Effect of Non-hydrogen Bonding Solvents on the Electronic Spectra of Aromatic N-Oxides

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In previous papers, the effect of solvents, including active hydrogen atoms, which can form a hydrogen bond, on the electronic absorption spectra of many aromatic *N*-oxides has been reported by us[1-4]. As a result it has been concluded that the absorption spectra of the above compounds show a remarkable blue shift with the increasing polarity of the solvents and that the hydrogen bonding, such as $\rangle$N—O···H (solvents), plays an important role in the blue shift phenomena. The effects of non-hydrogen bonding solvents on the absorption spectra of *N*-oxides, however, have hardly been investigated at all. For the present paper, particular interest has been taken in the case of solute-non-hydrogen bonding solvents interactions, and the results have quantitatively been analyzed on the basis of McRae's theory of the solute-solvent interaction[5]. The results thus obtained are compared with the previous results of the solvent effects due to hydrogen bonding polar solvents and the molecular orbital calculations which were carried out by one (T. K.) of the authors to elucidate the electronic structures of heterocyclic *N*-oxides.

Experimental

Ultraviolet absorption spectra were recorded by means of a Hitachi model EPS automatic recording spectrophotometer at room temperature(~25°C), at a scale expansion of 2 (which is just twice as expansible as the normal procedure), at a slow scanning speed (about ten minutes), and using a quartz cell of 1 cm. light path. Measurements of fluorescence spectra were made with a Beckman model DU spectrophotometer which was modified to record fluorescence spectra with good sensitivity[1]. Solvents were purified by the methods recommended by Weissberger and Proskauer[6], and special care was taken to remove contaminating water. Samples used here are pyridine *N*-oxide, 4-nitropyridine *N*-oxide, acridine *N*-oxide and *N*-methylbenzaldoxime. Pyridine *N*-oxide and acridine *N*-oxide were prepared and purified by the usual method[7,18]. 4-Nitro-pyridine *N*-oxide and *N*-methylbenzaldoxime were prepared by Tokuyama of our research laboratory and by Mori of Osaka University respectively. The physical properties and the purification method of the above samples are shown in Table I. The refractive index at the sodium D line (n_D) and the static dielectric constant of solvents used are shown in Table II. These data have been quoted from Ref. 6.

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[1] T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 916, 930 (1958).

[2] T. Kubota, *J. Pharm. Soc. Japan* (*Nippon Yakugaku Zasshi*), **75**, 1540 (1955).

[3] T. Kubota, ibid., **74**, 831 (1954), and the other papers.

[4] T. Kubota and H. Miyazaki, *Chem. Pharm. Bull.*, **9**, 948 (1961).

[5] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

[6] A. Weissberger and E. Proskauer, "Organic Solvent", 2nd Ed. Interscience Pub. , Inc., New York (1956).

[7] E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953); A. Kliegl and A. Brösamle, *Ber.*, **69**, 197 (1936).

TABLE I. COMPOUNDS USED AND THEIR PHYSICAL PROPERTIES AND PURIFICATION METHODS

Compound	Physical properties	Purification
Pyridine *N*-oxide	B. p. = 105°C/1.5 mmHg	Redistilled three times in vacuo
4-Nitropyridine *N*-oxide	M. p. = 162.5°C	Recrystallized several times from acetone
Acridine *N*-oxide	Decomp. p. = 169.8°C	Recrystallized twice from heptane-chloroform and twice from water-ethanol
N-Methylbenzaldoxime	M. p. = 83.5°C	Recrystallized from benzene-petroleum ether

TABLE II. THE VALUES[6] OF THE REFRACTIVE INDEX AT THE Na-D LINE AND THE STATIC DIELECTRIC CONSTANT OF THE SOLVENTS USED

No.	Solvent	n_D	D
1	*n*-Heptane	1.388	1.924
2	Cyclohexane	1.426	2.023
3	Methylcyclohexane	1.423	2.020
4	Carbon tetrachloride	1.463	2.238
5	Carbon disulfide	1.632	2.641
6	Dioxane	1.424	2.209
7	Benzene	1.501	2.284
8	Toluene	1.494	2.379
9	Acetonitrile	1.344	37.5
10	Nitromethane	1.379	35.87
11	Benzonitrile	1.527	25.20
12	Acetone	1.356	20.70
13	Methyl acetate	1.362	6.68
14	Ethyl acetate	1.370	6.02
15	*n*-Butyl acetate	1.394	5.01
16	Isoamyl acetate	1.405	4.63
17	Diethyl oxalate	1.410	8.1
18	Ethyl ether	1.353	4.335
19	*n*-Butyl ether	1.397	3.06
20	Isoamyl ether	1.409	2.82

