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Electronic Structures of Aromatic Amine N-Oxides*

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The electronic structures of heterocyclic amine N-oxides, nitrones, and nitrile N-oxides were systematically studied by the Pariser-Parr-Pople method. In addition, the intensity of $n-\pi^*$ transition pertinent to conjugated N-oxide systems has been calculated. The results of these calculations were compared with the experimental ones reported hitherto and also carried out in the present work. The electronic structure and spectra of aromatic amine N-oxides were thus discussed in detail.

Die elektronische Struktur heterozyklischer Amin-N-Oxide, Nitrone und Nitril-N-Oxide wird systematisch mit Hilfe der Pariser-Parr-Pople-Methode untersucht. Außerdem wurde die Intensität von $n-\pi^*$-Übergängen konjugierter N-Oxide berechnet. Die Resultate wurden mit bekannten sowie eigenen experimentellen Ergebnissen verglichen. Die Elektronenstruktur und die Spektren aromatischer Amin-N-Oxide wurden so im Detail diskutiert.

La structure électronique d'amine N-oxydes, de nitrones, et de nitrile N-oxydes ont été étudiés systématiquement par la méthode de Pariser-Parr-Pople. De plus, l'intensité de la transition $n-\pi^*$ des systèmes N-oxydes conjugués a été calculée. Les résultats de ces calculs ont été comparés aux résultats expérimentaux rapportés précédemment et également à ceux du présent travail. La structure électronique et le spectre des N-oxydes d'amines aromatiques ont ainsi été discutés en détail.

The electronic spectra and electronic structures of various substances of three kinds of aromatic tertiary amine N-oxides, i.e. heterocyclic amine N-oxides, nitrones, and nitrile N-oxides, were systematically studied hitherto [1–5]. The assignment of electronic spectra and the characteristics of electronic structures of these amine N-oxides were reasonably given on the basis of the experimental studies and also Hückel molecular orbital (HMO) and antisymmetrized MO (ASMO) calculations [1—5].

Quite recently, Kobinata and Nagakura [6], and Evleth [7][1] reported the SCF-MO calculation of pyridine N-oxide by means of the Pariser-Parr-Pople (P.P.P.) type π-electron approximation. Bene and Jaffé [8] also reported the transition energies of pyridine N-oxide obtained by a modified CNDO method. These recent calculations as well as the previous ASMO calculation based on the intramolecular charge transfer model [2] led to the same assignment for the $\pi-\pi^*$ bands of pyridine N-oxide. However, there still remains some question as to the $n-\pi^*$ assignment of the absorption band at 320 mμ ($f=0.016$) [9]. The reason for this question was reviewed in the paper by Evleth who assigned the band to a $\pi-\pi^*(^1B_1)$ band [7].

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[1] In this paper Evleth has misread Kubota's assignment [2b] of 215 mμ band of pyridine N-oxide in n-heptane. Kubota assigned this band as $^1A_1 \rightarrow {}^1B_1$ having the main characters of ^1L_b, $^1B_1(CT)$, and ^1B_b configurations. Thus, Evleth's assignment [7] agrees with the one by Kubota.

In this paper the authors will report the electronic structures of heterocyclic amine N-oxides, nitrones, and nitrile N-oxides in detail from the viewpoints of P.P.P. type SCF-MO calculations and experimental studies, and will compare those with the experimental and theoretical studies made hitherto [1—5]. Also, the above mentioned questions concerning the $n-\pi^*$ transition of pyridine N-oxide are discussed on the ground of the present theoretical and experimental studies.

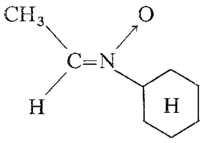
Experimental Section

Spectral Measurement

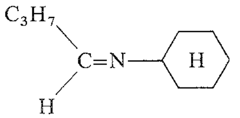
Electronic spectra in solutions were recorded with a Beckman DK-2A far-UV spectrophotometer located in an air-conditioned room operated at ~22° C. Usually 1 cm cells were employed to record the spectra except that the sandwich type thin cells (0.01—0.1 cm) were used in the region below ~220 mμ. All solvents were purified as previously reported [2—5]. Absorption spectra in the far-UV region of the vapor state of tertiarybutylnitrile and its N-oxide were obtained using the far-UV grating spectrometer [10] at the Institute for Solid State Physics, of the University of Tokyo[2]. Gas phase intensities were obtained with the aid of vapor pressure measurements.

Samples

The compounds used for the present studies are of the same quality as those employed in the previous physicochemical studies [11] of tertiaryamine N-oxides unless otherwise stated. Tertiarybutylnitrile (BCN) was obtained from Cilag-Chemie and sublimated twice in vacuum at about 0° C. The purity was checked by gas chromatographic analysis. The substances newly prepared are N-cyclohexyl acetoaldoxime (a quite stable aliphatic nitrone) (ANT), N-cyclohexylpropylaldimine (aliphatic azomethine) (AI), *t*-butylnitrile N-oxide (a quite stable aliphatic nitrile N-oxide) (BCNO), and 4-dimethylaminopyridine N-oxide.



ANT



AI

$(CH_3)_3C{-}C{\equiv}N{\rightarrow}O$,

BCNO

$(CH_3)_3C{-}C{\equiv}N$

BCN

These compounds were synthesized as follows. First, BCNO was synthesized from tertiarybutyl aldoxime using the method previously reported [5], where the corresponding aldehyde was yielded according to Campbell's description [12]. In those procedures, however, some modifications are needed; i.e. dehydrochlorination of tertiarybutylhydroxamic chloride with triethylamine should be

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[2] Authors wish to express their thanks to Professor S. Nagakura and Dr. K. Kaya for giving us their allowance to use the instrument and for advice.

carried out in ether. The ether solution was then filtered, and the filtrate was concentrated to obtain the crude BCNO as oil, which was distilled in reduced pressure (b.p. 24.5° C/2—3 mmHg). The BCNO thus obtained was sublimated twice in vacuum at ~0° C just before use. ANT was obtained by introducing acetoaldehyde vapor, under a nitrogen atmosphere, into N-cyclohexylhydroxylamine, which, in turn, was obtained from nitrocyclohexane by zinc powder reduction. Here, note that the above hydroxylamine should be extracted from the zinc residue with hot alcohol. ANT was recrystallized two times from cyclohexane (m.p. 86 ~ 87° C) and once more just before use. Elemental analyses gave agreement with the calculated values. AI was synthesized by a well-known method from cyclohexylamine and *n*-butylaldehyde. According to the Katritzky *et al.* [13] 4-dimethylaminopyridine N-oxide was synthesized from 4-chloropyridine N-oxide and dimethylamine (30% aqueous solution). This reaction yields a stable dihydrate (m.p. 226.5 ~ 228.0° C, from ethanol-ethylacetate).

Calculation

SCF-MO, transition energy, oscillator strength, dipole moment etc. were calculated with a Facom 270 – 30 computer in the Shionogi Computing Center and using the Kubota-Yoshitani-Yamakawa SCF-MO-CI programs.

Experimental Results

Electronic Spectra of Aliphatic Nitrone and Nitrile N-*Oxide and Related Substances*

The electronic spectra of ANT and AI are depicted in Fig. 1a, and those of BCNO and BCN are in Fig. 1b. Each value of these optical data is listed in Table 1. We see from Fig. 1a and Table 1 that ANT shows a strong $\pi - \pi^*$ band at 243.3 mμ in *n*-heptane which is blue shifted with increasing solvent polarity and in hydrogen bonding solvents. This behaviour is common to the $\pi - \pi^*$ bands of aromatic tertiaryamine N-oxides [1—5], in which N→O and C=C groups are in conjugated systems. The ultraviolet spectra of 1-pyrroline-1(N)-oxide and its related compounds [14] and of the other aliphatic nitrones [4], having conjugated systems and UV spectra similar to those of ANT, also show eminent blue shifts in polar solvents. However, note that a weak intensity absorption band attributable to a $n - \pi^*$ transition could not be clearly found in the longer wavelength region of the strong $\pi - \pi^*$ band of ANT (see Fig. 1a) in spite of the careful search. In addition, such a weak band has not been reported so far for the case of nitrones [4, 14, 15]. Thus, the $n - \pi^*$ transition pertinent to the C=N→O group may not appear in the above wavelength region, and it seems to be reasonable that the $n - \pi^*$ band should be hidden under the strong $\pi - \pi^*$ band or appears in a much shorter wavelength region with a weak intensity (see later discussions) if the $n - \pi^*$ transition arises. On the other band, compound AI exhibites two bands, 178 mμ ($\varepsilon = 12000$) and 246 mμ ($\varepsilon = 94$). On the basis of intensity and other

