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Electronic Properties of N-Heteroaromatics. XLVII.[1] Absorption Spectra and Electronic Structure of Some Quinoline 1-Oxides of Biological Interest

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Near-ultraviolet and visible absorption spectra of quinoline 1-oxides in aqueous and nonaqueous solutions were measured, with emphasis on 10 kinds of compounds known to be carcinogenic or non-carcinogenic, and the absorption bands were classified according to Platt's nomenclature system. Absorption spectra of 4-nitroquinoline 1-oxide and its derivatives in nonaqueous solution were separately assigned to the ^1L_b and ^1L_a bands, in addition to ^1B_b band. Molecular orbitals of quinoline 1-oxides were calculated by the simple LCAO-MO method. From the energy difference between molecular orbitals, each of the absorption bands was assigned to the electronic transition between specified molecular orbitals. The following relationship between band assignment and electronic transition was found for 4-nitroquinoline 1-oxide and its 2-methyl, 6-chloro, 6-carboxy, and 6-nitro derivatives: ^1L_b band, $\phi_m \rightarrow \phi_{m+1}$; ^1L_a band, $\phi_{m-1} \rightarrow \phi_{m+1}$; ^1B_b band, $\phi_m \rightarrow \phi_{m+2}$; ^1B_a band (for 6-nitro derivative), $\phi_{m-1} \rightarrow \phi_{m+2}$.

Since Nakahara, Fukuoka, and Sugimura[3] revealed a potent carcinogenic activity in 4-nitroquinoline 1-oxide, synthesized for the first time by Ochiai and Ishikawa,[4] biological activity of many of the quinoline 1-oxide derivatives has been examined. There have been a considerable number of theoretical and experimental reports on the absorption spectra of azanaphthalene N-oxides,[5] but that of quinoline 1-oxides of biological interest has not been taken up so much. We have been examining intermolecular interaction between carcinogens of the quinoline 1-oxide system and biopolymers[6] and, as a part of this study, near-ultraviolet and visible absorption spectra of some quinoline 1-oxides known to be carcinogenic or non-carcinogenic were measured, and $\pi \rightarrow \pi^*$ absorption bands were classified according to Platt's nomenclature system. At the same time, molecular orbitals of these compounds were calculated and the absorption bands were assigned to the electronic transition between specified molecular orbitals.

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1) Part XLVI: T. Okano and T. Kano, *Chem. Pharm. Bull.* (Tokyo), **19**, 1293 (1971).

2) Location: *Aobayama Sendai, 980, Japan.*

3) W. Nakahara, F. Fukuoka and T. Sugimura, *Gann*, **48**, 129 (1957).

4) E. Ochiai and M. Ishikawa, *Yakugaku Zasshi*, **63**, 280 (1943).

5) *a*) E. Ochiai and C. Kaneko, *Pharm. Bull.* (Japan), **5**, 56 (1957); *b*) C. Kaneko, *Yakugaku Zasshi*, **79**, 433 (1959); *c*) H. Hirayama and T. Kubota, *ibid.*, **72**, 1025 (1952); *d*) T. Kubota, *Nippon Kagaku Zasshi*, **79**, 930 (1958); *e*) *Idem*, *ibid.*, **80**, 578 (1959); *f*) *Idem*, *Yakugaku Zasshi*, **79**, 388 (1959); *g*) T. Kubota and H. Miyazaki, *Chem. Pharm. Bull.* (Tokyo), **9**, 948 (1961); *h*) T. Okamoto and M. Ito, *ibid.*, **11**, 785 (1963); *i*) T. Okamoto and M. Mochizuki, *ibid.*, **17**, 987 (1969); *j*) N. Kataoka, S. Shibata, A. Imamura, Y. Kawazoe, G. Chihara, and C. Nagata, *ibid.*, **15**, 220 (1967); *k*) M. Ito and N. Hata, *Bull. Chem. Soc. Japan*, **28**, 260 (1955); *l*) N. Hata, *ibid.*, 29, 82 (1956); *m*) T. Kubota and H. Miyazaki, *Nippon Kagaku Zasshi*, **79**, 916 (1958).

6) T. Okano, A. Niitsuma, A. Takadate and K. Uekama, *Gann*, **60**, 97 (1969); T. Okano, K. Uekama and E. Taguchi, *ibid.*, **60**, 295 (1969); T. Okano, S. Takenaka, and Y. Sato, *ibid.*, **60, 307 (1969)**; T. Okano, A. Takadate and T. Kano, *ibid.*, **60**, 557 (1969); T. Okano, A. Takadate and K. Uekama, *ibid.*, **61**, 541 (1970); T. Okano and T. Kano, *Chem. Pharm. Bull.* (Tokyo), **19**, 1293 (1971).

Material and Method

Chemicals——All the quinoline 1-oxides were synthesized in this laboratory according to published literature. The melting point and elemental analytical values of these compounds, and their referential literature (ref. 9) are listed in Table I.

Solvents——Three kinds of solvent were used. Aqueous solution was prepared with buffer solution of pH 7.0 containing 5.0 mM NaCl and 0.5 mM sodium cirtate. Cyclohexane was a commercial spectrograde. In preparing cyclohexane–EtOH mixture, unless otherwise noted 1 volume of 99% EtOH was mixed with 19 volumes of cyclohexane.