Results and Discussion

Theoretical Equation for the Solvent Effect of Absorption Spectra. — Theoretical investigation of solvent-solute interaction on electronic spectra have recently been made by Ooshika[8], by McRae[5] and by Longuet-Higgins and Pople[9] on the basis of applying the perturbation theory. As to the physical meaning, these authors obtained almost the same general expressions for the frequency shift. In this paper we shall use McRae's formula (Eq. 14 in the original paper) in order to analyze the experimental results, since this formula is well arranged for individual solute-solvent interaction terms such as the dispersion force, the solute dipole-solvent dipole thereby induced, the solute dipole-solvent dipole and the quadratic Stark effect. Nevertheless, the original formula is considerably complex and can not be applied to analyze the experimental data. The following simplifications, which are similar to those used by McRae to interpret the solvent effect of phenol blue[5], have been made with the aid of several assumptions. Firstly, the refractive index of the solvent at all frequencies involving the zero frequency has been replaced by the value at the Na-D line*[1]. Secondly, the quadratic Stark term representing the contribution from the interactions between the permanent dipoles of solvent molecules and the solute dipoles thereby induced has been neglected, since this term is small compared with the other contributions[5], especially for the relatively low polarity of most solvents used here. Lastly, the weighted mean wavelength (L_0) of the solvent introduced by McRae has been conveniently taken to be constant for all the solvents used, because L_0 values of most solvents may exist approximately in the far ultraviolet region (about 100∼125 mμ) and show considerable separation from the π-π^* absorption bands of *N*-oxide compounds*[2]. Thus we obtained

$$\tilde{\nu}_{\text{abs}} = \tilde{\nu}^{g}{}_{\text{abs}} + (A+B)\frac{n_D^2-1}{2n_D^2+1} + C\left[\frac{D-1}{D+2} - \frac{n_D^2-1}{n_D^2+2}\right] \tag{1}$$

where $\tilde{\nu}^{g}{}_{\text{abs}}$ is the band position at vapor state, and A, B and C are constants which are independent of the characters of the solvents, as is understood from Eqs. 2, 3 and 4 derived by McRae.

$$A = 1.07\times10^{-14}\cdot\frac{1}{a^3}\left[L_0\left\{-2f^{u}_{io} + \sum_{j\neq o,i}\left(f^{u}_{ji} - f^{u}_{jo}\right)\right\} + \sum_{j\neq o,i}\left(\frac{f^{u}_{jo}}{\tilde{\nu}^{u}_{jo}} - \frac{f^{u}_{ji}}{\tilde{\nu}^{u}_{ji}}\right)\right] \tag{2}$$

$$B = \frac{1}{hc}\left[\frac{(M^{u}_{oo})^2 - (M^{u}_{ii})^2}{a^3}\right] \tag{3}$$

$$C = \frac{2}{hc}\left[\frac{\vec{M}^{u}_{oo}(\vec{M}^{u}_{oo} - \vec{M}^{u}_{ii})}{a^3}\right] \tag{4}$$

In these equations, the notations and their meaning are the same as those in McRae's

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8) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954).

9) H. C. Longuet-Higgins and J. A. Pople, *J. Chem. Phys.*, **27**, 192 (1957).

*[1] n_D ordinarily differs little from n for infinite wavelengths except for special solvents (water, etc.).

*[2] In practice, it is difficult to estimate L_0 for all the solvents used because of a lack of their spectral data.

TABLE III. ABSORPTION MAXIMA OF THE COMPOUNDS USED IN VARIOUS SOLVENTS

Solvent	Pyridine *N*-oxide cm^{-1}	4-Nitropyridine *N*-oxide cm^{-1}	*N*-Methylbenzaldoxime cm^{-1}	Acridine *N*-oxide (ν^{I}) cm^{-1}	Acridine *N*-oxide (ν^{II}) cm^{-1}
n-Heptane	35400	28770	33550	23390	21990
Cyclohexane	35370	28690	33490	23340	21940
Methylcyclohexane	35320	28680	33540	23360	21950
Carbon tetrachloride	35160	28800	33250	23300	21920
Carbon disulfide	—	—	—	22900	21550
Dioxane	35780	28570	33580	23370	22020
Benzene	—	28380	33410	23300	21940
Toluene	—	28340	33410	23270	21920
Acetonitrile	36300	28970	33840	23570	22240
Nitromethane	—	—	—	23580	22250
Benzonitrile	—	28390	33190	23280	21990
Acetone	—	28790	—	23490	22180
Methyl acetate	36060	28780	33760	23510	22190
Ethyl acetate	35840	28740	33700	23470	22130
n-Butyl acetate	35780	28610	33630	23400	22080
Isoamyl acetate	35840	28650	33640	23410	22040
Diethyl oxalate	—	28610	—	23450	22100
Ethyl ether	35600	28750	33670	23440	22050
n-Butyl ether	35560	28680	33540	23370	21990
Isoamyl ether	—	28680	33550	23360	21990

paper5). It was possible to explain, within the range of experimental error, the experimental results by using Eq. 1[*3].

