Solvent Effects on the Absorption and Fluorescence Spectra of Naphthylamines and Isomeric Aminobenzoic Acids

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The solvent effects upon the absorption spectra and those upon the fluorescence spectra are different from each other.

From the study of this difference one may derive some information concerning the nature of the electronically-excited state in contrast to the ground state and also the nature of the interactions between solute and solvent molecules in the excited as well as the ground state.

On the other hand, the nature of the electronic states of such substituted aromatic hydrocarbons as hydroxy and amino derivatives seems to be not so well understood as that of the parent hydrocarbons[1-4] and their aza-derivatives[5-9].

Recently, a number of studies[10,11] have been carried out to elucidate the electronic structures and spectra of the former. Baba[10] has made comparative studies of the mono-substituted hydroxy and amino derivatives of benzene and naphthalene and has made the assignment of the electronic absorption bands of these molecules.

We present here a somewhat different approach to the electronic structures of naphthylamines. We are mainly interested in the electronically excited states and in the difference between the electronic structure in the excited state and that in the ground state. We shall demonstrate in the following the remarkable difference between the conjugation power of the hydroxy and that of the amino group by measuring the solvent effects on the electronic spectra.

Further, the results of similar measurements on isomeric aminobenzoic acids (ABA) will be described, with some discussion of the electronic structure of these molecules.

Experimental

Apparatus.—The absorption spectra were measured with a Beckman spectrophotometer model DU. Details of the fluorescence spectrophotometer have been described elsewhere[12]. The light source for *p*-ABA was a 300 W xenon discharge tube with a stabilizer. For other compounds used in the present study, a high-pressure mercury discharge tube was used as a light source.

The fluorescence of *p*-ABA was excited at 290 mμ, the monochromatic exciting light from the xenon discharge tube being taken out by a quartz prism monochromater. Doublet lines at 313 mμ, taken out from the high-pressure mercury discharge tube by the monochromator, were used for exciting the other compounds.

All measurements were carried out at room temperature (~20°C).

Materials. — The naphthylamines were recrystallized from ligroin and sublimated in a vacuum. The ABA's were purified by sublimation in a vacuum. Special grade benzene was dried over metallic sodium and distilled fractionally. Cyclohexane was dried over metallic sodium, distilled fractionally and the distillate was then passed through a column of activated silica gel for chromatographic use. *n*-Hexane was shaken with fuming sulfuric acid diluted with concentrated sulfuric acid, washed with water several times, dried over calcium chloride and distilled carefully. The acetic acid esters were dried over potassium carbonate and distilled fractionally. Acetonitrile was refluxed repeatedly over phosphorus pentoxide, distilled into potassium carbonate and fractionally distilled from it. Chloroform was shaken with concentrated sulfuric acid, washed with water, and after being dried over phosphorus pentoxide, distilled carefully. Methanol and ethanol were refluxed with silver nitrate, and after being refluxed with calcium-carbonate, fractionally distilled. Normal butanol was washed with dilute sulfuric acid and with a sodium bisulfate solution. The treated alcohol was then dried with potassium carbonate and fractionally distilled. Monochlorobenzene was dried with phosphorus pentoxide and fractionally distilled. Dioxane was refluxed with dilute hydrochloric acid, treated with potassium hydroxide, dried over metallic sodium and then fractionally distilled from it.

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[1] J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

[2] J. A. Pople, *Proc. Phys. Soc.*, **A68**, 881 (1955).

[3] R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

[4] N. Mataga, K. Nishimoto and S. Mataga, This Bulletin, **32**, 395 (1959).

[5] R. Mcweeny, *Proc. Phys. Soc.*, **A70**, 593 (1957).

[6] T. E. Peacock, ibid., **A70**, 654 (1957).

[7] N. Mataga and K. Nishimoto, *Z. Phys. Chem. N. F.*, **13**, 140 (1957).

[8] N. Mataga, ibid., **18**, 285 (1958); This Bulletin, **31**, 453, 459, 463 (1958).

[9] R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, **12**, 554 (1959).

[10] H. Baba. This Bulletin, **34**, 76 (1961); H. Baba and S. Suzuki, ibid., **34**, 82 (1961).

[11] K. Nishimoto and R. Fujishiro, ibid., **31**, 1036 (1958); **35**, 905 (1962).

[12] N. Mataga, Y. Torihashi and Y. Kaifu, *Z. Phys. Chem. N. F.*, **34**, 379 (1962).

Experimental Results

Naphthylamines. — Some examples of the solvent shifts of the absorption and fluorescence spectra of naphthylamines are shown in Figs. 1 and 2. In these figures, the intensity of the maximum of each fluorescence band is brought to the same value as that of the corresponding absorption band.

One may observe from Figs. 1 and 2 that the red shift of the absorption and fluorescence spectra becomes larger, the greater the dielectric constant of the solvent, and that the shift of the fluorescence band is much larger than that of the absorption band. This anomalous Stokes red shift can be ascribed to the change in solute-solvent interaction during the lifetime of the excited solute molecule[14-15].

In other words, according to the Franck-Condon principle, the configuration of the solvent molecules surrounding the solute molecule does not change during the light absorption. The momentary excited state (Franck-Condon excited state) is, in general, not the most stable equilibrium state appropriate to the excited solute molecule. The equilibrium-excited state can be reached completely or partially by reorganization of the configurations of the surrounding molecules during the lifetimes of the excited solute molecule.

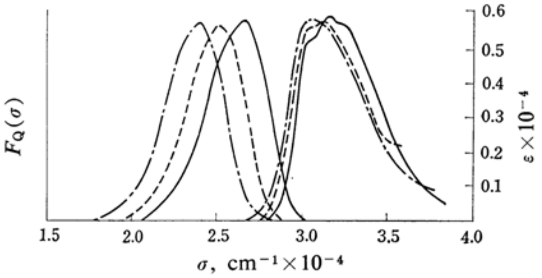

Fig. 1. Absorption and fluorescence spectra of α-naphthylamine.
Solvent: ——— n-Hexane
— — — Monochlorobenzene
—·—· Acetonitrile
Concn. of the naphthylamine ~0.8×10^{-4} mol./l.