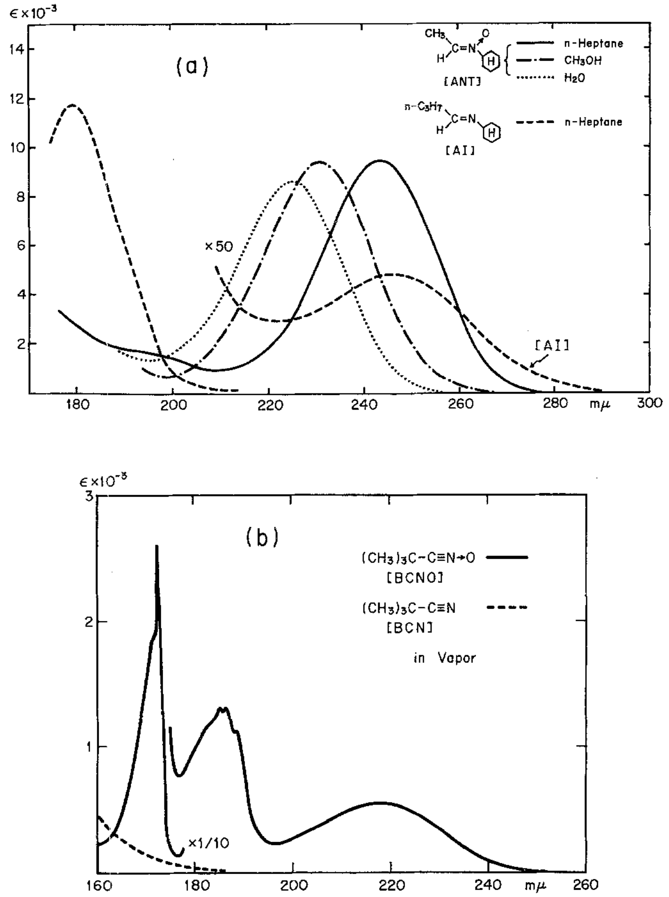

Fig. 1. Ultraviolet absorption spectra of ANT and AI in some solvents (*a*) and of BCNO and BCN in the vapor state (*b*)

experimental criteria [14, 16] these bands are assigned as being $\pi-\pi^*$ and $n-\pi^*$ transitions, respectively. This assignment is also confirmed from our theoretical results *(vide infra)*.

As is seen in Fig. 1a, b, the spectral features of ANT and BCNO are quite different. This difference is magnified by the fact that BCN exhibits no absorption band above 160 mμ. It has already been shown [5, 17] that the $C\equiv N\rightarrow O$ group has a linear structure and has the nature of a partial triple bond arising from the two π (π and $\bar{\pi}$) systems orthogonal to each other. The theoretical consequences of this linear structure will be discussed later but it suffices to say that the orthogonal nature of the π and $\bar{\pi}$ orbitals will dictate that certain $\pi-\bar{\pi}^*$ electronic transitions are forbidden. These results bring about quite large difference between the spectra of BCNO and ANT. Although only a limited number of solvents are suitable for this spectral region, it was shown that the weak 217 mμ transition of BCNO is blue shifted in more polar solvents; a feature characteristic of conjugated N-oxide groups.

Table 1. *Observed data of the absorption spectra of* ANT, AI, BCNO, *and* 4(*p*)- *or* 3(*m*)-*substituted pyridine* N-*oxides (see text for the abbreviation of substances)*

Compounds	Solvent	λ_{max}(mμ)	ε	*f*	λ_{max}(mμ)	ε	*f*	λ_{max}(mμ)	ε	*f*
ANT	*n*-heptane	243.3	9410	0.204—0.213	191.7 (*sh*)	1770	0.02—0.03			
	CH_3CN	239.4	9230							
	CH_3OH	230.6	9370							
	H_2O	224.5	8570							
AI	*n*-heptane	245.8	94	0.0023	178.3	11700				
BCNO	vapor	217.6	550	0.015—0.017	187.8	1100	0.021—0.024	172.6	26000	0.206
					186.1	1300		171.4 (*sh*)	19000	
					184.3	1300				
					183.0 (*sh*)	1200				

λ_{max}'s (ε_{max}'s) of substituted (R) pyridine N-oxides in *n*-heptane and acetonitrile

R	Solvent	I	II	III	IV and V
H	*n*-heptane	338.5 (*w*, 610), 325.9 (*m*, 1230), 315 (*sh*, 1840) $[f_{\mathrm{I}}=0.016]$	282.2 (11600) $[f_{\mathrm{II}}=0.205]$	220.9 (13300), 216.6 (14600), 213.9 (13100) $[f_{\mathrm{III}}=0.196]$	187.8 (11900) $[f_{\mathrm{IV}}=0.246]$
	CH_3CN	—	275.1 (13500)	218.4 (14400), 214.5 (16300)	184.1 (12000)
4-CH_3	*n*-heptane	346.3 (*w*), 332.0 (*m*), 320.6 (*sh*, *s*)	285.6 (—)	220.1 (—), 216.2 (—), 214.5 (—)	179.5 (—)
	CH_3CN	—	278.4 (17000)	217.6 (14100), 213.7 (15400)	—
4-Cl	*n*-heptane	353.6 (*w*), 338.7 (*m*), 326.4 (*sh*, *s*)	289.2 (—)	219.9 (*sh*, —), 215.4 (—)	187.1 (*sh*, —), 181.0 (—)
	CH_3CN	—	283.0 (17900)	218.6 (*sh*, 12700), 214.7 (14700)	186.0 (16700)
4-CH_3O	*n*-heptane	364.4 (*w*), 346.3 (*m*), 336.5 (*m*)	289.6 (—)	211.8 (*sh*, —), 209.0 (—), 207.1 (*sh*, —)	187.6 (—)
	CH_3CN	322.7 (*sh*, 2010)	281.8 (18400)	207.0 (14400)	185.4 (20200)
4-$N(CH_3)_2$	*n*-heptane	350 (*sh*, *m*)	307.1 (—)	—	—
	CH_3CN	347 (*sh*, *m*, 3700)	304.1 (33100)		205.1 (20900), 190.7 (21500)
3-CH_3	*n*-heptane	335.7 (590), 321.3 (*sh*, 1390)	282.4 (12200)	227.3 (16400), 222.2 (16200), 220.2 (*sh*, 13400)	191.5 (11800)
	CH_3CN	—	275.8 (13800)	223.9 (16500), 219.5 (17900)	188.6 (12000)
3-Cl	*n*-heptane	342.7 (780), 329.9 (1230), 328.0 (1240), 316 (*sh*, 1640)	283.2 (13100)	232.3 (16200), 227.1 (17400), 222.1 (12200)	202.6 (13100)
	CH_3CN	—	277.4 (16600)	228.7 (18900), 224.0 (21200)	201.0 (14000)
3-CH_3O	*n*-heptane	330.9 (2040), 321.7 (2650), 314.1 (2470), 306.1 (2400) $[f_{\mathrm{I}}=0.031]$	285 (*sh*, 10800), 279.1 (11500) $[f_{\mathrm{II}}=0.191]$	240.7 (14500), 235.7 (14500) $[f_{\mathrm{III}}=0.174]$	208.2 (13900) $[f_{\mathrm{IV}}=0.275]$ 196 (*sh*, 11800) $[f_{\mathrm{V}}=0.193]$
	CH_3CN	309.1 (2840)	274.4 (12800)	231.5 (15100)	210.5 (12400), 200.9 (*sh*, 10900)
3-NH_2	*n*-heptane	339.2 (*m*), 329.6 (*m*), 323.4 (*w*)	289 (*sh*, —), 282.0 (—)	254.0 (—), 247.9 (—), 244.4 (—), 239.7 (—)	227.0 (—)
	CH_3CN	327.3 (2940) $[f_{\mathrm{I}}=0.039]$	276.3 (11400) $[f_{\mathrm{II}}=0.157]$	241.4 (20800) $[f_{\mathrm{III}}=0.480]$	201.8 (8660) $[f_{\mathrm{IV}}=0.180]$

Electronic Spectra of Substituted Pyridine N-*Oxides*

Since there is no systematic study of the substituent effect on the electronic spectra of pyridine N-oxide, and also since the substituent effect is a useful criterion to distinguish the $n-\pi^*$ band from $\pi-\pi^*$ band, the spectra of pyridine N-oxides with electron donating substituents like OCH_3, NR_2, etc. have been recorded. The results are indicated in Figs. 2 and 3 and in Table 1. Observed absorption bands are tentatively designated from I to V as is shown in Figs. 2 and 3. The oscillator strength of each band recorded in a non-hydrogen bonding solvent is evaluated for the case of pyridine N-oxide and its m-OCH_3 and m-NH_2 substituents, whose band analyses are relatively easy, especially for the latter two, and is included in Table 1. In these spectra the following points are particularly noted. (i) The blue shift of the band I of pyridine N-oxide has not been observed by introducing the electron donating substituents. Conversely, the red shift of the band has been systematically observed according to the increasing substituent ability at para-position, but the red shift is small for the case of meta-substituents. That the elctron donating substituent causes the blue shift of the $n-\pi^*$ band is a characteristic property of it from experimental and theoretical viewpoints [18, 19]. Therefore, the above result may lead to the assignment that the band I may not be the $n-\pi^*$ band but it has a nature of a $\pi-\pi^*$ band. (ii) The band I of pyridine N-oxide is partly hidden under the strong band II. With meta-substituents of