Effect of Solvents on Absorption Spectra.—The absorption spectra of pyridine *N*-oxide, 4-nitropyridine *N*-oxide, acridine *N*-oxide and *N*-methylbenzaldoxime in *n*-heptane are shown in Fig. 1, and the π-π^* absorption bands under consideration are shown by arrows. The maxima of the π-π^* bands of the above compounds in various solvents are given in Table III. $\tilde{\nu}^{I}_{abs}$ and $\tilde{\nu}^{II}_{abs}$ of acridine *N*-oxide denote the band maxima (vibrational components of the π-$\pi^*-{}^1L_A$-band) at 427.5 mμ and at 454.8 mμ in *n*-heptane solution respectively. Thus $\tilde{\nu}^{g}_{abs}$, $A+B$ and C of Eq. 1 have been determined by applying the least square method to the data of Tables II and III[*4]. The numerical values of Eq. 1 thus obtained are given in Table IV. The relations of the calculated (these values were calculated from Eq. 1 using the values in Table IV) vs. the observed frequency shifts in the π-π^* bands of the above compounds are shown in Figs. 2—6. From the values in Table IV, it should be

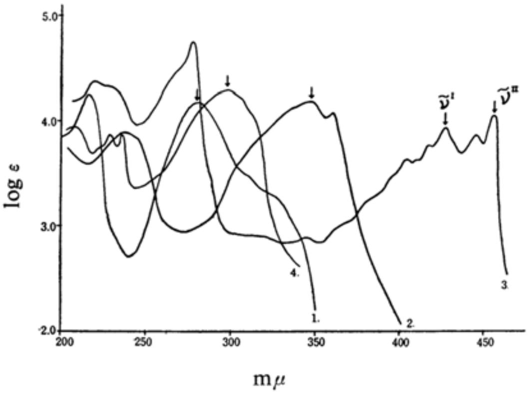

Fig. 1. The absorption spectra of the compounds in *n*-heptane. The absorption bands under consideration are shown by arrows.
1 Pyridine *N*-oxide
2 4-Nitropyridine *N*-oxide
3 Acridine *N*-oxide
4 *N*-Methylbenzaldoxime
Solvent : *n*-Heptane

TABLE IV. $\tilde{\nu}^{g}_{abs}$, $A+B$ AND C VALUES OBTAINED FROM EQ. 1 BY APPLYING THE LEAST SQUARE METHOD

Compound	$\tilde{\nu}^{g}_{abs}$ cm^{-1}	$A+B$ cm^{-1}	C cm^{-1}
Pyridine *N*-oxide	35980	−3260	1280
4-Nitropyridine *N*-oxide	30380	−8760	10
Acridine *N*-oxide	24410 22900	−5290 −4660	130 250
N-Methylbenzaldoxime	35130	−8000	90

[*3] What differs from the solvent effect of the weak $n\rightarrow\pi^*$ transitions, which were investigated recently by Ito et al.10), is that the dispersion term can hardly be considered independent of the solvents in the case of the strong π-π^* band of *N*-oxide compounds.

10) M. Ito, K. Inuzuka and S. Imanishi, *J. Am. Chem. Soc.*, **82**, 1317 (1960).

[*4] As is seen in Figs. 2—6, solvents showing a distinct discrepancy from a linear relation between the calculated and the observed values have been removed from the calculations by means of the least square method.

pointed out for all the *N*-oxide compounds that dispersion and dipole-dipole interaction terms cause a red shift and a blue shift respectively. Now let us consider how appropriate are the values of Table IV and Figs. 2—6. All the points, with the exception of anomalous solvents, fit a full straight line with a root mean square deviation of 90 cm^{-1} and 50 cm^{-1} for pyridine *N*-oxide and the other *N*-oxide compounds respectively, which is of the same order of magnitude as the experimental error in the determination of band frequency in solution spectra. Therefore it may be considered that Eq. 1 satisfactorily explains the experimental results. Moreover, it is also worth pointing out the following facts: Firstly, the *C*-value of 4-nitropyridine *N*-oxide is considerably small, 13 cm^{-1}; this result is reasonable because the dipole moment of this

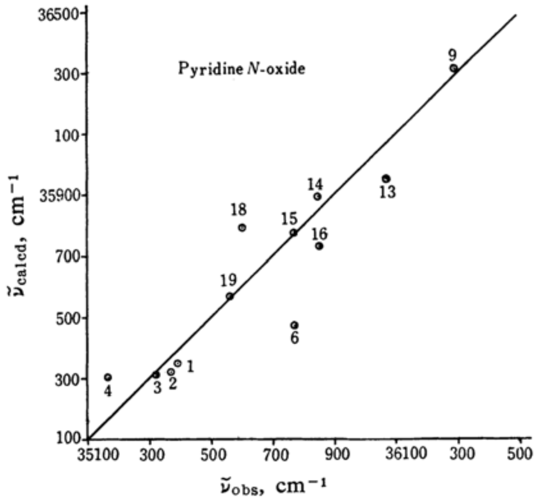

Fig. 2. Relation between $\tilde{\nu}_{obs}$ and $\tilde{\nu}_{calcd}$ for pyridine *N*-oxide.

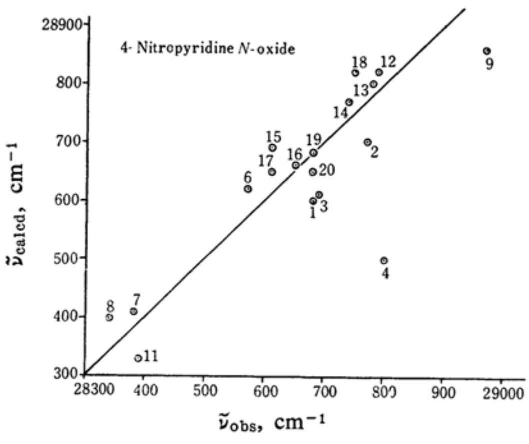

Fig. 3. Relation between $\tilde{\nu}_{obs}$ and $\tilde{\nu}_{calcd}$ for 4-nitropyridine *N*-oxide.

