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Molecular Interactions of *p*-(*N*,*N*-Dimethylamino)-Benzonitrile. Electrostatic Self-Complex and Hetero-Complex Formation in the Ground and Excited States

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Electrostatic self-complex formation of *p*-(*N*,*N*-dimethylamino)-benzonitrile and its hetero-complex formation with benzonitrile in cyclohexane matrix were studied in detail. The possibilities of ground state complex and excimer formation in various liquid solvents were examined thoroughly.

p-(*N*,*N*-Dimethylamino)-benzonitrile(DMABN) exhibits dual fluorescence bands in polar solvents, F_a at longer wavelength side (*ca.* 400—500 nm) and F_b at shorter wavelength side (*ca.* 360 nm). In nonpolar solvents and rigid matrix at low temperatures only the F_b band can be observed. Lippert *et al.*[2] ascribed this phenomenon to two emitting electronic states, a strongly polar one (^1L_a) and a less polar one (^1L_b).

On the other hand, Rotkiewicz *et al.* assigned the emissions to the existence of two isomers α and β differing in polarity and in the orientation of the dimethylamino group.[3] In the case of α form which is strongly polar and emits the F_a fluorescence, the lone pair of amino nitrogen is assumed parallel to the plane of benzene ring. In the case of less polar β form emitting the F_b fluorescence, the lone pair is considered to be perpendicular to the benzene ring.

Recently, we have measured time-resolved fluorescence spectra and fluorescence rise and decay curves of DMABN in MTHF (methyltetrahydrofuran) and have demonstrated clearly the relaxation process due to the interaction between the solvent and the strongly polar state of the solute, leading to the dual fluorescence.[4] Either of the above two interpretations by Lippert *et al.* and Rotkiewicz *et al.* may be consistent with our result of time-resolved fluorescence studies if we assume that α isomer is formed from the β isomer in the excited state. In the course of this study, we have found that the ground state DMABN forms self-complexes and also complexes with benzonitrile in cyclohexane matrix.[4] We have made more detailed investigations on these aggregation phenomena in cyclohexane matrix and, moreover, examined the possibilities of the ground state aggregates as well as excimer formations in various liquid solvents. We have found no definite ground state complex formation in the liquid solution.

On the other hand, McGlynn and co-workers have recently reported absorption and luminescence spectra which they ascribed to the dimer of DMABN.[5] Moreover, they claimed that the F_a band is an excimer emission. According to our present study, their dimer band is due to some unknown impurity and their claim of excimer fluorescence is erroneous.

Experimental

DMABN (K and K) was recrystallized several times from *n*-hexane (Wako, spectrograde). Diethyl ether (Merck, spectrograde), toluene (Merck, spectrograde), acetonitrile (Merck, spectrograde), tetrahydrofuran (THF) (Wako, spectrograde) and methylcyclohexane (Wako, spectrograde) were used without purification. Methanol, propylene glycol, benzonitrile and ethanol were all Wako analytical grade reagents and used without further purification.

The absorption spectra were measured by a Cary 15 and a Shimadzu MPS-50L spectrometer. Cells with optical paths of 1 mm, 400 μ, 25 μ and 2 μ were made by inserting thin packings between quartz plates. Fluorescence spectra were measured by an Aminco-Bowman spectrophotofluorometer. The detector for luminescence was photomultiplier of type RCA 1P28. The temperature of a solution for the measurement was controlled by a constant flow of cold nitrogen gas in a metal Dewar vessel with quartz windows or a cuvette was immersed in ethanol in a quartz Dewar vessel and the temperature of ethanol was controlled by dropping liquid nitrogen. Solutions for the measurement were not deaerated but some of them were flushed with nitrogen.

