2SO_4) as a standard ($\phi = 0.546$ in the excitation at 365 nm).[6] Determination of fluorescence lifetimes was made by N_2 laser (Molectron UV-12) excitation and analysis of exponential decay curve. The data were analyzed by a convolution method.[4]

Results and Discussion

Complex and Ion-pair Formations in the Ground State. The absorption spectrum of 3,5-dialkyl-4-hydroxybenzylidenemalononitrile (HO-BMN) shows an absorption band at 350—370 nm in aprotic solvent and in an acidic ethanol–water mixed solution, and another band at 465 nm in basic ethanol–water. The former and the latter were attributed to the neutral form and to the anion form of the compound, respectively.[4] Absorption spectra of 3,5-dimethyl- and 3,5-di-*t*-butyl-4-hydroxybenzylidenemalononitrile (Me$_2$- and *t*-Bu$_2$-HO-BMN) were measured in hexane solution in the presence of various amounts of ethanol (Figs. 1 and 2). The spectral change of Me$_2$-HO-BMN exhibiting an isosbestic point at 345 nm indicates the complex formation between this compound and ethanol in concentration greater than 0.1 mol dm^{-3}, while the spectra exhibit a conspicuous red-shift owing to the change of solvent polarity (general solvent effect) by the addition of small amount of ethanol. In 3,5-diisopropyl-4-methoxybenzylidenemalononitrile (Pr$_2$-MO-BMN),[7] however, no significant ethanol concentration dependence of absorption spectra was detected, though a considerable red-shift of the absorption band owing to the general solvent effect was observed with increasing ethanol concentration. Thus, the electronic interaction of HO-BMN with ethanol can be attributed to the hydrogen bonding between the OH

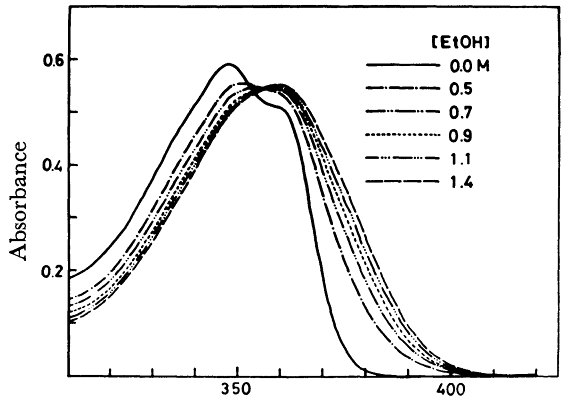


Fig. 1. Absorption spectra of t-Bu$_2$-HO-BMN (1.7×10^{-5} mol dm^{-3}) in hexane containing various amount of ethanol at room temperature (ethanol concentration <2 mol dm^{-3}) (1 M=1 mol dm^{-3}).

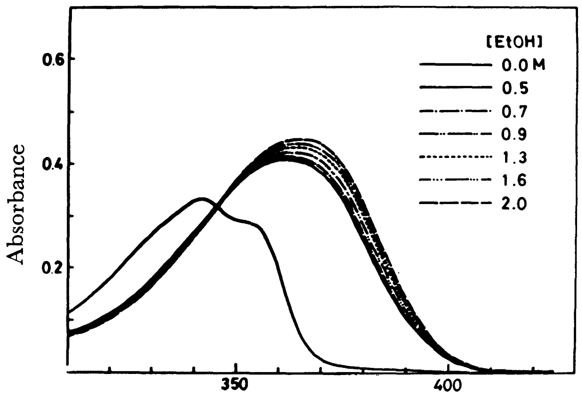


Fig. 2. Absorption spectra Me$_2$-HO-BMN (2.3×10^{-5} mol dm^{-3}) in hexane containing various amounts of ethanol (concentration $\simeq 2$ mol dm^{-3}) (1 M=1 mol dm^{-3}).