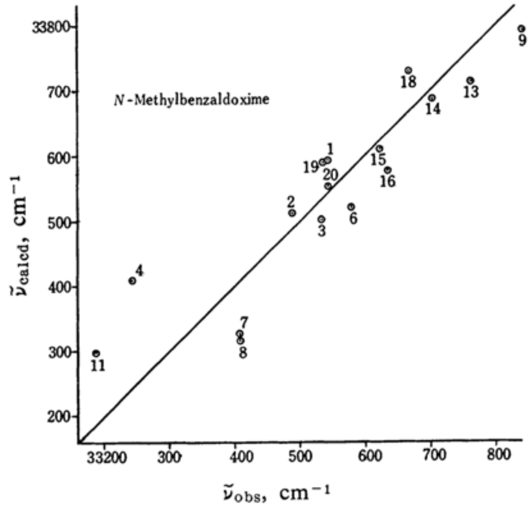

Fig. 4. Relation between $\tilde{\nu}_{obs}$ and $\tilde{\nu}_{calcd}$ for *N*-methylbenzaldoxime.

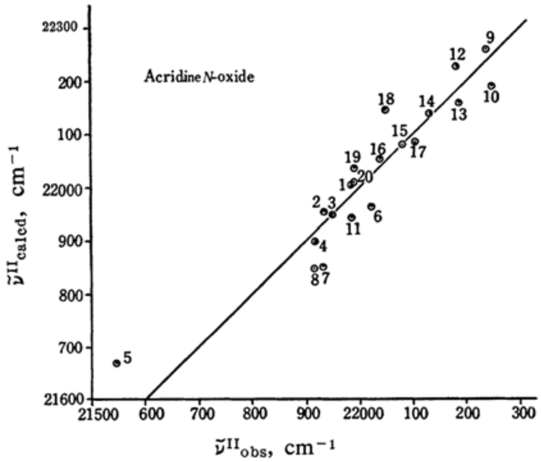

Fig. 5. Relation between $\tilde{\nu}^{II}_{obs}$ and $\tilde{\nu}^{II}_{calcd}$ for acridine *N*-oxide.

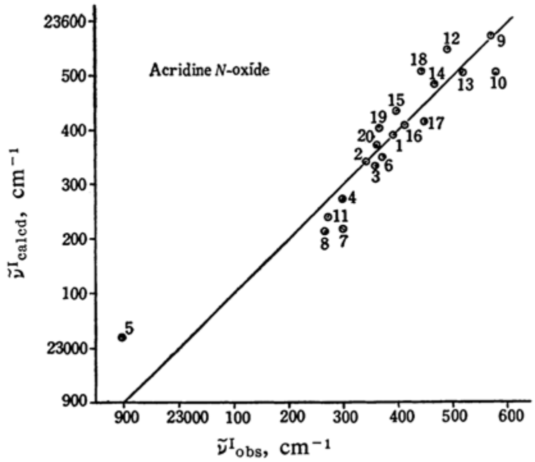

Fig. 6. Relation between $\tilde{\nu}^{I}_{obs}$ and $\tilde{\nu}^{I}_{calcd}$ for acridine *N*-oxide.

compound in the ground state is nearly zero[16]. Secondly, $\tilde{\nu}^{g}_{\mathrm{abs}}$ of pyridine *N*-oxide obtained from Eq. 1 is 35980 cm^{-1}; this value agrees well with the experimental value of 36080 cm^{-1} which was measured both by us and by Ito and Hata[11,*5]. On the other hand, calculated and observed frequencies frequently do not agree when dioxane and carbon tetrachloride have been used as a solvent; the former is especially irregular for substances having a large C value, and the latter, for those having a large $A+B$ value. The abnormal behavior of solvent dioxane is well known[5,10,12]. It is also common that carbon tetrachloride sometimes shows an anomalous behavior owing to short range intermolecular interactions such as molecular complex formation[13]. This fact may be regarded as one of the reasons why carbon tetrachloride shows an anomalous behavior, and some correlation may exist between such anomalous properties and $A+B$ values.