Results and Discussion

The extinction coefficient of the absorption band at 330—360 nm in propylene glycol solution decreased to about one-third or one-half of the initial value, respectively, when DMABN was recrystallized once from *n*-hexane or water. We observed that the extinction coefficient around 250 nm also decreased by recrystallization. After being recrystallized five times from *n*-hexane, DMABN did not show practically any absorption band at 330—360 nm region. Thus, it seems to be clear that the absorption band at 330—360 nm ascribed by McGlynn *et al.* to the dimer of DMABN is due to some unknown impurity. This impurity appears to show absorption band not only at 330—360 nm but also at about 250 nm. The impurity absorption band seems to become strong in such hydroxylic solvents as water and alcohols. However, it is quite weak in various non-hydroxylic solvents such as aliphatic as well as aromatic hydrocarbons, ethers and nitriles, even when a crude sample is used. Therefore, the intensity of the impurity band does not depend on the solvent polarity but seems to be affected by hydrogen bonding interaction.

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[1] To whom the correspondence should be adressed.

[2] E. Lippert, W. Luder, and H. Boos, "Advances in Molecular Spectroscopy," Pergamon Press, London (1962), p. 443.

[3] K. Rotkiewicz, K. H. Grellmann and Z. R. Grabowski, *Chem. Phys. Lett.*, **19**, 315 (1973).

[4] N. Nakashima, H. Inoue, N. Mataga, and C. Yamanaka This Bulletin, **46**, 2288 (1973).

[5] O. S. Khalil, R. H. Hofeldt, and S. P. McGlynn, *Chem. Phys. Lett.*, **17**, 479 (1972).

If there occurs the ground state dimerization of DMABN, its absorption spectra should show a concentration dependence. We have examined the concentration effect upon the absorption and fluorescence spectra of DMABN in propylene glycol by changing its concentration within the range 1×10^{-5} up to 5×10^{-3} M. We found no change in the spectra. This result is contrary to that of McGlynn *et al.*, and the fluorescence band assigned by them to the ground state dimer is clearly due to the unknown impurity.

We can observe true spectral change due to the ground state aggregation of DMABN in cyclohexane matrix at low temperatures as described in detail in section B. In the case of highly concentrated solutions (0.1—2 M), we can recognize a little change in the fluorescence spectra. We have confirmed, however, that this spectral change is not due to the excimer formation claimed by McGlynn *et al.*

A. On the Possibility of Excimer Formation in Highly Concentrated Solutions of DMABN. If F_a and F_b bands are an excimer and monomer emission of DMABN, respectively, as claimed by McGlynn *et al.*, the intensity ratio $I(F_a)/I(F_b)$ should increase as the concentration is increased. However, the ratio does not show any concentration dependence within the range 1×10^{-5} M up to 1×10^{-2} M in all solvents we have examined. Therefore, the excimer formation cannot be responsible for the F_a fluorescence. In toluene and ether solutions, the ratio increases and F_a band shows a red shift at very high concentration as indicated in Fig. 1 and Table 1. However, in such polar solvents as methanol and acetonitrile, the intensity ratio decreases and F_a band shows a little blue shift at a very high concentration as one can see from Fig. 2 and Table 1.

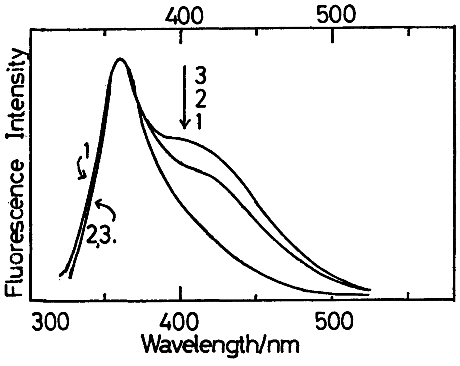

Fig. 1. Concentration effect of the fluorescence spectra of of DMABN in diethylether. [DMABN], 1: 5×10^{-5} M, 2: 1×10^{-1} M, 3: 2.5×10^{-1} M. The spectra were corrected for the response of the entire analyzing system.

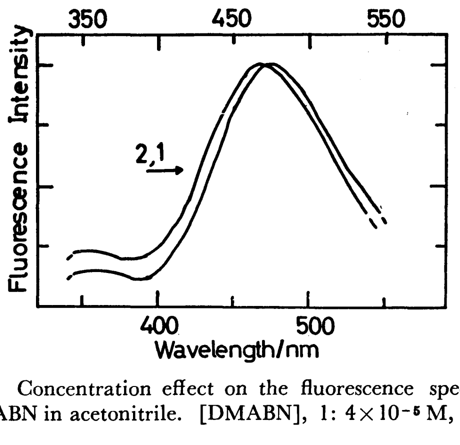

Fig. 2. Concentration effect on the fluorescence spectra of DMABN in acetonitrile. [DMABN], 1: 4×10^{-5} M, 2: 2M.