Spectrophotometry——All the spectra were recorded with Hitachi spectrophotometer Model EPU-2A. The cell was maintained at 25±0.1° with Haake Ultrathermostat. All the solutions were shielded from light before spectral measurement.

Molecular Orbital Calculations——Approximation was made by the simple LCAO-MO method.

Result and Discussion

Compound number, elemental analytical values and referential literature for syntheses are summarized in Table I. Of these compounds used in this work, carcinogenic activity of all, except IV and XII, has been reported.[7]

Absorption Spectra and Band Assignments

Figures 1 and 2 show the absorption spectra of compounds I to VI in nonaqueous and aqueous solutions, respectively, and Figs. 3 and 4 indicate those of compounds VII to XII

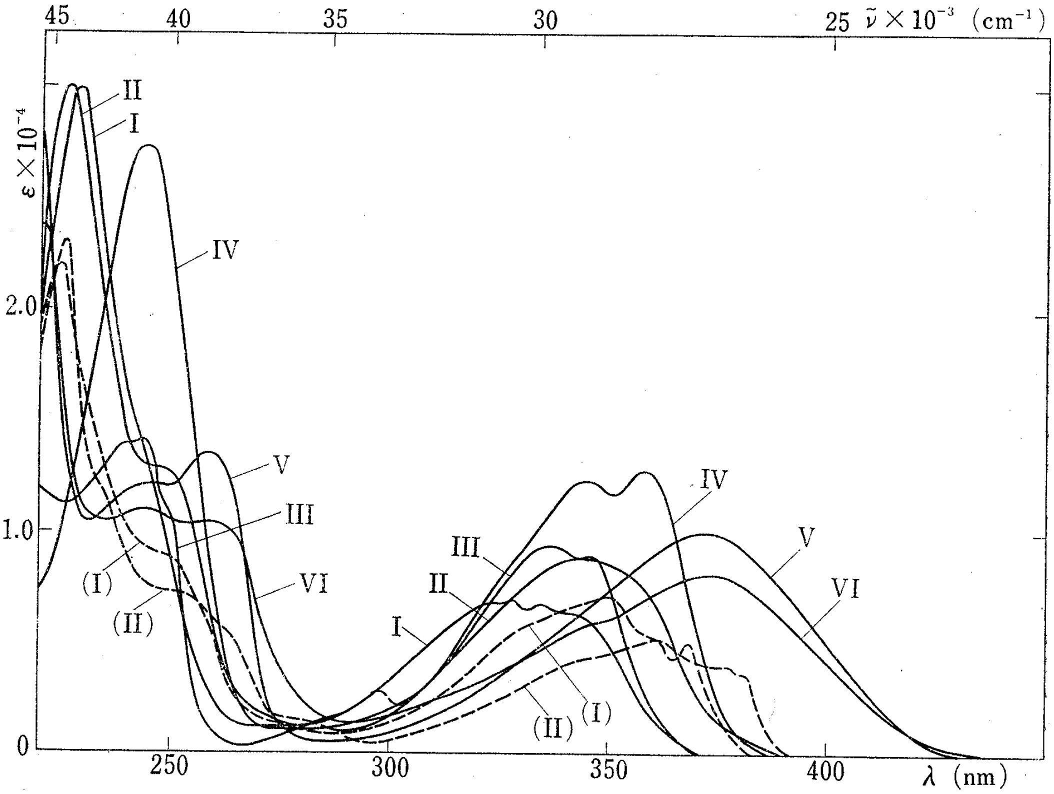

Fig. 1. Electronic Absorption Spectra of 4-Substituted Quinoline 1-Oxides in Nonaqueous Solution

——: cyclohexane–EtOH ------: cyclohexane

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[7] W. Nakahara, *Arzneimittelforschung*, **14**, 842 (1964); Y. Shirasu and A. Ohta, *Gann*, **54**, 221 (1963); W. Nakahara, F. Fukuoka, and T. Sugimura, *ibid.*, **48**, 129 (1957); W. Nakahara and F. Fukuoka, *ibid.*, **49**, 33 (1958); S. Takayama, *ibid.*, **53**, 167 (1962); T. Kawachi, Y. Hirata, and T. Sugimira, *ibid.*, **56**, 415 (1965).