Dipole Moment in the Excited State of Pyridine *N*-Oxide and Acridine *N*-Oxide.—Now it may be possible in principle to evaluate the dipole moment in an excited state from Eq. 4, but practically it is difficult (especially for the absolute $\vec{M}^{u}_{ii}$ value) because the appropriate "a" values ("a" is Onsager's reaction radius of the solute molecule) can not be easily determined and because the molecular symmetries in the ground and the excited states are, in general, not the same. In addition, various assumptions have been made to derive Eq. 4. Taking tentatively "a"$=3.5\sim4$ Å with reference to the reports of other authors[5,10,12,14] and assuming that $\vec{M}^{u}_{oo}$ and $\vec{M}^{u}_{ii}$ are parallel, the excited state dipole moments of pyridine *N*-oxide and acridine *N*-oxide are calculated to be $1.9\sim1.3$ D and $0.22\sim1.5$ D, ($\tilde{\nu}^{\mathrm{I}}{}_{\mathrm{abs}}$) and $0.3\sim0.4$ D ($\tilde{\nu}^{\mathrm{II}}{}_{\mathrm{abs}}$) respectively smaller than those of the ground state. It may be regarded in the first order approximation that such a decrease in excited state dipole moment is based on the change of the π-electron moment (π-moment) arising from an electronic excitation. It has been determined by Linton[15], by Katritzky, Bax et al.[16,17] and by Acheson et al.[18] that the dipole moments of pyridine *N*-oxide and acridine *N*-oxide in the ground state are 4.24 D and 3.90 D respectively and that the total moment ($\sigma+\pi$) is directed very closely from the ring to the oxygen atom along a C_2-axis, while the π-moment vector is in the opposite direction. Therefore, the above experimental fact clearly indicates that the π-electron transfer from the oxygen atom to the ring is much greater in the excited state than in the ground state. Assuming that "a" is taken to be 3.5 Å and 4 Å for pyridine *N*-oxide and acridine *N*-oxide respectively, and making a comparison of the degree of dipole moment decrease in the excited π-π^* state, the degree of pyridine *N*-oxide is $3.2\sim5.9$ times as great as that of acridine *N*-oxide. In the previous papers, one (T. K.) of the authors reported on the electronic structure of various heterocyclic *N*-oxides on the basis of various molecular orbital calculations[19,20]. It was then most reasonable to conclude that the π-π^* bands, that are the subject of discussion, belong to the group species $^1A_1$ and consist of a very large contribution of the single configuration which corresponds to one electronic excitation from the highest occupied orbital to the lowest empty orbital[*6]. The square values of the above two MO's coefficients are shown schematically in Figs. 7 and 8 for pyridine *N*-oxide and acridine *N*-oxide respectively. As is well understood from Figs. 7 and 8, the degree of the electron transfer from the oxygen atom to the ring of acridine *N*-oxide by an electron excitation is much smaller than that of pyridine *N*-oxide. Therefore, this fact shows a good correspondence with the above estimated values of the π-moment change by an electronic excitation for pyridine *N*-oxide and acridine *N*-oxide.

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11) M. Ito and N. Hata, This Bulletin, **28**, 260 (1955).

[*5] In this case, however, the reason why $\tilde{\nu}^{g}_{\mathrm{abs}}$ and $\tilde{\nu}^{\mathrm{max}}_{\mathrm{abs}}$ (in vapor state) experimentally determined must rigorously agree can not be found, owing to the several assumptions described above. Moreover, $\tilde{\nu}^{\mathrm{max}}_{\mathrm{abs}}$ in a vapor state of the other compounds could not be recorded because of the low vapor pressure.

12) E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955); *Z. für Elektrochem.*, **61**, 962 (1957).

13) A. Kuboyama, Symposium on Electronic States (in Japan), **9**, 13 (1954).

14) K. Mataga, Y. Kaifu and M. Koizumi, This Bulletin, **29**, 465 (1956).

15) E. P. Linton, *J. Am. Chem. Soc.*, **62**, 1945 (1940).

16) A. R. Katritzky, E. W. Randall and L. E. Sutton, *J. Chem. Soc.*, **1957**, 1769.

17) C. M. Bax, A. R. Katritzky and L. E. Sutton, ibid., **1958**, 1258.

18) R. M. Acheson, B. Adcock, G. M. Glover and L. E. Sutton, ibid., **1960**, 3367.

19) T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 916 (1958).

20) T. Kubota, This Bulletin, to be published.

[*6] In these calculations the values of SMO parameters are chosen so as to reproduce, by using Jaffé's relation[21], the electronic densities obtained from the experimentally determined Hammett's σ values of the *N*-oxide group in non-polar solvents[22]. The parameters obtained are equal to $k_{\mathrm{N}}=1.6\beta$, $k_{\mathrm{O}}=0.595\,\beta$ and inductive effect $=(1/3)^{n}k_{\mathrm{N}}$ respectively. $k_{\mathrm{O}}=0.595\beta$, however, is relatively small to interpret various physico-chemical properties, and $k_{\mathrm{O}}=0.8$ is the best value to reproduce the observed dipole moment, etc. The relative change of π-moments from pyridine *N*-oxide to acridine *N*-oxide will be almost independent of the selection of the k_{O}-values, either 0.595 or 0.8. In this paper we have used $k_{\mathrm{O}}=0.595$ for discussion, since all the MO calculations for parameter 0.8 are not complete at present.

21) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 778, 1554 (1952).

22) H. Shindo, *Chem. & Pharm. Bull.*, **6**, 117 (1958).