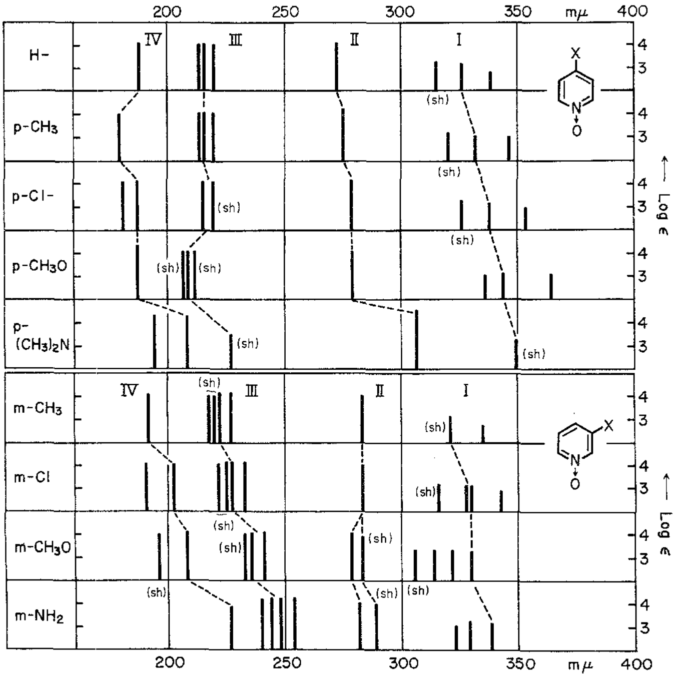

Fig. 2. The behavior of the absorption spectrum of pyridine N-oxide by replacing the *p*- or *m*-hydrogen atom by an electron donating substituent

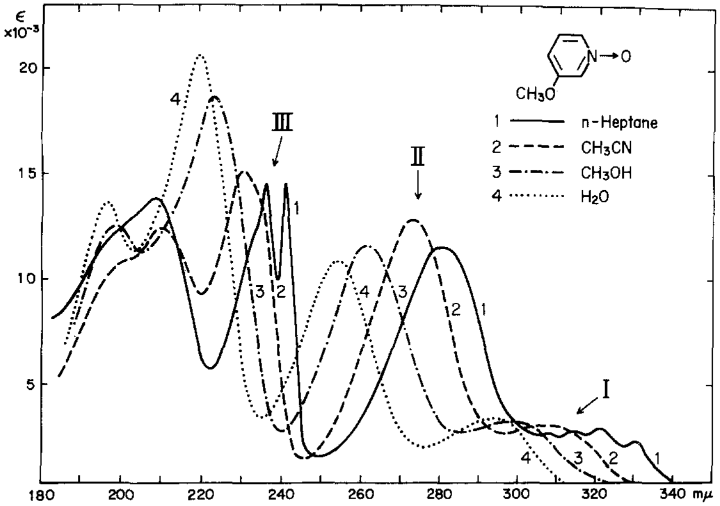

Fig. 3. Absorption spectra of *m*-methoxy-pyridine N-oxide in some solvents

increasing electron donating ability, this sort of overlapping is more reduced[3], and also the intensity of the band I is increased to a ε value more than 3000, which is very large if the band I is due to a $n-\pi^*$ transition (see later discussions). Although these two bands as well as the other bands show a blue shift in protic solvents, meta-methoxy- or meta-aminopyridine N-oxide exhibites clearly the band I, well separated from band II, in the longest wavelength region even in water or alcohol as the solvent (see Fig. 3)[3]. It is a usual phenomenon that the $\pi-\pi^*$ bands of aromatic N-oxides bring about the blue shift in protic solvents [1—5], so that the blue shift phenomenon of the $n-\pi^*$ band in protic solvent may fail to distinguish the $n-\pi^*$ band from the $\pi-\pi^*$ band of the N-oxide compounds. (iii) The red shift of bands II and III caused by an electron donating substituent is sensitive at the para-position for the former band but at the meta-position for the latter[4].

The experimental results of the electronic spectra of substituted pyridine N-oxides, ANT, BCNO etc. mentioned before seem to support the conclusion that the $n-\pi^*$ band pertinent to the functional group $\geqslant N \rightarrow O$ may not occur in a longer wavelength region of the $\pi-\pi^*$ band, or even if the $n-\pi^*$ transition is brought about in the above region its intensity should be weak. Therefore, the assignment of the band I of pyridine N-oxide may be either the $\pi-\pi^*$ band alone or the $\pi-\pi^*$ band overlapped with the weak $n-\pi^*$ band[3].

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[3] The fact that the band I of pyridine N-oxide disappears in water or alcohol as a solvent was the main reason to assign it to a $n-\pi^*$ transition [9]. Later, Hata [20] and Kubota [2a] pointed out independently that the band I of some other mono-azine N-oxides does not disappear completely even in water solvent and also is too strong to assign all its intensity to a $n-\pi^*$ transition, and that the band I consists of two bands, i.e., $\pi-\pi^*(^1L_b)$ [2a] and $n-\pi^*$ bands.

[4] Roughly speaking, it may be said that the band II has a nature of intramolecular charge transfer from the oxygen atom of the N→O bond to the ring residue, and symmetry $^1A_1$ (see text) [2]. Accordingly, the band II may be affected more by the perturbation at para-position.

SCF-Calculation

To elucidate the electronic structure of aromatic tertiaryamine N-oxides a P.P.P. type SCF-MO-CI calculation was carried out. Intrinsically, however, actual calculations correspond to the extension of the SCF-MO calculation made by Kobinata and Nagakura [6], since the estimation of the valence state ionization potential I_p and the electron affinity E_A of nitrogen and oxygen atoms in the N→O bond seems to be reasonable and to reflect well the valence state of the dative bond of the tertiaryamine N-oxide group[5]. But, in the present calcula-

Table 2. *Valence state I_p and E_A, one-center repulsion integral γ_{rr}, core resonance integral β_{rs}, bond length, and bond angle used in the present calculation*

Compounds	Bond	Bond length and bond angle	$-\beta_{rs}$	I_p[f]		E_A[f]
Heterocyclic amine N-oxides[a]	(C–C) ring	1.395 Å	2.370 eV	C:	11.22 eV	0.62 eV
	(C–N) ring	1.395	2.576	$N^{\delta+}$:	24.24	8.03
	N–O	1.28	2.00	$O^{\delta-}$:	22.45	4.38
	Ring: regular hexagon assumed.			δ	= 0.7 (see text)	
ANT[a]	C=N	1.31	2.658[d]	γ_{CC}	= 10.60 eV	
	N–O	1.28	2.00	γ_{NN}	= 16.21	
	<C=N→O	120°		γ_{OO}	= 18.07	
Benzylidene methyl amine N-oxide[a, 10]	(C–C) ring	1.390	2.370			
	C–C	1.464	2.190[d]			
	C=N	1.309	2.658[d]			
	N→O	1.284	2.00			
Fulminic acid[b]	C≡N	1.161	3.601[e]	$C(sp^2)$:	11.22	0.62
	N→O	1.207	2.164[e]	$C(sp)$:	11.24	0.68
				$N^{\delta+}$:	21.30	5.64
Benzonitrile N-oxide[c]	(C–C) ring	1.397	2.370	$O^{\delta-}$:	26.45	6.63
	C–C	1.435	2.273[d]	δ	= 0.5 (see text)	
	C≡N	1.147	3.601[e]	$\gamma_{CC}(sp^2)$	= 10.60	
	N–O	1.249	2.164[e]	$\gamma_{CC}(sp)$	= 10.56	
	<C≡N→O	180°		γ_{NN}	= 15.66	
	<C–C≡N	180°		γ_{OO}	= 19.82	

[a] See Ref. [1] to [5] in the text and other papers given therein on the molecular structures.

[b] Winnewisser, M., and H. K. Bodenseh: Z. Naturforsch. A **22**, 1724 (1967).

[c] See Ref. [17a] in the text.

[d] Estimated from the equations: $R_{CC} = 1.517 - 0.180P$, $R_{CN} = 1.451 - 0.180P$, $\beta_{CC} = -0.51P - 2.04$, and $\beta_{CN} = -0.53P - 2.24$, where P is the π bond order. Nishimoto, K., and L. S. Forster: Theoret. chim. Acta (Berl.) **4**, 155 (1966).

[e] See text for the derivation.

[f] See footnote 5 and Ref. [1] to [6] in text.

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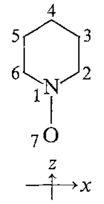
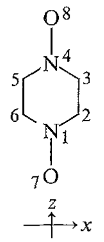
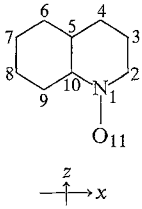
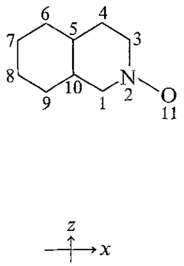
[5] Equations describing the I_p and E_A of nitrogen and oxygen atoms in an N-oxide dative bond are:

$$I_{p1}^{O} = E_A^{O}(s^2x^2y^{\delta}z^2 \rightarrow s^2x^2y^{\delta}z) = 14.89 - 20.25\delta + 7.47\delta^2,$$
$$I_{p2}^{O} = I_p^{O}(s^2x^2y^{\delta}z \rightarrow s^2x^2y^{\delta}) = 37.93 - 25.04\delta + 4.17\delta^2,$$
$$E_A^{N}(t_1t_2t_3^{2-\delta}z \rightarrow t_1t_2t_3^{2-\delta}z^2) = 4.315\delta^2 + 6.73\delta + 1.20,$$
$$I_p^{N}(t_1t_2t_3^{2-\delta}z \rightarrow t_1t_2t_3^{2-\delta}) = 1.555\delta^2 + 12.81\delta + 14.51.$$

Here, $\delta = 0.7$ is adopted [6] except for the case of nitrile N-oxide group where $\delta = 0.5$.

