January, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (1), 45—48 (1979)

Dimer and Excimer Fluorescence Spectra of Highly Polar Molecules, 3,5-Dialkyl-4-methoxybenzylidenemalononitrile

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(Received June 30, 1978)

Dual fluorescence of the ground state dimer of highly polar molecules of 3,5-dialkyl-4-methoxybenzylidenemalononitrile in 3-methylpentane solution at low temperature was investigated by steady-state and nonsecond fluorescence spectroscopies. The dimerization of these compounds was confirmed by concentration dependence of absorption and fluorescence spectra at 77 K. The dimer exhibits dual fluorescence consisting of a short-lived dimer fluorescence and a long-lived excimer fluorescence, while the monomer is almost nonfluorescent at room temperature to 77 K. The excimer formation by an orientational relaxation from the excited state of the dimer was discussed in terms of determination of the activation barrier and the fluorescence polarization.

Dual fluorescence of a highly polar molecule, *p*-dimethylaminobenzonitrile (MABN), was identified by Lippert[1)] as arising from two different excited states in polar solvent. However, Rotkiewicz *et al.*[2)] suggested that the dual fluorescence arose from states with the same fluorescence polarization, and that the two emitting states differed in the orientation of the dimethyl amino group with respect to the benzene ring. On the other hand, McGlynn and coworkers[3)] reported that the dual fluorescence of this compound was identified as arising from a ground state dimer in a number of different solvents and suggested that the dual fluorescence consisted of the dimer and an excimer. However, Nakashima and Mataga[4)] claimed that the dimer and the excimer assignment could not be correct by their concentration dependence of fluorescence spectra.

Very recently, Itoh *et al.*[5)] reported dual fluorescence of a ground state dimer of a highly polar molecule, 3,5-dialkyl-4-hydroxybenzylidenemalononitrile (dialkyl-HO-BMN), in 3-methylpentane (MP) solution at low temperature. The dual fluorescence was ascribed to the short-lived dimer and to the long-lived excited species generated by the duoble proton transfer reaction in the excited state of the dimer. The excited-state proton transfer of 3,5-di-*t*-butyl-4-hydroxybenzylidenemalononitrile (*t*-$\mathrm{Bu_2}$-HO-BMN) in the solid state was also reported.[6)]

This paper describes the dimer formation of several dialkyl-4-methoxybenzylidenemalononitrile (dialkyl-MO-BMN) in the ground state in MP solution at low temperature, and dual fluorescence consisting a short-lived dimer fluorescence and a long-lived excimer one by the steady-state and nanosecond (ns) fluorescence spectroscopies. The structure of the dimer is proposed to be a sandwich type dimer with a center of symmetry by taking account of a crystal structure of *t*-$\mathrm{Bu_2}$-HO-BMN.[6)] The excimer seems to be generated by an orientational relaxation in the excited state of the dimer. The dimer and excimer fluorescence spectra are discussed in terms of an activation barrier and fluorescence polarization at low temperature.

Experimental

Materials. The preparation of the model compounds are as follows. The products were purified by colum chromatography and recrystallizations, and chracterized by IR and NMR.

4-Methoxybenzylidenemalononitrile (MO-BMN) was prepared from 4-methoxybenzaldehyde with malonitrile in benzene solution containing small amount of acetic acid and piperidine.[7)] The product was recrystallized from benzene-hexane: Mp 113—116 °C.

Found: C, 71.90; H, 4.20; N, 15.09%. Calcd for $\mathrm{C_{11}H_8N_2O}$: C, 71.74; H, 4.35; N, 15.21%.

3,5-Dimethyl-4-methoxybenzylidenemalononitrile ($\mathrm{Me_2}$-MO-BMN) was prepared from 3,5-dimethyl-4-methoxybenzaldehyde by the same manner as described above. The product was recrystallized from benzene-hexane: Mp 120—122 °C.