TABLE V. CALCULATED RESULTS OF THE π-MOMENT IN THE GROUND AND THE EXCITED π^* STATES AND THE π-MOMENT CHANGE DURING π—π^* ONE ELECTRON TRANSITIONS SHOWN IN FIGS. 7 AND 8

Compound	$^{\pi}\overrightarrow{M}{}^{u}_{ii}$	$^{\pi}\overrightarrow{M}{}^{u}_{oo}$	$\overbrace{^{\pi}\overrightarrow{M}{}^{u}_{ii}-{}^{\pi}\overrightarrow{M}{}^{u}_{oo}}$	
	Calcd. value, D	Calcd. value, D	Calcd. value	Calcd. value[19,20]/1.6
Pyridine *N*-oxide	5.58	1.88	3.70	2.31
Acridine *N*-oxide	4.24	3.01	1.23	0.77

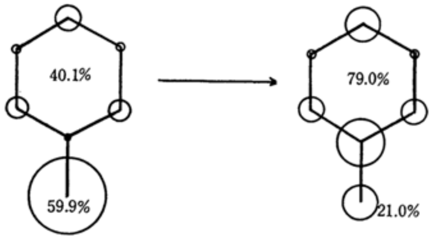

Fig. 7. Distribution of an electron in the highest occupied orbital and the lowest empty orbital of pyridine *N*-oxide.

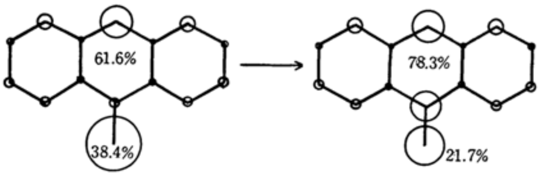

Fig. 8. Distribution of an electron in the highest occupied orbital and the lowest empty orbital of acridine *N*-oxide.

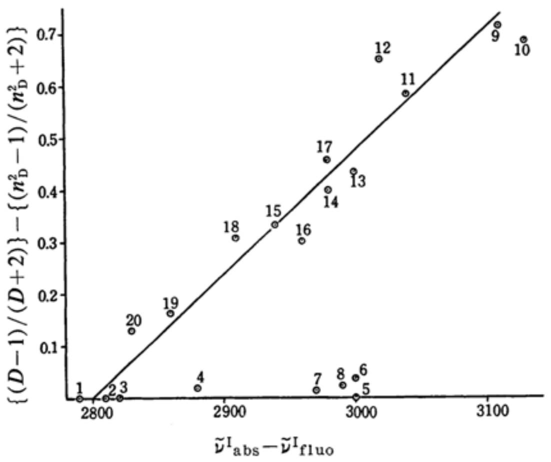

Fig. 9. Relation between ($\tilde{\nu}^{\mathrm{I}}{}_{\mathrm{abs}}-\tilde{\nu}^{\mathrm{I}}{}_{\mathrm{fluo}}$) and $\{(D-1)/(D+2)\}-\{(n_{\mathrm{D}}^2-1)/(n_{\mathrm{D}}^2+2)\}$ for acridine *N*-oxide.

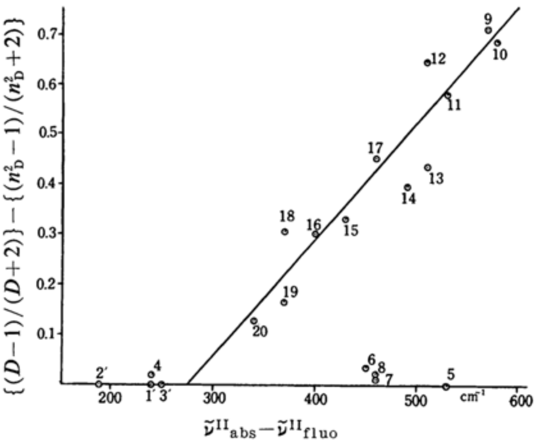

Fig. 10. Relation between ($\tilde{\nu}^{\mathrm{II}}{}_{\mathrm{obs}}-\tilde{\nu}^{\mathrm{II}}{}_{\mathrm{fluo}}$) and $\{(D-1)/(D+2)\}-\{(n_{\mathrm{D}}^2-1)/(n_{\mathrm{D}}^2+2)\}$ for acridine *N*-oxide.

Making the calculation of the π-moment change between the ground state and the excited π-π^* state shown in Figs. 7 and 8 by applying the molecular orbitals reported in previous papers[19,20], the results in Table V are obtained[*7]. As is seen from Table V, the absolute values ($^{\pi}\overrightarrow{M}{}^{u}_{ii}-{}^{\pi}\overrightarrow{M}{}^{u}_{oo}$) do not show a good agreement with those estimated from the *C* value, this discrepancy being based on the reason described in the beginning of this section. However, comparing the value ($^{\pi}\overrightarrow{M}{}^{u}_{ii}-{}^{\pi}\overrightarrow{M}{}^{u}_{oo}$) of pyridine *N*-oxide with that of acridine *N*-oxide, the former is 2.93~3.50 times as great as that of the latter; this result agrees well with the experimental value[*7,*8].

Effects of Hydrogen Bonding. — As stated above, the electronic spectra of aromatic *N*-oxide compounds show a remarkable blue

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[*7] In this calculation it has been assumed that the shape of these molecules is a condensed regular hexagon, the bond distance of which is 1.395 Å, and the N—O distance is taken to be equal to 1.28 Å. However, the ratio of the value ($^{\pi}\overrightarrow{M}{}^{u}_{ii}-{}^{\pi}\overrightarrow{M}{}^{u}_{oo}$) of pridine *N*-oxide to that of acridine *N*-oxide is almost insensitive in the selection of the N→O bond distance (1.28~1.40 Å). According to recent investigations of the crystal structure of phenazine mono-*N*-oxide and 4-nitropyridine *N*-oxide, the N—O distance is 1.24 Å and 1.26 Å for the former and the latter respectively[23,24].