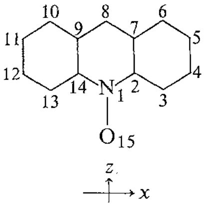
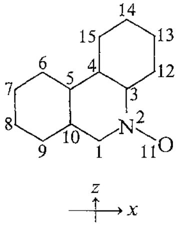
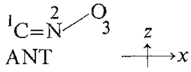
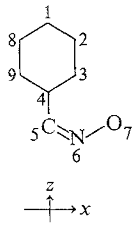
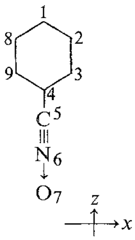
Table 3. *Calculated transition energies, oscillator strengths, and main singly excited configurations (%) under the condition of* $k_{\mathrm{N}^{\delta+}r} = 1/10$. *Observed values are also included*

Compounds	ΔE_{calc}	f_{calc}	Sym	ΔE_{obs} [a]	$f_{\mathrm{obs}}(\varepsilon_{\max})$	Main configurations (%)
	3.83 eV	0.026	$B_1(x)$	3.81 [b]	0.016	86.7 (4→6), 13.0 (3→5)
	4.55	0.489	$A_1(z)$	4.40	0.205	96.2 (4→5)
	5.65	0.338	$B_1(x)$	5.72	0.196	12.6 (4→6), 73.3 (3→5), 13.9 (2→6)
	6.36	0.401	$A_1(z)$	6.60	0.246	81.6 (3→6), 15.1 (2→5)
	6.93	0.004	$A_1(z)$			86.3 (4→7), 13.0 (2→5)
	7.31	0.644	$B_1(x)$			13.6 (3→5), 83.2 (2→6)
	3.22	0.038	$B_{3u}(x)$	~3.4 (*sh*) [b]	(2200)	91.7 (5→7)
	4.21	0.890	$B_{1u}(z)$	3.87	(22000)	95.8 (5→6)
	4.76	forb.	B_{2g}	4.80	(1100)	99.8 (4→7)
	4.99	forb.	A_g			99.7 (4→6)
	5.52	0.458	$B_{3u}(x)$	5.64	(15000)	88.4 (3→6), 8.2 (5→7)
	6.08	forb.	A_g			99.7 (5→8)
	6.45	0.770	$B_{1u}(z)$	6.84	(15000)	89.0 (3→7)
	7.56	0.100	$B_{1u}(z)$			91.0 (4→8)
	3.71	0.083		3.54	(8000)	17.3 (6→7), 57.5 (6→8), 20.5 (4→7)
	3.88	0.394				77.8 (6→7), 15.9 (6→8)
	4.67	0.006		4.53 (*sh*)	(1400)	89.9 (5→7)
	4.94	0.360		4.99	(15000)	16.3 (6→8), 30.3 (5→8), 43.9 (4→7)
	5.04	0.065				82.6 (6→9)
	5.56	0.966		5.55	(33000)	27.9 (5→8), 23.4 (4→7), 12.9 (4→9)
	6.15	0.272		5.96	(11000)	14.7 (6→10), 12.1 (5→8), 35.0 (4→8) 25.5 (3→7)
	6.28	0.177				30.4 (6→10), 11.8 (5→9), 39.4 (4→8) 10.7 (5→8)
	6.56	0.031				32.5 (6→10), 21.5 (5→9), 39.8 (3→7)
	6.75	0.252				54.9 (4→9), 13.1 (3→8), 10.4 (5→8)
	6.84	1.052		6.72	(29000)	56.8 (5→9), 19.5 (4→8), 10.1 (3→7)
	7.39	0.005				11.2 (4→9), 23.1 (3→8), 57.2 (2→7)
	7.62	0.042				19.4 (6→11), 14.0 (5→10), 50.3 (3→8) 12.1 (2→7)
	3.42	0.072		3.20*	(2100)	57.7 (6→7), 23.2 (6→8), 10.7 (5→7)
	4.11	0.224		3.95*	(22000)	35.3 (6→7), 25.3 (6→8), 36.7 (5→7)
	4.75	0.995		4.77	(19000)	44.5 (6→8), 43.8 (5→7)
	4.86	0.086				48.0 (5→8), 27.5 (4→7)
	5.44	0.040		5.19	(9000)	68.0 (6→9), 11.9 (4→7)
	5.78	1.078		5.62	(23000)	41.0 (5→8), 34.2 (4→7), 10.3 (5→9)
	5.94	0.093				16.6 (6→9), 29.9 (5→9), 14.7 (4→7), 16.6 (3→7)
	6.20	0.158				11.3 (5→9), 68.7 (3→7)
	6.49	0.033				83.6 (6→10)
	6.65	0.311		6.57	(10000)	27.0 (5→9), 63.9 (4→8)
	6.75	0.034				19.0 (4→9), 49.6 (3→8)
	7.20	0.019				71.6 (5→10), 20.0 (3→8)
	7.73	0.237				11.3 (5→10), 65.9 (4→9), 13.9 (2→7)

[a] The value at absorption maximum was usually taken as ΔE_{obs} except for the case that when spectra have well resolved vibrational structures the first strong vibrational peak was adopted and marked with asterisk.

[b] There is a possibility that the weak $n-\pi^*$ transition due to N-oxide group is obscured under this $\pi-\pi^*$ transition. See Ref. [8] in text and Table 4.

Table 3 (continued)

Compounds	ΔE_{calc}	f_{calc}	Sym	ΔE_{obs}[a]	$f_{\text{obs}}(\varepsilon_{\max})$	Main configurations (%)
	3.25	0.542	$A_1(z)$	2.73*	(11000)	95.5 (8→9)
	3.56	0.032	$B_1(x)$	3.38 (*sh*)	(900)	71.0 (8→10), 19.4 (6→9)
	4.26	0.011	$A_1(z)$			90.0 (7→9)
	4.30	0.003	$B_1(x)$			75.0 (8→11), 17.3 (6→9)
	4.40	0.142	$B_1(x)$			22.3 (8→11), 35.5 (6→9), 40.0 (5→9)
	4.72	1.630	$B_1(x)$	4.50	(74000)	25.9 (8→10), 25.5 (6→9), 44.8 (5→9)
	5.01	0.004	$A_1(z)$			75.0 (8→12)
	5.18	0.006	$A_1(z)$			37.8 (8→13), 29.8 (4→9), 10.7 (8→12)
	5.78	0.757	$B_1(x)$	5.33	(21000)	96.1 (7→10)
	5.96	0.005	$A_1(z)$			57.9 (8→13), 11.5 (6→10), 11.4 (5→10) 10.6 (4→9)
	6.11	0.045	$A_1(z)$			23.6 (6→10), 14.6 (5→11), 50.5 (4→9)
	6.28	0.233	$A_1(z)$			34.6 (6→10), 19.1 (6→11), 40.1 (5→10)
	6.43	0.042	$B_1(x)$			97.1 (7→11)
	6.89	0.186	$A_1(z)$			64.7 (6→11), 33.2 (5→10)
	7.05	1.114	$A_1(z)$	6.78	(31000)	15.5 (6→10), 76.8 (5→11)
	3.60	0.130		3.22*—3.41	(1200— 4100)	31.8 (8→9), 36.7 (8→10), 24.2 (7→9)
	3.88	0.429		3.62*—3.72	(10000—10000)	61.8 (8→9), 19.3 (8→10), 14.9 (7→9)
	4.48	0.468		4.22*—4.39	(17000—14000)	36.1 (8→10), 50.9 (7→9)
	4.69	0.132		4.74	(18000)	15.6 (8→11), 12.5 (7→10), 61.6 (6→9)
	4.93	0.150		4.96*—5.22	(27000—26000)	35.9 (8→11), 10.2 (7→11), 23.2 (6→9)
	5.08	0.904				30.0 (8→11), 47.8 (7→10)
	5.18	0.221				10.5 (8→11), 22.1 (7→10), 11.6 (7→11) 16.0 (6→10), 10.1 (5→9)
	5.46	0.234				44.7 (8→12), 33.9 (6→10)
	5.54	0.119				10.5 (7→11), 51.1 (5→9)
	5.87	0.183		6.04	(24000)	20.8 (8→12), 17.2 (6→10), 24.4 (5→9), 14.5 (4→9)
	6.04	0.136				11.6 (8→13), 22.8 (7→11), 52.2 (4→9)
	6.18	0.066				12.0 (8→12), 50.6 (8→13), 23.4 (5→10)
	6.42	0.236		6.60	(23000)	13.8 (8→13), 26.3 (7→11), 39.8 (5→10)
	6.50	0.504				11.6 (7→12), 54.3 (6→11), 19.4 (4→10)
 ANT	5.11	0.540		5.10	0.209	98.8 (2→3)
	9.80	0.281				98.8 (1→3)
	4.06	0.497		4.16	(19300)	93.7 (5→6)
	4.30	0.023				32.9 (5→7), 54.5 (4→6)
	5.23	0.097		5.26*	(7400)	24.8 (5→7), 47.0 (3→6), 16.4 (4→6)
	5.33	0.159				32.4 (5→7), 20.4 (5→8), 16.6 (4→6) 24.4 (3→6)
	5.87	0.188		5.98	(17500)	57.5 (5→8), 17.5 (4→7), 19.0 (3→6)
	6.16	0.006				40.1 (4→8), 47.4 (3→7)
	6.53	0.817				73.8 (4→7)
	7.22	1.040				51.4 (4→8), 42.2 (3→7)
	7.53	0.063				19.1 (3→8), 66.0 (2→6)
	4.60	0.001	$B_1(x)$	4.22	0.009	34.3 (5→7), 49.7 (4→6), 12.4 (3→7)
	4.91	1.048	$A_1(z)$	4.77	0.258	97.2 (5→6)
	6.06	0.167	$A_1(z)$	5.77	0.308	40.6 (4→7), 55.6 (3→6)
	6.11	0.503	$B_1(x)$			59.5 (5→7), 40.0 (4→6)
	6.52	0.364	$A_1(z)$	6.35	0.768	34.0 (5→8), 28.8 (4→7), 34.6 (3→6)
	6.92	0.155	$B_1(x)$			15.3 (4→8), 67.9 (3→7), 10.0 (4→6)
	6.97	0.167	$A_1(z)$			58.6 (5→8), 28.5 (4→7)
	7.59	0.459	$B_1(x)$			79.9 (4→8), 19.1 (3→7)