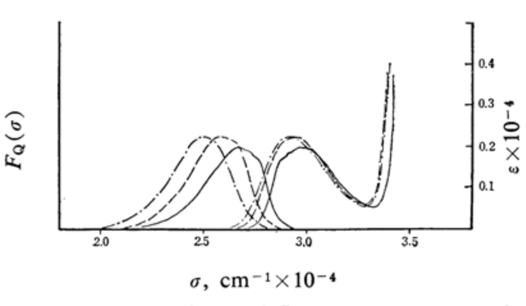

Fig. 2. Absorption and fluorescence spectra of β-naphthylamine.
Solvent: ——— n-Hexane
— — — Monochlorobenzene
—·—· Acetonitrile
Concn. of the naphthylamine ~2.0×10^{-4} mol./l.

We can use this difference between the solvent shifts of absorption and fluorescence spectra in order to get experimental information on the electronic structure of the excited molecule[13-15].

In the present study, we have used the method (Eq. 1) proposed by Lippert[14] and by the present author[15], for the evaluation of $\Delta\vec{\mu}$, the difference between the excited state dipole moment, $\vec{\mu}_e$, and that in the ground state, $\vec{\mu}_g$, i. e., $\Delta\vec{\mu}=\vec{\mu}_e-\vec{\mu}_g$, where the excited state is the fluorescent state.

$$hc\Delta\sigma \simeq \text{Const.}+2\cdot F(D,n)\cdot(\Delta\vec{\mu})^2/a^3$$

$$\Delta\sigma=\sigma_a{}^{\text{m}}-\sigma_f{}^{\text{m}}$$

$$F(D,n)=\left(\frac{D+1}{2D+1}+\frac{n^2+1}{2n^2+1}\right) \qquad (1)$$

In Eq. 1, $\sigma_a{}^{\text{m}}$ and $\sigma_f{}^{\text{m}}$: the wave number of a peak of the fluorescence band and that of the corresponding absorption band respectively; D and n: the dielectric constant and refractive index of the solvent and a: the cavity radius in Onsager's theory of the reaction field. The observed values of $\sigma_a{}^{\text{m}}$, $\sigma_f{}^{\text{m}}$ and $\Delta\sigma$ are given in Table I, together with the values of $F(D,n)$.

Thus, the observed values of $\Delta\sigma$ are plotted against the values of $F(D,n)$, in Fig. 3. As one can see from this figure, Eq. 1 is approximately satisfied, that is, an approximate linear

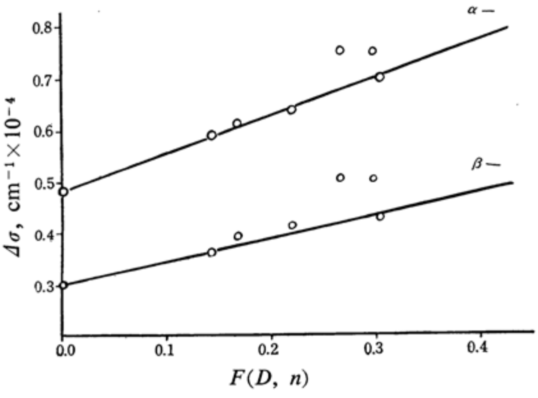

Fig. 3. $\Delta\sigma$ vs. $F(D, n)$ relation for naphthylamines.

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[13] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954); E. G. McRae, ibid., **61**, 562 (1957).

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

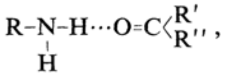
[15] N. Mataga et al., This Bulletin, **28**, 690 (1955); ibid., **29**, 465 (1956).

TABLE I*. THE WAVE NUMBERS OF THE BAND MAXIMA OF NAPHTHYLAMINES IN VARIOUS SOLVENTS

Solvent	$F(D, n)$	α-Naphthylamine			β-Naphthylamine		
		σ_a^m	σ_f^m	$\Delta\sigma$	σ_a^m	σ_f^m	$\Delta\sigma$
n-Hexane	0	3.14	2.66	0.48	2.96	2.66	0.30
Monochlorobenzene	0.143	3.10	2.51	0.59	2.93	2.58	0.35
n-Butyl acetate	0.171	3.07	2.46	0.61	2.90	2.51	0.39
Methyl acetate	0.220	3.06	2.43	0.63	2.92	2.51	0.41
n-Butanol	0.267	3.13	2.31	0.82	2.96	2.46	0.50
Ethanol	0.298	3.13	2.31	0.82	2.96	2.46	0.50
Acetonitrile	0.304	3.07	2.38	0.69	2.91	2.49	0.42

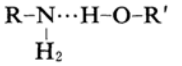
relation between $\Delta\sigma$ and $F(D, n)$ holds, although the $\Delta\sigma$ values of alcohol solutions deviate considerably from the linear relation.

Among the solvents used here, acetic acid esters and alcohols can form hydrogen bonds with naphthylamines of the types,



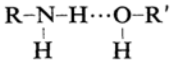
$$\mathrm{R{-}\underset{\displaystyle H}{\underset{|}{N}}{-}H\cdots O{=}C\left\langle{R' \atop R''}\right.},$$

and



$$\mathrm{R{-}\underset{\displaystyle H_2}{\underset{|}{N}}\cdots H{-}O{-}R'}$$

or



$$\mathrm{R{-}\underset{\displaystyle H}{\underset{|}{N}}{-}H\cdots \underset{\displaystyle H}{\underset{|}{O}}{-}R'}$$

or both, respectively. These hydrogen bonding interactions may somewhat complicate the interpretation of the observed results because only the long range dipolar interactions are taken into account in Eq. 1, and actually the values of alcohol solutions do not satisfy the linear relations. However, the hydrogen-bonding interactions with monochlorobenzene and acetonitrile are certainly very weak, and the $\Delta\sigma$ values for these solvents, together with that for *n*-hexane, well satisfy the approximate linear relation.