group in HO-BMN and ethanol molecule. With increase in ethanol concentration (>5 mol dm^{-3}), the absorption band of the H-bonded complex at 370 nm gradually decreased and another band at 465 nm appeared, increasing with an isosbestic point at 400 nm (Fig. 3). The second band corresponds to that of the anion form of the compound, mentioned above. Here, the equilibria are expressed as follows:

$$\underset{C_f}{\text{HO-BMN}} + \underset{C_B}{\text{EtOH}} \overset{K_1}{\rightleftharpoons} \underset{C_b}{\text{H-bonded complex}}$$

$$\underset{C_b}{\text{H-bonded complex}} + \underset{C_B}{\text{EtOH}} \overset{K_2}{\rightleftharpoons} \underset{C}{\text{Anion form}}$$

$$\text{HO-BMN} + 2\,\text{EtOH} \overset{K_3}{\rightleftharpoons} \text{Anion form} \qquad (1)$$

where K_1, K_2, and K_3 are the corresponding equilibrium constants, and $K_1\times K_2=K_3$. The constants were obtained by the following equations:[8,9]

$$(\varepsilon-\varepsilon_f)/C_B = K_1\varepsilon_b - K_1\varepsilon \qquad (2)$$

$$1/C_B^2 = c/A - K_3,\ c=\text{const} \qquad (3)$$

where C_f, C_B, and C_b are the equilibrium concentrations

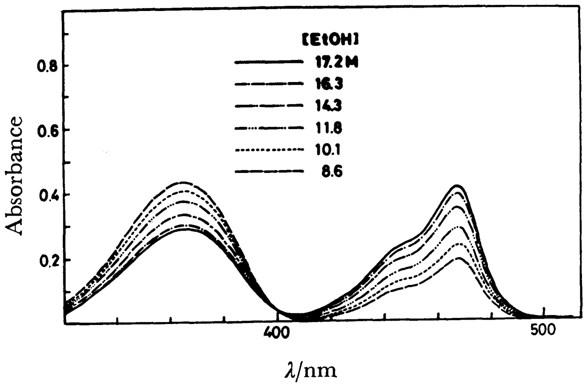


Fig. 3. Absorption spectra t-Bu$_2$-HO-BMN (1.7×10^{-5} mol dm^{-3}) in hexane containing various amounts of ethanol at room temperature (concentration >8 mol dm^{-3}) (1 M=1 mol dm^{-3}).

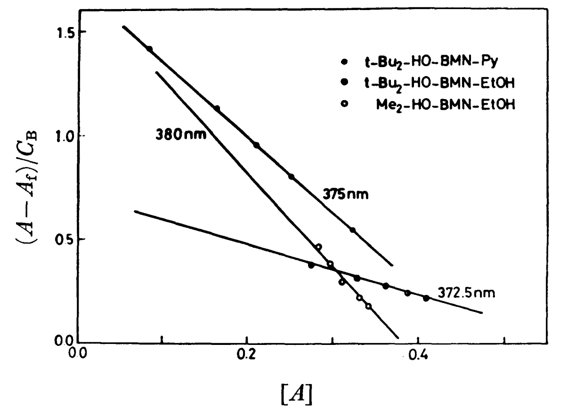


Fig. 4. Plots of $(A-A_f)/C_B$ *vs.* A, where ε and ε_f in Eq. 2 were replaced by the corresponding absorbance A and A_f, respectively (concentration of HO-BMN, 1—3 mol dm^{-3}).

of the free HO-BMN, ethanol and the H-bonded complex, respectively; and ε_f and ε_b are molar extinction coefficients of free HO-BMN and the complex, respectively; ε is apparent extinction coefficient. In Eq. 3, A is the absorbance of the anion form at 465 nm. A linear relationship of $(\varepsilon-\varepsilon_f)/C_B$ *vs.* A at 370 nm suggesting a 1:1 interaction of HO-BMN and ethanol is shown in Fig. 4. Plots of $1/C_B^2$ *vs.* $1/A$ suggesting also the reaction mechanism for the anion formation are shown in Fig. 5. The concentration dependence of the anion band at 465 nm shows remarkable deviation from Scot plots and Benesi Hildebrand plots of an ordinary 1:1 interaction between HO-BMN and ethanol molecule. Slopes of these linear plots (Figs. 4 and 5) afford equilibrium constants K_1 and K_3, respectively. The results are summarized in Table 1. Equilibrium constants K_1 and K_3 in the t-Bu$_2$-HO-BMN–ethanol system were determined at temperatures 5, 15, 20, and 30 °C. Conventional plots of ln K *vs.* $1/T$ showing a linear relation afford enthalpy changes of respective equilibrium ($\Delta H_1=-1.8$, $\Delta H_2=-1.0$, and $\Delta H_3=-2.8$ kcal mol^{-1}). The H-bonded complex formation of the other HO-BMN with ethanol was also observed (Table 1). Since the absorption band of the anion pair of the other HO-BMN was