Found: C, 73.78; H, 5.66; N, 13.01%. Calcd for $\mathrm{C_{13}H_{12}N_2O}$: C, 73.58: H, 5.66: N, 13.20%.

3,5-Di-isopropyl-4-methoxybenzylidenemalononitrie (*i*-$\mathrm{Pr_2}$-MO-BMN) was prepared by the same manner as described above. Though the product is noncrystalline syrup, the compound was identified by NMR and IR.

Measurements. Determination of the fluorescence and absorption spectra, and fluorescence polarization were described previously.[8,9)] Fluorescence lifetimes and time-resolved fluorescence were determined by analysing exponential decay curves measured by an oscilloscope and by a coaxial $\mathrm{N_2}$ gas-laser excitation. The decay curve was analyzed by a deconvolution method using a computer.[10)]

Results and Discussion

Dimer Formation in the Ground State. The MP solution of 4-methoxybenzylidenemalononitrile (MO-BMN) shows an absorption band in the 330—360 nm region at room temperature, which shows considerable red-shift (*ca.* 10—20 nm) at low temperature (<150 K), as shown in Fig. 1. Figure 2 shows concentration dependence of absorption spectra of MP solutions of MO-BMN at 77 K. Here, a monomer dimer equilibrium of this compound in MP solution is assumed, and an association constant (K) can be written as follows:[2)]

$$K = [\mathrm{D}]/([\mathrm{C}]-2[\mathrm{D}]),$$

where [C] and [D] are concentrations of MO-BMN and dimer. If an absorption band at 390 nm is due almost exclusively to the dimer, an absorbance [A] at 390 nm is expressed as $A=\varepsilon[\mathrm{D}]l$, where ε is a molar extinction coefficient of the dimer at this wavelength. The following equation is obtained:[11)]

$$[\mathrm{C}]/A = 2/\varepsilon+(1/\varepsilon K)^{1/2}(1/A)^{1/2}.$$

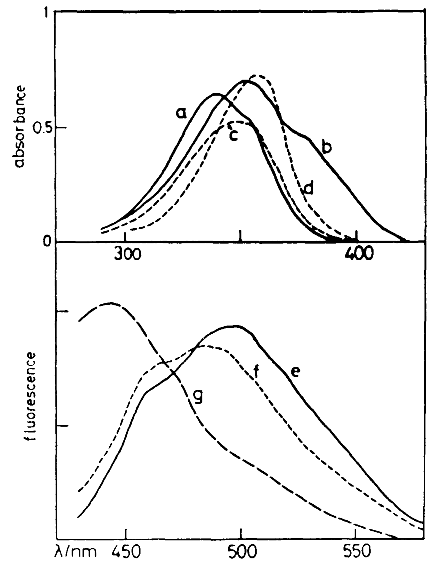


Fig. 1. Absorption spectra (a—d) of MO-BMN and fluorescence spectra (e—g) of dialkyl-MO-BMN: a) in MP solution (2.1×10^{-5} M) of MO-BMN at room temperature; b) at 77 K (2.6×10^{-5} M); c) MTHF solution (1.7×10^{-5} M) at room temperature; d) MTHF solution (1.3×10^{-5} M) at 77 K; e) fluorescence spectra of MO-BMN (1.3×10^{-5} M) at 77 K; f) of Me_2-MO-BMN in MP (2.7×10^{-5} M) at 77 K; and g) of *i*-Pr_2-MO-BMN in MP (3.3×10^{-5} M).