23) R. Curti, V. Riganti and S. Locchi, *Acta Cryst.*, **14**, 133 (1961).

24) E. L. Eichhorn, idid., **9**, 787 (1956).

[*8] The nature in the excited and the ground states of *N*-methylbenzaldoxime can not be discussed, since the molecular structure (cis or trans) and the electronic state of this compound have not been investigated as yet. At present we are investigating the electronic structures and the spectroscopic behaviors of nitron type compounds.

TABLE VI. VALUES OF ABNORMAL BLUE SHIFT (cm^{-1}) DUE TO THE HYDROGEN BONDING EFFECT APPROXIMATELY ESTIMATED BY USING EQ. 1 AND OBSERVED VALUES IN WATER AND ETHANOL

Compound		Solvent		
		Water (Obs. value)	Ethanol (Obs. value)	Water/Ethanol
Pyridine *N*-oxide		4860 (39440)	1410 (37660)	3.4
4-Nitropyridine *N*-oxide		5430 (31690)	1200 (30010)	4.5
N-Methylbenzaldoxime		3620 (34990)	940 (34290)	3.9
Acridine *N*-oxide	ν^{I}	2270 (24200)	700 (23980)	3.2
	ν^{II}	2260 (22980)	750 (22730)	3.0

shift in hydrogen bonding solvents, such as alcohol and water. This abnormal blue shift can not be explained by Eq. 1 and is mainly based on the hydrogen bonding complexes such as N→O……H. The contribution of the normal solvent effect to the frequency shift can be evaluated approximately from Eq. 1 by using n_{D} and D of the above solvents. The values thus obtained are small, and the remaining portion ($\tilde{\nu}_{\mathrm{hyd}}$) of the total frequency shift may mainly be owing to the hydrogen bonding effect, the calculated values being shown in Table VI. The value $\tilde{\nu}_{\mathrm{hyd}}$ of water is 3～4 times as great as that of ethanol in all the compounds used here. It may be considered from the above fact that the hydrogen bonding power of water is about 3～4 times as great as that of ethanol.

Relation between the Solvent-induced Frequency Shift of the Absorption and the Fluorescence Spectra of Acridine *N*-Oxide.—The difference in solvent effect on the maxima of the absorption and fluorescence spectra was given by Lippert[12)], by Mataga et al.[14)] and by McRae[5)] as in Eq. 5. Here K is approximately constant.

$$\tilde{\nu}_{\mathrm{abs}}-\tilde{\nu}_{\mathrm{fluo}}=\frac{2}{hc}\cdot\frac{[\vec{M}^{u}_{oo}-\vec{M}^{u}_{ii}]^{2}}{a^{3}}\times\left[\frac{D-1}{D+2}-\frac{n_{\mathrm{D}}^{2}-1}{n_{\mathrm{D}}^{2}+2}\right]+K \qquad (5)$$

TABLE VII. EXPERIMENTAL VALUES OF $\tilde{\nu}_{\mathrm{abs}}-\tilde{\nu}_{\mathrm{fluo}}$ OF ACRIDINE *N*-OXIDE IN VARIOUS SOLVENTS

Solvent	$\tilde{\nu}^{\mathrm{I}}_{\mathrm{abs}}-\tilde{\nu}^{\mathrm{I}}_{\mathrm{fluo}}$ cm^{-1}	$\tilde{\nu}^{\mathrm{II}}_{\mathrm{abs}}-\tilde{\nu}^{\mathrm{II}}_{\mathrm{fluo}}$ cm^{-1}
n-Heptane	2790	(240)[*9]
Cyclohexane	2810	(190)[*9]
Methylcyclohexane	2820	(250)[*9]
Carbon tetrachloride	2880	240
Carbon disulfide	3000	530
Dioxane	3000	450
Benzene	2970	460
Toluene	2990	460
Acetonitrile	3110	570
Nitromethane	3130	580
Benzonitrile	3040	530
Acetone	3020	510
Methyl acetate	3000	510
Ethyl acetate	2980	490
n-Butyl acetate	2940	430
Isoamyl acetate	2960	400
Diethyl oxalate	2980	460
Ethyl ether	2910	370
n-Butyl ether	2860	370
Isoamyl ether	2830	340

As was reported in the previous paper, the fluorescence spectra of acridine *N*-oxide show a good mirror image relative to the absorption band ($^{1}L_{a}$)[1)].