Table 1. pK_a and equilibrium constants in hexane at room temperature, and fluorescence lifetimes in MTHF at 77 K

	pK_a[a]	K_1/mol^{-1}	K_2/mol^{-1}	K_3/mol^{-2}	τ/ns[b]
			[C_2H_5OH]		
Me_2-HO-BMN	4.8	4.5	—	—	2.3
Pr_2-HO-BMN	—	2.3	—	—	2.6
t-Bu_2-HO-BMN	4.9	1.1	4.1×10^{-3}	4.5×10^{-3}	1.5
Me_2-MO-BMN	—	—	—	—	2.3
			[pyridine]		
t-Bu_2-HO-BMN	—	4.3	2.3×10^{-3}	1.0×10^{-2}	—
			[TEA]		
t-Bu_2-HO-BMN	—	—	—	2×10^{-3}	—

a) pK_a (100% aqueous solution) extrapolated from values determined in the mixed systems (aqueous ethanol, 50, 40, and 30 w/v%). b) Fluorescence lifetimes in 2-methyltetrahydrofuran at 77 K.

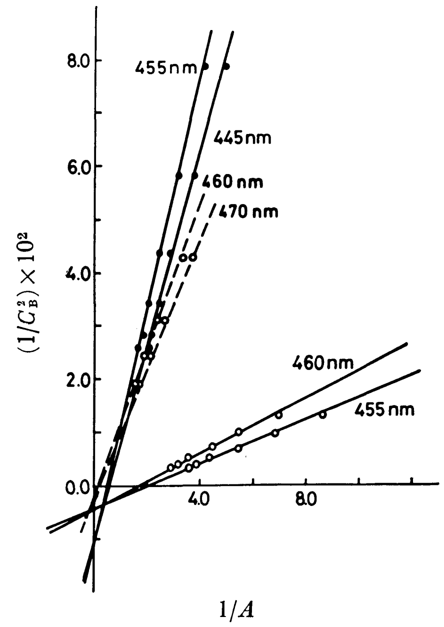


Fig. 5. Plots of $1/C_B^2$ *vs.* $1/A$; —○—, *t*-Bu_2-HO-BMN-ethanol system corresponding to spectra in Fig. 3; —●—, *t*-Bu_2-HO-BMN-pyridine system corresponding to spectra in Fig. 6; --○--, *t*-Bu_2-HO-BMN-TEA system corresponding to spectra of Fig. 8; concentrations of *t*-Bu_2-HO-BMN are 0.8—2.0×10^{-5} mol dm^{-3} (1 M = 1 mol dm^{-3}).

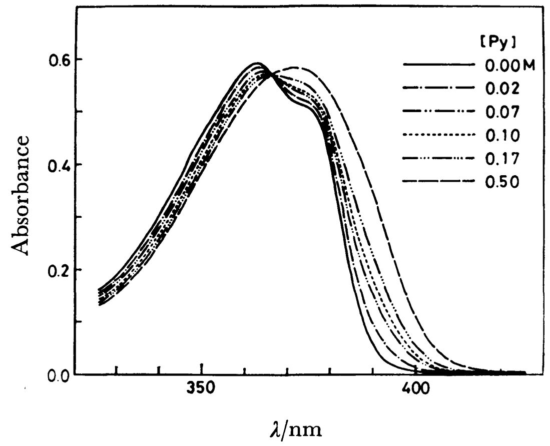


Fig. 6. Absorption spectra of *t*-Bu_2-HO-BMN (8.7×10^{-6} mol dm^{-3}) in hexane contaning various amounts of pyridine (1 M = 1 mol dm^{-3}).