Table 1. Concentration effect on the fluorescence spectra of DMABN in various solvents (at 20±2 °C)

Solvent	ε [a)] (°C)	[DMABN] (M)	$\lambda_{max}(F_b)$ (nm)	$\lambda_{max}(F_a)$ (nm)
Toluene	2.379	5×10^{-5}	360±2	c)
	(25)	1	360±5	428±2
Diethyl ether	4.335	5×10^{-5}	360±2	c)
	(20)	2.5×10^{-1}	360±2	427±2
Tetrahydrofuran	7.58	2×10^{-5}	360±2	435±2
	(25)	2	b)	460±2
Methanol	32.70	5×10^{-5}	b)	480±2
	(25)	1	b)	475±2
Acetonitrile	37.5	4×10^{-5}	b)	475±2
	(20)	2	b)	465±2

a) Dielectric constant of the solvent. Taken from J. A. Riddick and W. B. Bunger, "Techniques of Chemistry," 2. Organic Solvents., Third ed., John Wiley and Sons, New York (1970), p. 563. b) The intensity was too weak to determine the wavelength of the band maximum. c) Because of the overlapping of the F_b band which is much stronger than F_a band, the determination of the peak wavelength was not possible.

In highly concentrated solutions, DMABN seems to play not only the role of the solute but also that of the polar solvent molecule. Presumably, DMABN molecule may be more polar than toluene and ethers. Therefore, in the case of the highly concentrated solutions in these solvents, the electrostatic dipolar interactions between the strongly polar excited state and ground state DMABN molecules may facilitate the appearance and red shift of the F_a band. Contrary to this, dielectric constant of "DMABN solvent" may be smaller than those of methanol and acetonitrile, leading to the decrease of the intensity ratio and the blue shift of the F_a band at a very high concentration in these solvents.

The above electrostatic interactions, however, appear to involve not only the long range one determined by the bulk dielectric constant but also short range interactions which may be deemed 1 : 1 or 1 : *n* electrostatic loose "self-complex" formation. For the increase of the F_a band intensity in toluene and ethers starts already at 5×10^{-2} M where the increase of the bulk dielectric constant due to the added DMABN may certainly be neglected. The self-complex in the present case does not mean the formation of such a definite stoichiometric complex by a specific short range interaction as the typical exciplex, but loose association of excited DMABN with ground state DMABN molecules by means of dipole-dipole interactions.

The electrostatic self-complex formation may be rather difficult in strongly polar solvents such as methanol and acetonitrile, since the interaction between the polar solvent molecules and the excited DMABN may be quite strong. Therefore, the bulk electrostatic effect may be rather important in this case.

We have confirmed in the case of highly concen-

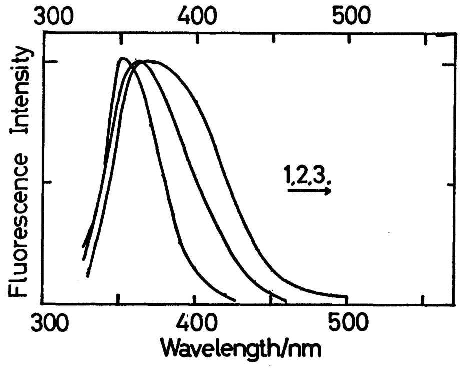

Fig. 3. Effect of the addition of benzonitrile upon the fluorescence spectra of DMABN in methylcyclohexane.
[DMABN] = 2×10^{-5} M.
1. [benzonitrile] = 0 M 21 °C.
2. [benzonitrile] = 4.9×10^{-2} M, 21 °C.
3. [benzonitrile] = 4.9×10^{-2} M, −17 °C.
The spectra were corrected.

trated solutions that the fluorescence excitation spectra measured at F_a band coincides with those measured at F_b band. Accordingly, the increase of the F_a band intensity at high concentration does not seem to be ascribed to the ground state complex formation. Moreover, it has been confirmed that the absorption spectra of highly concentrated solutions in methanol and ethanol are the same as those of 2×10^{-5} M solutions. Therefore, the electrostatic interactions leading to the fluorescence spectral changes are occurring in the excited state.

