The Electronic Structure of Excited N, N-Dimethyl-α-naphthylamine

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In the course of studying the effects of solvents on the electronic spectra of naphthalene derivatives, we have found that the solvent shifts of the first absorption band of *N, N*-dimethyl-α-naphthylamine (DMNA) are much smaller than those of α-naphthylamine (NA), whereas those of the fluorescence spectrum are quite large and are almost comparable to the shifts of NA.

On the other hand, Smith[1] has studied the dipole moments of various aromatic amines and their *N, N*-dimethyl derivatives. His results indicate that, in DMNA as compared with NA, the steric repression of the resonance effect of the substituent is very strong. This argument is in accordance with the fact that, as is shown in Table I, the wave numbers of the absorption band maximum ($\sigma_a{}^m$) of DMNA in several solvents are considerably larger than those of NA. The apparent first absorption bands of both NA and DMNA are composed of two electronic bands, ^1L_a and ^1L_b[2,3]. In Table I, the $\sigma_a{}^m$ values given for NA are those of ^1L_a, while for DMNA the $\sigma_a{}^m$ values of both ^1L_a and ^1L_b are given. In the case of NA, the fluorescent state seems to be ^1L_a[3], although the lowest absorbing singlet state is ^1L_b. It is quite probable that the lowest absorbing state of DMNA is ^1L_b. However, it is not quite clear whether the fluorenscent state of this molecule is ^1L_a or ^1L_b. Nevertheless, this circumstance will not affect the essential conclusion of the present study.

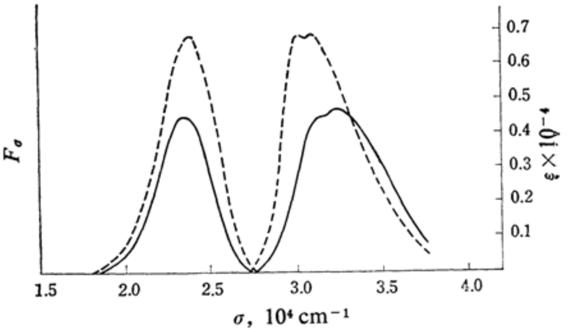

Fig. 1. Absorption and fluorescence spectra of DMNA (——) and NA (----) in acetonitrile. Concentrations of the solute: DMNA, 0.875×10^{-4} mol./l., NA, 0.8×10^{-4} mol./l.

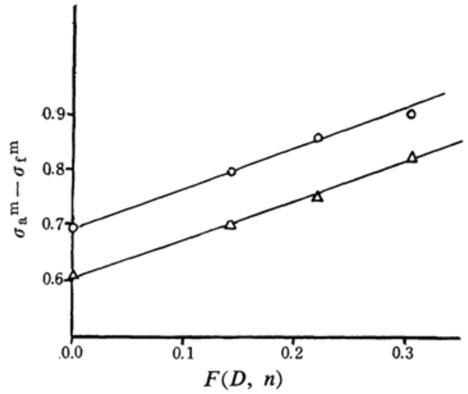

Fig. 2. $(\sigma_a{}^m - \sigma_f{}^m) \sim F(D, n)$ relations for DMNA.
○ $\sigma_a{}^m(^1L_a) - \sigma_f{}^m$ △ $\sigma_a{}^m(^1L_b) - \sigma_f{}^m$

As an example of the difference between the absorption and fluorescence spectra of DMNA and NA, the spectra in acetonitrile are indicated in Fig. 1. The smaller absorption intensity of DMNA compared with NA is also in accordance with the findings of Smith[1].

Thus, the resonance interaction between the substituent and the naphthalene ring in DMNA is rather small in the ground state and in the excited Franck-Condon state. Moreover, the interaction energy between DMNA and the surrounding solvent molecules is not very differemt in the ground state and in the Franck-Condon excited state respectively. However, the very large solvent shift of the fluorescence spectra indicate a rather large difference between the solute-solvents interaction energies in the Franck-Condon state and in the equilibrium excited state of DMNA, and, consequently, a large difference between the electronic structures of DMNA in the ground and in the fluorescent states respectively.