Table I. Compound Number and Analytical Data of Quinoline 1-Oxides Used

Compound	No.	mp (°C)	Formula	Elemental analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Reference for synthesis
Quinoline 1-oxide	I	(bp 192 (6 mmHg))	C_9H_7ON	74.48	4.86	9.65	74.38	5.25	9.62	9*a*)
4-Chloroquinoline 1-oxide	Ⅱ	133—134	C_9H_6ONCl	60.18	3.36	7.80	60.47	3.45	7.86	9*b*)
4-Hydroxyquinoline 1-oxide	Ⅲ	241—242	$C_9H_7O_2N$	67.07	4.38	8.69	66.96	4.93	8.44	9*c*)
4-Carboxyquinoline 1-oxide	IV	258 (decomp.)	$C_{10}H_7O_3N$	63.49	3.73	7.41	63.52	3.85	7.18	9*d*)
4-Aminoquinoline 1-oxide	V	272—273 (decomp.)	$C_9H_8ON_2$	67.48	5.03	17.49	67.32	5.25	16.87	9*e*)
4-Hydroxyaminoquinoline 1-oxide	VI	198—200 (decomp.)	$C_9H_8O_2N_2$	60.36	4.58	15.90	60.80	4.61	16.41	9*f*)
4-Nitroquinoline 1-oxide	Ⅶ	153—154	$C_9H_6O_3N_2$	56.84	3.18	14.73	56.93	3.29	14.64	9*g*)
4-Nitroquinalidine 1-oxide	Ⅷ	158	$C_{10}H_8O_3N_2$	58.82	3.95	13.72	58.95	4.18	13.69	9*h*)
6-Chloro-4-nitroquinoline 1-oxide	IX	193—195	$C_9H_5O_3N_2Cl$	48.12	2.24	12.47	48.08	2.30	12.47	9*b*)
6-Carboxy-4-nitroquinoline 1-oxide	X	241 (decomp.)	$C_{10}H_6O_5N_2$	51.29	2.58	11.98	51.37	2.91	11.27	9*i*)
4,6-Dinitroquinoline 1-oxide	XI	218 (decomp.)	$C_9H_5O_5N_3$	45.97	2.14	17.87	45.63	2.44	17.29	9*b*)
6-Nitroquinoline 1-oxide	Ⅻ	224—225	$C_9H_6O_3N_2$	56.84	3.18	14.73	56.75	3.23	15.03	9*j*)

in nonaqueous and aqueous solutions, respectively. The position and molar extinction coefficient (ε) of the absorption maxima (λ_{max}) of main bands in these spectra are given in Tables II and III. From the size of ε value, it is clear that all the absorption bands have arisen from the $\pi \rightarrow \pi^*$ transition.[8] The band assignments given in the last columns of Tables II and III were derived from the following considerations.

As will be clear from Figs. 1—4, absorption bands of compounds I to XII became broader with increasing polarity of the solvent. This phenomenon was especially marked in the absorption bands of VII and its derivatives in a longer wavelength side. For example (*cf.* Table III), the three bands in the region of 364—402 nm of VII in cyclohexane–EtOH mixture became one broad band around

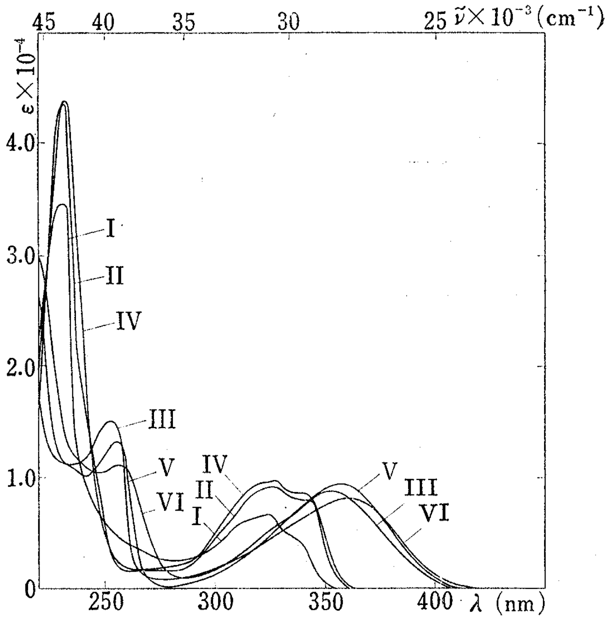

Fig. 2. Electronic Absorption Spectra of 4-Substituted Quinoline 1-Oxides in Aqueous Solution, pH 7.0

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8) T. Kubota, *Yakugaku Zasshi*, **74**, 831 (1954).

9) *a*) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953); *b*) T. Okamoto, *Yakugaku Zasshi*, **71**, 727 (1951); *c*) *Idem*, *ibid.*, **71**, 297 (1951); *d*) M. Katada, *ibid.*, **68**, 123 (1948); *e*) E. Ochiai and T. Naito, *ibid.*, **64**, 206 (1944); *f*) Y. Kawazoe and M. Tachibana, *Chem. Pharm. Bull.* (Tokyo), **15**, 1 (1967); *g*) M. Hamana and T. Nagayoshi, *ibid.*, **14**, 319 (1966); *h*) M. Ishikawa, *Yakugaku Zasshi*, **65**, 98 (1945); *i*) E. Ochiai, S. Suzuki, Y. Utsunomiya, T. Okamoto, K. Nagatomo, and M. Ito, *ibid.*, **70**, 339 (1960); *j*) M. Ishikawa, *Proc. Imp. Acad. Tokyo*, **20**, 599 (1944).