The excited DMABN molecule will make the electrostatic complex not only with the same kind of molecules but also with different kind of polar molecules. We have examined its interaction with benzonitrile in methylcyclohexane. As shown in Fig. 3, one can recognize a considerable change of the fluorescence spectra at 5×10^{-2} M of added benzonitrile. The spectra show an apparent red shift and intensity increase at the long wavelength side of the band by temperature lowering, which may be ascribed to the appearance of the F_a band caused by electrostatic "hetero-complexes" formation with benzonitrile molecules. In this case too, we have confirmed that the absorption spectra of DMABN do not show any change by the addition of 5×10^{-2} M benzonitrile. Therefore, the interaction with benzonitrile molecules leading to the appearance of F_a band is occurring in the excited state. The present hetero-complex also is not a definite complex but loose aggregation of excited DMABN with benzonitrile by means of dipole-dipole interactions, since one cannot recognize a definite isoemissive point in the emission spectra. Electrostatic loose complex formation of an excited polar solute molecule with polar solvent molecules has been assumed, for example, in the case of indole or tryptophan in alcohol or aqueous solution[6,7] as well as DMABN-propionitrile-methylcyclohexane system.[8]

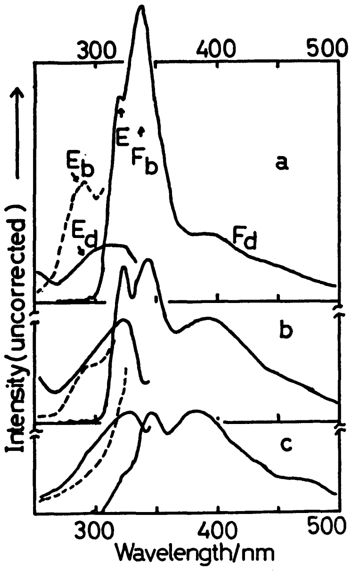

Fig. 4. Concentration effect on the fluorescence and excitation spectra of DMABN in cyclohexane matrix at −45 ±3 °C.
[DMABN]: a. 5×10^{-5} M, b. 5×10^{-4} M, c. 5×10^{-3} M.
E: exciting light. E_b: excitation spectra of F_b band.
E_d: excitation spectra of F_d band.

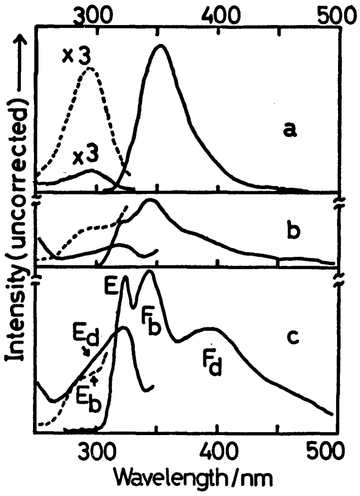

Fig. 5. Temperature effect on the fluorescence and excitation spectra of DMABN in cyclohexane matrix.
[DMABN] = 5×10^{-4} M.
a. 20±3 °C, b. −24±3 °C, c. −45±3 °C.
The meanings of E, E_b and E_d are the same as those in Fig. 4.

At any rate, the above results in nonpolar and slightly polar solvents may be well understood as due to the loose 1 : 1 or 1 : *n* electrostatic self-complex or hetero-complex formation and the results in strongly polar solvents may be ascribed mainly to an electrostatic bulk effect. Change of the fluorescence spectra due to the complex formation of DMABN occurs also in cyclohexane matrix at low temperatures as we have briefly reported previously. In the case of cyclohexane matrix, however, the complex is formed already in the ground state. The studies in cyclohexane matrix may be quite useful for the elucidation of the aggregation phenomena of DMABN. We have made a de-

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[6] N. Mataga, Y. Torihashi, and K. Ezumi, *Theor. Chim. Acta*, **2**, 158 (1964).