Equation 1 for naphthylamines can be written approximately as follows:

$$\beta\text{-},\quad \Delta\sigma = 2900 + 4800\,F(D, n)$$
$$\alpha\text{-},\quad \Delta\sigma = 4800 + 7300\,F(D, n)$$

From these equations, $\overrightarrow{\Delta\mu}$ values for naphthylamines can be evaluated as follows, assuming $a \sim 3$ Å: α-, 4.4 D, β-, 3.5 D. By the same method and with the same value of the cavity radius, the $\overrightarrow{\Delta\mu}$ values for naphthols were estimated to be 0.5D∼1D[15]. In the latter case, the $\overrightarrow{\Delta\mu}$ value of the β-derivative was evidently greater than the $\overrightarrow{\Delta\mu}$ value of the α-derivative, in contrast with the former case.

At any rate, it is quite certain that the $\overrightarrow{\Delta\mu}$ values of naphthylamines are much larger than those of naphthols and that the relative order of magnitude of this value for α- and β-derivatives is reversed in naphthylamines when compared with naphthols.

ABA's. — The absorption and fluorescence spectra of *o*- and *m*-isomers in a benzene solution are shown in Fig. 4, while those of *p*-isomer in benzene and methyl acetate are given in Fig. 5.

The values of σ_a^m, σ_f^m, $\Delta\sigma$ and $F(D, n)$ for isomeric ABA's are collected in Table II. The relations between the $\Delta\sigma$ values and $F(D, n)$ are shown in Fig. 6.

It appeares, from Fig. 6, that Eq. 1 is not so well satisfied in these cases as in the case of naphthylamines. In particular, the deviations of the $\Delta\sigma$ values of alcohol solutions from the linear relation is quite remarkable.

We have not attempted to evaluate the $\overrightarrow{\Delta\mu}$

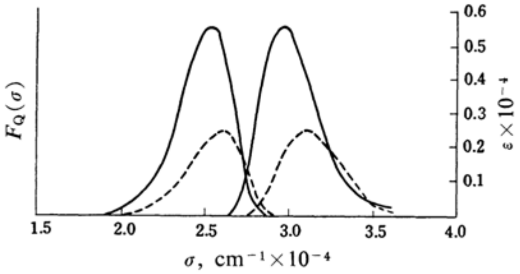


Fig. 4. Absorption and fluorescence spectra of *o*- and *m*-ABA in benzene.
—— *o*- – – – *m*-
Concn. of the solutes:
o-, 1×10^{-4} mol./l. *m*-, 2×10^{-4} mol./l.

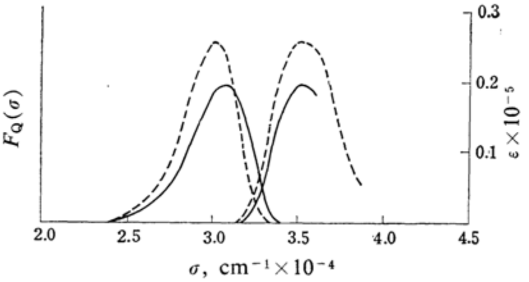


Fig. 5. Absorption and fluorescence spectra of *p*-ABA.
Solvent: —— Benzene
– – – Methyl acetate
Concn. of *p*-ABA in benzene $\sim 3.4 \times 10^{-5}$ mol./l. and 2.5×10^{-5} mol./l. in methyl acetate.

TABLE II*. THE WAVE NUMBERS OF THE BAND MAXIMA OF ISOMERIC AMINOBENZOIC ACIDS IN VARIOUS SOLVENTS

Solvent	$F(D, n)$	*o*-ABA			*m*-ABA			*p*-ABA		
		σ_a^m	σ_f^m	$\Delta\sigma$	σ_a^m	σ_f^m	$\Delta\sigma$	σ_a^m	σ_f^m	$\sigma\Delta$
Cyclohexane	0	2.98	2.58	0.40	—	—	—	—	—	—
Benzene	0.002	2.96	2.52	0.44	3.10	2.60	0.50	3.51	3.07	0.44
Monochlorobenzene	0.143	2.96	2.51	0.45	3.08	2.56	0.52	3.47	3.04	0.43
Chloroform	0.185	—	—	—	—	—	—	3.53	3.04	0.49
Acetonitrile	0.304	2.99	2.50	0.49	3.10	2.46	0.64	3.51	2.99	0.52
Dioxane	0.028	2.97	2.51	0.46	3.09	2.57	0.52	3.54	3.01	0.53
n-Butyl acetate	0.171	2.97	2.52	0.45	3.10	2.54	0.56	3.56	3.02	0.54
Ethyl acetate	0.202	2.98	2.51	0.47	3.10	2.52	0.58	3.55	3.01	0.54
Methyl acetate	0.220	2.98	2.50	0.48	3.11	2.46	0.65	3.53	3.00	0.53
n-Butanol	0.267	2.99	2.45	0.54	3.13	2.27	0.87	3.47	2.92	0.55
Ethanol	0.298	2.98	2.42	0.56	3.13	2.27	0.86	3.46	2.90	0.56
Methanol	0.308	3.00	2.42	0.58	3.15	2.25	0.90	3.46	2.90	0.56

* σ's and $\Delta\sigma$'s are in unit of $10^4\,\text{cm}^{-1}$.

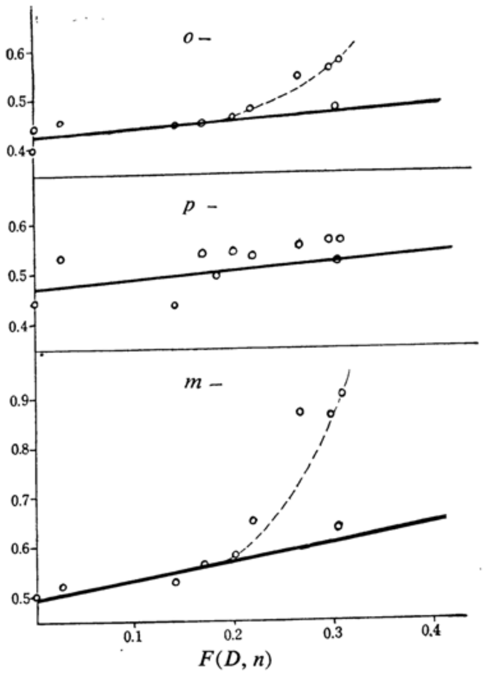


Fig. 6. $\Delta\sigma$ vs. $F(D, n)$ relation for aminobenzoic acids.

values of ABA's because the points are rather scattered and the more specific short-range interactions between solute and solvent molecules seem to be rather dominant. However, the inclinations of the full lines in Fig. 6 may give an approximate measure of th $\overrightarrow{\Delta\mu}$ values for these compounds, because the $\Delta\sigma$ values involved here mainly correspond to solvent molecules which make very weak hydrogen bond with solute molecules. The observed inclination is the largest for the *m*-isomer and the smallest for the *o*-isomer.

