This compound was refluxed with 10% HCl for 15 hr. and gave the corresponding bis(aminomethyl)anisole hydrochloride, m.p. 265°(decomp.). *Anal.* Calcd. for $C_9H_{16}ON_2Cl_2$: C, 45.19; H, 6.74; N, 11.71. Found: C, 45.30; H, 6.86; N, 11.58.

N-(4-Methoxybenzyl)formamide (XIV)——In an autoclave, 7.5 g. of anisaldehyde oxime (XIII), 4.5 g. of $HCONH_2$, 20 cc. of EtOH, and Raney Ni catalyst (1 g. as 50% alloy) were placed and given 96 atm. (at 20°) of initial H_2 pressure. The mixture was shaken at 125~140° and in about 10 min., approximately 0.2 moles of H_2 was absorbed. The reaction mixture was filtered and the filtrate was evaporated. The residue was distilled in a reduced pressure giving a solid distillate of $b.p_2$ 128~131°. Yield, 7.3 g. Plates (from EtOH), m.p. 75~76°. *Anal.* Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.62; H, 6.69; N, 8.49.

4-Methoxybenzylamine Hydrochloride (XII)——To 20 cc. of 10% HCl, 3 g. of (XIV) was added and the mixture was refluxed for 2 hr. The solution was concentrated to leave crystals, which were recrystallized form EtOH to needles, m.p. 232~233°.

The authors are grateful to Prof. M. Ishidate of Tokyo Biochemical Research Institute for his kind encouragement during the course of this work. The authors are indebted to Miss Saito for the elemental analyses.

Summary

Acetamidomethylation of phenol and anisole was carried out by heating with N,N′-methylenediacetamide and phosphoryl chloride. Formation of N-(2- and 4-hydroxybenzyl)acetamides resulted in the case of phenol and formation of N-(4-methylbenzyl)acetamide in the case of anisole.

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147. Tanekazu Kubota and Hiroshi Miyazaki: Spectrophotometric Studies on Organic Substances. IX.[1] Ultraviolet Absorption Spectra of Derivatives of Heterocyclic N-Oxides. General Properties on the Solvent Effect and the Substituting Effect.

(*Shionogi Research Laboratory, Shionogi & Co., Ltd.*[*1])

In a series of previous papers, the ultraviolet absorption spectra[2~7] and electronic structure[8,9] were reported of various basic heterocyclic N-oxides, such as pyridine, quinoline, and acridine N-oxides, and their simple derivatives. From the above investigations it was well established that ultraviolet absorption spectra bands pertinent to heterocyclic N-oxides exhibit a marked blue shift (frequency shift to a shorter wave-length) in polar solvents containing active hydrogen atoms from those in nonpolar solvents. As

*1 Fukushima-ku, Osaka (窪田種一, 宮崎 寛).

1) Part Ⅷ. T. Kubota: Yakugaku Zasshi, **77**, 785 (1957).
2) H. Hirayama, T. Kubota: Ann. Rept. Shionogi Research Lab., **2**, 121 (1952).
3) *Idem*: Yakugaku Zasshi, **72**, 1025 (1952).
4) T. Kubota: *Ibid.*, **74**, 831 (1954).
5) *Idem*: *Ibid.*, **75**, 1540 (1955).
6) T. Kubota, H. Miyazaki: Nippon Kagaku Zasshi, **79**, 916 (1958).
7) T. Kubota: *Ibid.*, **79**, 930 (1958).
8) *Idem*: *Ibid.*, **80**, 578 (1959).
9) *Idem*: Yakugaku Zasshi, **79**, 388 (1959).

one of the reasons for this blue shift phenomenon, it was clearly shown[1,4~6] from investigations on three-component systems that the hydrogen bonding of N-oxides with various proton donors plays an important rôle. On the other hand, a relationship between the wave lengths of absorption bands and the position of substituting groups was found by the present authors[3,7] and by other workers,[10~13] mainly on naphthalene N-heterocyclic compounds and their N-oxides. For example, the positions of a substituent group in a molecule shown in Fig. 1 were classified into two classes, I and II. Positions 4, 5,

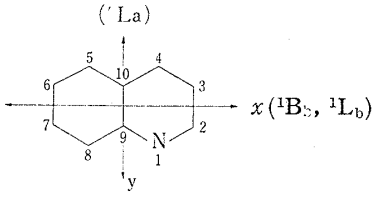

Fig. 1.

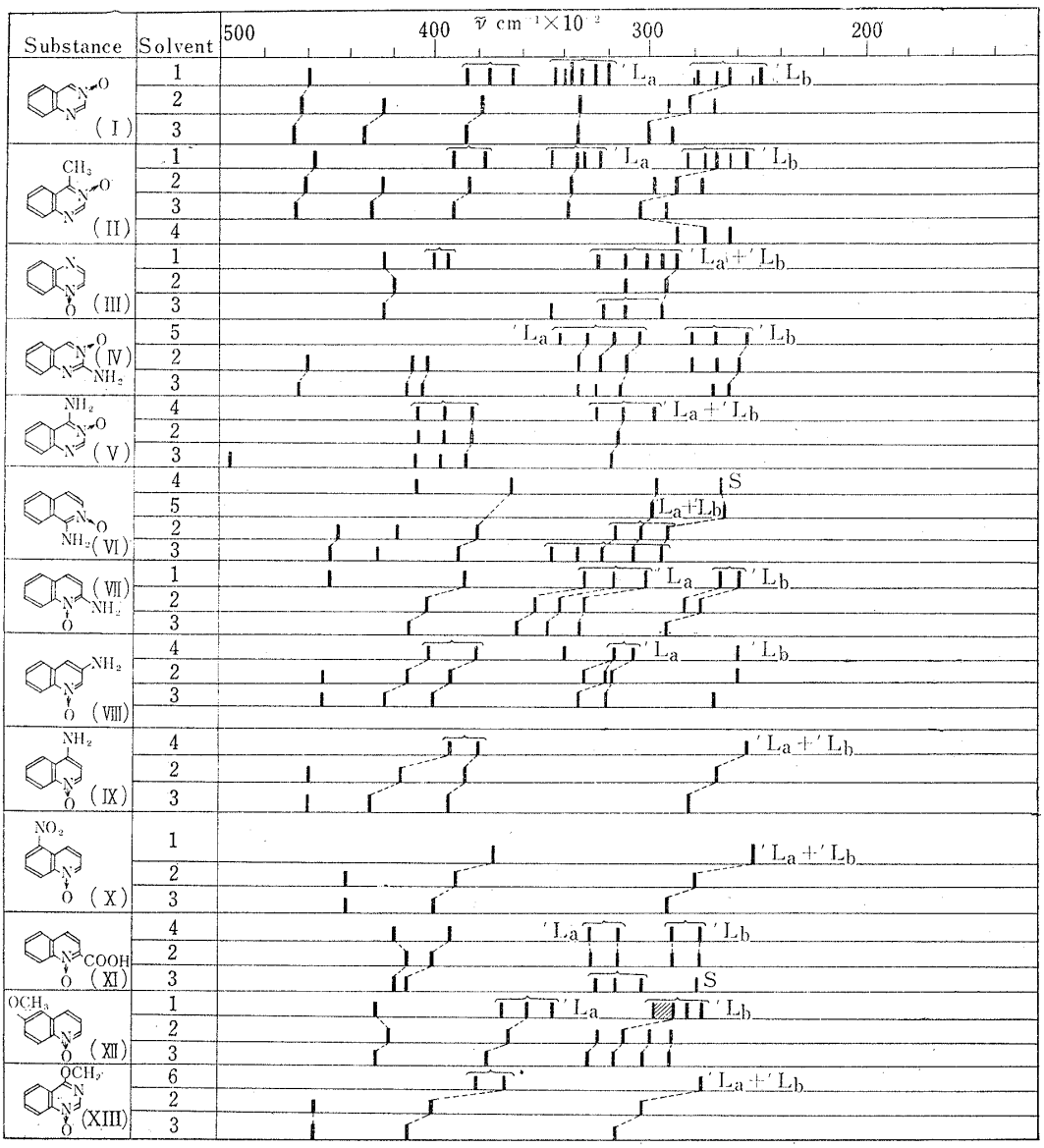

Fig. 2a.

