Electronic Spectra and Electronic Structures of Some Basic Heterocyclic N-Oxides

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In a series of previous papers[1,2], we reported on the electronic spectra and electronic structures of various basic heterocyclic *N*-oxides such as pyridine, quinoline, acridine *N*-oxides, etc. and also on their derivatives. The assignment of ultraviolet absorption bands and the interpretation of other physicochemical properties (such as dipole moments, infrared spectra, molecular diagrams, reactivities, dissociation constants, etc.) of basic heterocyclic *N*-oxides were made from the experimental and theoretical points of view. It was concluded that the strongest band near 280 mμ observed with pyridine *N*-oxide and its simple derivatives can not be assigned to the ^1L_b band whose transition moment is parallel to the x-axis as shown in Fig. 4 and that, on the other hand, it may reasonably be interpreted as a new band (charge transfer band) whose transition is associated with the charge displacement from the oxygen atom to the pyridine nucleus[*1].

As to the absorption bands of polyheterocyclic *N*-oxides, however, band assignments by means of Platt's treatment were possible. In the present work, the spectra and the electronic structures of some basic *N*-oxides are reported in a development of our previous work[*2]. The electronic absorption spectra of pyrazine mono- and di-*N*-oxides and 4-methylpyrimidine *N*-oxide and the electronic structures of pyrazine di-*N*-oxide and some other compounds have been studied and compared with the results in the previous studies.

Experimental

Materials. — Pyrazine mono- (m. p. 108°C) and di- (d. p. 260°C) *N*-oxides were prepared by the oxidation of pyrazine with an equivalent and an excess of hydrogen peroxide respectively, and were purified by sublimation in vacuum. A pure sample of 4-methylpyrimidine *N*-oxide (m. p. 76~79°C) was supplied by Dr. Yamanaka of Tohoku University[7]. Organic solvents such as *n*-heptane, dioxane, alcohol, etc. for spectrophotometric measurements were purified according to the standard method[8].

Measurement. — A Hitachi recording spectrophotometer model EPS-2 and a Beckman spectrophotometer model D. U. were used for the ultraviolet absorption measurements of solutions. Measurements were usually carried out at room temperature (20~25°C), using the quartz cell with a stopper of a 1 cm. light path. For measurements of weak absorption bands, quartz cells of 2, 5 and 10 cm. light path were also used. If necessary, however, the temperature of the absorption cell was kept constant by circulating water of a desired constant temperature through the cell jacket.

Experimental Results

Absorption Spectra of Pyrazine Di-*N*-oxide.— As is shown in Fig. 1, the spectrum in an absolute dioxane solution[*3] apparently consists of the three main bands (i. e., 324, ~260 and 223 mμ[*4]) and of some bands of a lower intensity superposed on the main absorption band near 350~370 mμ. Figure 1 also shows our band analysis based on the method which was used by Stephenson for the interpretation of the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands of pyridine and its simple derivatives[9]. Oscillator strengths of each band obtained by the above analysis were calculated in terms of Eq. 1,

$$f=4.32\times10^{-9}\int\varepsilon d\bar{\nu} \qquad (1)$$

where the value of the integral, $\int\varepsilon d\bar{\nu}$, was estimated by the approximate formula, $\int\varepsilon d\bar{\nu}\fallingdotseq$ [(half wide value in cm^{-1})$\times\varepsilon_{\max}$] and the

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1) T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 930 (1958), etc.

2) T. Kubota, ibid., **80**, 578 (1959), etc.

[*1] The concept of the intramolecular charge transfer spectra was first introduced by Nagakura and Tanaka[3-5] to interpret the spectra of substituted benzenes.

3) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

4) J. Tanaka and S. Nagakura, ibid., **24**, 1274 (1956).

5) S. Nagakura, *Molecular Physics*, 3, 152 (1960).

[*2] Moreover, many spectra of heterocyclic *N*-oxides with much more complex constitutions have also been recorded, and we have found some general properties on these spectra[6].

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

7) Cf. E. Ochiai and H. Yamanaka, *Pharm. Bull.*, **3**, 175 (1955).

8) A. Weissberger and E. Proskauer, "Organic Solvent", 2nd Edition, Interscience Pub., Inc., New York (1956).

[*3] Accurate measurement of the spectrum in the *n*-heptane solution could not be carried out because of the much lower solubility.

[*4] This value, cited in the previous papers, was obtained in an absolute ethanol solution[2,6].

9) H. P. Stephenson, *J. Chem. Phys.*, **22**, 1077 (1954).

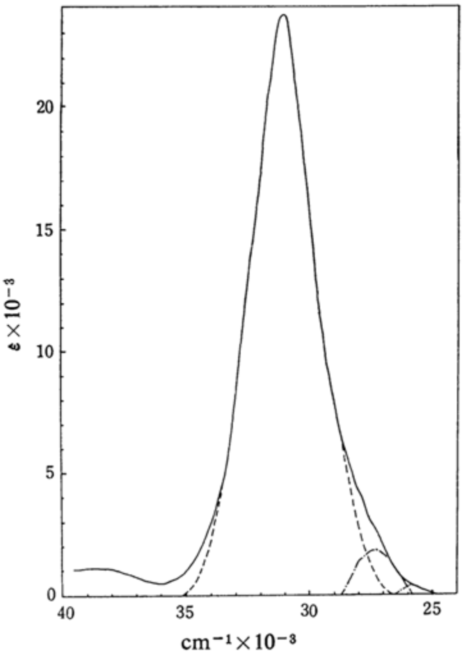

Fig. 1. Absorption spectrum in absolute dioxane solution and band analysis of pyrazine di-*N*-oxide.

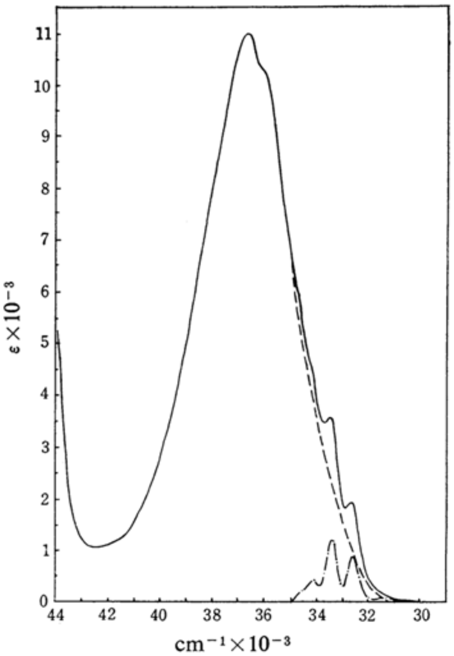

Fig. 2. Absorption spectrum in *n*-heptane solution and band analysis of pyrazine mono-*N*-oxide.

graphic integration for the main band and the weak bands respectively. The results are shown in Table I. In solvents such as alcohol and water, the absorption bands show a blue shift with the increase in solvent polarity. Especially, the weak band which appeared obviously in the longest wavelength region in non-polar solvents could not be observed even by careful measurement using the cell of a 10 cm. light path[6]. It may be possible that the blue shift of the above weak bands due to the change from non-polar to polar solvents is much greater than that of the main $\pi\rightarrow\pi^*$ band[*5], and that therefore we could not find the weak bands in polar solvents, which are hidden below the main $\pi\rightarrow\pi^*$ band.