An MP solution of MO-BMN exhibits a strong green fluorescence at 77 K as shown in Fig. 1, while the solution is almost non-fluorescent at room temperature. MP solutions of 3,5-dimethyl- and 3,5-di-isopropyl-4-methoxybenzylidenemalononitrile (Me_2-MO-BMN and *i*-Pr_2-MO-BMN) also show strong fluorescence at 77 K as shown in Fig. 1. However, an MTHF solution of dialkyl-MO-BMN exhibits no significant temperature dependence of fluorescence and absorption spectra. The green fluorescence in the MP solution markedly increases in intensity with increasing concentration of MO-BMN, but the fluorescence due to the monomer does not seem to exhibit even in the dilute solution, as shown in Fig. 3. Since intensity (I) of the green fluorescence may be proportional to the concentration of the dimer [D], the following equation is obtained for the monomer dimer equilibrium;

$$[C]/I = 2/q + (1/qK)^{1/2}(1/I)^{1/2},$$

where q is a constant including several experimental

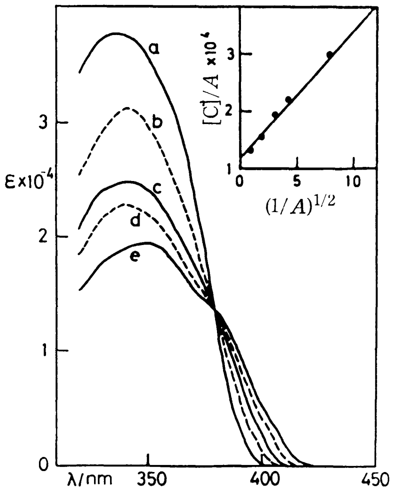


Fig. 2. Concentration dependence of absorption spectra of the MP solution of MO-BMN at 77 K and plot of $[C]/A$ *vs.* $(1/A)^2$.
a) 3.2×10^{-6} M; b) 1.0×10^{-5} M; c) 2.9×10^{-5} M; d) 4.8×10^{-5} M; e) 7.2×10^{-5} M.

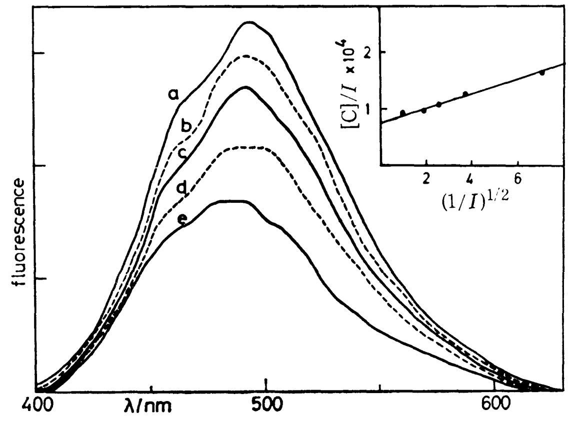


Fig. 3. Concentration dependence of fluorescence spectra of the MP solution of MO-BMN at 77 K and plot of $[C]/I$ *vs.* $(1/I)^{1/2}$.
a) 3.8×10^{-5} M; b) 2.0×10^{-5} M; c) 1.1×10^{-5} M; d) 6.2×10^{-6} M; e) 2.9×10^{-6} M. Flurorescence intensity is q unit (see in the text).

factors. Plots of $[C]/A$ and $[C]/I$ exhibit linear relationship *vs.* $(1/A)^{1/2}$ and $(1/I)^{1/2}$, respectively, as shown in Figs. 2 and 3. Two straight lines confirm an assumption of the monomer dimer equilibrium, and

TABLE 1. EQUILIBRIUM CONSTANTS (K) FOR THE DIMERIZATION OF DIALKYL-MO-BMN IN MP AT 77 K, AND FLUORESCENCE PROPERTIES OF THE DIMER (D*) AND THE EXCIMER (E*), AND THEIR ACTIVATION ENERGY (E_a)