10) E. Ochiai, C. Kaneko: This Bulletin, **5**, 56 (1957).
11) C. Kaneko: Yakugaku Zasshi, **79**, 433 (1959).
12) H. Baba, T. Suzuki: "Progress Reports on Electronic Processes in Chemistry," **1**, 9 (1959).
13) *Idem*: Nippon Kagaku Zasshi, **81**, 366 (1960).

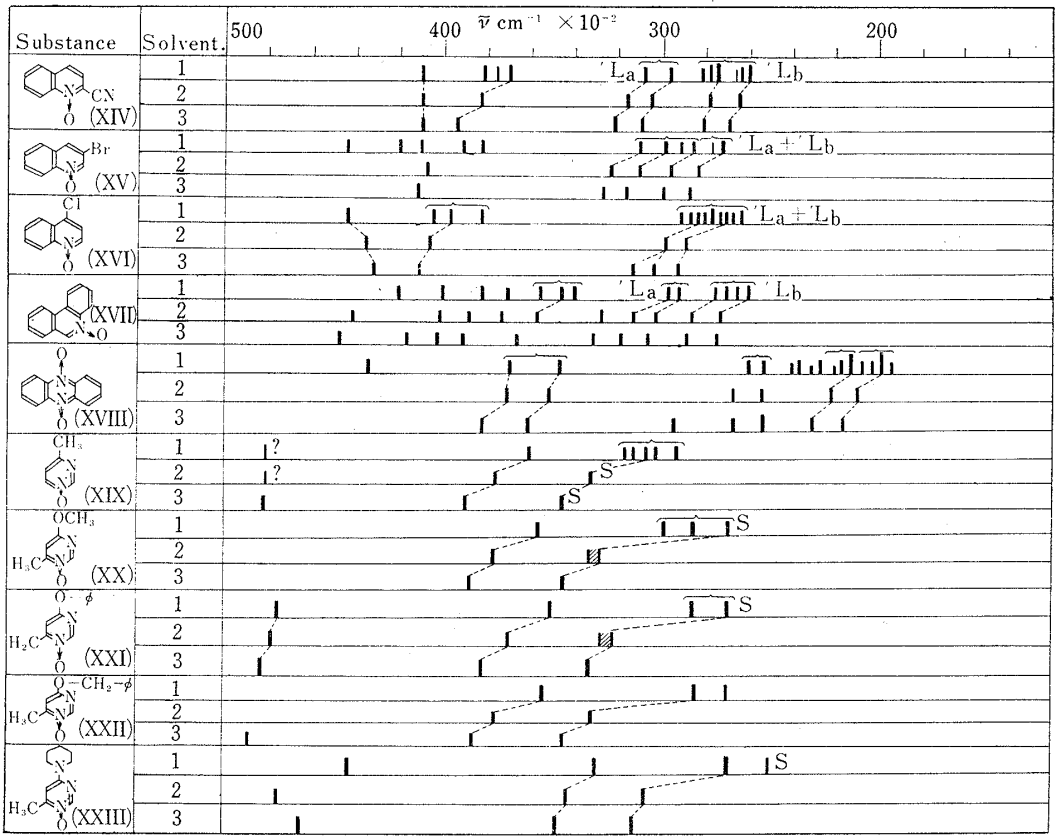

Fig. 2b.

Solvent: 1. Heptane 2. 95% EtOH 3. Water 4. Dehyd. dioxane
5. Benzene 6. CCl_4 S: Shoulder

and 8 belong to Class I, and positions 2, 3, 6, and 7 to Class II. When a substituent was introduced at any position in Class I, ^1L_b and ^1L_a bands*2 which appear in a longer wavelength region, were apparently recorded at the nearly equal wave lengths. In the case of Class II, however, both bands were apparently recorded at the well separated wave lengths. Thus, this relationship gives the most useful information for the determination of the position of a substituent.

It is now of interest to see how the above two properties (namely, the solvent effect and substitution effect) of the basic heterocyclic compounds change with much more complex compounds. In the present work, ultraviolet and fluorescence spectra of many derivatives of benzene, naphthalene, and anthracene heterocyclic N-oxides were measured in detail, and the solvent and substitution effects were examined. As to the substitution effect, especially, the results obtained in the present work were compared with many spectral data of N-heteronaphthalene and naphthalene derivatives reported in the past literatures, and two general properties were found from the present work.

(A) Solvent Effect on Absorption Bands

The solvent effect was examined with heptane, 95% ethanol, water, and other solutions, and the results obtained on all the compounds used here are summarized in Fig. 2, where the abbreviation of these compounds is also given. The spectral curves of each compound in the above solvents are shown in Figs. 3~28. From the spectral data, it should be pointed out that the ultraviolet absorption bands (especially π-π^* band at the

*2 This notation is used by J. R. Platt.[14]

14) J. R. Platt: J. Chem. Phys., **17**, 484 (1949).

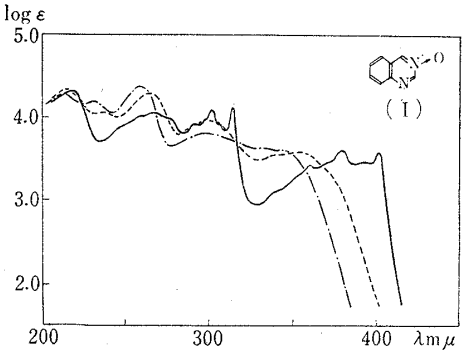

Fig. 3.

—— Heptane
------ 95% EtOH
–·–· H_2O

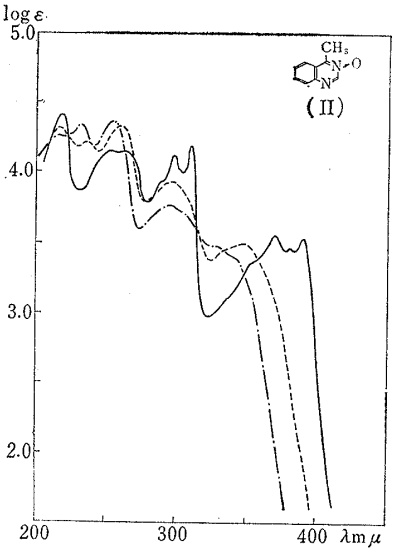

Fig. 4.

—— Heptane
------ 95% EtOH
–·–· H_2O

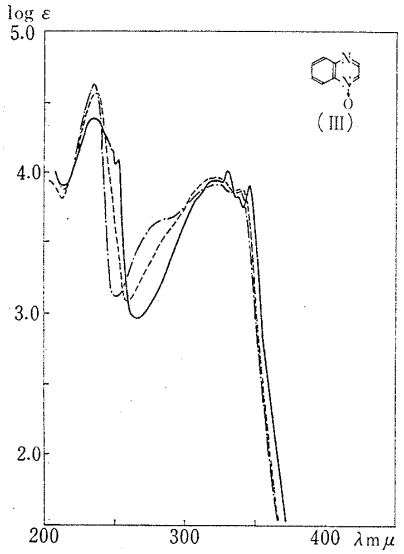

Fig. 5.