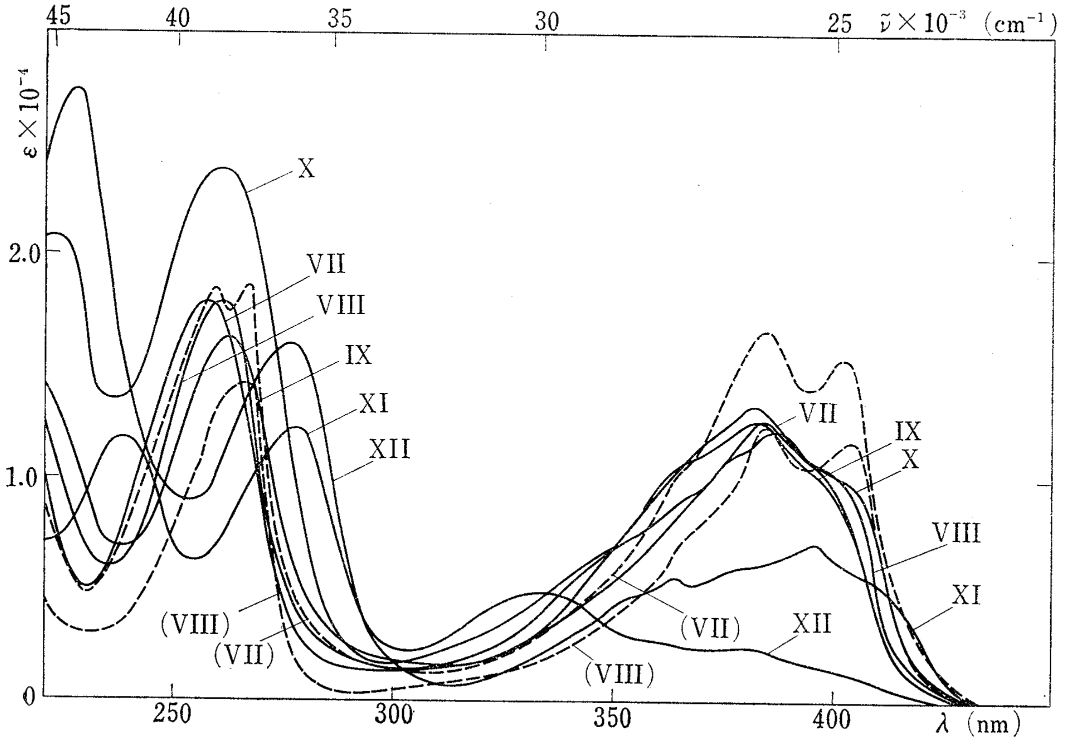

Fig. 3. Electronic Absorption Spectra of 4-Nitroquinoline 1-Oxides in Nonaqueous Solution

——: cyclohexane–EtOH ------: cyclohexane

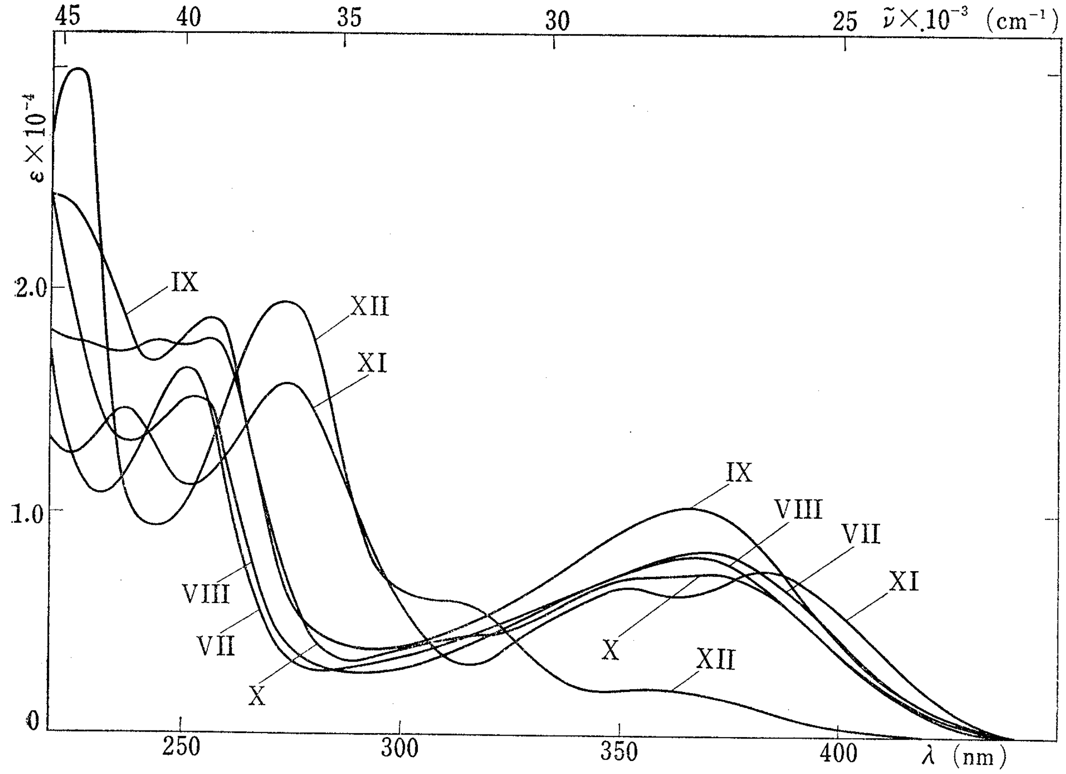

Fig. 4. Electronic Absorption Spectra of 4-Nitroquinoline 1-Oxides in Aqueous Solution, pH 7.0

368 nm in aqueous solution, and the four absorption bands in the region of 363—415 nm of XI in cyclohexane–EtOH mixture became two broad bands with absorption maxima at 352 and 383 nm in aqueous solution. With the exception of the bands of III in a longer wavelength region, all the absorption bands tended to show a blue shift with increasing polarity of the solvent. This blue shift is due chiefly to the hydrogen bonding between aromatic N-oxides and hydroxylic solvents.[10] The spectral shift due to substitution effect showed a similar tendency in both the aqueous and nonaqueous solutions (Tables II and III).