Absorption Spectra of Pyrazine Mono-*N*-oxide. —As is shown in Fig. 2, the spectrum of this compound in an *n*-heptane solution shows distinct maxima at 275 and 222 mμ[*6] which exhibits three fine structures. The spectrum also shows some fine structures superposed on the long wavelength side of the $\pi\rightarrow\pi^*$ band. Our band analysis of the above spectrum is also shown in Fig. 2. It may be inferred that the above weak band has a fine structure consisting of three peaks. The behavior of the spectra in polar solvents is similar to that of pyrazine di*N*-oxide[6], while the weak band could not be observed in polar solvents. The results of our band analysis are shown in Table I.

Absorption Spectra of 4-Methylpyrimidine *N*-oxide. — The spectra of this compound in *n*-heptane and water solutions are shown in Fig. 3 and in Table I. A distinct difference compared with the above two compounds is that the low intensity band which appears obviously in non-polar solvents at the longest wavelengh region can also be found partly in water. Our band analysis was carried out by the following method. First, the tail of the strong longest wavelength $\pi\rightarrow\pi^*$ band in water was extended as smooth as possible; the $\pi\rightarrow\pi^*$ band thus obtained was symmetrical with respect to the band's center line. This band was then subtracted from the total absorption band. Thus we obtained band I. Second, the same procedure was applied to the spectrum in *n*-heptane, and band II was obtained. Finally, it was assumed that band I had almost the same intensity in *n*-heptane as in water, and band I′ (the absorption band in *n*-heptane corresponding to the band I in water) was subtracted from band II as shown in Fig. 3. This

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[*5] According to the general rule for the UV spectra of heterocyclic *N*-oxides, these $\pi\rightarrow\pi^*$ bands show a remarkable blue shift with the above-described variation in solvent[1,6]. On the other hand, the hydrogen bonding such as $\gg$N$\rightarrow$O······H (solvent) is an essential mechanism in such general spectral behavior[10,11].

10) T. Kubota, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **74**, 831 (1954); **75**, 1540 (1955), etc.

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

[*6] This value was taken from the previous papers[2,6].

TABLE I

Substance	Solvent	Weak band ($n\rightarrow\pi^*$)		CT band		$\frac{f_{n\rightarrow\pi^*}}{f_{CT}}$	Weak band (^1L_b band)	
		cm^{-1}	f-Value	cm^{-1}	f-Value		cm^{-1}	f-Value
Pyrazine di-*N*-oxide	1,4-Dioxane	27250 25800	0.001 0.014 (+ 0.015	30900	0.303	0.050	—	
	Water		—	32670	—	—	—	
Pyrazine mono-*N*-oxide	*n*-Heptane	34050 33350 32520	0.006	36500	0.186	0.033	—	
	Water		—	37880	—	—	—	
4-Methyl-pyrimidine *N*-oxide*3	*n*-Heptane*3		0.011	35970	0.180	0.064	32180	0.020
	Water		—	38820	0.183	—	34750	0.020
Pyridine *N*-oxide*2	*n*-Heptane	~32000	0.012*1	35520	0.173*1	0.079*1	—	

*1 See Ref. 22.

*2 See Ref. 1.

*3 If we should assume that all weak bands in the longest wavelength region are due to $n\rightarrow\pi^*$ transition, the value of $[f_{n\rightarrow\pi^*}/f_{CT}]$ is 0.174. This value, however, is abnormally large.

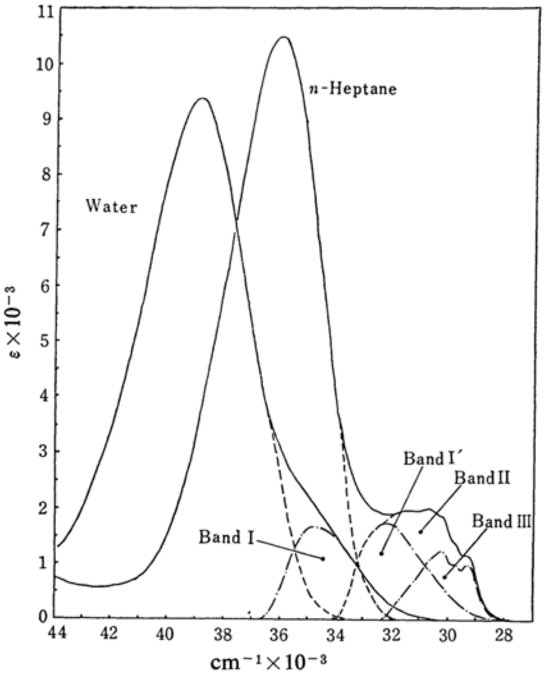

Fig. 3. Absorption spectra in *n*-heptane and water solutions and band analysis of 4-methylpyrimidine *N*-oxide.

way of subtraction would be fairly reasonable. The weak band in *n*-heptane was thus divided into bands I′ and III. The results obtained by the above band analysis are shown in Table I.

Theoretical

Electronic State and Electronic Spectrum of Pyrazine Di-*N*-oxide. — Theoretical calculation based on π-electron approximation, in which electron repulsion terms are taken into account, was carried out on pyrazine di-*N*-oxide. The method is almost the same as that of the previous calculation on pyridine *N*-oxide. Following the procedure of Longuet-Higgins and Murrell, pyrazine di-*N*-oxide is divided into two parts, pyrazine nucleus and two oxygen atoms, and self-consistent field (SCF) calculations for the above two parts are carried out. Then the interaction between the above two parts is calculated. Now, let us explain the procedure in some detail.

SCF Calculation of the Pyrazine Residue.— The electronic structure of pyrazine residue may differ considerably from that of the normal pyrazine molecule, because the N–O bond may be considered to be like a semi-polar bond. In view of the above point[2], a virtual proton model, which was used to calculate the electronic structure of pyridine *N*-oxide, is also adopted in the present calculation. This model is shown in Fig. 4. Hamiltonian calculations for the total π-electrons may be written as:

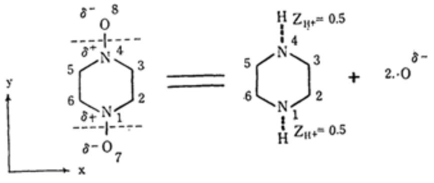

Fig. 4. The model of pyrazine di-*N*-oxide for MO calculation by composite system method. The proton potential, where Z_{H^+} was taken equal to 0.5, should be regarded as representing the core potential due to the formally charged nitrogen atom "N$^{\delta+}$".

$$H=\sum_i\left[H_i^{\text{core}}-\sum_p\frac{Z_{\text{H}^+}\cdot e^2}{r_{pi}}\right]+\sum_{i<j}\frac{e^2}{r_{ij}} \tag{2}$$

Here, r_{pi} represents the distance (1.032 Å)[2] between a virtual proton and an *i*th electron, while $Z_{\text{H}^+}\cdot e$ represents the effective charge of the virtual proton, the value being 0.5. We have used here the semiempirical SCF MO method, including zero-differential overlap approximation, as developed by Pople[12]. According to this method, the matrix elements of Fock's Hamiltonian calculation in terms of AO's can be written as follows:

$$F_{\mu\mu}=\alpha_\mu^{\text{core}}+V_\mu^p+\frac{1}{2}p_{\mu\mu}\cdot\gamma_{\mu\mu}+\sum_{k(\neq\mu)}(p_{kk}-1)\gamma_{\mu k} \tag{3}$$

$$F_{\mu\nu}=\beta_{\mu\nu}^{\text{core}}-\frac{1}{2}p_{\mu\nu}\cdot\gamma_{\mu\nu} \tag{4}$$