tion some modification of the diagonal term of well-known matrix elements was made to take into account the inductive effect of the $N^{\delta+}$ atom of the N-oxide group at carbon atoms. The use of the mutual relation [2, 21] between HMO and P.P.P. calculations may allow the following expression for the diagonal term.

$$F_{rr}^{n+1} = F_{rr}^{n} + \sum_{s \neq r} k_{sr} [F_{ss}^{n} - C_s] . \tag{1}$$

F_{rr}^{n+1} is the diagonal element for $(n+1)$th iterative calculation; here $F_{rr} = -I_p^r + (1/2) P_{rr} \cdot \gamma_{rr} + \sum_{s \neq r} (P_{ss} - n_s) \cdot \gamma_{sr}$. The off-diagonal element is $F_{rs} = \beta_{rs} - (1/2) P_{rs} \cdot \gamma_{rs}$. Each notation is the one used commonly. k_{sr} is the inductive effect parameter, and generally $k_{sr} \neq k_{rs}$: s means the atom which brings about the inductive effect ($N^{\delta+}$ atom for the present case) and r represents the one which suffers the inductive effect caused by the atom (carbon atoms for the present case). C_s corresponds to the F value taken as standard, and the value at each carbon atom in benzene ring is adopted: $C_s = -5.92$ eV (constant). First, this kind of calculation was tested for ANT and pyridine N-oxide under various conditions. Especially, in the case of ANT there is only one $\pi - \pi^*$ band in a near UV region, moreover it was already verified [4] that the electronic and molecular structures of nitrone are quite similar to those of heterocyclicamine N-oxides such as pyridine N-oxide etc. Accordingly, ANT as well as pyridine N-oxide is a valuable compound to get the best integral values and to check how these calculations can explain the experimental results of aromatic amine N-oxides. Using the best set of the integral values thus determined the electronic structures of the other N-oxide compounds were calculated to compare those with experimental results reported hitherto. In Table 2 are given valence state I_p and E_A, one center repulsion integral γ_{rr}, core resonance integral β_{rs}, bond length R_{rs}, and bond angle of some bonds appearing in the present calculation with the references cited here. Two center repulsion integrals, γ_{rs}, were obtained by the Mataga-Nishimoto approximation [2, 22].

The parameters adjusted are β_{NO} and the inductive effect parameter k_{sr} due to the $N^{\delta+}$ atom. For the case of pyridine N-oxide and ANT[6] (model compounds) the SCF-MO-CI calculations have been done using the values in a reasonable range: β_{NO} is 1.50, 2.00, and 2.50 eV, and k_{sr} is 0, $(1/10)^n$, $(1/5)^n$, and $(1/3)^n$. The calculated values of transition energy[7], dipole moment[8] etc. are thus compared with the observed ones [1—5]. The best sets of the parameters were found to be $\beta_{NO} = 2.00$ eV except for nitrile N-oxides and $k_{sr} = (1/10)^n$ or $(1/5)^n$ with $n \leqq 3$. The values of β_{NO}, β_{CN}, I_p, and E_A of the $-C{\equiv}N{\rightarrow}O$ group were evaluated using the ones of the best parameters just mentioned above and also by taking into account the previous MO calculation results [5] which indicate a π charge displacement of about 0.2 from the oxygen to the nitrogen in the $\bar{\pi}$ system, no contribution from which appears for ANT, pyridine N-oxide etc. The above

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[6] The effect of CH_3 and cyclohexyl groups on the spectra was neglected.

[7] Configuration interactions involved in the calculations are, for example, within 10 eV for pyridine N-oxide but 7 eV for acridine N-oxide.

[8] Dipole moment was calculated by the same method as that in the foregoing papers [23].

charge displacement in the $\bar{\pi}$ system has been taken in the calculation of I_p and E_A of the nitrile N-oxide group by means of Kobinata and Nagakura's procedure [6] [5]. In turn, β_{NO} and β_{CN} of the nitrile N-oxide group were put as [$2.00 \cdot S$(at $R_{NO} = 1.21$ Å)$/S(R_{NO} = 1.28)$] and [$2.66 \cdot S(R_{C\equiv N} = 1.16)/S(R_{C=N} = 1.31)$], respectively, S being the overlap integral. $R_{NO} = 1.28$ Å is for the nitrone and pyridine N-oxide, and $R_{CN} = 1.31$ Å is for nitrone (see Table 2). Thus, the SCF-MO-CI calculation of various N-oxide compounds has been carried out using the parameter values discussed above and shown in Table 2. The results are included in Table 3 with the experimental ones reported hitherto [1—5] for the purpose of comparison.

Intensity Calculation of the *n*—*π** Transition

If the $n-\pi^*$ transition pertinent to the N-oxide group occurs, there is a problem how the intensity of this transition is, since the intensity of band I of pyridine N-oxide is too strong to assign it to a $n-\pi^*$ transition. This is one of the reasons why Sidman [24], Murrell [15] and others [7, 25] doubt the $n-\pi^*$ assignment given by Ito *et al.* [9]. The calculation was made on ANT, pyridine N-oxide, pyrazine di-N-oxide, and their corresponding amines using the π^* orbitals obtained here for the N-oxides and cited from Ref. (22] for the corresponding amines. As to the non-bonding orbitals of the oxygen atom of the N-oxide group we assumed two cases: there is no hybridization or sp^2 hybridization for the oxygen atom. The lone pair orbital of the amines of pyridine or AI types was, however, supposed always to be in the sp^2 hybridization. Here it should be noted that the assumption of a sp^2 hybridization of the oxygen atom of the N-oxide group is only for the purpose of calculation itself in order to see which value of the intensity one can get, because the oxygen atom spectroscopic n orbitals seem to be almost free from hybridization, as was already discussed in the previous papers [5, 26]. The actual calculation is similar to that of Goodman's paper [19a]. The transition dipole [26] length Q of the $n-\pi^*$ transition is now given by $Q = \sqrt{2}\,\langle\phi_n|\boldsymbol{r}|\psi_{i\pi^*}\rangle = \sqrt{2}\sum_j C_{ij}\langle\phi_n|\boldsymbol{r}|\phi_j^\pi\rangle$, where Slater atomic orbitals are employed. Q is sometimes zero due to the nature of the orbital symmetry entering into a $n-\pi^*$ transition. It is convenient to write the ϕ_n^{2p} as $\phi_n^{2p} = \phi_n^{2p\sigma}\cdot\cos\theta + \phi_n^{2p\eta}\cdot\sin\theta$: $\phi_n^{2p\sigma}$ and $\phi_n^{2p\eta}$ are each component parallel and perpendicular, in the molecular plane, to the axis connecting atoms $n(\phi_n)$ and $j(\phi_j^\pi)$, respectively. The analytical form of the ϕ_n in sp^2 hybridization is easily written by the standard procedure [27]. When there are two ϕ_n orbitals in a molecule just like pyrazine, the linear combination of ϕ_{n1} and ϕ_{n2} is taken to construct the $\phi_{n+} = 1/\sqrt{2}(\phi_{n1}+\phi_{n2})$ and $\phi_{n-} = 1/\sqrt{2}(\phi_{n1}-\phi_{n2})$. The selection rule and the intensity of $n-\pi^*$ transitions are then determined and calculated using the ϕ_{n+} and ϕ_{n-} orbitals. Analytical forms in atomic units of the integrals necessary to do the calculation are as follows: here the axis along the $2p\pi$ orbital (perpendicular to molecular plane) is put as y axis (see Table 3) [9].