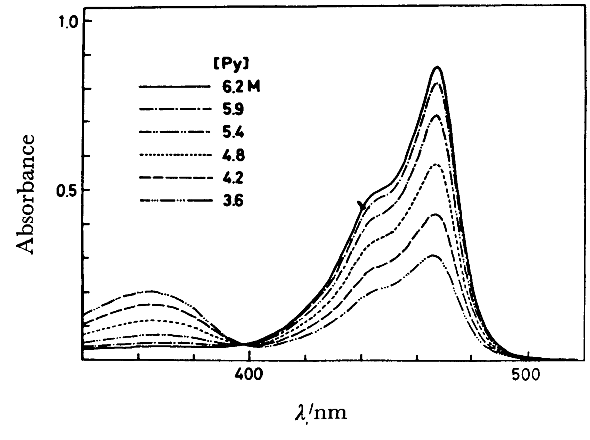


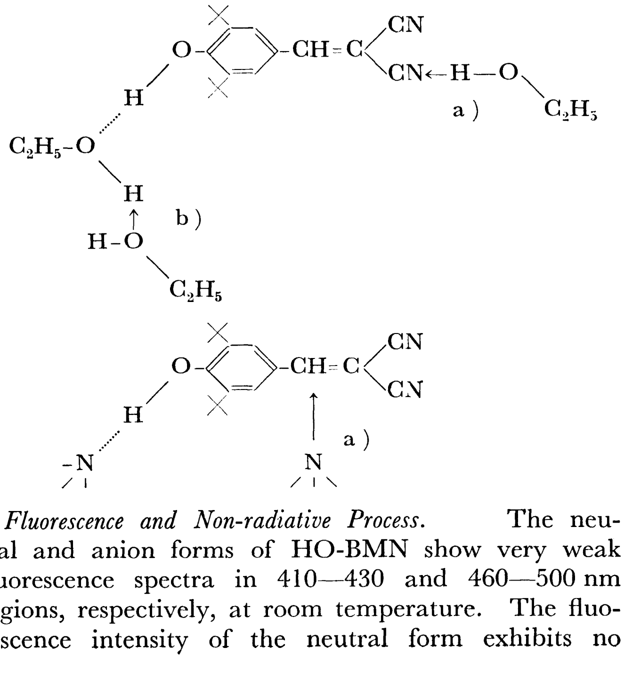
Fig. 7. Absorption spectra of *t*-Bu_2-HO-BMN (8.7×10^{-6} mol dm^{-3}) in hexane containing various amounts of pyridine (concentration >3 mol dm^{-3}) at room temperature (1 M = 1 mol dm^{-3}).

small in intensity even in ethanol, the exact equilibrium constant K_3 was not obtained.

The H-bonding formation of *t*-Bu_2-HO-BMN and further anion pair formation were also observed in the interaction with pyridine and triethylamine (TEA). Figures 6 and 7 show the absorption spectra of *t*-Bu_2-HO-BMN in hexane with various concentrations of pyridine. Similarly, plots of $(\varepsilon-\varepsilon_f)/C_B$ *vs.* A, and of $1/C_B^2$ *vs.* $1/A$ afford K_1 and K_3, respectively. In the *t*-Bu_2-HO-BMN and TEA system, the concentration dependence of TEA upon the absorption band of the H-bonded complex in hexane exhibits no significant isosbestic points because of considerable red shift with increasing concentration of TEA (<2 mol dm^{-3}). Therefore, K_1 was not obtained in this system. Figure 8 shows absorption spectra of the anion band of *t*-Bu_2-HO-BMN in various concentrations of TEA (>4 mol dm^{-3}) in hexane. It is seen that the increase of the anion band follows Scheme 1 and not the ordinary 1:1 interaction. Plots of $1/C_B^2$ *vs.* $1/A$ (Fig. 5) afford K_3 (Table 1). The constants K_3 obtained in the three systems show almost similar values, though ethanol, pyridine and TEA differ considerably in dielectric property.

Baba *et al.*[8] reported the H-bonded complex formation between *p*-nitrophenol and TEA in several solvents, and subsequent proton transfer in the ground state. The proton transfer *i.e.*, anion pair formation of phenol in the H-bonded complex, takes place from nitrophenol to amine to yield a H-bonded ion pair, no further concentration dependence of amine upon the ion pair formation being detected. In these HO-BMN–ethanol, –pyridine, and –TEA systems, another ethanol (pyridine and TEA) molecule is involved in the ion pair formation from the H-bonded complex. The concentration dependence of the anion formation might be ascribed to the change of the dielectric property of the solvent system by the addition of ethanol (dielectric constant, $\varepsilon=24.6$),[10,11] pyridine (12.4) and TEA (2.42) in the hexane solution (1.88). However, the results of the anion pair formation in the interaction with three proton acceptors do not seem to be correlated with their dielectric constants. This shows that the ionization of the H-bonded complex can be attributed to a specific interaction between the complex and ethanol (pyridine and TEA) molecule.