V_μ^p in Eq. 3 can be written as

$$V_\mu^p=-Z_{\text{H}^+}\cdot e^2\int\sum_p(\phi_\mu^2(i)/r_{pi})\mathrm{d}\tau_i \tag{5}$$

where ϕ_μ represents a 2pπ-AO of atom μ. V_μ^p was calculated by Roothaan's formula[13] using Slater type AO for ϕ_μ. As for the molecular dimensions of the pyrazine residue, it was assumed for the sake of simplicity that the pyrazine residue was a regular hexagon of V_h symmetry. The virtual proton potential as shown in Eq. 5 does not necessarily mean the simple electrostatic potential; it can be regarded as representing the modifications of core potentials due to the formally charged nitrogen atom "$N^{\delta+}$" in the pyrazine residue. Z_{H^+} is taken to be 0.5 in view of the fact that, in the previous calculation of pyridine *N*-oxide by the method of the composite system, SCF MO's of the pyridine residue obtained by the virtual proton model[*7], where Z_{H^+} was taken to be equal to 0.5, were in nice agreement with the SMO's (simple molecular orbitals) of the pyridine residue obtained by the following procedures[*8]. The values of parameter k_N and k_O in Eqs. 7 and 8 are chosen so as to reproduce the electron densities obtained from the experimentally-determined Hammett's σ-value of the aromatic *N*-oxide group in non-polar solvents, using Jaffe's relation[2]. In this case

$$\alpha_N=\alpha+k_N\cdot\beta \tag{7}$$

$$\alpha_O=\alpha+k_O\cdot\beta \tag{8}$$

all resonance integrals including β_{NO} are assumed equal to β, and the inductive effect is put at $(1/3)^n\cdot k_N$. The SMO's of the pyridine residue were calculated by using the parameters k_N and $(1/3)^n\cdot k_N$ thus obtained.

The values of the two center electronic repulsion integrals $\gamma_{\mu\nu}$ have been evaluated by Mataga's method[15], where the point-charge model[12] was modified by means of Pariser-Parr's treatment[16]. The values of the integrals α_N^{core}, α_C^{core}, γ_{NN}, γ_{CC}, β_{CC}^{core} and β_{CN}^{core} are taken to be the same as those used in the previous paper[2]. The values of V_N^p and V_C^p are -8.107 and -5.455 eV. respectively.

As for the starting MO in the SCF procedure, the SMO obtained by the use of parameters $k_N=k_1=\alpha+1.6\beta$ and $\alpha_2=\alpha+0.711\beta$ (0.711 is a sum of inductive effects—$(1/3)^n\cdot k_N$—contributed from each nitrogen atom) from the above point of view was used; this SMO is near to the SCF MO's obtained by the iterative calculation of Eq. 9.

$$\sum_\nu F_{\mu\nu}\cdot C_{i\nu}=\varepsilon_i\cdot C_{i\mu} \tag{9}$$

The SCF MO's, eigen-values and symmetries of orbitals obtained in this way are shown in Table II and in Fig. 5. Here, symmetries of the orbitals are the same as those described in the previous paper[2].

Energy Levels of Oxygen Atoms.—The MO's of two oxygen atoms can be written as follows:

$$(b_{2u})\psi_7=1/\sqrt{2}(\phi_7+\phi_8) \tag{10}$$

$$(b_{3g})\psi_8=1/\sqrt{2}(\phi_7-\phi_8) \tag{11}$$

Here, ϕ_7 and ϕ_8 represent the 2pπ AO of oxygen atoms 7 and 8 respectively. ψ_7 and ψ_8 are nearly degenerate, and the eigen-value for these MO's was evaluated using Eq. 12, were $\overline{F^c}_{\mu\mu}$ and $\overline{F^c}_{\mu\nu}$ represent the mean value of $F_{\mu\mu}$'s for carbon atoms and that of $F_{\mu\nu}$'s for the nearest neighbor carbon atoms respectively, because the matrix elements ($F_{\mu\mu}$ and $F_{\mu\nu}$) in the SCF MO method correspond reasonably to the matrix elements in the SMO method (for example, Eq. 7 and 8):

$$F_{00}=\overline{F^c}_{\mu\mu}+k_O\cdot\overline{F^c}_{\mu\nu} \tag{12}$$

k_O was taken to be 1, since the F_{00} value obtained from the previous ASMO CI calculation on pyridine *N*-oxide corresponds to the case $k_O=1$[1], and thus $F_{00}=-15.34$ eV. was obtained.

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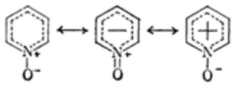
12) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

13) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

[*7] This treatment for heterocyclic compounds was carried out first by S. Mataga and N. Mataga[14].

14) S. Mataga and N. Mataga, *Z. physik. Chem.*, *N. F.*, **19**, 231 (1959).

[*8] $Z_{\text{H}^+}=0.5$ may be a reasonable value, since the following resonance formulas can be conceived:



15) N. Mataga and K. Nishimoto, ibid., **13**, 140 (1957).

16) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

TABLE II. SCF MO'S, EIGEN-VALUES AND SYMMETRIES OF EACH ORBITAL OF PYRAZINE RESIDUE

Symmetry	SCF MO	Eigen-value
b_{2u}	$\psi_1=0.5207(\phi_1+\phi_4)+0.3383(\phi_2+\phi_3+\phi_5+\phi_6)$	−21.249 eV.
b_{3g}	$\psi_2=0.6318(\phi_1-\phi_4)+0.2245(\phi_2-\phi_3-\phi_5+\phi_6)$	−19.374 eV.
b_{1g}	$\psi_3=1/2(\phi_2+\phi_3-\phi_5-\phi_6)$	−16.322 eV.
b_{2u}	$\psi_4=0.4784(\phi_1+\phi_4)+0.3682(-\phi_2-\phi_3-\phi_5-\phi_6)$	− 8.566 eV.
a_u	$\psi_5=1/2(\phi_2-\phi_3+\phi_5-\phi_6)$	− 6.926 eV.
b_{3g}	$\psi_6=0.3174(\phi_1-\phi_4)+0.4468(-\phi_2+\phi_3+\phi_5-\phi_6)$	− 4.588 eV.

TABLE III. ENERGIES AND EXCITED STATE WAVE FUNCTIONS OF PYRAZINE RESIDUE, AND ENERGIES OF CHARGE TRANSFER CONFIGURATIONS AND INTERCONFIGURATIONAL MATRIX ELEMENTS (Energies are in unit of eV.)