	K (M^{-1})	λ_{max} (nm) and lifetimes (ns) in bracket		E_a (kcal M^{-1})
		D*	E*	
MO-BMN	1.6×10^5	480$^{a)}$ (4)	500$^{a)}$ (21)	—
Me_2-MO-BMN	4.5×10^4	470—480$^{a)}$ (4)	490$^{a)}$ (21)	0.9
i-Pr_2-MO-BMN	2.8×10^4	450$^{b)}$ (4)	470—480$^{a)}$ (18)	1.1

a) The fluorescence maxima determined by time-resolved spectra (error appeoximately±5 nm) and lifetimes analyzed by a computer deconvolution (error approximately ±1 ns). b) The fluorescence maximum determined by a steady-state spectrum.

afford equilibrium constants; $K=1.6\times10^5\ \mathrm{M}^{-1}$ from absorption spectra and $1.5\times10^5\ \mathrm{M}^{-1}$ from fluorescence spectra. Concentration dependence of the absorption spectra of the other alkyl-MO-BMN in MP solution also shows the dimer formation at 77 K, whose K are summarized in Table 1.

Excimer Fluorescence. Nanosecond time-resolved fluorescence spectra of an MP solution of MO-BMN at 77 K shown in Fig. 4 demonstrate that the fluorescence consists of two fluorescence spectra; a short-lived fluorescence (λ_{max} 480—490 nm, $\tau=4$ ns) and a long-lived one (λ_{max} 500 nm, $\tau=21$ ns). The dual fluorescence of the dimer was also observed in the other dialkyl-MO-BMN. Figure 4 shows a fluorescence decay curve of an MP solution of MO-BMN at 77 K in comparison with a computer simulated one. Table 1 summarizes the fluorescence maxima and lifetimes in the dimers of these compounds at 77 K. The excitation spectra of the short-lived fluorescence and the long-lived one are identical each other, and are corresponding to the dimer absorption spectra (Fig. 5). Taking account of a large Stokes shift of the long-lived fluorescence, the fluorescence may be ascribed to the excited species (E*) generated from the excited state of the MO-BMN dimer (D*), while the short-lived one to the dimer (D*).

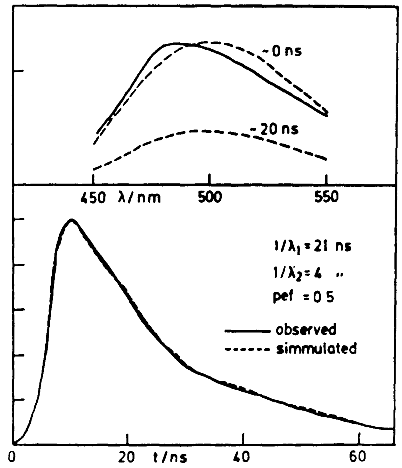


Fig. 4. Time-resolved fluorescence spectra of the MP solution of MO-BMN (3.9×10^{-5} M) at 77 K. A fluorescence decay curve monitored at 490 mn, and a simulated one; (——) and (----) are time-resolved spectra of a short-lived and a long-lived components depicted on the obtained time constants and pre-exponential factor (pef). Time indicated in the time-resolved spectra is virtually after a signal maximum of the fluorescence.

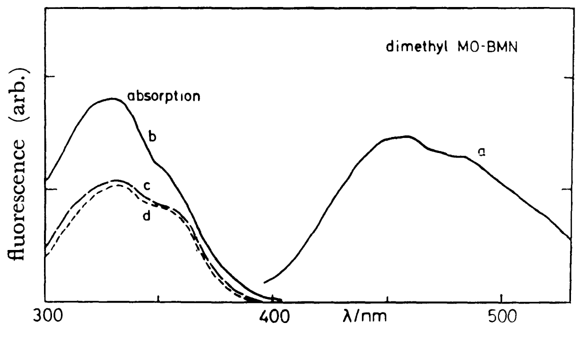


Fig. 5. Fluorescence (a) and absorption (b) spectra of an MP solution of $\mathrm{Me_2}$-MO-BMN (5.1×10^{-5} M) at 77 K; fluorescence excitation spectra (c) monitored at 420 nm and (d) at 520 nm.