We can now roughly estimate the change of electronic structure in the fluorescent state, as

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[1] J. W. Smith, *J. Chem. Soc.*, **1961**, 81.
[2] H. Baba and S. Suzuki, This Bulletin, **34**, 82 (1961).
[3] N. Mataga, to be published.

TABLE I. WAVE NUMBERS OF BAND MAXIMA IN SEVERAL SOLVENTS (in unit of $10^4\,\mathrm{cm}^{-1}$)

Solvent	$F(D, n)$	DMNA			NA	
		$\sigma_a{}^m({}^1L_a)$	$\sigma_a{}^m({}^1L_b)$	$\sigma_f{}^m$	$\sigma_a{}^m({}^1L_a)$	$\sigma_f{}^m$
n-Hexane	0	—	—	—	3.14	2.66
Cyclohexane	0	3.28	3.20	2.59	—	—
Monochlorobenzene	0.1429	3.27	3.17	2.47	3.10	2.51
Dichloroethane	0.2199	3.27	3.16	2.41	—	—
Acetonitrile	0.3054	3.25	3.17	2.35	3.07	2.38

compared with the ground state, by the following equation[4,5]:

$$hc(\sigma_a{}^m-\sigma_f{}^m)=\mathrm{const}+2\cdot F(D,n)\cdot\delta$$

$$F(D,n)=\left[\frac{D-1}{2D+1}-\frac{n^2-1}{2n^2+1}\right],\ \delta=(\vec{\mu}_e-\vec{\mu}_g)^2/a^3$$

where D and n: the dielectric constant and the refractive index of the solvent, $\vec{\mu}_e$ and $\vec{\mu}_g$: the dipole moments of the solute molecule in the excited and ground states respectively, and a: the cavity radius in Onsager's theory of the reaction field.

The approximate linear relations between $(\sigma_a{}^m-\sigma_f{}^m)$ and $F(D, n)$ are satisfied for DMNA, as is shown in Fig. 2. From the linear relations, the δ value can be estimated to be 7500 cm^{-1} for either value of $\sigma_a{}^m(\sigma_a{}^m({}^1L_a)$ or $\sigma_a{}^m({}^1L_b))$. This δ value is very close to and a little larger than the δ value of NA (7300 cm^{-1}). Thus the change of the electronic structure of DMNA in the fluorescent state is quite large in spite of the steric repression of the resonance effect of the substituent in the ground state. The ionization potential of the nitrogen lone pair orbital of the dimethylamino group may be much smaller than that of the amino group. (The difference between the ionization potentials of methylamine and trimethylamine and the difference between those of ammonia and dimethylamine are both ca. 1 eV.[6]) Therefore, the energy of the CT (charge transfer) configuration, where one electron is transfered from the nitrogen lone pair orbital to a vacant orbital of naphthalene, is much smaller in DMNA than in NA. Accordingly, the interaction between the CT configurations and the locally excited states of naphthalene may be very strong if the core resonance integral between the nitrogen lone pair orbital and the carbon $2p\pi$AO's of naphthalene is not so small.

The large value of δ for DMNA observed in the present study indicates the structural change, i.e., the rotation of the dimethylamino group around the C–N bond during the life time of the excited state, leading to an increase in the overlap between the lone pair orbital and the π-orbital of naphthalene. This structural change is perhaps possible because the considerable increase of CT interaction in the excited state compensates for the increase in the steric repulsion.

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[4] E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955); *Z. Elektrochem.*, **61**, 962 (1957).

[5] N. Mataga et al., This Bulletin, **28**, 690 (1955); ibid., **29**, 465 (1956).

[6] K. Watanabe and J. R. Mottle, *J. Chem. Phys.*, **26**, 1773 (1957).