$[{}^1\chi_{3\to4} \mid H \mid {}^1\chi_{3\to4}]=4.7855$	$(34 \mid G \mid 34)=\ 5.3527$
	$(34 \mid G \mid 43)=\ 1.1911$
$[{}^1\chi_{3\to5} \mid H \mid {}^1\chi_{3\to5}]=6.4808$	$(35 \mid G \mid 35)=\ 5.8662$
	$(35 \mid G \mid 53)=\ 1.4754$
$[{}^1\chi_{2\to4} \mid H \mid {}^1\chi_{2\to4}]=7.7151$	$(24 \mid G \mid 24)=\ 6.1655$
	$(24 \mid G \mid 42)=\ 1.5360$
$[{}^1\chi_{2\to5} \mid H \mid {}^1\chi_{2\to5}]=7.9208$	$(25 \mid G \mid 25)=\ 5.4130$
	$(25 \mid G \mid 52)=\ 0.4426$
$[{}^1\chi_{7\to5} \mid H \mid {}^1\chi_{7\to5}]=4.8299$	$(75 \mid G \mid 75)=\ 3.5887$
$[{}^1\chi_{8\to5} \mid H \mid {}^1\chi_{8\to5}]=[{}^1\chi_{7\to5} \mid H \mid {}^1\chi_{7\to5}]$	
$[{}^1\chi_{8\to4} \mid H \mid {}^1\chi_{8\to4}]=2.7922$	$(84 \mid G \mid 84)=\ 3.9863$
$[{}^1\chi_{7\to4} \mid H \mid {}^1\chi_{7\to4}]=[{}^1\chi_{8\to4} \mid H \mid {}^1\chi_{8\to4}]$	
$[{}^1\chi_{7\to4} \mid H \mid \Psi_0]=\sqrt{2}\cdot[C_{77}\cdot C_{41}\cdot\beta_{71}{}^{\mathrm{core}}+C_{78}\cdot C_{44}\cdot\beta_{84}{}^{\mathrm{core}}]=\sqrt{2}\cdot\varepsilon_{74}=-1.9135$	
$[{}^1\chi_{3\to4} \mid H \mid {}^1\chi_{2\to5}]=-1.0221$	$(24 \mid G \mid 53)=-0.7261$
	$(24 \mid G \mid 35)=-0.4301$
$[{}^1\chi_{3\to5} \mid H \mid {}^1\chi_{2\to4}]=0.3940$	$(25 \mid G \mid 43)=-0.0180$
	$(25 \mid G \mid 34)=-0.4301$
${}^1\mathrm{L_b}({}^1\mathrm{B_{3u}}:x)=0.9586({}^1\chi_{3\to4})+0.2849({}^1\chi_{2\to5})\ :\ 4.4817$	
${}^1\mathrm{B_b}({}^1\mathrm{B_{3u}}:x)=0.2849({}^1\chi_{3\to4})-0.9586({}^1\chi_{2\to5})\ :\ 8.2246$	
${}^1\mathrm{L_a}({}^1\mathrm{B_{1u}}:y)=0.9599({}^1\chi_{3\to5})-0.2803({}^1\chi_{2\to4})\ :\ 6.3657$	
${}^1\mathrm{B_a}({}^1\mathrm{B_{1u}}:y)=0.2803({}^1\chi_{3\to5})+0.9599({}^1\chi_{2\to4})\ :\ 7.8301$	
$[{}^1\chi_{8\to4} \mid H \mid {}^1\chi_{3\to5}]=0$	
$[{}^1\chi_{8\to4} \mid H \mid {}^1\chi_{2\to4}]=-\varepsilon_{28}=1.7871$	
$[{}^1\mathrm{L_a} \mid H \mid {}^1\chi_{8\to4}]=-0.5009$	
$[{}^1\mathrm{B_a} \mid H \mid {}^1\chi_{8\to4}]=1.7155$	
$[{}^1\chi_{8\to5} \mid H \mid {}^1\chi_{3\to4}]=0$	
$[{}^1\chi_{8\to5} \mid H \mid {}^1\chi_{2\to5}]=-\varepsilon_{82}=1.7871$	
$[{}^1\mathrm{L_b} \mid H \mid {}^1\chi_{8\to5}]=0.5091$	
$[{}^1\mathrm{B_b} \mid H \mid {}^1\chi_{8\to5}]=-1.7131$	

Obtained energy levels are shown in Fig. 5. Now, it may be possible that electronic transitions, as shown by arrows in Fig. 5, make a great contribution to the near-ultraviolet absorption of pyrazine di-*N*-oxide. Therefore, these transitions were taken into account. The calculation of the excitation energies was made as follows. First, the energy values of the locally excited states were calculated on the basis of the results shown in Table II, using the method of configuration interaction. These results are shown in Table III. In this table, for example, ${}^1\chi_{3\to4}$ denotes the configuration produced by one electron transition from ψ_3 to ψ_4, and the necessary formulas for transition energies and interaction energies between these configurations are shown in the footnote[*9].

The energy values of the charge transfer configurations due to electron transfers from ψ_7 and ψ_8 to the orbitals of pyrazine nucleus are also shown in Table III. In this case, it is assumed that r_{NO}, $r_{77}=r_{88}$ and $\beta_{71}{}^{\mathrm{core}}=\beta_{84}{}^{\mathrm{core}}$ are equal to 1.27 Å, 14.127 eV. and −2.00 eV. respectively, owing to the same reason as described in a previous paper2). The values

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[*9]
$$[{}^1\chi_{i\to j} \mid H \mid {}^1\chi_{i\to j}]$$
$$=\varepsilon_j-\varepsilon_i+2(ij \mid G \mid ji)-(ij \mid G \mid ij)$$
$$[{}^1\chi_{i\to j} \mid H \mid {}^1\chi_{k\to l}]$$
$$=2(kj \mid G \mid li)-(kj \mid G \mid il)$$
$$[{}^1\chi_{i\to j} \mid H \mid \Psi_0]=\sqrt{2}\,\varepsilon_{ij}$$
$$[{}^1\chi_{i\to j} \mid H \mid {}^1\chi_{k\to j}]$$
$$=-\varepsilon_{ik}+2(kj \mid G \mid ji)-(kj \mid G \mid ij)$$
$$[{}^1\chi_{i\to j} \mid H \mid {}^1\chi_{i\to l}]$$
$$\varepsilon_{jl}+2(ij \mid G \mid li)-(ij \mid G \mid il)$$

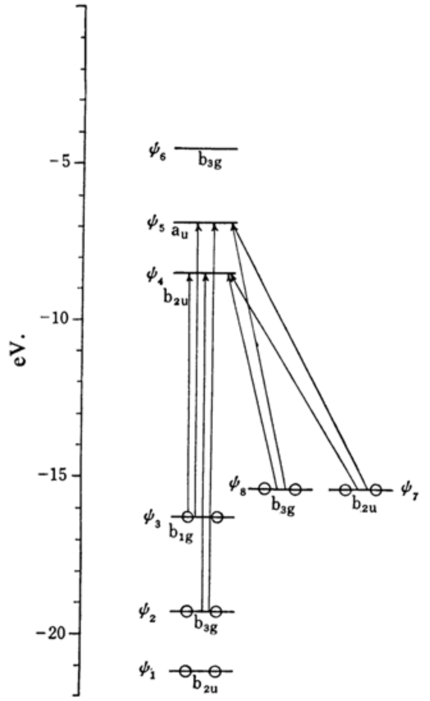


Fig. 5

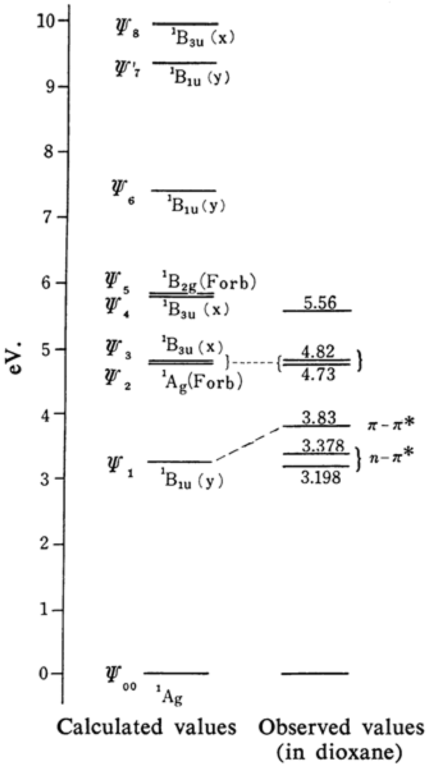


Fig. 6. The calculated energy levels and observed values in dioxane solution of pyrazine di-*N*-oxide.