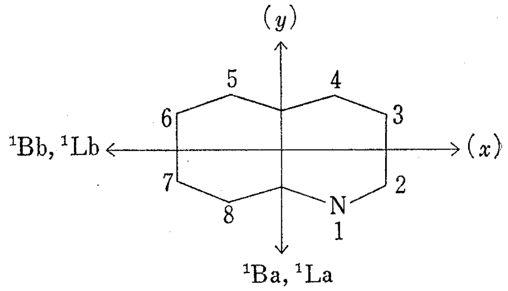

Fig. 5. Polarization Diagram of Azanaphthalene on the Basis of Platt's Free Electron Model

TABLE II. Near-ultraviolet and Visible Absorption Bands of 4-Substituted Quinoline 1-Oxides and Their Classification

Compound No.	λ_{max} nm (ε)$^{a)}$			Assignment
	H_2O (pH 7.0)	Cyclohexane–EtOH	Cyclohexane	
I		228 (29900)	224 (22020)	
	231 (34520)	247 (11370)(s)	243 (9630)	^1B_b
			250 (8920)	
			260 (5580)(s)	
	311 (5450)(s)	318 (6410)	330 (5810)	$^1L_a+^1L_b$
	323 (6560)	327 (7010)	336 (6410)	
	336 (3900)(s)	334 (6780)	350 (7210)	
		342 (6560)	362 (5220)	
			368 (5160)	
II		226 (29900)	225 (23160)	
	231 (43590)	250 (12540)(s)	236 (11180)(s)	^1B_b
			251 (7290)	
			267 (2200)(s)	
	315 (8130)(s)	344 (8830)	340 (3900)	$^1L_a+^1L_b$
	327 (9120)	361 (6480)(s)	362 (5190)	
	342 (8000)		367 (4500)	
			377 (3960)	
			381 (3610)	
III	253 (14900)	240 (14060)		^1B_b
		244 (14150)		
		250 (10900)		
	327 (5610)(s)	320 (6160)(s)		$^1L_a+^1L_b$
	355 (8770)	335 (9420)		
		346 (8950)		
IV	232 (43890)	244 (27190)		^1B_b
	301 (5610)(s)	322 (6890)(s)		$^1L_a+^1L_b$
	316 (8700)(s)	344 (12200)		
	327 (9790)	358 (12650)		
	342 (8400)			
V	234 (13230)(s)	246 (12180)		^1B_b
	255 (11400)	260 (13390)		
	357 (9350)	339 (5760)(s)		$^1L_a+^1L_b$
		370 (9840)		
VI	256 (11240)	244 (10930)		^1B_b
		260 (10380)		
	358 (8220)	341 (5400)(s)		$^1L_a+^1L_b$
		374 (8110)		

a) (s) denotes a shoulder

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[10] T. Kubota, *Shionogi Kenkyusho Nempo*, **6**, 31 (1936); *idem*, *Yakugaku Zasshi*, **77**, 785 (1957); *idem*, *ibid.*, **75**, 1540 (1955); *idem*, *Nippon Kagaku Zasshi*, **79**, 916 (1958).

Classification of absorption bands according to Platt's nomenclature system (*cf.* Fig. 5) will now be made, dividing the compounds, for the sake of convenience, into 4-substituted quinoline 1-oxides (I to VI) and 4-nitroquinoline 1-oxides (VII to XII). Unless otherwise noted, all the spectral data refer to those in a mixed solvent.

4-Substituted Quinoline 1-Oxides——Of the compounds shown in Table II, band assignments have been made by Ochiai and Kubota for the band (${}^1B_b$) around 247 nm and bands (${}^1L_a+{}^1L_b$) in the region longer than 300 nm in I (unsubstituted quinoline 1-oxide),[5d,11] and the bands (${}^1L_a+{}^1L_b$) in the region longer than 300 nm in II and V.[5g] I and II exhibited one absorption band of strong intensity in the shorter wavelength region than the ${}^1B_b$ band and, as will be seen in Table II, these bands showed a red shift with increasing polarity of the solvent. Such a direction of the shift is reverse of the direction of the solvent effect characteristic to heterocyclic N-oxides.[11] The shoulder around 250 nm in II is considered to be the result of a red shift of ${}^1B_b$ band in I. 4-Hydroxy (III), 4-carboxy (IV), 4-amino (V), and

Table III. Near-ultraviolet and Visible Absorption Bands of 4-Nitroquinoline 1-Oxidses and Their Classification