Hoshino and Koizumi[12] reported a two-step interaction of ethanol molecule with *p*-amino- and *p*-dimethylaminobenzophenone in cyclohexane. They suggested the interactions of one ethanol molecule to the NH_2 group (or $N(CH_3)_2$) and one molecule to C=O of these compounds. The first specific interaction of ethanol with HO-BMN is ascribed to the hydrogen bonding with OH group, since ethanol, as well as TEA and pyridine, is a proton acceptor. In the interaction of the second ethanol molecule leading to the ion pair formation, there seem to be two possibilities: (a) a specific interaction of another ethanol molecule with malononitrile group, and (b) further interaction of the second ethanol molecule with an oxygen atom of the H-bonded OH group of HO-BMN or with a hydrogen atom of the first ethanol. However, since TEA and pyridine exhibit almost the same behavior as ethanol, (a) seems preferable.



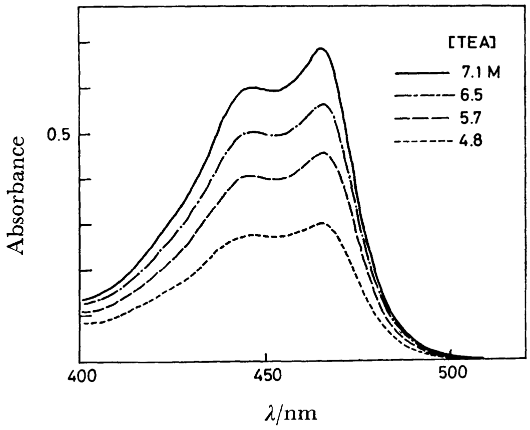


Fig. 8. Absorption spectra of *t*-Bu_2-HO-BMN in hexane containing various concentrations of TEA at room temperature (concentration of *t*-Bu_2-HO-BMN, 3.7×10^{-5} mol dm^{-3}) (1 M=1 mol dm^{-3}).

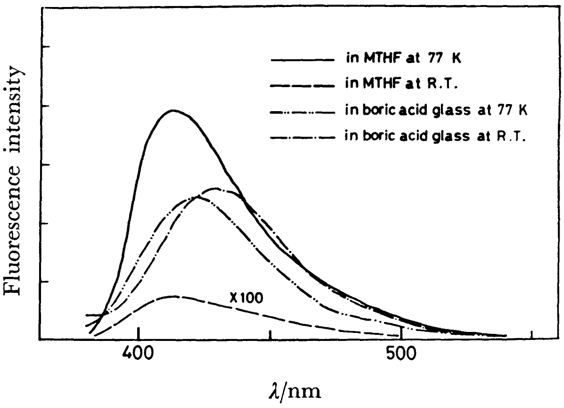


Fig. 9. Fluorescence spectra of *t*-Bu_2-HO-BMN in 2-methyl-tetrahydrofuran and in boric acid glass; Intensities are arbitrary unit.

Fluorescence and Non-radiative Process. The neutral and anion forms of HO-BMN show very weak fluorescence spectra in 410—430 and 460—500 nm regions, respectively, at room temperature. The fluorescence intensity of the neutral form exhibits no significant difference between free (λ_{max} 410 nm in hexane) and H-bonded HO-BMN (λ_{max} 430 nm in ethanol). Fluorescence quantum yields of HO-BMN (neutral form) and MO-BMN in several solvents were determined approximately to be $1—5\times10^{-4}$ at room temperature. The fluorescence intensity of these compounds in various solvents remarkably increased with decreasing temperature at 150—77 K. Figure 9 shows fluorescence spectra of *t*-Bu_2-HO-BMN (neutral form) in MTHF, at 77 K and at room temperature. Figure 10 shows the temperature dependence of fluorescence intensity of *t*-Bu_2-HO-BMN in various solvents. Fluorescence intensity of *t*-Bu_2-HO-BMN increased in the temperature region below $\approx$100 K in MTHF and in methylcyclohexane (MCH). However, in 3-methylpentane–MCH mixed system (1:3), it increased markedly at temperatures below $\approx$90 K. A similar temperature dependence of fluorescence was also observed in MO-BMN. The temperature region in which fluorescence intensities increase seems to correspond to the increase of solvent rigidity (viscosity) from fluid to rigid glass. In order to confirm the influence of the rigidity of solution on fluorescence intensity, the fluorescence spectrum of HO-BMN in the solid solution of boric acid glass was determined at room temper-