of $\gamma_{7\mu}$ etc. were evaluated in the same way as that for the pyrazine nucleus. Next, the matrix elements of the interactions between each state of ^1L_b, ^1B_b, ^1L_a and ^1B_a and each state of the above charge transfer configurations were calculated. Therefore, we could obtain the energy levels of pyrazine di-*N*-oxide as solutions of secular equations belonging to the same symmetry, such as Eq. 13 etc. (Eq. 13 is for $^1B_{3u}$ (x)).

$$\begin{array}{ccc} {}^1\chi_{8-5} & {}^1L_b & {}^1B_b \\ \hline \end{array}$$
$$\begin{vmatrix} 4.8299-E & 0.5091 & -1.7131 \\ 0.5091 & 4.4817-E & 0 \\ -1.7131 & 0 & 8.2246-E \end{vmatrix} = 0 \qquad (13)$$

The results obtained by the above treatment were shown in Table IV and Fig. 6, together with the experimental results.

The Electronic States of Isoquinoline *N*-Oxide and Acridine *N*-Oxide. — The following values of parameters for SMO can be shown to be suitable for interpreting various physicochemical properties of heterocyclic *N*-oxides[2]. Namely,

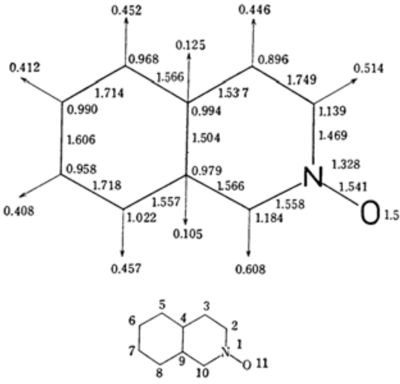


Fig. 7

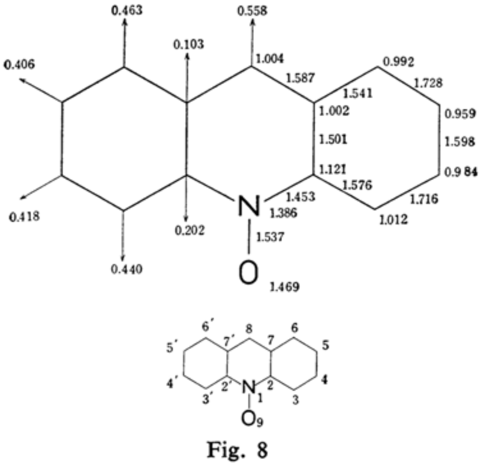
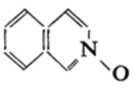
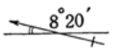
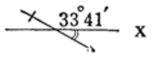
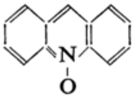
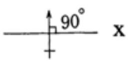
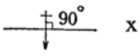


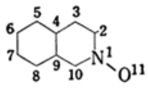
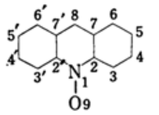
Fig. 8

TABLE IV. GROUND STATE AND EXCITED STATE WAVE FUNCTIONS AND EIGEN VALUES OF PYRAZINE DI-*N*-OXIDE (Energies are in unit of eV.)

$\Psi_{00}(^1A_g)=0.8915(\Psi_0)+0.4531(^1\chi_{7\to4})$	-0.9726
$\Psi_1(^1B_{1u}:y)=0.9502(^1\chi_{8\to4})+0.1145(^1L_a)-0.2899(^1B_a)$	2.2084
$\Psi_2(^1A_g)=0.4531(\Psi_0)-0.8915(^1\chi_{7\to4})$	3.7648
$\Psi_3(^1B_{3u}:x)=0.7747(^1\chi_{8\to5})-0.5671(^1L_b)+0.2969(^1B_b)$	3.7920
$\Psi_4(^1B_{3u}:x)=0.5088(^1\chi_{8\to5})+0.8225(^1L_b)+0.2543(^1B_b)$	4.7967
$\Psi_5(^1B_{2g})=1(^1\chi_{7\to5})$	4.8299
$\Psi_6(^1B_{1u}:y)=0.0872(^1\chi_{8\to4})-0.9906(^1L_a)-0.1053(^1B_a)$	6.4098
$\Psi_7(^1B_{1u}:y)=0.2993(^1\chi_{8\to4})-0.0748(^1L_a)+0.9512(^1B_a)$	8.3699
$\Psi_8(^1B_{3u}:x)=0.3884(^1\chi_{8\to5})+0.0443(^1L_b)-0.9204(^1B_b)$	8.9475

TABLE V. DIPOLE MOMENTS AND REACTIVITIES ESTIMATED FROM SMO CALCULATIONS

Substance	π-Moment (Debye unit)		Total moment (Debye unit)*		
	$\pi/1.6$	The angle between x-axis and π-moment	Calculated values	The angle between x-axis and total moment	Observed value
	0.76		4.33		—
	1.88		3.14		3.90[20]

Substance	Electrophilic reaction**	Nucleophilic reaction	Radical reaction
	10≫6≈8>2	10≈3>5≈8	10≫3>8
	8>6>4	8>6>4≈3	8>6>4

* Following Katritzky's analysis[30], total moments were calculated with vector addition between π-moment and observed value (5.02 D) of trimethylamine *N*-oxide.

** Recently, bromination and nitration of acridine *N*-oxide which were investigated by R. M. Acheson et al. gave 8-Br- and 8-NO_2- acridine *N*-oxides[20]. This fact agrees with present theoretical prediction.

k_N, k_O and inductive effects in Eqs. 7 and 8 were set equal to 1.6, 0.595 and $(1/3)^n\cdot k_N$ respectively. We also carried out the SMO calculations on isoquinoline *N*-oxide and acridine *N*-oxide, because the calculations using the above parameters were not carried out on these compounds in the previous paper[2]. Molecular diagrams and MO's obtained in this way are shown in Figs. 7 and 8 and in an appendix respectively, while the calculated dipole moments $(\overrightarrow{\mu})$ and active points for electrophylic, nucleophylic and radical reactions are shown in Table V. The π-moments $(\overrightarrow{\mu_\pi})$ obtained from the present calculations are considerably larger than those estimated from the observed value. Therefore, by Orgel et al.'s procedure[17], $\overrightarrow{\mu_\pi}$ was divided by 1.6.

The geometrical structure of the molecules used to calculated the dipole moments was the same as that described in the previous paper[2]. Namely, it was assumed that the shape of these molecules was a condensed regular hexagon the bond distance of which was 1.395 Å, and r_{NO} was taken to be equal to 1.27~1.28 Å. The prediction of reaction centers was based upon the frontier orbital method as used in previous papers[2,18].

The reaction centers of acridine *N*-oxide obtained from the above calculations are in approximate agreement with those of the

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[17] L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

[18] K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, ibid., **22**, 1433 (1954).

previous calculation in which parameters for *N*-oxide molecules in polar solvents were employed instead of the present ones.

As for isoquinoline *N*-oxide, it is interesting that even if the reaction types are different from one another, the tenth position in Fig. 7 is always the most active position[*10].