We can get only a rough estimate of the inclination for the *p*-isomer because the points in this case are scattered considerably. However, the inclination for the *p*-isomer is certainly rather close to that of the *o*-isomer.

Discussion

Deviations of $\Delta\sigma$ Values from the Linear Relation and Hydrogen Bonding Effects. — The lowest excited electronic state of naphthalene is ^1L_b, and the next one is ^1L_a[1-4]. Owing to the substitution by the hydroxy and amino groups, the electronic spectrum of naphthalene is modified considerably. Nevertheless, the lowest excited electronic states of naphthols and naphthylamines can be assigned to modified ^1L_b's and next ones to modified ^1L_a's[10].

It is well known that the electron migration or the charge transfer interaction between the substituent and the aromatic hydrocarbon is the most important factor which affects and determines the electronic spectra of aromatic derivatives[10,11,16-25].

In general, the extent of electron migration or the charge transfer interaction is greater in the excited electronic state than in the ground state. The observed $\overrightarrow{\Delta\mu}$ values presumably arise mainly from this difference.

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16) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1959).

17) K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).

18) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).

19) S. Nagakura and H. Baba, ibid., **74**, 5693 (1952).

20) L. Goodman and H. Shull, *J. Chem. Phys.*, **27**, 1388 (1957).

21) S. Nagakura and J. Tanaka, ibid., **22**, 236 (1954); S. Nagakura, ibid., **23**, 1441 (1955); J. Tanaka, S. Nagakura and M. Kobayashi, ibid., **24**, 311 (1956); J. Tanaka and S. Nagakura, ibid., **24**, 1274 (1956).

22) J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 969 (1955).

23) N. Mataga and S. Mataga, This Bulletin, **32**, 600 (1959).

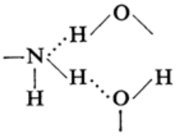
24) I. Fischer-Hjalmars, *Ark. för Fys.*, **21**, 123 (1962).

25) K. Nishimoto, to be published.

Baba[10] calculated the changes (decrease) in π-electron density on the substituent of naphthols and naphthylamines accompanying electronic transitions by a semiempirical ASMO CI method. The calculated results show that this decrease is much larger for naphthylamines than for naphthols, which is in accordance with the observed $\Delta\vec{\mu}$ values of these compounds, at least qualitatively.

This decrease of π-electron density on the substituent in the excited state is probably responsible also for the observed deviations of the $\Delta\sigma$ values of alcohol solutions in Fig. 3.

The hydrogen-bonding interaction in alcohol solutions probably involves both the types of hydrogen bonds indicated in Experimental Results, simultaneously, i. e., a bonding of the type:



The hydrogen bonding of the type, $_{H}{>}N-H\cdots O{<}$, causes a red shift of the absorption spectrum, whereas the other type of hydrogen-bonding interaction cause a blue shift of the absorption spectrum, because the former is favorable but the latter is unfavorable for the charge migration from the substituent to the aromatic ring.

As one can see from the tables, the $\sigma_a{}^m$ values of alcohol solutions are almost the same as or even larger than those in non-polar solvents.

This fact indicates that the effect of the latter type of hydrogen-bonding interaction on the spectral shift is rather important.

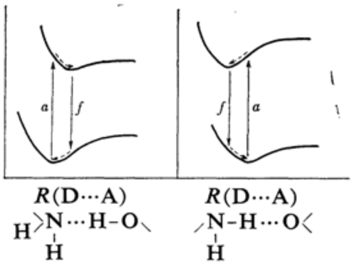


Fig. 7. Potential energy curves for the hydrogen bondings of the types: $-\underset{H_2}{N}\cdots H-O-$ and $-\underset{H}{N}-H\cdots O{<}$, respectively. $R(D\cdots A)$ is the distance between the proton donor and the acceptor. a and f indicate the light absorption and fluorescent transitions, respectively, and broken lines represent radiationless processes due to the reorganization of the hydrogen bond.

As is indicated in Fig. 7, the hydrogen-bonding interaction of the type, $-\underset{H_2}{N}\cdots H-O-$, is certainly very weak in the excited state of naphthylamines, and the other type of hydrogen-bonding interaction is a little stronger in the excited state than in the ground state.

The broken lines in Fig. 7 represent radiationless processes, which are reorganizations of hydrogen-bonding interactions. This sort of radiationless process may cause a large value of $\Delta\sigma$, leading to considerable deviations from the linear relation between $\Delta\sigma$ and $F(D,n)$.

The effect of hydrogen-bonding interaction of this type may be much stronger in the case of ABA's than in the case of naphthylamines because of the existence of the carboxyl group in the former. The near-ultraviolet absorption spectra of the ABA molecule have been interpreted as being due to the intramolecular charge-transfer transition from the aniline residue to the antibonding orbital of the carboxyl group[20]. Thus, the electron-accepting character of the carboxyl group results in a stronger decrease in the π-electron density on the amino group in the excited electronic state. This circumstance is probably responsible for the remarkable deviations in the $\Delta\sigma$ values of alcohol solutions in the case of *m*-ABA.