Compound No.	λ_{max} nm (ε)$^{a)}$			Assignment
	H_2O (pH 7.0)	Cyclohexane–EtOH	Cyclohexane	
VII	251 (16480)	257 (18130)	249 (13980)(s)	${}^1B_b$
			258 (18560)	
			266 (18710)	
		363 (10570)(s)	364 (10170)(s)	${}^1L_a$
		382 (13470)	382 (16830)	${}^1L_b$
	368 (8400)$^{b)}$	402 (9020)(s)	402 (15600)	
VIII	252 (15090)	260 (17860)	250 (8000)(s)	${}^1B_b$
			258 (12620)(s)	
			266 (14240)	
		363 (8220)(s)	365 (7330)(s)	${}^1L_a$
		384 (12620)	384 (12180)	${}^1L_b$
	366 (8090)$^{b)}$	404 (9420)(s)	404 (9420)	
IX	255 (18710)	261 (16590)		${}^1B_b$
		362 (10320)(s)		${}^1L_a$
		382 (12750)		${}^1L_b$
	363 (10230)$^{b)}$	403 (8360)(s)		
X	230 (17460)	261 (23880)		${}^1B_b$
	243 (17860)			
	256 (17860)			
	350 (6900)	363 (8640)(s)		${}^1L_a$
		374 (10580)(s)		
	370 (7410)	387 (12110)		${}^1L_b$
		408 (8640)(s)		
XI	236 (14610)	238 (11770)		${}^1B_a$
	273 (15810)	277 (12320)		${}^1B_b$
	352 (6670)	363 (5510)		${}^1L_a$
		375 (5850)		
	382 (7450)	395 (7210)		${}^1L_b$
		415 (4350)		
XII	225 (29930)	228 (27540)		${}^1B_a$
	273 (19380)	262 (11630)(s)		${}^1B_b$
		277 (16000)		
	312 (6020)	334 (4880)		${}_1L_a$
		355 (2760)		
	355 (2110)	381 (2250)		${}^1L_b$
		401 (1250)		

a) (s) denotes a shoulder. *b)* (${}^1L_a+{}^1L_b$) band

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[11] E. Ochiai, "Aromatic Amine Oxides," Elsevier Publishing Company, Amsterdam, 1967, pp. 126—147.

4-hydroxyamino (VI) derivatives showed 1—3 absorption bands in the position corresponding to the ^1B_b band in I. This band in III showed an apparent red shift in an aqueous solution. Since it is assumed from the pK_a (=5.76[12]) of 4-hydroxypyridine 1-oxide that III is present as a mixture of dissociated and non-dissociated molecular species under the experimental condition, it would not be possible to make a direct comparison of spectral patterns of III in aqueous and nonaqueous solution. The bands in longer wavelength region than 300 nm in III, IV (pK_a=2.67 (25°)[13]) and VI (pK_a=3.96 (25°)[13]) may be considered as a mixture of ^1L_a and ^1L_b bands, in analogy with the band assignments for I, II, and V. In compounds III, IV, and VI, similar to the case of II and V, the absorption bands are greatly affected by the substitution in the position influencing polarization in the direction of y axis (*cf.* Fig. 5), and red shift of the ^1L_a band in quinoline (which has ^1L_a and ^1L_b bands respectively at around 270 and 313 nm)[14] has overlapped it with the ^1L_b band, making it difficult to discriminate these two kinds of bands.

4-Nitroquinoline 1-Oxides——Of the compounds shown in Table III, the absorption bands around 251 and 273 nm of VII and XII (6-nitro compound), respectively, in aqueous solution have been assigned to ^1B_b band.[11] These bands appeared at around 257 (VII) and 277 (XII) nm in the nonaqueous solution. The bands corresponding to these in VIII, IX, X, and XI appeared respectively at around 260, 261, 261, and 277 nm, indicating the red shift of ^1B_b in VII by 3—20 nm due to the effect of a substituent in 2- or 6-position of VII. The ^1B_b band in the 6-nitro compound (XI and XII) appear in the longer wavelength region by 20 nm, indicating that nitration of the 6-position has greatly aided polarization in the direction of the x axis (*cf.* Fig. 5). The molar extinction coefficient of the ^1B_b band in the 6-carboxy compound (X) is greater than that of VII by about 5500 but the ε value is smaller in other compounds.