—— Heptane
------ 95% EtOH
–·–· H_2O

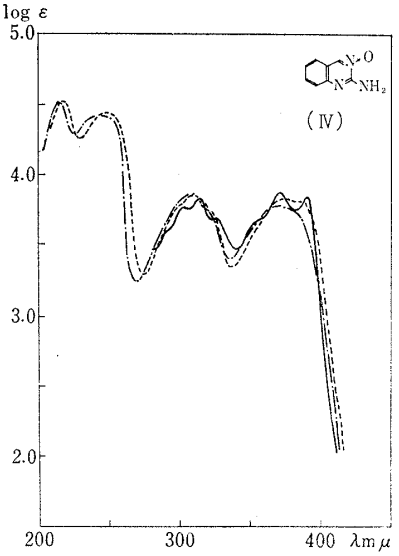

Fig. 6.

—— Benzene*
------ 95% EtOH
–·–· H_2O

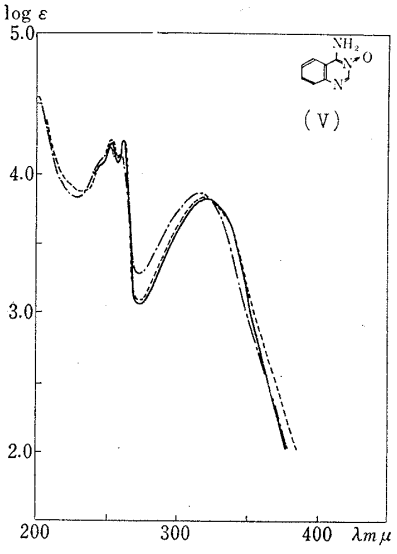

Fig. 7.

—— Dehyd. dioxane
------ 95% EtOH
–·–· H_2O

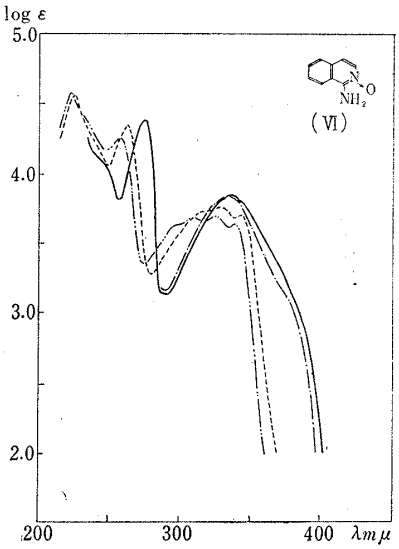

Fig. 8.

—— Dioxane
–·–· Benzene
------ 95% EtOH
–··– H_2O

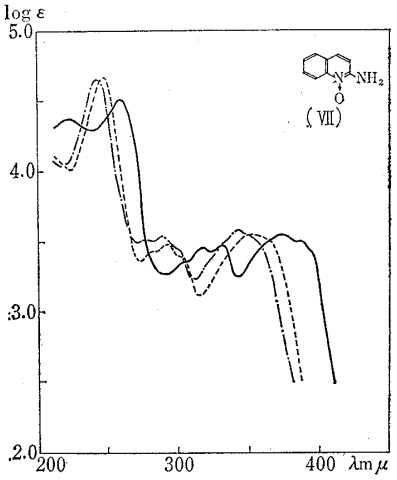

Fig. 9.
—— Heptane*
----- 95% EtOH
-·-·- H_2O

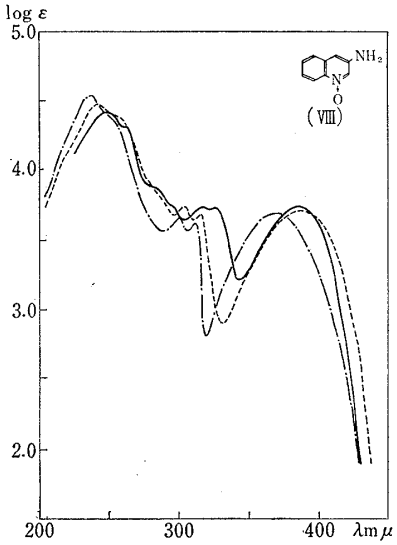

Fig. 10.
—— Dioxane*
----- 95% EtOH
-·-·- H_2O

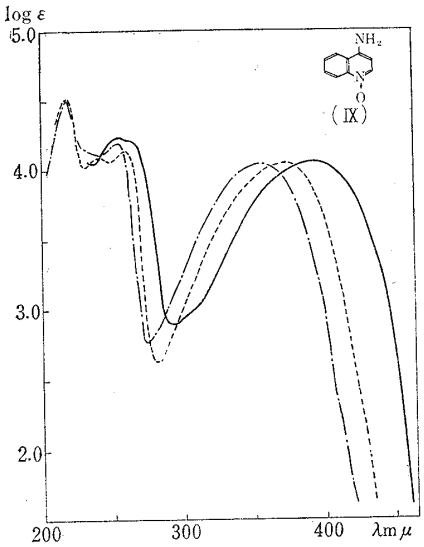

Fig. 11.
—— Dioxane*
----- 95% EtOH
-·-·- H_2O

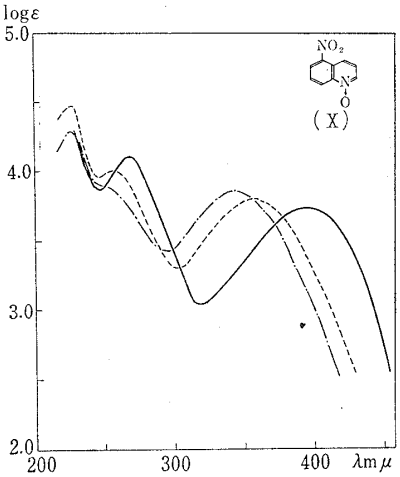

Fig. 12.
—— Heptane
----- 95% EtOH
-·-·- H_2O

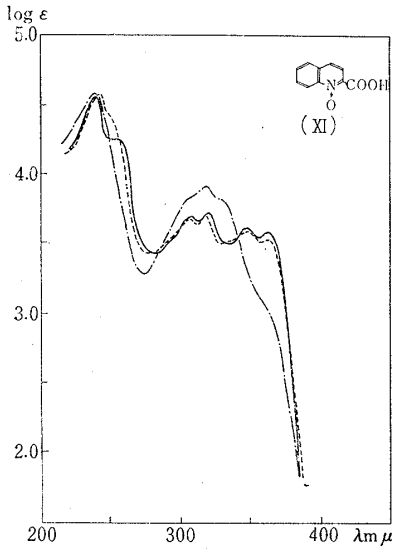

Fig. 13.
—— Dioxane
----- 95% EtOH
-·-·- H_2O

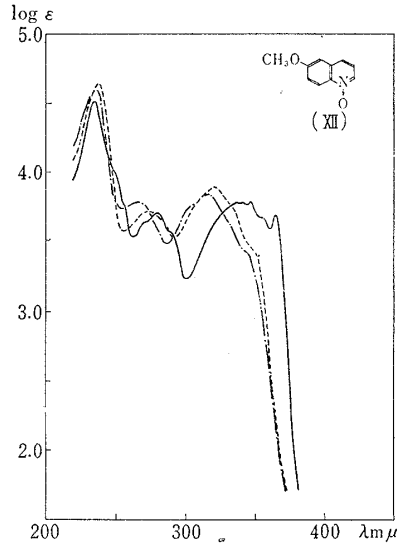

Fig. 14.
—— Heptane
----- 95% EtOH
-·-·- H_2O

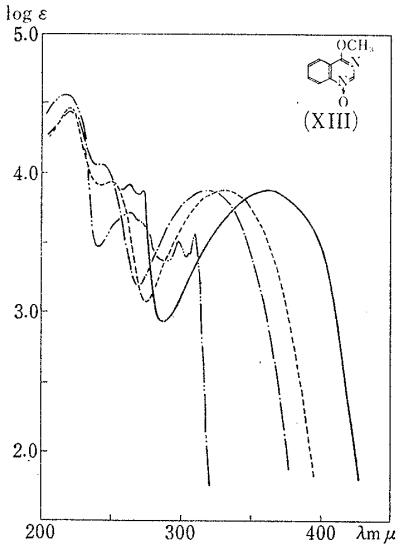

Fig. 15.