The photochemical reaction scheme is as follows:

$$\begin{tikzcd} \mathrm{D} \arrow[rr, "h\nu"] & & \mathrm{D}^* \arrow[rr, shift left, "k_3"] \arrow[dl, "k_1"'] \arrow[d, "k_2"] & & \mathrm{E}^* \arrow[ll, shift left, "k_4"] \arrow[dl, "k_5"'] \arrow[dr, "k_6"] & \\ & \mathrm{D}+h\nu' & \mathrm{D} & \mathrm{D}+h\nu'' & & \mathrm{D} \end{tikzcd}$$

Time dependent concentrations of D* and E* are expressed by the following well known equations:[12,13)]

$$[\mathrm{D}^*] = C_1 \exp(-\lambda_1 t) + C_2 \exp(-\lambda_2 t), \tag{1}$$

$$[\mathrm{E}^*] = C_3 \exp(-\lambda_1 t) - C_3 \exp(-\lambda_2 t), \tag{2}$$

$$\lambda_1, \lambda_2 = 1/2[k_1+k_2+k_3+k_4+k_5+k_6 \mp (\{k_1+k_2+k_3 - (k_4+k_5+k_6)\}^2+4k_3k_4)^{1/2}].$$

Here, if $k_3 \gg k_4 \approx 0$, [D*] may be approximately represented by the second term of Eq. 1. The fluorescence lifetimes of D* and E* are expressed as follows:

$$\tau_{\mathrm{D}} = \lambda_2^{-1} = (k_1+k_2+k_3)^{-1},$$

$$\tau_{\mathrm{E}} = \lambda_1^{-1} = (k_5+k_6)^{-1}.$$

Since two fluorescence decay curves of D* and E* at a certain wavelength overlap each other, actual decay curves at several wavelengths were analyzed by the following equation:

$$[\mathrm{D}^*] + [\mathrm{E}^*] \propto \exp(-\lambda_1 t) + \frac{C_2-C_3}{C_3} \exp(-\lambda_2 t).$$

Fluorescence lifetimes of D* and E* of an MP solution of MO-BMN at 77 K were determined to be 4 ns and 21 ns, respectively, by computer simmulation mentioned above. Unfortunately, the fluorescence rise of E* was not detectable, because the D* fluorescence overlaps on the decay curve of E*.

Fluorescence spectra of an MP solution of i-$\mathrm{Pr_2}$-MO-BMN at several temperatures shown in Fig. 6 reveal remarkable decrease of the short-lived fluorescence with increasing temperature (77 to 130 K). Since no significant shift of the monomer dimer equilib-

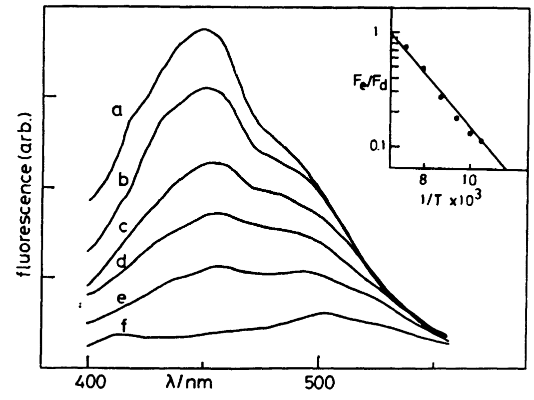


Fig. 6. Temperature dependence of fluorescence spectra of an MP solution of i-$\mathrm{Pr_2}$-MO-BMN (3×10^{-5} M); a) 100 K; b) 108 K; c) 115 K; d) 120 K; e) 125 K; f) 132 K.

rium was detected in this temperature region, and since no monomer fluorescence was detected, the remarkable temperature dependence may be attributable to a dynamic process between D* and E* requiring a small amount of activation energy. From the fluorescence spectra shown in Fig. 6, the activation energy can be obtained to be 1.1 kcal/mol by the aid of the conventional method and assumption reported previously.[8] The activation energy in the dimer of Me_2-MO-BMN was also obtained to be 0.9 kcal/mol. However, an MP solution of MO-BMN shows no significant temperature dependence of fluorescence spectra which seems to imply a very small amount of activation energy in this photochemical process.