In the case of *o*-ABA, however, the circumstance may be somewhat different because of the existence of an intramolecular hydrogen bond between the amino group and the carbonyl group. Because electronic delocalization through the hydrogen bond is possible[26-29], the charge separation between the two substituents may be smaller in this molecule than in the other isomers. This delocalization is certainly stronger in the excited state than in the ground state because the electronic orbital is more extended, the ionization potential of the carbonyl becomes smaller, and the electron affinity of the amino group becomes larger in the excited electronic state than in the ground state.

In this way, the electronic delocalization through the intramolecular hydrogen bond may result in smaller deviations in the $\Delta\sigma$ values of *o*-ABA in alcohol solutions than is the case with *m*-isomer.

The same factor may be responsible also for

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26) H. Tsubomura, This Bulletin, **27**, 445 (1954); *J. Chem. Phys.*, **23**, 2130 (1955); ibid., **24**, 927 (1956).

27) K. Nukasawa, J. Tanaka and S. Nagakura, *J. Phys. Soc. Japan*, **8**, 792 (1953).

28) S. Nagakura and M. Gouterman, *J. Chem. Phys.*, **26**, 881 (1957).

29) N. Mataga and Y. Kaifu, ibid., **36**, 2804 (1962); N. Mataga and S. Tsuno, This Bulletin, **30**, 711 (1957).

the small inclination of *o*-ABA in Fig. 6. However, the distance between the two substituents is the smallest for this isomer, and this may be the main cause for the small inclination. Because the distance between the two substituents is the largest for the *p*-isomer, one may expect the largest inclination for this compound. However, this expectation is not in agreement with the observed result.

As shown in Fig. 5, the absorption intensity of the *p*-isomer is much stronger than those of other isomers and naphthylamines. This very strong absorption intensity indicates a short life time of the fluorescent state, although the observed value of the life time is not available for this molecule. During the very short life time of the fluorescent state, the rearrangement of the solvent molecules surrounding the excited solute molecule may be reached only partially or it may be almost impossible. Such a circumstance has already been observed in the case of *p*-dimethylaminocinnamic-nitrile³⁰⁾.

It is quite probable that the rearrangement of the solvent molecules during the life time of the excited state occurs only incompletely for *p*-ABA and that, accordingly, the observed inclination is so small as shown in Fig. 6.

Theoretical Calculation of the $\overrightarrow{\Delta\mu}$ Values of Naphthylamines and Naphthols. — As has been mentioned in Experimental Results, the observed $\overrightarrow{\Delta\mu}$ value for α-naphthylamine was larger than that for β-naphthylamine, contrary to the case of naphthols.

To interpret these facts, the observed results may be compared with the results of theoretical calculation as follows.

The Method of Calculation. — The semiempirical ASMO CI method³⁾ was used. In this treatment, an electronic state function, Ψ, for the π-electrons is approximated by a linear combination of the ground configuration function, χ_0, and singly excited configuration functions, χ_{ik}'s, where one electron is excited from an occupied MO ψ_i to an unoccupied MO ψ_k.

The orthonormal MO's are themselves linear combinations of 2pπAO's, ϕ_μ's:

$$\psi_i=\sum_{\mu} c_{i\mu}\phi_\mu \tag{2}$$

The theoretical expression for $\overrightarrow{\Delta\mu}$ in terms of the state function, Ψ, is given by:

$$\overrightarrow{\Delta\mu}=\langle\Psi_e|M|\Psi_e\rangle-\langle\Psi_g|M|\Psi_g\rangle \tag{3}$$

where

$$M=\sum_{t} e_t r_t \tag{4}$$

e_t and r_t are the charge and the position vector of t-th particle, respectively. In the π-electron approximation, M can be separated into two parts:

$$M=e\sum_{\mu} r_\mu+\sum_{s} e_s r_s \tag{5}$$

e is the electronic charge, the first summation being over the π-electrons and the second over the cores. The necessary formulas for the expansion of 3 in terms of integrals over MO's are given as follows:

$$\left.\begin{aligned}
&\langle\chi_0|M|\chi_0\rangle=2\sum_{i}^{\text{occ}} M_{ii}+\sum_{s} e_s r_s\\
&\langle{}^1\chi_{ik}|M|{}^1\chi_{ik}\rangle=2\sum_{i}^{\text{occ}} M_{ii}-M_{ii}\\
&\qquad\qquad\qquad\qquad+M_{kk}+\sum_{s} e_s r_s\\
&\langle\chi_0|M|{}^1\chi_{ik}\rangle=\sqrt{2}\,M_{ik}\\
&\langle{}^1\chi_{ik}|M|{}^1\chi_{jk}\rangle=-M_{ij}\\
&\langle{}^1\chi_{ik}|M|{}^1\chi_{il}\rangle=M_{kl}\\
&\langle{}^1\chi_{ik}|M|{}^1\chi_{jl}\rangle=0\\
&M_{ik}=\langle\psi_i|M|\psi_k\rangle
\end{aligned}\right\} \tag{6}$$

In Eq. 6, occ means the summation over the occupied MO's in χ_0.

In the present calculations, the wave functions calculated by Baba³¹⁾ were used. In his treatment, $\Psi_g\sim\chi_0$ and $\Psi_e\sim a\,{}^1\chi_{ik}+b\,{}^1\chi_{jl}$; therefore Eq. 3 reduces to the following:

$$\overrightarrow{\Delta\mu}=a^2(M_{kk}-M_{ii})+b^2(M_{ll}-M_{jj}) \tag{7}$$

In the expansion of M_{ii}'s in terms of integrals over AO's, the following approximation was used:

$$M_{ll}=\sum_{\mu,\nu} c_{i\mu}c_{i\nu}\langle\phi_\mu|M|\phi_\nu\rangle\simeq e\left[\sum c^2_{i\mu}R_\mu\right] \tag{8}$$

where R_μ is the position vector of the μ-th atom.

All bond distances in naphthylamines and naphthols are assumed to be 1.39Å.

Calculated Results. — The $\overrightarrow{\Delta\mu}$ values for the ^1L_b state of naphthols were calculated as follows: α-, 1.63 D and β-, 2.75 D, which are much larger than the observed values.