The values ($\tilde{\nu}_{\mathrm{abs}}-\tilde{\nu}_{\mathrm{fluo}}$) in various solvents are given in Table VII. Here $\tilde{\nu}^{\mathrm{I}}_{\mathrm{fluo}}$ and $\tilde{\nu}^{\mathrm{II}}_{\mathrm{fluo}}$ correspond to $\tilde{\nu}^{\mathrm{I}}_{\mathrm{abs}}$ and $\tilde{\nu}^{\mathrm{II}}_{\mathrm{abs}}$ respectively. Thus the coefficients of Eq. 5 have been determined by means of the least square method by using the above data, and Eqs. 6 and 7 have thereby been obtained[*9].

$$\tilde{\nu}^{\mathrm{I}}_{\mathrm{abs}}-\tilde{\nu}^{\mathrm{I}}_{\mathrm{fluo}}=2800+420\left[\frac{D-1}{D+2}-\frac{n_{\mathrm{D}}^{2}-1}{n_{\mathrm{D}}^{2}+2}\right] \qquad (6)$$

$$\tilde{\nu}^{\mathrm{II}}_{\mathrm{abs}}-\tilde{\nu}^{\mathrm{II}}_{\mathrm{fluo}}=270+430\left[\frac{D-1}{D+2}-\frac{n_{\mathrm{D}}^{2}-1}{n_{\mathrm{D}}^{2}+2}\right] \qquad (7)$$

In Figs. 9 and 10, the values $\left(\frac{D-1}{D+2}-\frac{n_{\mathrm{D}}^{2}-1}{n_{\mathrm{D}}^{2}+2}\right)$ are plotted against the values ($\tilde{\nu}_{\mathrm{abs}}-\tilde{\nu}_{\mathrm{fluo}}$) of the $\tilde{\nu}^{\mathrm{I}}$ and $\tilde{\nu}^{\mathrm{II}}$ bands, and it is found that a good linear relation comes into existence between the above two values, but solvents such as dioxane, toluene and benzene cause a large deviation from the linear relation. The abnormal behavior of dioxane is owing to the same reason as that described in the previous section. The exceptional behavior of benzene and toluene (which in main arises

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[*9] In solvents 1, 2 and 3, $\tilde{\nu}^{\mathrm{II}}_{\mathrm{fluo}}$ has a tendency to be divided into doublets, but not so in the other solvents. To correct this difference, we used the weighted mean wave number given by the following equation for the determination of $\tilde{\nu}^{\mathrm{II}}_{\mathrm{fluo}}$ in solvents 1, 2 and 3. The values thus obtained were used to obtain Eq. 7 and are indicated by 1′, 2′ and 3′ in Fig. 10.

$$\tilde{\nu}_{\mathrm{max}}=\left[\int\varepsilon\cdot\tilde{\nu}\cdot\mathrm{d}\tilde{\nu}\Big/\int\varepsilon\cdot\mathrm{d}\tilde{\nu}\right]\fallingdotseq\left[\sum_{i}\varepsilon_{i}\cdot\tilde{\nu}_{i}\Big/\sum_{i}\varepsilon_{i}\right]$$

from the abnormal frequency shift in the fluorescence spectra) is caused by mutual short-range interaction between the solute molecules and the π-electrons of the aromatic solvents and coincides with the analogous result that was found previously in the experiment concerning the fluorescence quenching of acridine *N*-oxide[1]. Making the same assumption as that described in the previous section and using the coefficients of Eqs. 6 and 7, the value $({}^{\pi}\vec{M}^{u}_{ii} - {}^{\pi}\vec{M}^{u}_{oo})$ can be evaluated to be 1.6~1.8 D. This value, however, does not agree well with the data obtained from the analysis of the absorption spectra. It may reasonably be inferred that this is because the solute-solvent interaction of various types in the excited state differs in some measure from that of the ground state. Therefore, considering the Franck-Condon principle, the frequency shifts of absorption and fluorescence bands do not agree well[12]. In our case, $(\vec{M}^{u}_{oo} > \vec{M}^{u}_{ii})$, the shift of the latter is smaller than that of the former[12]. Indeed, $\tilde{\nu}^{\mathrm{I}}{}_{\mathrm{fluo}}$ and $\tilde{\nu}^{\mathrm{II}}{}_{\mathrm{fluo}}$ show almost the same wave number in the polar solvents used here, although $\tilde{\nu}^{\mathrm{I}}{}_{\mathrm{abs}}$ and $\tilde{\nu}^{\mathrm{II}}{}_{\mathrm{abs}}$ do not[*10]. As a result, some simplifications concerning the treatment of the second term of Eq. 1 have been made, but such simplifications are unnecessary in Eq. 5. Moreover, the character in the excited π-π^* state generally may be considered to be locally more polar than in the ground state, as is understood from the general character of molecular orbitals. The special solute-solvent interactions, which are negligible in the ground state, may be expected in some measure in the excited state, since fluorescence is emitted from the equilibrium state in the excited π-π^* state.

Summary

The strong π-π^* absorption bands of pyridine *N*-oxide, 4-nitropyridine *N*-oxide, acridine *N*-oxide and *N*-methylbenzaldoxime were measured in various solvents, and the frequency shifts induced by solvents were quantitatively analyzed by applying the McRae's theory of the solvent effect. On the other hand, the fluorescence spectra of acridine *N*-oxide have also been recorded in various solvents, and the solvent effect has been discussed in connection with that of the absorption spectra. The results show that the π-electron transfer from the oxygen atom to the ring is much greater in the excited state than in the ground state.

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[*10] In a hydrogen bonding effect previously investigated[1], such phenomena were frequently found; they have also been discussed by Pimentell[25].

[25] G. C. Pimentel, *J. Am. Chem. Soc.*, **79**, 3323 (1957).