Moreover, some molecular constants (charge densities and bond orders) obtained by the present calculation on isoquinoline *N*-oxide, and also those of isoquinoline obtained by the use of parameters close to the present ones, are shown in Fig. 9 for the purpose of comparison[21].

As can be well understood from Fig. 9, electron migration from the oxygen atom to ring, which does not include the *N*-oxide group, is quite small. Therefore, it may be reasonable to consider the reactivity for such a ring as almost the same as that of isoquinoline.

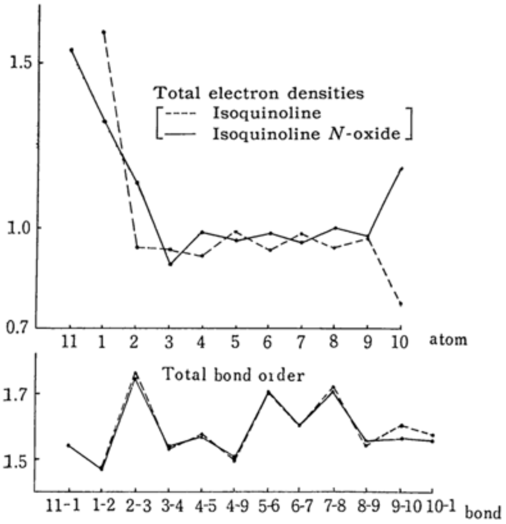

Fig. 9. The comparison of total electron densities and bond orders between isoquinoline *N*-oxide and isoquinoline ($k_N=2$; $k_{C'}=0.25$ on isoquinoline)[21].

Discussion

On the Absorption Bands of Pyrazine Mono-*N*-Oxide and 4-Methylpyrimidine *N*-Oxide. — According to our previous investigations[1,2] and those of the other authors[22,23], it is evident that the near ultraviolet absorption of pyridine *N*-oxide and related compounds exhibit three main absorption bands from both experimental and theoretical points of view. These bands are the $n\rightarrow\pi^*$ band (this is due to electron transitions from lone pair orbitals of oxygen to π^*-orbitals), the charge transfer (CT) band and the ^1L_b band (this corresponds to the $^1B_{2u}$ band of benzene). We can make an approximate interpretation of the electronic spectra of pyrazine mono*N*-oxide and 4-methylpyrimidine *N*-oxide based on the previous results of ASMO CI calculation for pyridine *N*-oxide[2] because the effects of the replacement of –CH= by –N= and the substitution for ring hydrogen of methyl on the electronic spectra are rather small and because the intrinsic natures of the absorption bands of the parent compound seem to be scarcely affected by such replacement and substitution[*11].

As can be seen in Table I, Fig. 2 and Fig. 3, it would be moderately possible for the weak bands which pyrazine mono-*N*-oxide and 4-methylpyrimidine *N*-oxide show at 300 mμ and at 331 mμ respectively to be assigned to the $n\rightarrow\pi^*$ bands, because these weak bands having fine structures in non-polar solvents shift obviously toward a shorter wavelength with an increase of solvent polarity and can not be found in water or alcohol solutions.

According to Ito's rule[22], obtained from the comparison in oscillator strength (f) between the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands of conjugated compounds, the value of $f(n\rightarrow\pi^*)/f(\pi\rightarrow\pi^*)$ should be about 0.05 and may not exceed ~ 0.1[*12].

[*10] Whenever a nitration is tried for isoquinoline *N*-oxide in the usual manner, the nitro group is introduced into a benzene ring[19]. This fact does not agree with the above theoretical prediction. As has been reported in a previous paper as well as in the present paper[2], however, theoretical predictions on pyridine *N*-oxide, quinoline *N*-oxide and acridine *N*-oxide[20] agree with the experimental results. The discrepancy in the case of isoquinoline *N*-oxde may perhaps be due to the so-called ortho effect. Namely, the main reason of this discrepancy between experimental results and theoretical predictions may be attributed to steric effects and to various mutual interactions between *N*-oxide and the nitro groups, which are very polar bulky substituents and occupy the ortho position relative to each other.

19) a) E. Ochiai and Z. Sai, *J. Pharm. Soc. Japan Yakugaku Zasshi*, **65**, 418 (1945). b) E. Ochiai and N. Ikehara, ibid., **73**, 666 (1953).
c) E. Ochiai and Y. Kawazoe, *Chem. Pharm. Bull.*, **8**, 24 (1960).

20) R. M. Acheson, B. Adcock, G. M. Glover and L. E. Sutton, *J. Chem. Soc.*, **1960**, 3367,

21) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).

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

23) M. Ito and W. Mizushima, *J. Chem. Phys.*, **23**, 495 (1956).

[*11] Recent theoretical investigations on *N*-heterocyclic compounds indicate that the k_N of Eq. 7 is equal to about 0.5 and that the UV spectra of the free base of *N*-heterocyclic compounds can be interpreted on the basis of those of corresponding hydrocarbons[15,24,25].

24) N. Mataga, *Z. physik. Chem., N.F.*, **18**, 516 (1958).

25) H. Tubomura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 293 (1957).

[*12] We have examined whether or not Ito's rule is valid for many other compounds. For example, the above ratios on pyridine, 2-pycoline, 3-pycoline, 4-pycoline, 3-fluoro-, 3-chloro- and 3-bromopyridine are 0.073, 0.040, 0.049, 0.072, 0.045, 0.032 and 0.023 respectively[26]. It seems that the rule is approximately applicable to the other compounds.

26) The experimental values of these compounds are cited from Stephenson's paper[9].

Testing the above rule for each band obtained from the band analysis, we can find that the rule is approximately valid for the compounds used here, as is shown in Table I.

The band I′ near 310 mμ in 4-methylpyrimidine *N*-oxide (Fig. 3) can also be found in a water solution and may perhaps be the ^1L_b band which could not be found experimentally in the cases of pyridine *N*-oxide and pyrazine mono-*N*-oxide. It may be considered that the band can be observed in this case because the band has shifted slightly from that of pyridine *N*-oxide owing to the lower symmetry of this compound. A band which may be assigned to the ^1L_b band has also been found on many other compounds, such as 4-aminopyridine *N*-oxide[6,27,28].

The high intensity bands which 4-methylpyrimidine *N*-oxide and pyrazine mono-*N*-oxide show near 278 mμ with $\varepsilon=10480$ and near 274 mμ with $\varepsilon=10980$ respectively can reasonably be assigned to the CT band as it was reported in a previous paper in the case of pyridine *N*-oxide[2].

Absorption Spectra of Pyrazine Di-*N*-oxide.—As shown in Table I, this compound has weak bands in the longest wavelength region. The behavior of these bands is similar to that of the corresponding bands of pyrazine mono-*N*-oxide and 4-methylpyrimidine *N*-oxide, and the bands can conceivably be ascribed to the $n\rightarrow\pi^*$ transition. As can be seen from Fig. 2, they are apparently two $n\rightarrow\pi^*$ bands. We can explain the above two weak bands from two different points of view, but it is difficult to determine which point of view is valid. The one is to ascribe the apparent two weak bands to vibrational structures. The other is as follows. In the case of pyrazine di-*N*-oxide, two group orbitals, whose wave functions are similar to Eqs. 10 and 11, can be obtained from the lone pair orbitals belonging to the O_7 and O_8 atoms as shown in Fig. 4. Consequently, two bands may be expected, owing to the electron transitions from the above two lone pair orbitals to the π^* orbital of the pyrazine nucleus, just as in the case of two $n\rightarrow\pi^*$ bands found on pyrazine[23].