The usual MO method seems to overestimate the values of dipole moments and also $\overrightarrow{\Delta\mu}$ values. Thus, the calculated $\overrightarrow{\Delta\mu}$ values for the ^1L_b state of naphthols were four times as large as the observed values.

Because we are concerned here with only the relative values of $\overrightarrow{\Delta\mu}$ for these molecules, the calculated values were divided by this factor. Then, one quarter of the $\overrightarrow{\Delta\mu}$ values for the ^1L_b state of naphthols was calculated

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30) E. Lippert, *Angew. Chem.*, 73, 695 (1961).

31) H. Baba, private communication; see also Ref. 10.

as: α-, 0.41 D and β-, 0.69 D. The same quantities (i. e., one quarter of the theoretical values) for the ^1L_b state of naphthylamines were: α-, 0.92 D and β-, 1.16 D. These values are considerably smaller than the observed values. However, a more serious disagreement with the experimental results is that the $\overrightarrow{\Delta\mu}$ value of the α-isomer is smaller than that of the β-isomer.

One-quarter of the theoretical value of $\overrightarrow{\Delta\mu}$ for the ^1L_a state of α-naphthylamine (abbreviated as $\overrightarrow{\Delta\mu}(^1L_a{}^\alpha)$) was 1.35 D, which was larger than $\overrightarrow{\Delta\mu}(^1L_b{}^\beta)$. Moreover, the ratio $\overrightarrow{\Delta\mu}(^1L_b{}^\beta)/\overrightarrow{\Delta\mu}(^1L_a{}^\alpha)$ is 0.86 for the calculated values, which is very close to the observed ratio, 0.80. These facts seems to indicate rather strongly that the fluorescent state of α-naphthylamine is not the ^1L_b but the ^1L_a state.

If all of the structures of the absorption band in *n*-hexane as shown in Fig. 1 belong to the same electronic band, the fluorescence band should have the corresponding structures and the absorption and fluorescence bands should present the "mirror image" appearance*. However, this seems not to be the case in the observed spectrum, because the shortest wavelength shoulder in the fluorescence band, which corresponds to the longest wavelength shoulder in the absorption band, seems to be missing. The latter shoulder was assigned[10] to ^1L_b, which seems to be quite reasonable. These facts also appear to support the above interpretation. Thus, the ^1L_a state of α-naphthylamine may probably become the lowest excited singlet state during the radiationless process from the Franck-Condon to the equilibrium excited state.

The Mechanism of the Level Reversal during the Life Time of the Excited State.—There is a noticeable difference between spectral changes caused by substitutions at the α- and β-positions of naphthalene. Several explanations have been already given for this interesting phenomenon[10,25,32,33].

The reversal of the ^1L_b and the ^1L_a states of α-naphthylamine during the life time of the excited state may be closely related to the factor which determine the spectral characteristics of the α- and β-isomers respectively.

The characteristic difference between the α- and β-isomers may be understood well if we write down the matrix elements of the interactions between the locally excited states of naphthalene and the charge transfer (CT) configurations which arise from the transfer of one electron from the occupied orbital of the substituent to the vacant orbitals of naphthalene.

Using the method developed by Longuet-Higgins and Murrell[22,34], the necessary matrix elements can easily be calculated as follows.

If the SCF MO's of naphthalene are written $\psi_1 \cdots \psi_n$ and those of the substitutent, $\theta_1 \cdots \theta_m$, then the energy of the CT configuration, $^1\chi_{sk}$, where one electron is transferred from an occupied orbital, θ_s, to a vacant MO, ψ_k, is given by:

$$\langle {}^1\chi_{sk} | \mathscr{H} | {}^1\chi_k \rangle = \varepsilon_k - \varepsilon_s - \langle \theta_s(1)\psi_k(2) | G_{12} | \theta_s(1)\psi_k(2) \rangle \tag{9}$$

where ε_k and ε_s are linear combinations of ψ_k and θ_s respectively, and ψ_k's are linear combinations of 2pπAO's $\phi_1 \cdots \phi_n$,

$$\psi_k = \sum_\mu c_{k\mu}\phi_\mu \tag{10}$$

G_{12} is the two-electron operator, e^2/r_{12}, r_{12} being the inter-electronic distance.

For naphthylamines, ε_s will be given, to a good approximation, by the observed ionization potential of ammonia, i. e., $\varepsilon_s = -10.154$ eV.[35] The difference between the observed and calculated values of the electron affinity of benzene, $\Delta A = A_B{}^{obs} - A_B{}^{calc}$[4], has been added to the calculated values of ε_k.

With neglect of differential overlap,

$$\langle \theta_s(1)\psi_k(2) | G_{12} | \theta_s(1)\psi_k(2) \rangle = \sum_\mu c^2{}_{k\mu}\gamma_{s\mu} \tag{11}$$

$$\gamma_{s\mu} = \langle \theta_s(1)\phi_\mu(2) | G_{12} | \theta_s(1)\phi_\mu(2) \rangle$$

For the evaluation of $\gamma_{s\mu}$, the equation[4,7,8], $\gamma_{s\mu} = e^2/(\rho + R_{s\mu})$, was used, where $\rho = 1.197$ Å. The value of ρ is the harmonic mean of the ρ for carbon[4,7,8] and that for nitrogen. The latter value was obtained from the one center value of γ for nitrogen calculated by Brown[36] using the VESCF method.

The matrix elements of the interactions between the CT configurations and various local configurations in naphthalene can be evaluated from the following formulas:

$$\langle {}^1\chi_{sk} | \mathscr{H} | {}^1\chi_{jl} \rangle = -\delta_{kl} \langle \theta_s(1) | H(1) | \psi_j(1) \rangle \tag{12}$$

where δ_{kl} is Kronecker's delta.

$$\langle {}^1\chi_{sk} | \mathscr{H} | \chi_0 \rangle = \sqrt{2} \langle \theta_s(1) | H(1) | \psi_k(1) \rangle \tag{13}$$

where χ_0 is the ground configuration.

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* See, for example, Th. Förster, "Fluoreszenz organischer Verbindungen", Vandenhoeck and Ruprecht Göttingen (1951).