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[9] Note that $\langle\phi_n^{2p\eta}|\boldsymbol{y}|\phi_j^{2p\pi}\rangle = 0$. The equations previously given by Kubota, Yamakawa, and Tanaka [26] for the integrals, $\langle\phi_n^{2p\sigma}|\boldsymbol{y}|\phi_j^{2p\pi}\rangle$ and $\langle\phi_n^{2s}|\boldsymbol{y}|\phi_j^{2p\pi}\rangle$, where the Mulliken approximation $\mu = 1/2(\mu_n + \mu_j)$ was adopted, gave also almost the same values as those calculated here.

$$\langle\phi_n^{2p\sigma}|y|\phi_j^{2p\pi}\rangle = \frac{(4\mu_n\cdot\mu_j)^{5/2}R^6}{2048}[A_5(B_1-B_3)+A_3(B_5-B_1)+A_1(B_3-B_5)+B_4(A_2-A_0)+B_2(A_0-A_4)+B_0(A_4-A_2)]\,, \tag{2}$$

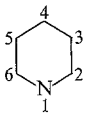
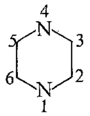
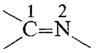
$$\langle\phi_n^{2s}|y|\phi_j^{2p\pi}\rangle = \frac{\sqrt{3}(4\mu_n\mu_j)^{5/2}R^6}{6144}[A_5(B_0-B_2)+A_3(B_4-B_0)+A_1(B_2-B_4)+B_5(A_2-A_0)+B_3(A_0-A_4)+B_1(A_4-A_2)]\,, \tag{3}$$

$$\langle\phi_n^{2s}|y|\phi_n^{2p\pi}\rangle = \frac{5}{2\sqrt{3}}\,\frac{1}{\mu_n}\,. \tag{4}$$

The calculation of A and B functions appearing in the Eqs. (2) and (3) is performed directly by the well-known method [28] or using the table [28]. Thus, the intensity is obtained from the equation, $f_{\text{calc}} = 1.085\times 10^{-5}\cdot\tilde{\nu}_{\max}\cdot Q^2\cdot G$ ($G=1$ for the present case), and by adopting the molecular geometry and coordinates given in Tables 2 and 3, and the π MO's obtained here. The calculated results are listed in Table 4.

Table 4. *Calculated oscillator strengths for the $n-\pi^*$ transition of amine groups, and for the assumed $n-\pi^*$ transition of* N-oxide *groups. The values of each integral appearing in this calculation are also given*

Compounds	$\nu_{\max}$(*K.K.*)	$f_{\text{calc}}(sp^2)\times 10^3$		$f_{\text{calc}}(p)\times 10^5$		$f_{\text{obs}}\times 10^3$
Pyridine	37.0[a]	8.63	$B_2(y)$	—		3.0[a]
Pyrazine	30.5[a]	15.97	$B_{2u}(y)$	—		10.4[a]
AI	40.7	13.84	$A''(y)$	—		2.3
Pyridine NO	(30.7)[b]	5.57	$B_2(y)$	4.79	$B_2(y)$	—
Pyrazine di NO	(27.25)[b]	10.47	$B_{2u}(y)$	9.26	$B_{2u}(y)$	—
ANT	(35.7)[b]	8.73	$A''(y)$	5.74	$A''(y)$	—

Compound	Bond	R (Å)	$\langle\phi_n^{2s}|y|\phi_j^{2p\pi}\rangle$	$\langle\phi_n^{2p\sigma}|y|\phi_j^{2p\pi}\rangle$
	1—1	0	0.740 au	0 au
	1—2	1.340	0.249	0.238
	1—3	2.413	0.034	0.040
	1—4	2.810	0.014	0.018
	1—2	1.334	0.252	0.239
	1—3	2.377	0.036	0.043
	1—4	2.810	0.008	0.011
	1—2	1.30	0.265	0.249
Pyridine NO	7—7	0	0.6706	0
	7—1	1.28	0.1670	0.1808
	7—2	2.32	0.0289	0.0332
	7—3	3.58	0.0013	0.0017
	7—4	4.07	0.0004	0.0005
Pyrazine di NO	7—4	4.07	0.0001	0.0001
ANT	3—1	2.24	0.0389	0.0449

[a] Mason, S. F.: J. chem. Soc. (London) **1959**, 1240.

[b] Assumed wave number for the N-oxide groups. See also Refs. [2, 8, 9].

Discussions

Comparison of Observed UV *Spectra with Calculated Energy Levels*

First, the comparison will be made with the observed spectra of benzylidene methylamine N-oxide (BMANO) [4][10], 2,6-dimethylbenzonitrile N-oxide (BNO) [5], and ANT. The absorption bands of BMANO and BNO were already assigned [4, 5] from the experimental evidences, and on the basis of the calculation of the spectroscopic β method presented by Baba [29] and Goodman [30], where partial configuration interaction was included to get the ^1L_b and ^1B_b bands. The inspection of Table 3 shows that the agreement between calculated and observed values of BMANO, BNO, and ANT is very good, and that the band assignment made previously [4, 5] coincides with the one obtained here for the near UV spectra of the above compounds except that the observed bands at ~216 mμ (BNO) and ~233 mμ (BMANO) consist of the ^1B_b band and the other moderately weak band ($^1A_1$ for BNO); the latter band went to much higher energy in the case of the previous calculations [4, 5] because no configuration interaction was adopted for the $^1A_1$ transition. Note that the spectroscopic facts that the weak ^1L_b band may be hidden under the strong ^1L_a band (~298 mμ and ~260 mμ for BMANO and BNO, respectively) for BMANO but appears as shoulder at the longer wavelength side of the ^1L_a band in the case of BNO, are well explained from the present calculation as well as the previous one.

Next, attention should be directed to the spectra of the N-oxides of acridine, phenanthridine, quinoline, isoquinoline, pyrazine, and pyridine (basic hetero-

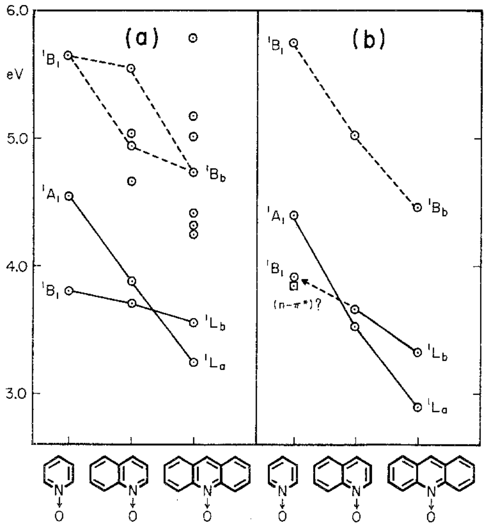


Fig. 4 a and b. The correlation curves of transition energies among the N-oxides of pyridine, quinoline, and acridine. a: the mutual relation among main transition energies obtained from the present calculation. b: experimentally obtained correlation curves (see Refs. [1–3] in text)

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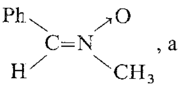
[10] The structure is  $\mathrm{Ph(H)C{=}N(\rightarrow O)CH_3}$, a typical aromatic nitrone.

cyclic amine N-oxides). The absorption bands of these N-oxides and others were first assigned by Kubota [1, 2, 3] based on the systematic study of the electronic spectra. These results are shown in Fig. 4b. It is worthwhile to note that the ^1L_b and ^1L_a bands of basic heterocyclic amine N-oxides show generally the following spectral behaviors. (1) The absorption spectra of proton addition species ($\geqslant N^+$–OH) are quite similar to those of the species ($\geqslant N^+$–H) of the corresponding N-heterocyclic compounds [1, 3]. The absorption bands of the latter were already assigned reasonably by Zanker *et al.* [31], so that the assignment of the former species was certainly made based on the spectral analogy of the above two species. (2) When the protonated species ($\geqslant N^+$–OH) become free species ($\geqslant N \rightarrow O$) in aqueous solution, the intensity of ^1L_a band increases quite strongly, but that of the ^1L_b band decreases strongly (for the N-oxides of acridine, phenanthridine, isoquinoline) or there is almost no change (this is the case for quinoline N-oxide, but note that the ^1L_a and ^1L_b bands for this compound are strongly overlapped to each other)[11]. This property seems to be similar to the corresponding behavior (change from $\geqslant N^+$–H to $\geqslant N$ species) of ^1L_b and ^1L_a bands of basic N-heterocyclic compounds [31]. (3) Large red shifts of the bands occur due to the solvent change from water to *n*-heptane, and well resolved vibrational structures appear in hydrocarbon solvents, particularly for isoquinoline N-oxide and acridine N-oxide (see later discussion). On the other hand, there is an exceptional case for the before mentioned general properties: the strong ~281 mμ band of pyridine N-oxide in *n*-heptane behaves as though the band is ^1L_a viewed from the above property 2. This is the one of reasons why the 281 mμ band of pyridine N-oxide was not assigned to be of ^1L_b character [3]. In other words we can say that the band characters of basic N-heterocyclic compounds will be more or less kept even with the N-oxidation for the compounds having more than 2 rings, since the modification of the total π MO's is not so severe with the N-oxidation. However, the N-oxidation affects the MO's of pyridine (monocyclic azine) quite strongly, so that the band analogy between pyridine and pyridine N-oxide is no longer kept so well. In addition, referring to the substituent effect on the UV spectra of quinoline, isoquinoline, acridine, and their N-oxides [32], and also based on the results of HMO and ASMO-CI calculations [2, 23] the absorption bands of the N-oxides were previously assigned as it is shown in Fig. 4b. Now, the correlation curve corresponding to the Fig. 4b is drawn in Fig. 4a on the ground of the present SCF-MO-CI calculation. As one can see from Table 3 and Figs. 4a, b, the band assignment of various heterocyclic N-oxides in the present study seems to be in agreement with the one given in the previous reports, and the transition energies and the intensities assessed here agree almost with the observed ones, although the agreement is not so sufficient in the strict sense.