—— CCl_4*
------ 95% EtOH
-·-· H_2O
-··- (XXIV)**

** shows the spectrum of 4-methoxy-quinazoline (XXIV) in 95% EtOH.

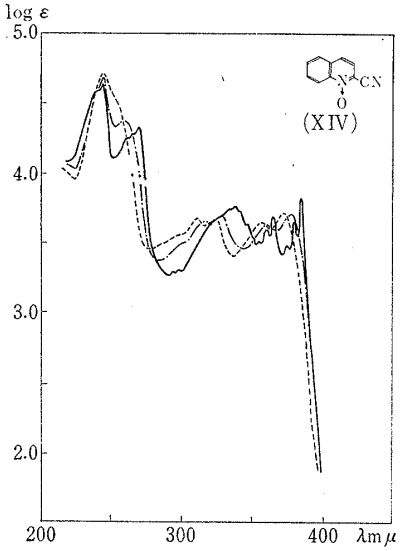

Fig. 16.

—— Heptane
------ 95% EtOH
-·-· H_2O

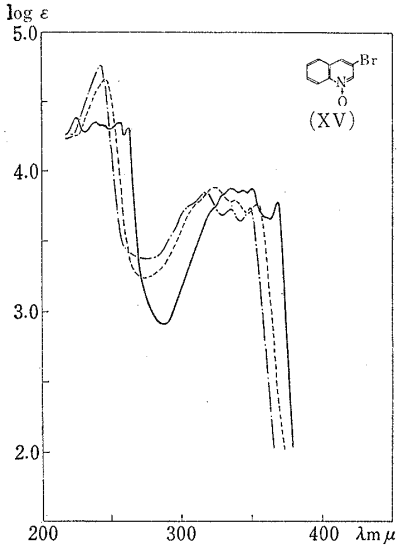

Fig. 17.

—— Heptane
------ 95% EtOH
-·-· H_2O**

** Solvent used contains a little amount of 95% EtOH.

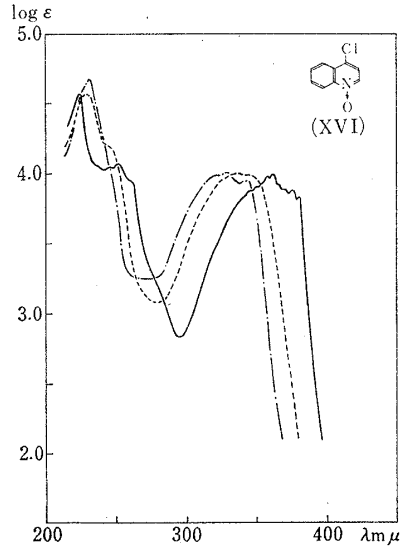

Fig. 18.

—— Heptane
------ 95% EtOH
-·-· H_2O**

** Solvent used contains a little amount of 95% EtOH.

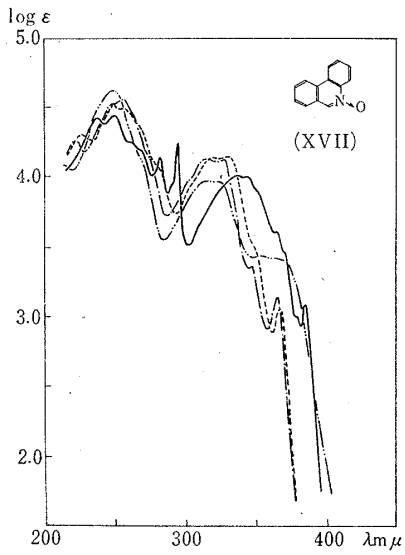

Fig. 19.

—— Heptane*
------ 95% EtOH
-·-· H_2O**
-··- 10% H_2SO_4

** Solvent used contains a little amount of 95% EtOH.

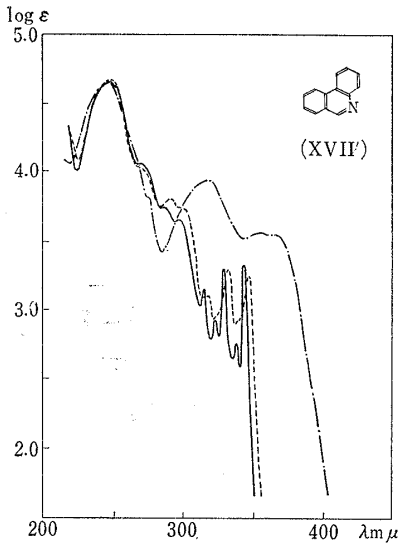

Fig. 20.