[32] D. Peters, *J. Chem. Soc.*, **1957**, 646, 1993, 4182.

[33] E. Döller, Th. Förster and H. Renner, *Z. Phys. Chem. N. F.*, **15**, 34 (1958).

[34] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955).

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

[36] R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, **12**, 319 (1959).

$$\begin{aligned}\langle {}^1\chi_{sk}|\mathscr{H}|{}^1\chi_{sl}\rangle &= -\langle\theta_s(1)\psi_k(2)|G_{12}|\theta_s(1)\psi_l(2)\rangle \\ &= -\sum_{\mu} c_{k\mu}c_{l\mu}\langle\theta(1)\phi_\mu(2)|G_{12}|\theta_s(1)\phi_\mu(2)\rangle\end{aligned} \tag{14}$$

The integral $\langle\theta_s(1)|H(1)|\psi_j(1)\rangle$ can be reduced to $c_{jr}\langle\theta_s(1)|H(1)|\phi_r(1)\rangle = c_{jr}\beta^c$, the substituent being attached to the carbon atom '*r*'.

Now, by means of these formulas and the SCF MO's and state functions of naphthalene[4)], the energy matrices for naphthylamines are calculated as follows (in units of eV.):

α-Naphthylamine

$$\begin{array}{ccccccc} \chi_0 & {}^1\mathrm{B}_{3u}^- & {}^1\mathrm{B}_{2u}^+ & {}^1\mathrm{B}_{3u}^+ & {}^1\mathrm{B}_{2u}^- & {}^1\chi_{s6} & {}^1\chi_{s7} \\ 0 & & & & & 0.5995\beta^c & -0.3749\beta^c \\ & 3.99 & & & & 0.0023\beta^c & -0.2997\beta^c \\ & & 4.51 & & & -0.4081\beta^c & -0.0009\beta^c \\ & & & 5.61 & & -0.0023\beta^c & -0.2997\beta^c \\ & & & & 7.30 & -0.1145\beta^c & 0.0032\beta^c \\ & & & & & 6.1679 & -0.0734\beta^c \\ & & & & & & 7.3736 \end{array}$$

β-Naphthylamine

$$\begin{array}{ccccccc} \chi_0 & {}^1\mathrm{B}_{3u}^- & {}^1\mathrm{B}_{2u}^+ & {}^1\mathrm{B}_{3u}^+ & {}^1\mathrm{B}_{2u}^- & {}^1\chi_{s6} & {}^1\chi_{s7} \\ 0 & & & & & -0.3749\beta^c & -0.5602\beta^c \\ & 3.99 & & & & 0.2801\beta^c & -0.1875\beta^c \\ & & 4.51 & & & -0.2553\beta^c & -0.1069\beta^c \\ & & & 5.61 & & -0.2801\beta^c & -0.1875\beta^c \\ & & & & 7.30 & -0.0716\beta^c & 0.3814\beta^c \\ & & & & & 6.5635 & -0.1573\beta^c \\ & & & & & & 7.3829 \end{array}$$

In these matrices, observed values are used for the locally excited states of naphthalene.

The calculated matrix elements correspond quite well to the observed characteristics of the electronic spectra of α- and β-derivatives respectively. That is, there are weak interactions between the ${}^1\mathrm{B}_{3u}^-$ and CT configurations and strong interactions between the ${}^1\mathrm{B}_{2u}^+$ and CT configurations for the α-isomer, whereas either ${}^1\mathrm{B}_{3u}^-$ or ${}^1\mathrm{B}_{2u}^+$ interacts moderately with the CT configurations and the interactions of the ${}^1\mathrm{B}_{3u}^-$ with CT configurations are a little stronger than those of ${}^1\mathrm{B}_{2u}^+$, in the β-isomer. In the case of naphthylamines, the energies of CT configurations are considerably smaller than those of naphthols*. Moreover, the core resonance integral, β^c, for naphthylamines may be a little larger than that for naphthols**. Therefore, only in the case of α-naphthylamine, the ${}^1\mathrm{L}_a$ state will be very close to the ${}^1\mathrm{L}_b$ state.

Now, in the excited state of naphthylamine, the more flattened structure of the amino group and the more stretched form of the N–H bond compared with those in the ground state may probably be favored because the gain of the CT interaction energy due to these changes in the structure of the amino group is much larger in the excited electronic state than in the ground state. In other words, these structural changes result in the lowering of the ionization potential of the lone-pair orbital of the amino group and the increase of β^c.

Thus, the excitation energies of the CT configurations becomes smaller and the CT interactions becomes stronger. Because the energy differences between the lower excited states of naphthalene and the CT configurations are much smaller than those between the ground configuration and CT configurations, the CT interactions are considerably larger in the excited electronic state.

Because of these circumstances, ${}^1\mathrm{B}_{2u}^+$ mixed with ${}^1\chi_{s6}$ is lowered rather strongly, but the lowering of ${}^1\mathrm{B}_{3u}^-$ may be small because of the very small interaction with ${}^1\chi_{s6}$ in the case of α-naphthylamine. Thus, the order of the ${}^1\mathrm{L}_b$ and ${}^1\mathrm{L}_a$ states may be reversed during the radiationless process in the excited state. This level reversal may be demonstrated by calculations using a simplified model, which are similar to those of an earlier treatment by Nagakura and Tanaka[21)] but which take into account the inter-electronic interactions to some extent. In this treatment, we discuss the case of the structural change of the amino group from the pure sp³ hydride to the pure sp₂ hydrid without a stretching of the N–H bond, and take into consideration only interactions among ${}^1\mathrm{B}_{3u}^-$, ${}^1\mathrm{B}_{2u}^+$ and ${}^1\chi_{s6}$.

We assume the proportionality of β^c to the corresponding overlap integral, *S*. Then we must evaluate the overlap integrals for the tetrahedral and trigonal hybrids respectively.