However, there arises a problem for the assignment of band I of pyridine N-oxide and of the moderately weak bands at about 367 mμ of pyrazine di-N-oxide.

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[11] Such notations as ^1L_b, ^1L_a, etc. have no longer such a strict meaning as it was originally applied to unsaturated hydrocarbons, for the case of the present, especially, low symmetry N-oxides. Actually it was obtained, that the transition moments of the ^1L_b and ^1L_a bands of, for example, quinoline N-oxide and isoquinoline N-oxide are not so largely different from each other. This theoretical result is comparable to that of a polarized emission study of some N-oxides [25] in which the presence of a $n - \pi^*$ transition was not indicated.

In the foregoing papers [2] the above bands were attributed to the $n-\pi^*$ transition arising from the oxygen lone pair orbital on reference to Ito's assignment [9]. And, the intramolecular charge transfer calculation [2] indicated that the $^1L_b(^1B_1)$ band of pyridine N-oxide would be hidden under the $^1A_1$ band ($\sim$281 mμ) and the one of pyrazine di-N-oxide will take place in the shorter wavelength region of the $^1B_{1u}$ band ($\sim$324 mμ, CT character). According to the present calculation the bands attributed to the $n-\pi^*$ transition in the aforesaid discussions may be reassigned to be the ones having a $^1B_1$ character as Fig. 4a shows. This assignment would reproduce so well the experimentally obtained correlation curves (see Fig. 4b), and is in agreement with the one given by Evleth [7]. Therefore, the $n-\pi^*$ transition of the N-oxide group may be covered more or less with the $^1B_1$ band. See later section on the detailed discussion.

Characteristics[12] *of the π MO's and Molecular Diagrams*

It seems to be valuable to note the characteristics of the SCF-MO's obtained, which are quite close to the HMO derived in the previous studies with the parameter values, for example, $\alpha_{O^{\delta-}}=\alpha+0.8\beta$, $\alpha_{N^{\delta+}}=\alpha+1.6\beta$, $\beta_{NO}=1\cdot\beta$, Ind. $=1.6\times(1/3)^n$ for heterocyclic amine N-oxides. The most important feature is in the highest occupied (HO) and the lowest vacant (LV) MO's, that is, the coefficient of the oxygen (of N→O bond) $2p\pi$ atomic orbital is very large in HOMO but is quite small in LVMO (see Fig. 5). The $^1A_1$ band at about 281 mμ of pyridine N-oxide as well as the ^1L_a bands of the other N-oxides is mainly contributed from the configuration with a one-electron transition from the HOMO to the LVMO, so that those spectra are of the nature of an intramolecular charge transfer band from the oxygen to the π residue (pyridine ring for pyridine N-oxide). The above characteristic of the LVMO was well confirmed by Kubota *et al.* from the systematic ESR study of the anion radicals of many heterocyclic amine

Table 5. *Comparison of the calculated dipole moments with the observed ones*

	μ_{calc}	μ_{obs}
Pyridine NO	4.18 D	4.18[a] D
Quinoline NO	3.93	4.07[b]
Isoquinoline NO	4.59	4.47[b]
Acridine NO	3.72	3.90[c]
Phenanthridine NO	4.09	—
ANT	3.19	3.82[d]
Benzylidene methyl amine NO	2.88	3.49[e]
Fulminic acid	3.18	3.06[f]
Benzonitrile NO	3.52	4.00[g]

[a] Sharpe, A. N., and S. Walker: J. chem. Soc. (London) **1961**, 2974.
[b] Tsoucaris, G.: J. Chim. physique **58**, 619 (1961).
[c] Acheson, R. M., B. Adcock, G. M. Glover, and L. E. Sutton: J. chem. Soc. (London) **1960**, 3367.
[d] Our measurement.
[e] See Ref. [4b] in the text.
[f] Winnewisser, M., and H. K. Bodenseh: Z. Naturforsch. **22A**, 1724 (1967).
[g] Speroni, G.: Ricerca Sci. **27**, 1199 (1957).

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[12] To save the space each MO is eliminated from this paper. The MO's will be distributed with the reprint requested.

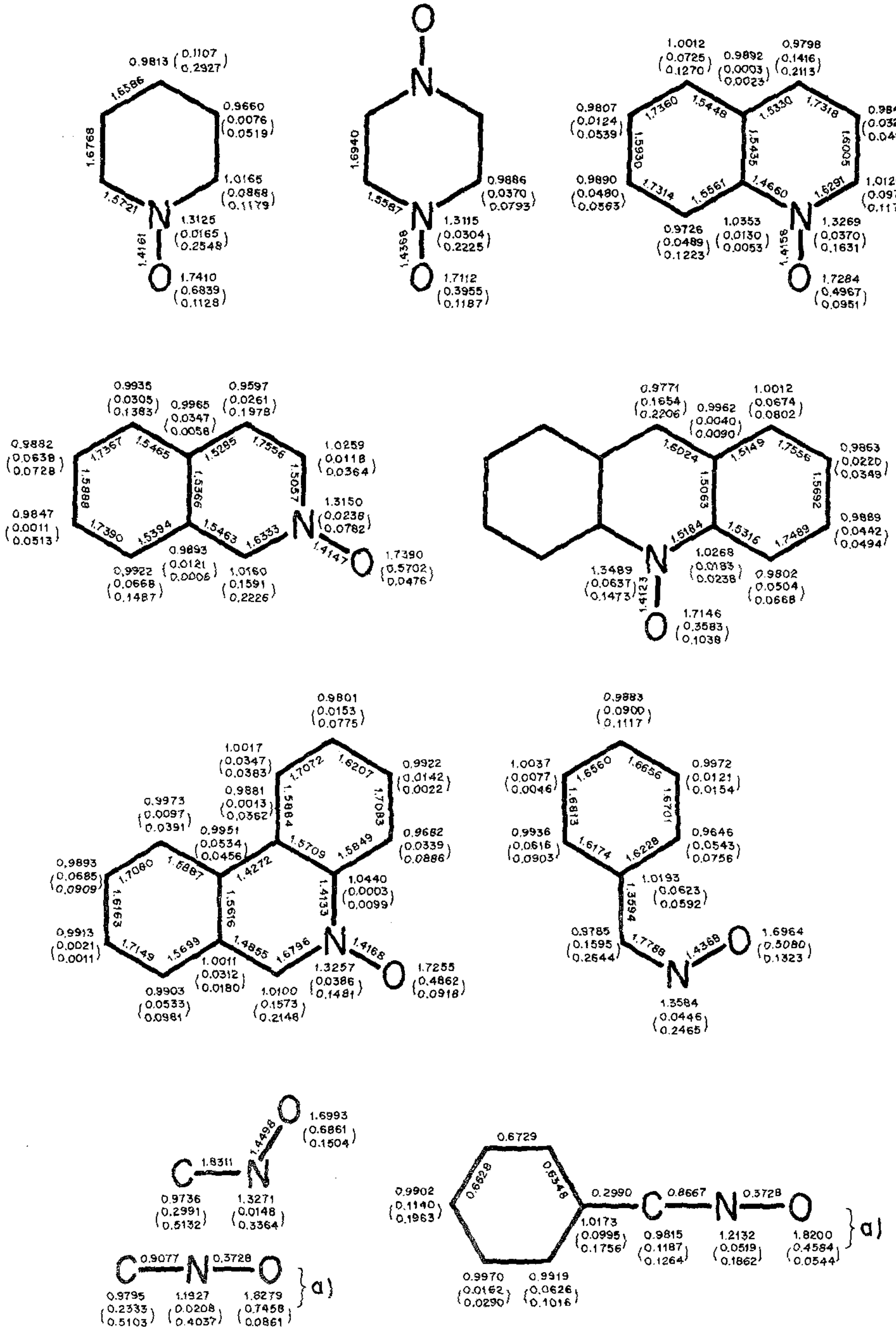

Fig. 5. Molecular diagrams of various aromatic amine N-oxides calculated here using the inductive parameter $k_{N^{\delta+},r} = 1/10$. The values written in parentheses are the orbital charge densities in the highest occupied MO (upper number) and the lowest vacant MO (under number). a) The values concerning the $\bar{\pi}$ system have been omitted, which are the same as those of the C–N–O π system

N-oxides [11]. The molecular diagrams of the N-oxides studied are shown in Fig. 5, in which the values written in parentheses are the orbital charge densities in HOMO (upper number) and LVMO (lower number)[13]. Based on these molecular diagrams dipole moments have been calculated, and compared with the experimental ones. The results are given in Table 5. It is now understood that the calculated dipole moments seem to be in agreement with the experimental ones within the accuracy of the experiments and also within the approximation (the separation of σ and π moments, etc.) of the model adopted for the calculation. The electronic state of the ground state of aromatic N-oxides is regarded to be well explained by the present SCF-MO calculation results.