—— Heptane
------ 95% EtOH
-·-· 10% H_2SO_4

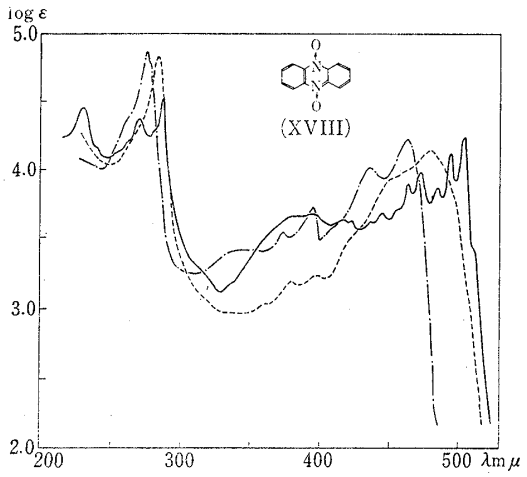

Fig. 21.
—— Heptane* ------ 95% EtOH -·-· H_2O

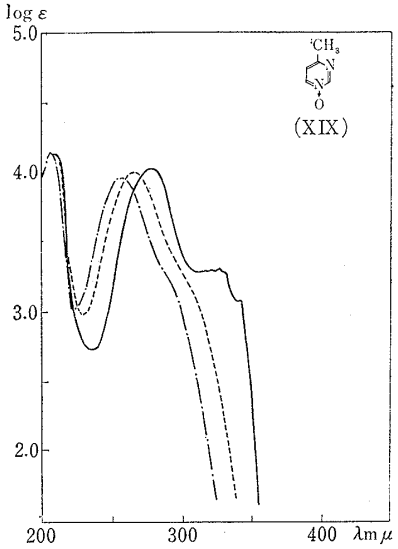

Fig. 22.
—— Heptane*
------ 95% EtOH
-·-· H_2O

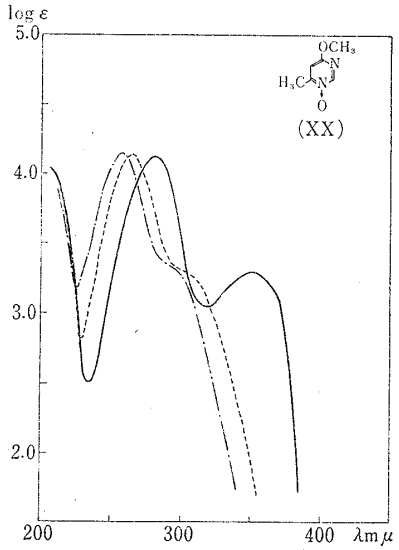

Fig. 23.
—— Heptane
------ 95% EtOH
-·-· H_2O

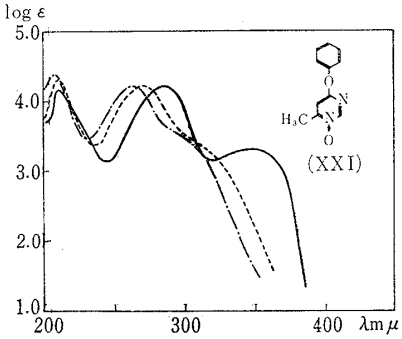

Fig. 24.
—— Heptane
------ 95% EtOH
-·-· H_2O

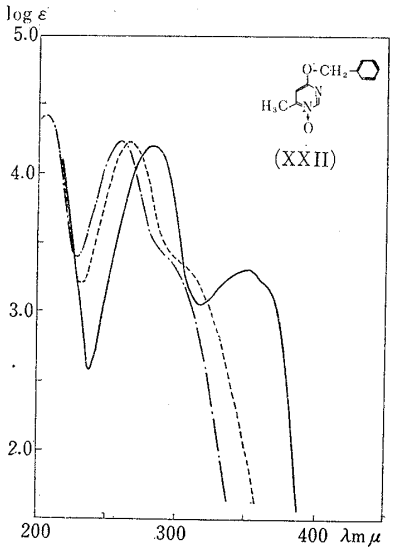

Fig. 25.
—— Heptane
------ 95% EtOH
-·-· H_2O

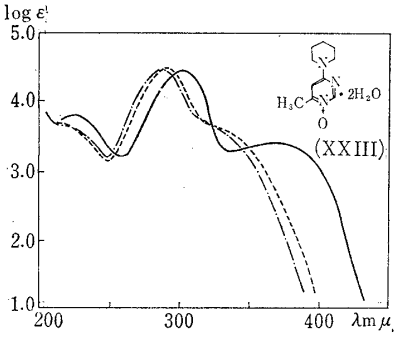

Fig. 26.
—— Heptane
------ 95% EtOH
-·-· H_2O

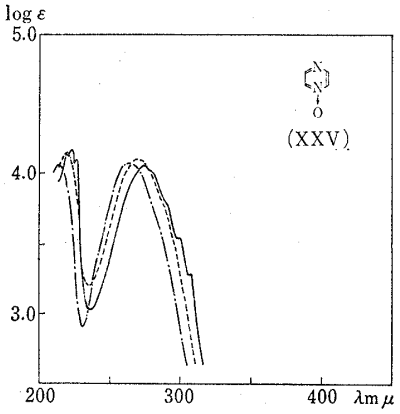

Fig. 27.
—— Heptane
------ 95% EtOH
-·-· H_2O

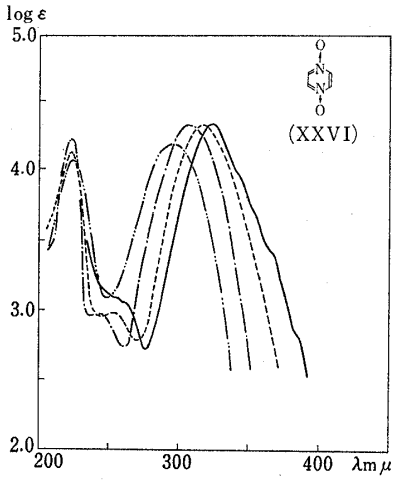

Fig. 28.
—— Dioxane
------ Dehyd. EtOH
-·-· H_2O
-··- 50% H_2SO_4

longest wave-length) of all N-oxides listed in Fig. 2 show increasing blue shift with increasing polarity of the solvents used. In spite of a considerably complex structure of these compounds, this property is similar to that of relatively simple N-oxides and it may be said that this is one of the general properties of heterocyclic N-oxides, since π-π^* transition bands of ordinary aromatic or hetero-aromatic compounds normally exhibit a red shift with increasing polarity of the solvent (even if a blue shift is recorded, the degree is small) and do not show such a large blue shift as heterocyclic N-oxides. As is shown in Fig. 29, the frequency shift can be explained as the difference in stabilization

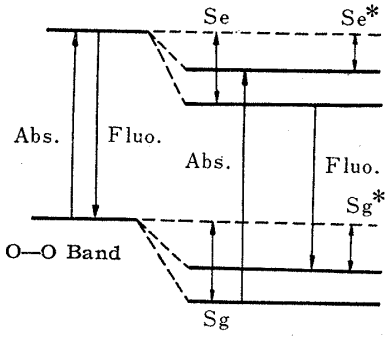

Fig. 29.
Stabilization energies shown by S_e^* and S_g^* may mean those at Franck-Condon equilibrium states reported by Bayliss and McRae.[15]

energies between the ground state and excited state. To cause a blue shift, the ground state must be more stabilized than the excited state, so that $S_g > S_e^*$ is concluded. The majority of these stabilization energies in polar solvents may be caused by the solute-solvent interaction such as hydrogen bonding, etc., because polar solvents used contain active hydrogen atoms within a molecule. Moreover, aromatic and heteroaromatic compounds having the following structure may generally show a blue shift of ultraviolet absorption bands based on solute-solvent effect. Namely, in the electronic structure of these compounds, the contribution of ionic structure to a resonance hybrid in the ground state can be considered to be much greater than that in the excited state (in a wide sense, these compounds are meso-ionic compounds).

Actually, Sydnone,*3 antipyrine,[18,19] and N-phenylbenzophenone oximes*3 also show

*3 Unpublished data. Moreover, the same experimental results were reported by the other workers on some derivatives of pyridine 1-oxide.[16,17]

15) N. S. Bayliss, E. G. McRae : J. Phys. Chem., **58**, 1002 (1954).
16) N. Ikekawa, Y. Sato : This Bulletin, **2**, 400 (1954).
17) N. Hata : Bull. Chem. Soc. Japan, **31**, 224 (1958).
18) T. Kubota : Yakugaku Zasshi, **77**, 818 (1957).
19) H. Hirayama, T. Kubota : Ann. Rept. Shionogi Research Lab., **1**, 53 (1951).

a remarkable blue shift of ultraviolet absorption bands, and in this case, it may also be inferred that hydrogen bonding is the most important effect of the solute-solvent interactions.*4

(B) Solvent Effect on Fluorescence Spectra

It was shown previously[7] that the fluorescence spectra of basic heterocyclic N-oxides also cause a blue shift when ultraviolet absorption bands of these compounds shift towards shorter wave-lengths with increasing polarity of solvents having active hydrogen atoms. Such a phenomenon was explained by the fact that the hydrogen-bonding power of these N-oxides in the excited state is smaller than that in the ground state.[6] As will be seen in Table I, however, the red shift of fluorescence spectra due to change of the solvent from nonpolar to 95% ethanol has been observed in almost all compounds.*5 It is easily recognized that each of the compounds listed in Table I contains some active group for hydrogen bonding such as $\rangle N\rightarrow O$, $\rangle N$, NH_2, etc. It may be considered that proton-donating power of $\rangle C\text{-}NH_2$ radical in the excited π-π^* state is much greater than that in the ground state, since the electron-migration from NH_2 to the ring may more increase in the excited π-π^* state.[21] On the other hand, $\rangle N$ in the ring may also be considered