The lone-pair orbital used in this calculation for tetrahedral nitrogen is of the form:

$$\zeta = (1/2)s + (2/3)^{1/2}p_x - (1/12)^{1/2}p_z \tag{15}$$

where the x axis is taken perpendicular to the

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* Calculations using similar approximations give for naphthols:

α-, $\langle {}^1\chi_{s6}|\mathscr{H}|{}^1\chi_{s6}\rangle = 8.3435$ eV.
$\langle {}^1\chi_{s7}|\mathscr{H}|{}^1\chi_{s7}\rangle = 9.6003$ eV.
β-, $\langle {}^1\chi_{s6}|\mathscr{H}|{}^1\chi_{s6}\rangle = 8.7971$ eV.
$\langle {}^1\chi_{s7}|\mathscr{H}|{}^1\chi_{s7}\rangle = 9.5860$ eV.

** If we assume the proportionality of the core resonance integral to the corresponding overlap integral, taking $\beta_c(-2.388$ eV.) and $S(0.25)$ between the nearest neighbor 2pπAO's of benzene as a reference, then the β_c for naphthylamines is calculated to be -1.7 eV., whereas it is -1.4 eV. for naphthols. In this calculation, the AO's on the substituents are assumed to be pure 2pπAO's perpendicular to the molecular plane, and the orbital exponent in the Slater AO of the heteroatom is the simple arithmetic mean of the values for the neutral atom and the singly ionized one respectively.

molecular plane. Taking the simple arithmetical mean of the values of neutral and singly ionized atoms for the orbital exponent in the Slater AO of nitrogen, the overlap integrals have been calculated, and from these the core reasonance integrals have been evaluated by the same procedure as described before**: β^c (tetrahedral)~ -1.43 eV., β^c (trigonal)~ -1.75 eV.

The change of the ionization potential of the lone pair orbital on nitrogen caused by this structural change was estimated by means of the following equation:

$$I(\mathrm{tr})/I(\mathrm{tet}) = I/I(\mathrm{NH_3})$$

where I(tr) and I(tet) are the ionization potentials of lone pair orbitals in the trigonal and tetrahedral valence states respectively. These values are evaluated from the valence state quantities given by Hinze and Jaffé[37]: $I(\mathrm{tr}) = 11.958$ eV., $I(\mathrm{tet}) = 14.157$ eV. $I(\mathrm{NH_3})$ is the observed ionization potential of ammonia. Thus, $I = 8.5768$ eV. Using these values of β^c's and I's, the relevant energy matrices can be written as follows:

(a) Tetrahedral $-NH_2$ (b) Trigonal $-NH_2$

$$\begin{array}{ccc} {}^1B_{3u}^- & {}^1B_{2u}^+ & {}^1\chi_{s6} \\ \left(\begin{array}{c} 3.99 \\ \\ \\ \end{array}\right. & \begin{array}{c} 0 \\ 4.51 \\ \\ \end{array} & \left.\begin{array}{c} -0.0033 \\ 0.5836 \\ 6.1679 \end{array}\right) \end{array} \qquad \begin{array}{ccc} {}^1B_{3u}^- & {}^1B_{2u}^+ & {}^1\chi_{s6} \\ \left(\begin{array}{c} 3.99 \\ \\ \\ \end{array}\right. & \begin{array}{c} 0 \\ 4.51 \\ \\ \end{array} & \left.\begin{array}{c} -0.0040 \\ 0.7142 \\ 4.5909 \end{array}\right) \end{array}$$

The interaction between ${}^1B_{3u}^-$ and ${}^1\chi_{s6}$ is very small and can be neglected practically. The lower energies and state functions for the interaction of ${}^1B_{2u}^+$ with ${}^1\chi_{s6}$ may then be given as follows:

(a) 4.325 eV. $\Psi = 0.953\,{}^1B_{2u}^+ - 0.302\,{}^1\chi_{s6}$

(b) 3.835 eV. $\Psi = 0.727\,{}^1B_{2u}^+ - 0.687\,{}^1\chi_{s6}$

Thus, the level is reversed and the ${}^1L_a$ state in the latter case contains a large amount of the CT configuration.

Of course, the above calculations are too simplified and the transformation from the tetrahedral to the trigonal structure may be realized only partially. However, the stretching of the N–H bond may also contribute to the level reversal, and the occurence of the latter seems to be plausible.

This change in the structure of the amino group, leading to the stronger CT interaction, may be responsible for the large difference between the theoretical $\overrightarrow{\Delta\mu}$ values (one-quarter of the calculated values) and the observed $\overrightarrow{\Delta\mu}$ values of the fluorescent state.

In the case of naphthols, such effects may not be important because the CT configurations are considerably higher and β^c is smaller than in naphthylamines.

Summary

The absorption and fluorescence spectra of naphthylamines and isomeric aminobenzoic acids in various solvents have been measured.

From the observed results, the difference in the dipole moments in the fluorescent and ground states respectively, i. e., $\overrightarrow{\Delta\mu} = \overrightarrow{\mu_e} - \overrightarrow{\mu_g}$, has been estimated for naphthylamines.

The effect of hydrogen bonding between solute and solvent molecules on the spectral shifts has been discussed. The hydrogen bonding between alcohol and amino nitrogen exerts a especially remarkable influence on the spectra, and the reorganization of this hydrogen bond during the life time of the excited solute molecule has been concluded from the observed results.

The intramolecular hydrogen bond of *o*-aminobenzoic acid considerably decreases the $\overrightarrow{\Delta\mu}$ value and the effect of the intermolecular hydrogen bonding on the spectra. This result has been explained as due to the charge transfer through the intramolecular hydrogen bond.

The $\overrightarrow{\Delta\mu}$ values for naphthylamines and naphthols have been calculated using the ASMO CI method and compared with the observed results.

This comparison, together with the theoretical interpretation of the characteristics in the spectra of α- and β-isomers, respectively, has indicated that the lowest excited singlet state in the light absorption is ${}^1L_b$, whereas the fluorescent state is ${}^1L_a$ in the case of α-naphthylamine and ${}^1L_b$ is the relevant excited state for both light absorption and fluorescence in the case of β-naphthylamine and naphthols.

The mechanism of this level reversal has been discussed as being due to the change in the structure of the amino group during the life time of the excited state.

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[37] J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 540 (1962).