Compounds VII to XII exhibit 3—4 bands or shoulders in the wavelength region longer than 300 nm. Of the three bands of VII in a longer wavelength region, the band at 282 nm and a shoulder at 402 nm appear in VIII, IX, X (pK_a=3.08 (25°)[13]) and XI respectively at 384 and 404 (shoulder) nm, 382 and 403 (shoulder) nm, 387 and 408 (shoulder) nm, and at 395 and 415 nm. Introduction of a substituent in 2- or 6-position of VII has resulted in red shift of the two absorption bands of VII in the longest wavelength region by 1—13 nm. The band corresponding to the shoulder at 363 nm in VII appears at 362 or 363 (shoulder) nm in VIII, IX, X, and XI. These facts indicate that while the band at 363 nm in VII is hardly affected by substitution in 2- or 6-position, the bands at around 382—402 nm in VII were greatly affected by substitution into these positions. It is apparent that the introduction of a substituent into 2- or 6-position of VII will affect polarization mainly in the direction of x axis, and the absorption bands in longer wavelength region in VII to XI may be assigned separately to ^1L_a and ^1L_b bands. Absorption bands of XII at around 312 and 355 nm in aqueous solution have been separately assigned to ^1L_a and ^1L_b bands.[5h] The shoulders at around 402—404 nm in VII and VIII appeared as distinct absorption bands in cyclohexane. In the case of X and XI with strong electron-withdrawing group in 6-position, absportion band not seen in VII to IX appeared at around 374—375 nm. This band is assumed to be the ^1L_a band exposed from the overlapping ^1L_b band in VII. The ^1L_a and ^1L_b bands were overlapped in compounds VII to IX due to the red shift of the ^1L_b band by the effect of a substituent in 6-position of VII. Separation of ^1L_a and ^1L_b bands became more apparent in cyclohexane. Although these two bands of X and XI were separately assigned in the spectra taken in aqueous solution, they appeared as one broad band in VII, VIII, and IX in aqueous solution and were unseparable.

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12) H.H. Jaffè, *J. Am. Chem. Soc.*, **76**, 3527 (1964).
13) Determined by spectrophotometric method (unpublished data).
14) V. Zanker, *Z. Physik. Chem.*, *N.F.*, **2**, 52 (1954).

6-Nitro compounds (XI and XII) showed a similar spectral pattern, and they exhibited one band of strong intensity at 238 and 228 nm, respectively, a shorter wavelength region than the position of their ^1B_b band. This band was not observed in the spectra of I and VII. The strong absorption band in XI and XII is considered to be the ^1B_a band which appeared in the observable wavelength region due to a red shift by the effect of nitration of the 6-position. In this connection, it is known that the nitration of 6-position in quinoline 1-oxide aids polarization in the direction of y axis and nitration of 4-position is promoted.[5c,7b] Although Hata and others[5k,5l,15] observed n→π^* and intramolecular charge transfer bands, besides the $\pi\rightarrow\pi^*$ band, in azabenzene N-oxides, such absorption bands were not found in quinoline 1-oxides in the present work.

Electronic Structure

Molecular Orbital Calculations——The parameters used for the molecular orbital calculations in the present work are summarized in Table IV. These values, except those of the hydroxyamino group, were obtained from the existing literature (Ref. 16). The Coulomb integrals of nitrogen and oxygen atoms and the resonance integral of N-O of hydroxyamino group were taken as given in this Table, according to Nagata's suggestion.

Table IV. Parameters Used for the MO Calculation

Substituent	Coulomb integral	Resonance integral	Reference
$\gg$N→O	$h_{\dot{N}}=3.5$ $h_{\ddot{O}}=0.6$	$k_{N-O}=1.0$	16*a*)
–NO$_2$	$h_{\ddot{N}}=1.0$ $h_{\ddot{O}}=1.0$	$k_{N-O}=1.0$	16*b*)
–COOH	$h_{\dot{O}}=2.08$ $h_{\ddot{O}}=2.22$	$k_{C-O}=1.14$ $k_{C-O}=0.80$	16*c*)
–NHOH	$h_{\ddot{N}}=1.0$ $h_{\ddot{O}}=0.6$	$k_{N-O}=0.6$	16*d*)
–OH	$h_{\ddot{O}}=0.6$	$k_{C-O}=0.7$	16*e*)
–NH$_2$	$k_{\ddot{N}}=0.4$	$k_{C-N}=0.6$	16*f*)
–Cl	$h_{Cl}=2.0$	$k_{C-Cl}=1.0$	16*g*)
–CH$_3$$^{a)}$	$h_X=3.0$	$k_{C-X}=1.0$	16*h*)

a) heteroatom model $\equiv$C—X

Energy levels of molecular orbitals in quinoline 1-oxides (compounds I to XI), calculated by the simple LCAO-MO method using the parameters given in Table IV, are listed in Table V. The values for ϕ_8 and ϕ_9 of compound VII we obtained are close to those obtained by Nagata and others.[17] The energy difference (ΔE) of all the compounds, obtained from the values listed in Table V, is given in Table VI. In this Table, the wave number ($\bar{\nu}$) of the main peaks of absorption bands of quinoline 1-oxides in the longest wavelength region, taken from the absorption spectra of these compounds in a cyclohexane–EtOH mixture (Figs. 1 and 3), are also shown.

In Fig. 6, the $\bar{\nu}$ values of Table VI are plotted against the difference between the energy of the lowest-empty molecular orbital (E_{m+1}) and that of the highest-occupied molecular orbital (E_m) ($\Delta E=E_{m+1}-E_m$). As will be apparent from this graph, a comparatively good linear relation was established between the ΔE and $\bar{\nu}$ values. Similar parallel relationship

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15) T. Kubota and H. Watanabe, *Bull. Chem. Soc. Japan*, **35**, 946 (1962).