Table I. Frequency Shifts of Ultraviolet and Fluorescence Spectra due to the Solvent change from 95% ethanol to Heptane

Compounds	$\Delta\tilde{\nu}_{ab}$ (95% EtOH-heptane) on main absorption bands (cm^{-1})	$\Delta\tilde{\nu}_{fluo}$ (95% EtOH-heptane) on main fluorescence bands (cm^{-1})	$(\Delta\tilde{\nu}_{ab}+\Delta\tilde{\nu}_{fluo})/2$	
			cm^{-1}	kcal/mole
(XXVII)[a]	30080−27210=2870 29190−25740=3450	24630−24270=360 25510[b]−25060=450	1610 1950	4.61 5.57
(I)	28170−26390=1780	23150−23420=−270	755	2.16
(II)	28820−27030=1790	23640−23920=−280	755	2.16
(VIII)	25910−25910[c]=0	21880−22680[c]=−800	−400	−1.14
(VI)	29150−26670[c]=2480	22730−22940[c]=−210	1135	3.24
(IX)	26850−25450[c]=1400	20200−19920[c]=280	840	2.40
(XXVIII)[a]	29850−30120=−270	26040−27030=−990	−630	−1.80
(XXIX)[a]	28410−28410=0	24510−25250=−740	−370	−1.06
(XXIII)	30770−27030=3740	22520−22520=0	1870	5.35
(XXI)	23790−28570=4220	24690−24880=−190	2015	5.76
(XX)	32790−28490=4300	24690−24880=−190	2055	5.87

a) Compounds (XXVII), (XXVIII) and (XXIX) denote isoquinoline N-oxide, 2-aminoquinoline and 2-dimethyl-aminoquinoline respectively.
b) The datum was obtained in dehyd. ethanol.
c) These data were obtained in dehyd. dioxane because of much lower solubility in heptane.

as a much greater proton acceptor in the excited π-π^* state, since much more increase in electron density is expected at the nitrogen atom in the excited state, such as in acridine.[22] Therefore, even if proton-accepting power of $\rangle N\rightarrow O$ group in the π-π^* state is smaller than that in the ground state, as is seen in Fig. 29, the stabilization energy S_e which may represent the energy in the equilibrium state (because it can approximately be considered that a life time of solute-solvent interaction such as hydrogen bonding is shorter than that of fluorescence[6,22]) may indicate a relatively large value. Now, for

*4 From the latest data, such an abnormally large effect of hydrogen bonding on frequency shift was well established by quantitative experiments based on McRay's theory concerning the solvent effect.[20]

*5 Fluorescence spectra could not be recorded for the substances in Fig. 2 except the compounds in Table I.

20) E.G. McRae: J. Phys. Chem., **61**, 562 (1957); T. Kubota, M. Yamakawa: Bull. Chem. Soc. Japan, **35**, 3 (1962).
21) K.F. Helzfeld: Chem. Revs., **41**, 233 (1947).
22) N. Mataga, Y. Kaifu, M. Koizumi: Bull. Chem. Soc. Japan, **29**, 115 (1956).

estimation of (S_g-S_e), the values of $[(\Delta\tilde{\nu}_{ab}+\Delta\tilde{\nu}_{fluo})/2]$,[6] which are shown in Table I, are more reasonable. For example, this value is 2.16 kcal/mole in quinazoline 3-oxide which means that S_g is more stable than S_e and (S_g-S_e) is equal to 2.16 kcal/mole.

The same treatment can be applied to other substances. It should, however, be pointed out that the (S_g-S_e) value obtained with the above treatment is only a qualitative value owing to the fact that the values of $\Delta\tilde{\nu}_{ab}$ and $\Delta\tilde{\nu}_{fluo}$ are considerably different from each other. This fact means that potential functions in the ground and excited states are somewhat different.[23] As some examples of fluorescence spectra, the recorded curves of compound (II) and 2-dimethylaminoquinoline are shown in Figs. 30 and 31, respectively.

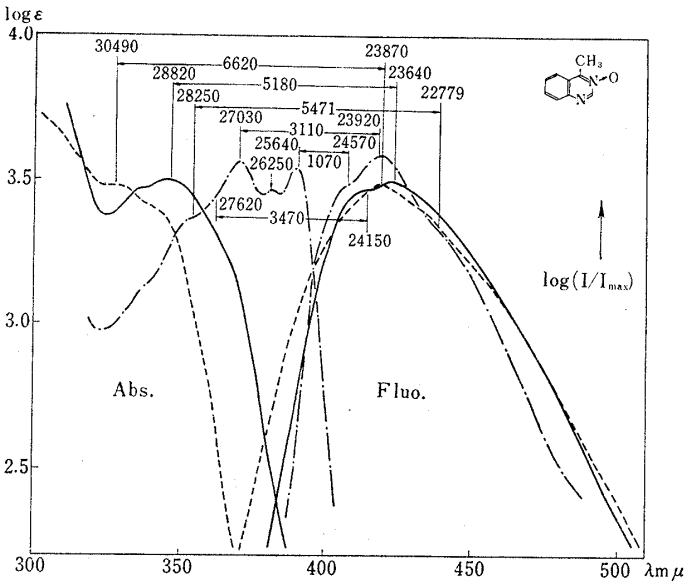

Fig. 30.
---- Heptane
—— 95% EtOH
------ H_2O

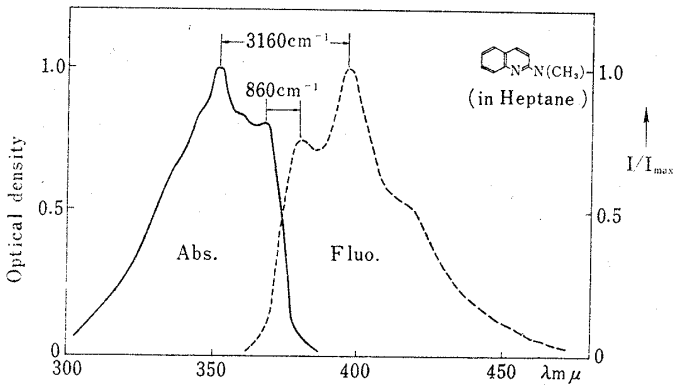

Fig. 31.

(C) Relationship between Absorption Bands and Structure of Compounds

The assignment of ultraviolet spectral absorption bands of various basic alternant hydrocarbons such as benzene, naphthalene, anthracene, etc., and their N-heterocyclic compounds was obviously determined by the semi-empirical A.S.M.O.-C.I. or S.C.F. calculations.*6 These assignments correspond well with Platt's notation[14] derived from a free-electron model. As will be seen in Fig. 1, the transition moments of ^1L_b and ^1B_b bands are directed very close to the x-axis and those of ^1L_a and ^1B_a to the y-axis. According to theoretical and experimental studies,*6 the wave length of each band will be in the following order : For benzene, naphthalene, and their N-heterocyclic compounds (free

*6 See the reviews in (12) and (28).