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tailed investigation along this line.

B. Aggregation in Cyclohexane Matrix. The effects of DMABN concentration as well as temperature upon the luminescence and excitation spectra have been investigated as shown in Figs. 4 and 5. When temperature is kept constant at -45 ± 3 °C and concentration is increased, the intensity of the band at 390 nm (F_d band) increases and its peak wavelength does not depend on the concentration as one can see from Fig. 4. When the temperature is lowered keeping the concentration at 5×10^{-4} M, the F_d band intensity increases as indicated in Fig. 5. In both of Figs. 4 and 5, we can observe the F_b band at *ca.* 340 nm together with the F_d band. The excitation spectrum of F_b band is observed at *ca.* 290 nm, the wavelength of the absorption band of DMABN. However, that of the F_d band is observed at about 320 nm which is different from the absorption peak of DMABN monomer. Since the excitation spectra at shorter wavelengths than 250 nm were not accurate, they are not shown here.

In view of its concentration and temperature dependences and its excitation spectra different from those of the monomer, the F_d band may be ascribed to an aggregated state of DMABN. In order to confirm the change of absorption spectra in cyclohexane matrix, we have measured directly the absorption spectra at several temperatures as shown in Fig. 6. Temperature lowering causes the intensity increase of the bands at 320 ± 10 nm and at 240 ± 5 nm. The absorption peak at 320 nm is in good agreement with the peak of the excitation spectra of F_d band. One can see also in Fig. 6 that the temperature lowering causes the intensity decrease of the 285 nm band. Presumably, the absorption bands at 320 and 240 nm may be assigned to the dimer of DMABN and the F_d band to its fluorescence. The F_d band may be mainly due to the F_a band appeared as a result of the electrostatic interaction between the halves in the dimer. However, the wavelength of the F_d band is a little shorter than that of the F_a band in highly concentrated toluene solution or diethyl ether solution. This result may be ascribed to the fact that the ground state of the aggregate is stabilized considerably and there is no reorientation stabilization due to the surrounding solvent dipoles in the case of the cyclohexane matrix. Moreover higher aggregate may be formed in the excited state of highly concentrated liquid solution, leading to the larger red shift of the F_a band.

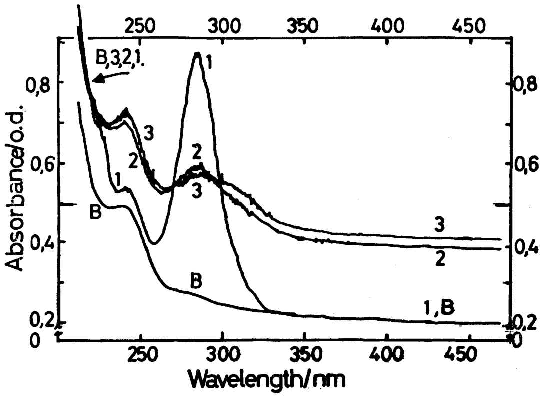

Fig. 6. Absorption spectra of DMABN in cyclohexane matrix.
Optical path ~400 μ. B. Base line (absorbance of the Dewar vessel and cell containing cyclohexane only).
[DMABN] = 5×10^{-4} M.
1. −20 °C, 2. -30 ± 2 °C, 3. -46 ± 1°C,
Because of the increase of scattering of light by the crystallization of cyclohexane, the base line is elevated at lower temperatures. However, it is elevated almost uniformly at all observed wavelengths.

Since the absorption bands of the aggregate as well as the F_d band do not show any shift caused by the temperature lowering and the concentration increase, higher aggregates do not appear to be formed in the ground state as well as in the excited state. In the case of the most concentrated solution in Fig. 4(c), we can recognize a fluorescence band at 460 nm in addition to the 390 nm band. In the previous report we also assigned this band to the dimer. However, we have confirmed that the excitation spectra of 460 nm band appears at longer wavelength (~360 nm) than 320 nm and there occurs a considerable decrease in the intensity of 460 nm band after repeated recrystallization of DMABN from *n*-hexane. Moreover, this band was not detectable in a concentrated liquid solution. Therefore, we conclude here that this fluorescence band is due to an aggregate of unknown impurity in DMABN.