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Table V. Energy Levels of Quinoline 1-Oxides

Compound No.	E (β)								
	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9	ϕ_{10}	ϕ_{11}	ϕ_{12}	ϕ_{13}
I	1.033	0.585	−0.341	−0.918					
II		0.949	0.385	−0.266	−0.999				
III		0.716	0.320	−0.423	−0.957				
IV			0.953	0.441	−0.160	−0.888			
V		0.695	0.328	−0.505	−0.995				
VI			0.448	0.210	−0.493	−0.966			
VII			0.682	0.404	−0.058	−0.481			
VIII				0.566	0.397	−0.095	−0.478		
IX				0.881	0.392	−0.049	−0.739		
X						0.437	0.420	−0.087	−0.154
XI					0.889	0.398	−0.039	−0.730	

Table VI. Calculated Transition Energies (ΔE) of Quinoline 1-Oxides

Compound No.	ΔE ($-\beta$)			$\bar{\nu}\times 10^{-2}$ [a] (cm^{-1})
	$E_{m+1}-E_m$	$E_{m+1}-E_{m-1}$	$E_{m+2}-E_m$	
I	0.926	1.374	1.503	305.81
II	0.651	1.215	1.384	290.69
III	0.743	1.139	1.277	298.50
IV	0.601	1.113	1.329	270.27
V	0.833	1.200	1.323	270.27
VI	0.703	0.941	1.176	267.37
VII	0.462	0.740	0.885	261.78
VIII	0.492	0.661	0.875	260.41
IX	0.441	0.930	1.131	261.78
X	0.507	0.524	0.574	258.39
XI[b]	0.437	0.928	1.128	253.16

a) wave number of the main peaks of absorption bands of quinoline 1-oxides in the longest wavelength region

b) $E_{m+1}-E_{m+2}=1.619$ (β)

was observed between the lowest-empty orbital energy and polarographic half-wave potential[18] of 4-nitroquinoline 1-oxides (VII to XI). These facts indicate the reasonableness of the result of the foregoing molecular orbital calculations.

Electronic Transition——Discussion will now be made on the correlation between the ΔE values of compounds listed in Table VI and the absorption bands classified as above. In the following paragraphs, the spectral data refer to those obtained by measurement in cyclohexane–EtOH mixture.

Band assignments were made for compounds I to VI as given in Table II. From the ΔE values listed in Table VI, it is possible to assume that the mixed bands of ^1L_b and ^1L_a in these compounds correspond to mixture of the electronic transition from the highest-occupied molecular orbital to the lowest-empty molecular orbital ($\phi_m \rightarrow \phi_{m+1}$) and the electronic transition from the second-highest occupied molecular orbital to the lowest-empty molecular orbital ($\phi_{m-1} \rightarrow \phi_{m+1}$), while the ^1B_b band corresponds to the electronic transition from the highest-occupied to the second lowest molecular orbital ($\phi_m \rightarrow \phi_{m+2}$).

The spectral bands of 4-nitroquinoline 1-oxides (VII to XI) were all assigned to ^1L_b, ^1L_a, and ^1B_b bands sequentially from the longer to shorter wavelength side. From the ΔE

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values in Table VI, ^1L_b, ^1L_a, and ^1B_b bands in these compounds can be understood to correspond respectively to the electronic transitions of $\psi_m \rightarrow \psi_{m+1}$, $\psi_{m-1} \rightarrow \psi_{m+1}$, and $\psi_m \rightarrow \psi_{m+2}$. The band at 238 nm in XI was assigned to the ^1B_a band and this band is thought to originate in the electronic transition of $\psi_{m-1} \rightarrow \psi_{m+2}$ (*cf.* footnote to Table VI). Consequently, the relation between the electronic transition and band assignment in 4-nitroquinoline 1-oxides (VII to XI) may be depicted as shown in Fig. 7.

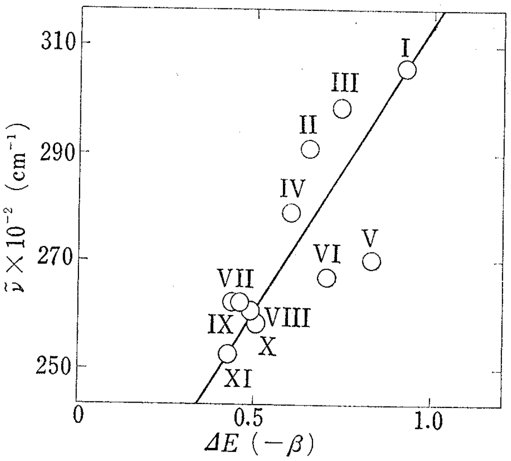

Fig. 6. Relationship between Wave Numbers ($\tilde{\nu}$) of the Longest Wavelength Bands of Quinoline 1-Oxides and the Energy Difference (ΔE) between the Highest-occupied and Lowest-empty Molecular Orbitals

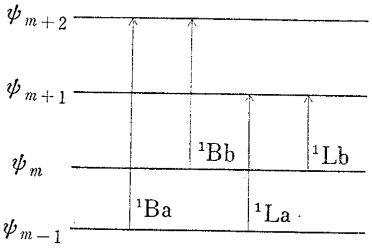

Fig. 7. A Schematic Diagram for the Electronic Transition of 4-Nitroquinoline 1-Oxides

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