23) G.C. Pimentel : J. Am. Chem. Soc., **79**, 3323 (1957).

bases), each absorption band shifts to a shorter wave-length in the descending order of ^1L_b (the longest wave-length), ^1L_a, ^1B_b, and for anthracene and N-hetero-anthracene (both free bases and cations) the order is $^1L_a > ^1L_b > ^1B_b$. The order for cations of quinoline and isoquinoline is $^1L_a > ^1L_b > ^1B_b$ and $^1L_b > ^1L_a > ^1B_b$, respectively, and care must be taken in the determination of the band assignment of these cations. As a standard example, the spectrum and band assignment of naphthalene are shown in Fig. 32. In a previous

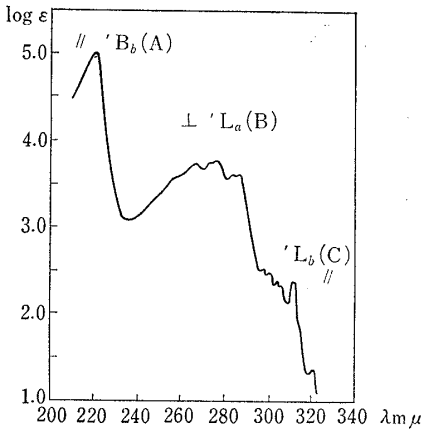

Fig. 32.
Spectrum and Band Assignments of Naphthalene in Hydrocarbon Solution.
In this figure A, B and C, and ^1L_b, ^1L_a and ^1B_b show Jones' notation[27] and Platt's notation,[14] respectively.

work the band assignment of various basic heterocyclic N-oxides was made according to Platt's notation from the experimental[7] and theoretical[8,9] points of view, and each band of quinoline 1-oxide, isoquinoline 2-oxide, acridine N-oxide, etc. could be interpreted by Platt's notation, but that of pyridine N-oxide could not be interpreted by the notation alone, because in this case a new band, namely, charge transfer band appears in the spectrum. Assuming that Platt's notation can reasonably be extended to much more complex naphthalene and anthracene heterocyclic derivatives (except the more complex benzene heterocyclic N-oxides), the notation may be used for discussion of the results obtained in the present work. As will be seen in Fig. 2 and Figs. 3~28, three distinct absorption bands have also been observed in a near ultraviolet absorption spectra region as for heterocyclic naphthalene derivatives. From a view-point of the band assignment for basic heterocyclic compounds, the assignment*7 for the three main bands in the above compounds (free bases) has tentatively been made as follows: Each band appears in a shorter wave length in the order of ^1L_b, ^1L_a, and ^1B_b. When a substituent is introduced into the position which belongs to Class II, the red shift of ^1L_b band may especially be expected, because the direction of electron migration or electron drawing arising from a substituent is directed nearly to the x-axis in Fig. 1. In view of the resonance theory, the above relation concerning the effect of a substituent is described in Fig. 33. Therefore, an excited

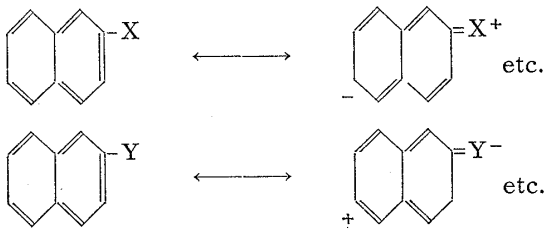

Fig. 33.
X and Y show electron donating and accepting substituents respectively.

state having the transition moment directed to the x-axis may be more stabilized, and red shift of ^1L_b or ^1B_b state occurs as the result. A similar treatment can now be made for the effect of a substituent on the ^1L_a band and, in this case, ^1L_b and ^1L_a bands may

*7 A more detailed discussions on the ultraviolet spectra shown in Figs. 22, 27, and 28, will be reported in a later paper based on detailed experimental and theoretical cosiderations.

be recorded apparently as one absorption band, since frequency shift (red shift) of ^1L_a becomes much greater, and ^1L_b and ^1L_a may overlap each other. This relationship is shown in Fig. 2. Confining to ^1L_b and ^1L_a bands, it may be possible to say that this relation is a general property. Some other examples of these spectra are shown in Figs. 34 and 35.*8

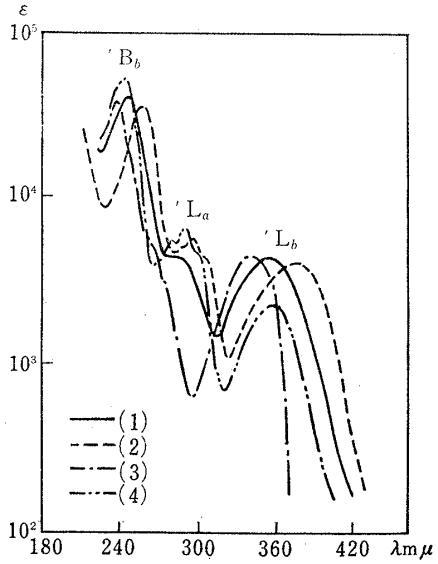

Fig. 34. Absorption Spectra*8 of Monoamino Derivatvies of Quinoline and Naphthalene in 95% EtOH

(1) 6-aminoquinoline
(2) 6-dimethylaminoquinoline
(3) 2-aminoquinoline
(4) β-aminonaphthalene

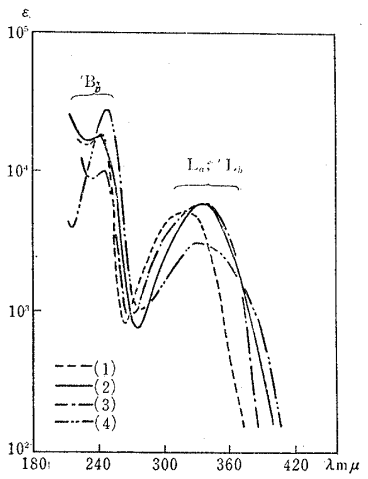

Fig. 35. Absorption Spectra*8 of Monoamino Derivatives of Quinoline, Isoquinoline and Naphthalene in 95% EtOH

(1) α-aminonaphthalene
(2) 5-aminoisoquinoline
(3) 4-aminoisoquinoline
(4) 8-aminoquinoline

When some substituents were introduced into a molecule, the following treatment was employed concerning the prediction of band positions. It was assumed that the degree of substituting power of electron-donating groups is in the descending order of $N(R)_2 \approx NH_2 > OR \approx OH \approx \gg N\text{-}O \gg CH_3$, halogens, etc., and that of electron-accepting groups $NO_2 > C{=}O \approx COOR(H) > \gg N \rightarrow O \gg \gg N$ (in the ring)> halogens, etc. When each of these substituents was introduced at positions of the same class, their substituting effects, on the whole, will stress the relationship shown in Table II. On the other hand, these substituents introduced at the positions of different classes will infer that substituents belonging to the most powerful substituting effect according to the above orders will show the relationship shown in Table II. In view of the above assumption, the experimental results shown in Fig. 2 and Figs. 3~28 can be explained. For example, compound (V) has

Table II. Relationship between Substituted Position and Frequency Shift of ^1L_b and ^1L_a bands

Type	Classification of positions in Fig. 1	Effect of substituted position on ^1L_b and ^1L_a bands[a]
1	1, 4, 5, 8 (Class I)	Degree of red shift of ^1L_a is larger than ^1L_b, so that ^1L_b and ^1L_a bands may apparently be overlapped as one band
2	2, 3, 6, 7 (Class II)	Degree of red shift of ^1L_b is larger than ^1L_a, so that ^1L_b and ^1L_a bands may distinctly be separated as two bands

a) ^1B_b band usually shows the highest intensity ($\log \varepsilon \geqslant 4$), so that the assignment of ^1B_b band can easily be made. Our attention is confined to ^1L_b and ^1L_a bands.