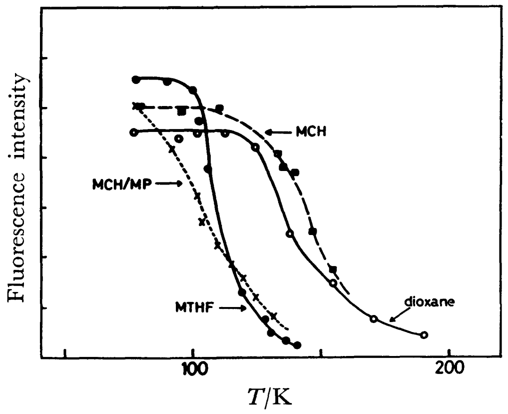


Fig. 10. Temperature dependence of fluorescence intensity (arbitrary unit) of *t*-Bu_2-HO-BMN in various solvents.

ature.[13] The spectrum shows fairly strong fluorescence at room temperature (Fig. 9), but no significant temperature dependence. Fluorescence lifetimes of these compounds in various solvents were determined to show also remarkable temperature dependence. The lifetimes in the rigid glass at 77 K are 1—3 ns (Table 1), while those decrease to within a duration of a laser pulse in fluid medium at 100—150 K. Fluorescence lifetimes of these compounds may be in the order of picosecond at room temperature.

Semi-empirical molecular orbital calculation (Pariser-Parr-Pople type) indicates that the first electronic transition of HO-BMN as well as MO-BMN is allowed, corresponding to an absorption band at 340—360 nm. Thus, natural radiative lifetimes τ_0 of these compounds were obtained as $1—3\times10^{-9}$ s (in ethanol, THF, and hexane) from absorption bands at 340—360 nm. The lifetimes of these compounds were estimated to be $10^{-12}—10^{-13}$ s from fluorescence quantum yield ($\approx10^{-4}$) and τ_0 ($\approx10^{-9}$ s). This suggests that the decay process of the compounds is mostly non-radiative. In the non-radiative process of HO-BMN in fluid medium, there are two possible mechanisms: (a) the excited-state proton transfer of OH group leading to the anion formation, *i.e.*, a photoionization, and (b) a torsional non-radiative relaxation process of the excited state.[14] (a) is ruled out from similar fluorescence behavior of MO-BMN to HO-BMN. Thus, (b) can be attributed to the non-radiative process, since the torsional non-radiative process seems to be frozen out in rigid solution at 77 K and in the boric acid glass at room temperature.

Hui and Rice reported a torsional non-radiative process in the excited state of styrene.[15] The non-radiative process of styrene consists of $S_1\rightarrow T_1$ and cis-trans isomerization, suggesting a plausible schematic potential energy surface for the torsional motion that leads to cis-trans isomerization. On the other hand, El-Bayoumi reported torsional relaxation of the excited state of 1,1,4,4-tetraphenylbutadiene (TPB).[16] In fluid media, TPB exhibits large Stokes shifts and their fluorescence spectra are diffuse, while the fluorescence maximum shifts to higher energy, and the vibrational structure being resolved by preventing this torsional relaxation in the rigid medium at low temperature. In HO-BMN, however, no longer-wavelength fluorescence corresponding to the large Stokes shift was observed in fluid medium. If the torsional equilibrium of S_1 state of this compound is in a low level and the intersystem crossing from S_1 to T_1 is predominant in the decay process, no fluorescence would be observed. According to this argument, HO-BMN dimer (or MO-BMN) as well as the double proton transfer species (or the excimer) should be fluorescent.[4] This is becuase the torsional relaxation in a component molecule of the dimer can be prevented by its sandwich-type structure. However, no exact potential energy curves concerned with C–C bond rotations of malononitrile double bond and of phenyl-malononitrile single bond were obtained at the present stage.

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