The high intensity $\pi\rightarrow\pi^*$ band near 323.6 mμ of pyrazine di-*N*-oxide can reasonably be assigned to the CT band, the excited state wave function of which has a great contribution from $^1\chi_{8\rightarrow4}$ configuration in view of the results of the calculation described in the Theoretical section, and the direction of the transition moment of this band is expected to be parallel to the y-axis. In the case of these *N*-oxide compounds, however, it may be considered that the character of absorption bands was emphasized by using the method of the composite system adopted here, and that the degree of charge transfer from the oxygen atoms to the ring is smaller than that expected from the present calculation[29]. The calculated energy levels of pyrazine di-*N*-oxide do not give such a nice agreement with the experimental results as in the case of pyridine *N*-oxide. The main reason for this discrepancy may be ascribed to the fact that the various energy integrals are assumed to be the same as those of pyridine *N*-oxide.

The weak band near 260 mμ in Fig. 1 may probably be due to the transition from the ground state to the $^1A_{1g}$ (Ψ_2: forbidden) state or the $^1B_{3u}$ (Ψ_3: x) state in view of the calculated results, as indicated in Table IV. However, it can not be concluded which assignment is more plausible. It is probable that the ^1A_g (Ψ_2) band appears near 260 mμ with a low intensity due to the vibrational interactions.

Moreover, the stabilization energy (0.973 eV.) for the ground state of pyrazine di-*N*-oxide is about twice as large as that (0.437 eV.) of pyridine *N*-oxide[2]. From this fact, it is probable that the electronic structure for the ground state of pyrazine di-*N*-oxide may be represented by a resonance hybrid in which each of two oxygen atoms makes resonance with the pyrazine residue almost independently.

On the Parameter of Oxygen Atoms of Heterocyclic *N*-Oxides.—It has been pointed in a previous paper[2] and in a previous section of this paper that the π-electron densities obtained from the SMO calculation using $\alpha_0=\alpha+0.595\beta$ were an over-estimation of the electron migration from the oxygen atom to the heterocyclic nucleus. For example, about the same values as observed dipole moments were obtained by dividing the π-moments obtained from the above calculation by 1.6. These results are ascribed to the use of a small k_O value in Eq. 8. On the other hand $k_O\approx1$ was derived from the ASMO CI calculation for the ultraviolet spectra of pyridine *N*-oxide. However, the dipole moment calculated by the SMO method using $k_O\approx1$ is somewhat smaller compared to the observed one. To estimate a reasonable k_O value, pyridine *N*-oxide has been selected as a model compound, and SMO calculations have been undertaken under various sets of k_O values. The values of dipole moments obtained by the same treatment as that described in the previous paper[2] are shown by curve 1 in Fig.

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[27] T. Kato, F. Hamaguchi and T. Oiwa, *Ann. Rept. Tokyo Coll. Pharm.*, 27 (1956).

[28] N. Hata, This Bulletin, 29, 82 (1956).

[29] T. Kubota and M. Yamakawa, ibid., 35, 555 (1962).

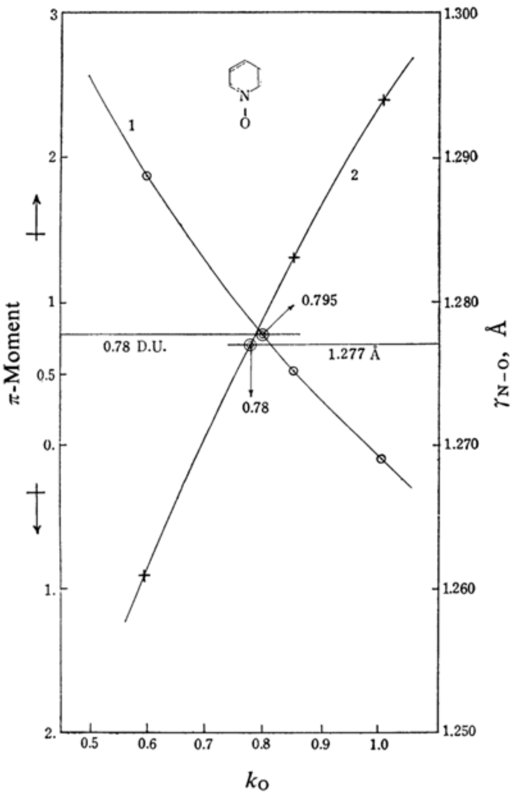

Fig. 10

10*[13]. The value (0.78 Debye unit) of the π-moment estimated from the analysis of the observed total moment was taken from Katritzky's paper[30]. As shown in Fig. 10, $k_O \approx 0.8$ is the best value, and a nice agreement with the observed dipole moment was obtained with this value of k_O. Moreover, as shown by curve 2 in Fig. 10, the N–O distance (this is calculated by the same method as in footnote 13) obtained from the SMO calculation using $k_O \approx 0.8$ is nearly equal to the value (1.277 Å) obtained from an empirical relation between the N–O stretching frequency and the N–O bond length; this fact means that $k_O \approx 0.8$ is reasonable.

Summary

The ultraviolet absorption spectra of pyrazine mono-*N*-oxide, 4-methylpyrimidine *N*-oxide and pyrazine di-*N*-oxide have been measured under various conditions, and band analyses of those spectra have been carried out. In order to interpret the spectra and other physicochemical properties of pyrazine di-*N*-oxide, semi-empirical LCAO MO calculations including the treaments of configuration interactions, have been undertaken in a manner similar to previous calculations on pyridine *N*-oxide. On the other hand, the spectra of pyrazine mono-*N*-oxide and 4-methylpyrimidine *N*-oxide have been interpreted on the basis of the calculated results on pyridine *N*-oxide described in a previous paper. The high intensity bands (278, 274 and 323.6 mμ for 4-methylpyrimidine *N*-oxide, pyrazine mono- and di-*N*-oxides respectively) can reasonably be assigned to charge transfer bands such as the 282 mμ band of pyridine *N*-oxide.

The above substances also exhibit weak bands in the longest wavelength region in non-polar solvents. These weak bands may possibly be due to the $n \rightarrow \pi^*$ transitions. SMO calculations on isoquinoline *N*-oxide and acridine *N*-oxide have also been carried out with the same parameters as those in the case of pyridine *N*-oxide in non-polar solvents, and various physicochemical properties have been discussed on the basis of these calculations. As has been pointed out in a previous paper, the parameter for the oxygen atom used here is too small. To estimate the most reasonable value, SMO calculations were carried out many times on pyridine *N*-oxide, which was used as a model compound. As a result, it was found that k_O (in Eq. 8) ≈ 0.8 is the best value.

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[13]* The bond order of N-O changes somewhat according to the selection of the k_O value. Therefore, the N-O distance may also change to some extent. However, whether or not the change in bond distance estimated from the order-length relation for the N-O bond described in the previous paper[2] is taken into account, the calculated results of dipole moment are almost the same.

30) C. M. Bax, A. R. Katritzky and L. E. Sutton, *J. Chem. Soc.*, **1958**, 1258.