If the dimer takes the sandwich configuration where the dimethylamino group lies over the cyano group, the simplified exciton resonance model predicts that the transition between the higher energy exciton state and the ground state is allowed. However, we cannot observe the intensification of the absorption at shorter wavelength side of the monomer band, but we can see only the appearance of the 320 nm band in Fig. 6. The 240 nm band is too much blue shifted from the 285 nm band to be assigned to the higher energy excited state, if we assume the 320 nm band is the lower energy one. The appearance of the 320 and 240 nm bands can be well understood as due to the electrostatic interaction between the excited and non-excited halves in the dimer causing the red shift of the monomer bands at 285 nm and at shorter wavelength than 235 nm, respectively. Of course, we cannot reject entirely the exciton type interaction mechanism

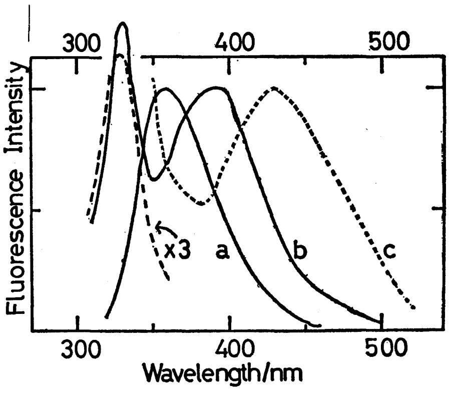

Fig. 7. Fluorescence spectra of DMABN-benzonitrile system in cyclohexane matrix.
[DMABN] = 2×10^{-5} M, [benzonitrile] = 4.9×10^{-2} M.
a. 20 °C, b. 0 ± 1 °C, -17 ± 2 °C.
The spectra were corrected.

on the basis of the above experimental results. There might be more or less contribution of the exciton type interaction to the excited state of the dimer, leading to a little longer fluorescence lifetime of the dimer than that of the monomer.[4] However, it may not be important for the shift of the spectra.

We have examined also the interaction of DMABN with benzonitrile in cyclohexane matrix as shown in Fig. 7. We reported similar spectra in the previous report,[4] where the concentration of DMABN was 5×10^{-4} M. At this concentration, self-complex formation in addition to the formation of hetero-complexes with benzonitrile might be possible. Therefore, we have studied the interaction with benzonitrile, keeping the concentration of DMABN at 2×10^{-5} M, where the self-complex formation can be neglected.

One can see from Fig. 7 that the fluorescence spectra show a remarkable red shift by temperature lowering. As shown in Table 2, not only the fluorescence band but also the excitation spectra show a considerable red shift by the temperature lowering. Whether this hetero-complex is 1 : 1 or 1 : n ($n\geqq 2$) aggregate is not very clear at the present stage of the investigation.

We should note here that, we can see only one fluorescence band at 20 °C in Fig. 7. However, we observe two bands at 0 °C as well as at −17 °C, of which the longer wavelength band may be assigned to the complex as discussed above. In the previous report, we have assigned tentatively the short wavelength band to the uncomplexed DMABN. However, this assignment is not well-founded. We cannot make final conclusion at present about the nature of this band.

At any rate, we have proved that DMABN forms (classical) electrostatic complexes with polar molecules, including the self-complex formation and that the complexation is facilitated in cyclohexane matrix.

TABLE 2. TEMPERATURE EFFECT ON THE FLUORESCENCE AND EXCITATION SPECTRA OF DMABN-BENZONITRILE-CYCLOHEXANE SYSTEM

[Benzonitrile] (M)	Temperature (°C)	λ^{f}_{max} (nm)	λ^{e}_{max} (nm)
0	20±1	350±3	284±2
5×10^{-2}	20±1	360±3	288±2
5×10^{-2}	0±1	390±3	292±2
5×10^{-2}	−17±1	430±3	297±2

λ^{f}_{max}: fluorescence band maximum (corrected).
λ^{e}_{max}: maximum of excitation spectra (uncorrected).