*8 These spectra were cited from E. A. Steck and G. W. Ewing's data.[24]

24) E. A. Steck, G. W. Ewing: J. Am. Chem. Soc., **70**, 3397 (1948).

three substituents involving ring-nitrogen, namely, NH_2, $\rangle N \rightarrow O$, and $\rangle N$. NH_2 is the most powerful substituent among these three substituents. In addition, NH_2 and $\rangle N$ belong to the position of the same Class I. Therefore, ^1L_b and ^1L_a bands of this compound are expected to appear as one absorption band and this prediction agrees well with the experimental result. Phenomena seen in the other compounds can also be explained in the same manner. As was seen from Table II, Fig. 2, etc., the above relationship may also be called a general property.*9 The spectra of the compounds (XVII) and (XVIII) shown in Figs. 19, 20, and 21, and those of the acridine and anthracene derivatives examined by other workers[25~28],*6 show that the above property may also be applied to three-ring systems, but in such a case, care must be taken in band assignments. In this case, as was described in the previous section, ^1L_a band absorbs at the longest wave length. Quantum mechanical calculations associated with this property have not been undertaken as yet with the treatments involving electronic repulsion terms except for a few naphthalene derivatives.[12] Nevertheless, the substituting effect of some groups such as CH_3, halogens, etc. can reasonably be explained by the application of electron migration theory[21] because of their relatively small substituting effect. In other words, above property can be explained on the basis of comparison of coefficients of molecular orbitals associated with the electron transition.[28]

Experimental

Materials——Pure samples of 2-aminoquinazoline 3-oxide, m.p. 265~270°(decomp.), 4-aminoquinazoline 3-oxide, m.p. 220~222°(decomp.), quinazoline 3-oxide, m.p. 150~152°, quinoxaline 1-oxide, m.p. 130°, and 4-methylquinazoline 3-oxide, m.p. 170~172°, were supplied by Dr. Adachi[29] of the University of Kanazawa. Pure samples of 4-methoxyquinazoline 1-oxide, m.p. 80~81°, 4-methoxyquinazoline, m.p. 35°, phenanthridine 5-oxide, m.p. 235~236°, phenanthridine, m.p. 108~109°, 4-methylpyrimidine 1-oxide, m.p. 76~79°, 4-methoxy-6-methylpyrimidine 1-oxide, m.p. 134~136°, 4-benzyloxy-6-methylpyrimidine 1-oxide, m.p. 95~97°, 4-phenoxy-6-methylpyrimidine 1-oxide, m.p. 120° and 4-piperidino-6-methylpyrimidine 1-oxide dihydrate, m.p. 85~87°, were supplied by Prof. Hayashi and Dr. Yamanaka[30~32] of Shizuoka College of Pharmacy. Pure samples of 2-aminoquinoline, m.p. 125°, 2-dimethylaminoquinoline, m.p. 71~72°, 2-aminoquinoline 1-oxide, m.p. 109~112°; 155~157°(anhydride substance), and 1-aminoisoquinoline 2-oxide, m.p. 170~171°, were supplied by Dr. H. Tanida in this laboratory. Pure samples of 2-carboxyquinoline 1-oxide, m.p. 168~169°(decomp.), 5-nitroquinoline 1-oxide, m.p. 161°, 4-aminoquinoline 1-oxide, m.p. 274°(decomp.), 6-methoxyquinoline 1-oxide, m.p. 117°, 3-bromoquinoline 1-oxide, m.p. 104~105°, and 4-chloroquinoline 1-oxide, m.p. 134~134.5° were supplied by Dr. R. Maeda in this laboratory. A pure sample of 3-aminoquinoline 1-oxide, m.p. 178~179°(decomp.), was supplied by Dr. Kaneko of the Faculty of Pharmaceutical Sciences, University of Tokyo. Phenazine di-N-oxides prepared by oxidation of phenazine with perhydrol were purified by repeating recrystallization from MeOH, m.p. 190~191°(decomp.). Pyrazine mono-N-oxide,[33] m.p. 108° and di-N-oxide, m.p. 260°[33] were respectively prepared by oxidation of pyrazine with equivalent and excess of perhydrol, and were purified by sublimation in vacuum. The methods of preparations and purifications of samples supplied by the above workers were respectively reported elsewhere.[29~39]

*9 There are, of course, some exceptions to this rule. For example, 4-methoxyquinazoline should obey type I in Table II. Distinct separation of ^1L_b and ^1L_a bands, however, has been recorded in the spectrum of this substance (see Fig. 15). On the other hand, the spectrum of 4-methoxyquinoline agrees well with presumption in Table II.[28]

25) A. Wittwer, V. Zanker: Zeit. Phys. Chem. N.F., **22**, 417 (1959).
26) V. Zanker, A. Wittwer: *Ibid.*, **24**, 183 (1960).
27) R.N. Jones: Chem. Revs., **41**, 353 (1947).
28) T. Kubota: "Progress Reports on Electronic Processes in Chemistry," **2**, 42 (1960).
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31) E. Ochiai, H. Yamanaka: *Ibid.*, **3**, 175 (1955).
32) E. Hayashi, Y. Hotta: Yakugaku Zasshi, **80**, 834 (1960).
33) H. Shindo: This Bulletin, **8**, 33 (1960).
34) N.A. Lange, *et al.*: J. Am. Chem. Soc., **52**, 3696 (1930).
35) J.K. Landquist: J. Chem. Soc., **1953**, 2816.

Measurement of Ultraviolet Absorption Spectra in Solution——Hitachi Recording Spectrophotometer Model EPS-2 and Beckman Spectrophotometer Model DU were used for the ultraviolet absorption measurements in solutions. Measurements were ordinarily carried out at room temperature (20~25°) and quartz cell of 1-cm. light path having a good stopper was used. Some of the samples used were scarcely soluble in nonpolar solvents used and, therefore, accurate determination of the concentration was difficult. In such a case, spectra were recorded with a suitable solutions prepared from saturated solutions at suitable temperatures, and intensities of these absorption bands were estimated on the ground that ultraviolet absorption of substances having similar structure will indicate similar intensities. Spectral curves obtained in such a manner are denoted by an asterisk (*) on each solvent.

Fluorescence Spectra of Solution——Measurement of fluorescence spectra was carried out at almost the same temperature as ultraviolet measurement and the apparatus*10,6) described in a previous paper was used. In this case, the temperature of the fluorescence cell was kept constant by circulating water of a desired temperature through the cell jacket. The wave lengths used for excitation of fluorescence solutions were Hg-365 mμ and Hg-435 mμ lines.

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Summary

Ultraviolet absorption spectra and fluorescence spectra of many derivatives of benzene and naphthalene heterocyclic N-oxides and a few derivatives of anthracene and phenanthrene heterocyclic N-oxides were recorded in various solvents. Experimental results were discussed from the point of solvent effect and substituting effect. Ultraviolet spectra of all N-oxides used showed increasing blue shift with increasing polarity of the solvent. These results agreed well wlth the behavior in the solvent effect which was reported in previous papers for basic heterocyclic N-oxides and their simple derivatives. It is suggested that this solvent effect is a general property for heterocyclic N-oxides. As for the fluorescence spectra of N-oxides, such a general property as was observed on ultraviolet spectra was not observed. A main reason for this solvent effect is attributed to hydrogen bonding such as $\rangle N \rightarrow O \cdots H$ (in solvent). On the other hand, a relationship was found to exist between the effect of substituting positions and the spectra. By arranging many substituents in the order of substituting ability and classifying the positions in a molecule belonging to two ring systems into two classes, it has been found that the above relationship is present between ^1L_b and ^1L_a absorption bands. This property may also be considered as a general property.

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*10 This apparatus was made by a modification of Beckman Spectrophotometer Model DU.

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38) H. Tanida: This Bulletin, **7**, 540 (1959).
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