$n-\pi^*$ *Transition on the Conjugated Tertiaryamine* N-*Oxides*

As was mentioned in the introduction of this paper there may be doubt for assigning the band I of pyridine N-oxide to a $n-\pi^*$ transition. The experimental and theoretical results carried out in this study may suggest the conclusion that the band I may be due to the ${}^1B_1$ $\pi-\pi^*$ transition which overlaps with a weak $n-\pi^*$ transition[3] if the $n-\pi^*$ transition arises in this wavelength region as it was shown by Bene and Jaffé's calculation [8]. As the reason we can enumerate the following facts. (1) The intensity is very large to attribute it to a $n-\pi^*$ transition regardless of taking into account the hybridization of the oxygen lone pair orbitals, as Table 4 indicates. Here note that the calculated intensity of the $n-\pi^*$ transition of pyridine type (sp^2 hybridization) comes out to be about 1.5—5.9 times larger than the observed values[14], depending on the substances used. In other words, calculated values on the ground of the present treatment overestimate the observed ones. Despite this fact the calculated values of pyridine N-oxide become considerably smaller than the observed ones. Also it should be remembered that the spectroscopic non-bonding orbitals of the oxygen atom of the N→O bond are almost free from the hybridization[14]. Keeping in mind these arguments the conclusion has been drawn that the band I of pyridine N-oxide is too large for assigning it to a $n-\pi^*$ transition. Moreover, since these N-oxide compounds are good plane molecules, the mixing, as it was firstly observed by Cookson and Wariyar [34], of $n-\pi^*$ and $\pi-\pi^*$ transitions may be very small. Thus, the intensification of the $n-\pi^*$ transition due to this kind of factor would be very small. Of course, there is vibronic coupling due to the Herzberg-Teller effect, which causes the interaction of $n-\pi^*$ electronic state with vibrational state. Some vibronic states of this kind may bring about the mixing of $n-\pi^*$ and $\pi-\pi^*$

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[13] The order of orbital charge densities at each atom in LVMO of heterocyclic amine N-oxides (see Fig. 5) agrees completely with the one of calculated spin densities (MHMO method [11]) of the corresponding anion radicals [11].

[14] It is necessary to point out that the assumed lone pair sp^2 orbital is an extreme case because the lone pair is not completely localized at a specified atom in a molecule as theoretical calculations and experiments support this result [33]. The delocalization of lone pair electrons results in the decrease of the s-character in the hybridization. The one center integral (Eq. 4) involving $2s$ orbital contributes mainly to the $n-\pi^*$ intensity, so that the above delocalization decreases the calculated f value of the $n-\pi^*$ transition. Also note that the observed weak ($n-\pi^*$) transition of alkylnitrite etc. has the ε values less than 100. In other words, the hybridization in the oxygen lone pair orbitals is almost negligible.

states. The intensification of the $n-\pi^*$ transition due to this Herzberg-Teller effect seems to be smaller than that caused by Cookson's effect mentioned above [35]. (2) The band I undergoes a red shift by replacing the ring hydrogen atom with an electron donating substituent (see Fig. 2) and also shows a clear absorption band even in water solvent, especially for the case of a meta-substituent (see Fig. 3). In addition, that the orbital energy of pyridine N-oxide LVMO is pushed up by the interaction with an electron donating substituent was verified experimentally by the study of non-aqueous polarography [11]. This fact may not lead to the red shift of the $n-\pi^*$ transition by introducing the substituent. (3) It is reasonably expected from the correlation curves shown in Figs. 4a, b that the $^1B_1$ band exists in the longer wavelength region of the $^1A_1$ ($\sim$281 mμ) strong band of pyridine N-oxide. (4) ANT, the most simple chromophore of the conjugated N-oxides, does not show a clear $n-\pi^*$ band at the longer wavelength side of the strong $\pi-\pi^*$ band in spite of the appearance of the $n-\pi^*$ band in the case of the compound AI (see Fig. 1). Also Murrell pointed out the same fact as the above [15]. (5) The fact that the band I of pyridine N-oxide exhibits resolved vibrational structures is attributed to a reason to assign it to a $n-\pi^*$ transition [36]. From a viewpoint of vibronic interaction, however, it is understood that if the first and the second bands are suitably separated the first band may show resolved vribrational structures [37]. In fact, the moderately weak $\pi-\pi^*$ band (^1L_b) occuring in the longest wavelength region of isoquinoline N-oxide has fine structures in *n*-heptane, but the corresponding bands of quinoline N-oxide and pyrazine di N-oxide have not. Moreover, it is thought to be necessary[15] that the vibrational analyses of band I of the pyridine N-oxide vapor spectrum should be reexamined because some assignments of fundamental vibrations of pyridine N-oxide were altered [1] from the ones given first by Ito and Hata [9][16].

On the Spectrum of BCNO

It is noted that the spectrum and the band positions of BCNO are very different from those of ANT in spite of the simple chromophores similar to each other, namely $C{=}N(CH_3){\rightarrow}O$ and $C{\equiv}N{\rightarrow}O$. The interaction between π and $\bar{\pi}$ systems in addition to that among π electrons within π or $\bar{\pi}$ system itself of the $C{\equiv}N{\rightarrow}O$ group may produce the electronic states as $\pi \cdot \pi = \Sigma^+ + \Sigma^- + \Delta$ under $C_{\infty v}$ symmetry. The transition $\Sigma^+ \rightarrow \Sigma^+$ is allowed with the transition moment along the molecular axis, but $\Sigma^+ \rightarrow \Sigma^-$ and $\Sigma^+ \rightarrow \Delta$ are both forbidden. Also it is said that the spectral pattern of BCNO shown in Fig. 1b is quite similar to that [38] of nitrous oxide $N{\equiv}N{\rightarrow}O$ except that the spectrum of the latter arises in a shorter wavelength region than in the former. Referring to the spectrum of nitrous oxide the strong 172 mμ band (band III) of BCNO would be assigned to the allowed $\Sigma^+ \rightarrow \Sigma^+$ transition. Here Σ^+ and Δ states may be produced by the mutual interaction of two locally excited states, $\langle {}^1\chi_{2\rightarrow 3} | \mathscr{H} | {}^1\chi_{\bar{2}\rightarrow\bar{3}} \rangle$; ${}^1\chi_{2\rightarrow 3}({}^1\chi_{\bar{2}\rightarrow\bar{3}})$ stands for the singlet excited configuration from the $\psi_2(\psi_{\bar{2}})$ molecular orbital to $\psi_3(\psi_{\bar{3}})$ of the $\pi(\bar{\pi})$ system of BCNO. In addition there is an interaction between the

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[15] Sidman [24] discussed this problem also.

[16] For example, the $N \rightarrow O$ stretching vibration (A_1) of pyridine N-oxide appears at 1266 cm^{-1} (CCl_4) [1] which differs considerably from that (832 cm^{-1}) assigned by them [9].

charge transfer configurations $^1\chi_{2\to\bar{3}}$ and $^1\chi_{\bar{2}\to 3}$, producing the Δ and Σ^- states. The transition to these states might have a weak intensity. The weak bands I and II (see Fig. 1b) of BCNO seem to be due to the transition to the above Σ^- and Δ states, although it is not sure which band corresponds to which transition at the present step. All of the discussions made above are based on the π-electron approximation alone. In the case of a small π electron system like $C{\equiv}N{\to}O$, so called $\pi-\sigma$ interaction would comparatively affect the band positions of the spectra, since the spectra appear in quite shorter wavelength regions. Quantitative discussions, therefore, have not made here.

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Note Added in Proof: After the manuscript of this paper had been sent to the Theoretica Chimica Acta, we learned the paper by K. Seibold, G. Wagnière, and H. Labhart; Helv. chim. Acta **52**, 789 (1969); in which they studied the effect of an electric field on the UV spectrum of pyridine N-oxide and determined experimentally that the 282 mμ band in *n*-heptane is molecular-axis polarized and a $^1A_1 \to {}^1A_1$ $\pi-\pi^*$ band. Their results agree with the theoretical and experimental conclusions reported in this paper.

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