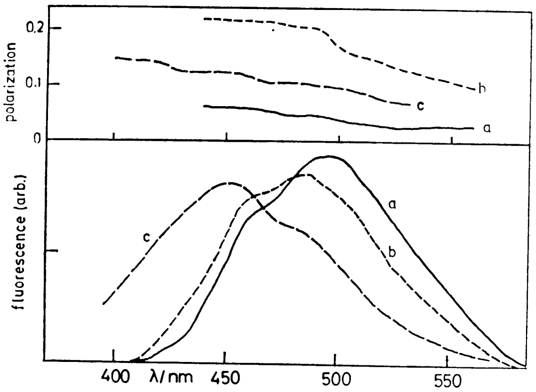
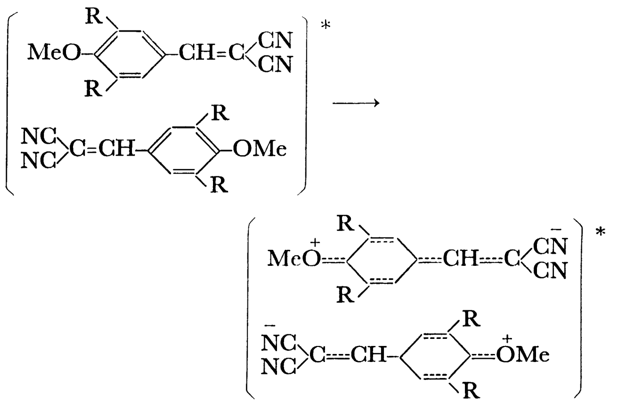


Fig. 7. Fluorescence spectra and their polarizations of MP solutions at 77 K; a) MO-BMN (4.6×10^{-5} M); b) Me_2-MO-BMN (5.9×10^{-5} M); c) i-Pr_2-MO-BMN (6.8×10^{-5} M).

Figure 7 shows the fluorescence polarizations of MP solutions of MO-BMN and dialkyl-MO-BMN at 77 K.[14] The fluorescence polarization were observed to decrease from 0.22 to 0.1 with increasing wavelength in Me_2-MO-BMN. Further, a similar behavior of the polarization was observed in i-Pr_2-MO-BMN, though no significant change of the polarization was detected in MO-BMN. The shorter wavelength (also lifetime) fluorescence and the longer wavelength (also lifetime) one were ascribed to the dimer and the excimer, respectively, as mentioned above. Therefore, the larger and the smaller polarizations may be attributable to the dimer and the excimer. The results indicate that the dimer and excimer fluorescence spectra have considerably different character of electronic transition each other. Since these compounds are highly polar molecules with strong electron donor and acceptor groups, the dimer formation may be attributable to the exciton and the charge transfer interactions between two component molecules in the sandwich dimer with a center of symmetry.[6] It seems that the photoexcitation of the dimer leads to an access of the electronic polarization of the component molecules including an orientational relaxation in the excited state, as follows:



R = H, CH_3, and i-$CH(CH_3)_2$

Here, a small amount of activation energy may be required in the orientational relaxation in the excited state of the dimer. The relaxation process leading to the formation of the excimer (E*) seems to include a rotation of 4-CH_3O– group with respect to the benzene ring. The rotation of this group may be hindered by a steric effect of 3,5-dialkyl groups.[15] The argument is consistent with the activation barriers (MO-BMN < Me_2-MO-BMN < i-Pr_2-MO-BMN) as summarized in Table 1. However, it is difficult to depict the concrete structure of the dimer as well as the excimer at this stage.

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