Appendix

SIMPLE MOLECULAR ORBITALS OF ISOQUINOLINE *N*-OXIDE ($k_N=1.6$; $k_O=0.595$; Ind.$=(1/3)^n\cdot k_N$)

ψ_i	Eigen value ε_i	C_{i1}	C_{i2}	C_{i3}	C_{i4}	C_{i5}	C_{i6}	C_{i7}	C_{i8}	C_{i9}	C_{i10}	C_{i11}
ψ_1	3.03113	$\overset{+}{0.72279}$	$\overset{+}{0.36183}$	$\overset{+}{0.18099}$	$\overset{+}{0.15460}$	$\overset{+}{0.06238}$	$\overset{+}{0.03371}$	$\overset{+}{0.03967}$	$\overset{+}{0.08605}$	$\overset{+}{0.21607}$	$\overset{+}{0.37587}$	$\overset{+}{0.29669}$
ψ_2	2.18861	$\overset{+}{0.30840}$	$\overset{+}{0.06799}$	$\overset{-}{0.19587}$	$\overset{-}{0.46184}$	$\overset{-}{0.34676}$	$\overset{-}{0.29280}$	$\overset{-}{0.29286}$	$\overset{-}{0.34455}$	$\overset{-}{0.44080}$	$\overset{-}{0.07998}$	$\overset{+}{0.19353}$
ψ_3	1.55933	$\overset{+}{0.09375}$	$\overset{-}{0.44456}$	$\overset{-}{0.54986}$	$\overset{-}{0.31511}$	$\overset{-}{0.18154}$	$\overset{+}{0.03426}$	$\overset{+}{0{\cdot}23483}$	$\overset{+}{0.32902}$	$\overset{+}{0.25872}$	$\overset{+}{0.34353}$	$\overset{+}{0.09721}$
ψ_4	1.32388	$\overset{+}{0.15812}$	$\overset{+}{0.05882}$	$\overset{-}{0.11162}$	$\overset{-}{0.18675}$	$\overset{+}{0.28609}$	$\overset{+}{0.56197}$	$\overset{+}{0.45558}$	$\overset{+}{0.03554}$	$\overset{-}{0.41064}$	$\overset{-}{0.31942}$	$\overset{+}{0.21694}$
ψ_5	0.88856	$\overset{+}{0.07049}$	$\overset{-}{0.44659}$	$\overset{-}{0.22913}$	$\overset{+}{0.28373}$	$\overset{+}{0.47937}$	$\overset{+}{0.13630}$	$\overset{-}{0.35882}$	$\overset{-}{0.45071}$	$\overset{-}{0.01495}$	$\overset{+}{0.15634}$	$\overset{+}{0.24010}$
ψ_6	0.47457	$\overset{-}{0.08776}$	$\overset{-}{0.18298}$	$\overset{+}{0.09851}$	$\overset{+}{0.21221}$	$\overset{-}{0.12440}$	$\overset{-}{0.26971}$	$\overset{-}{0.00249}$	$\overset{+}{0.26856}$	$\overset{+}{0.11402}$	$\overset{-}{0.44694}$	$\overset{+}{0.72868}$
ψ_7	-0.37522	$\overset{-}{0.31905}$	$\overset{-}{0.16383}$	$\overset{+}{0.46789}$	$\overset{-}{0.09492}$	$\overset{-}{0.32307}$	$\overset{+}{0.22013}$	$\overset{+}{0.23957}$	$\overset{-}{0.31298}$	$\overset{-}{0.10359}$	$\overset{+}{0.46518}$	$\overset{+}{0.32884}$

$\varepsilon_8=-0.67$ $\varepsilon_9=-1.135$ $\varepsilon_{10}=-1.37$ $\varepsilon_{11}=-2.15$

SIMPLE MOLECULAR ORBITALS OF ACRIDINE *N*-OXIDE ($k_N=1.6$; $k_O=0.595$; Ind.$=(1/3)^n\cdot k_N$)

ψ_i	Eigen value ε_i	Symmetry	C_{i1}	C_{i2}	C_{i3}	C_{i4}	C_{i5}	C_{i6}	C_{i7}	C_{i8}	C_{i9}
ψ_1	3.15620	b_2	$\overset{+}{0.67255}$	$\overset{+}{0.39201}$	$\overset{+}{0.15321}$	$\overset{+}{0.06432}$	$\overset{+}{0.04597}$	$\overset{+}{0.08021}$	$\overset{+}{0.20244}$	$\overset{+}{0.13074}$	$\overset{+}{0.26259}$
ψ_2	2.19741	a_2	0	$\overset{+}{0.36769}$	$\overset{+}{0.30593}$	$\overset{+}{0.25018}$	$\overset{+}{0.22899}$	$\overset{+}{0.25018}$	$\overset{+}{0.30593}$	0	0
ψ_3	2.07512	b_2	$\overset{+}{0.41223}$	$\overset{-}{0.04133}$	$\overset{-}{0.10756}$	$\overset{-}{0.16275}$	$\overset{-}{0.22053}$	$\overset{-}{0.29214}$	$\overset{-}{0.36839}$	$\overset{-}{0.36549}$	$\overset{+}{0.27851}$
ψ_4	1.50721	b_2	$\overset{+}{0.02851}$	$\overset{-}{0.01695}$	$\overset{-}{0.32246}$	$\overset{-}{0.41173}$	$\overset{-}{0.27371}$	$\overset{+}{0.00257}$	$\overset{+}{0.27743}$	$\overset{+}{0.38321}$	$\overset{+}{0.03126}$
ψ_5	1.20982	a_2	0	$\overset{+}{0.39174}$	$\overset{+}{0.13250}$	$\overset{-}{0.25499}$	$\overset{-}{0.42589}$	$\overset{-}{0.25499}$	$\overset{+}{0.13250}$	0	0
ψ_6	1.12027	a_2	0	0	$\overset{+}{0.36386}$	$\overset{+}{0.34294}$	0	$\overset{-}{0.34294}$	$\overset{-}{0.36386}$	0	0
ψ_7	1.02660	b_2	$\overset{+}{0.19434}$	$\overset{-}{0.28085}$	$\overset{-}{0.30762}$	$\overset{+}{0.01974}$	$\overset{+}{0.32671}$	$\overset{+}{0.31163}$	$\overset{-}{0.02526}$	$\overset{-}{0.05222}$	$\overset{+}{0.45027}$
ψ_8	0.30475	b_2	$\overset{-}{0.17995}$	$\overset{-}{0.19344}$	$\overset{+}{0.16901}$	$\overset{+}{0.21490}$	$\overset{-}{0.11626}$	$\overset{-}{0.24890}$	$\overset{+}{0.05515}$	$\overset{+}{0.44934}$	$\overset{+}{0.61997}$
ψ_9	-0.25300	b_2	$\overset{-}{0.39519}$	$\overset{+}{0.13313}$	$\overset{+}{0.22312}$	$\overset{-}{0.22925}$	$\overset{-}{0.15153}$	$\overset{+}{0.26946}$	$\overset{+}{0.06739}$	$\overset{-}{0.43162}$	$\overset{+}{0.46603}$

$C_{i2}=\pm C_{i2'}$; $C_{i3}=\pm C_{i3'}$; $C_{i4}=\pm C_{i4'}$; $C_{i5}=\pm C_{i5'}$; $C_{i6}=\pm C_{i6'}$; $C_{i7}=\pm C_{i7'}$ (+ and − represent b_2 and a_2 orbitals respectively). $\varepsilon_{10}=-0.77215(a_2)$; $\varepsilon_{11}=-0.88324(a_2)$; $\varepsilon_{12}=-1.07(b_2)$. ε_{13}, ε_{14} and ε_{15} were not calculated.