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The Electronic Spectra of Nitrile *N*-Oxides and the Solvent Effect on Them

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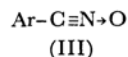
The electronic spectra of several substituted benzonitrile *N*-oxides and 9-anthronitrile *N*-oxide were recorded in various solvents and compared with those of the corresponding nitriles. The following results were thus obtained. (1) Substituted benzonitrile *N*-oxides showed a characteristic strong π - π^* band at wavelengths much longer than those of the 1L_a band of the corresponding nitriles. (2) The π - π^* band showed a blue shift with an increase in the polarity of the solvents. Quantitative analyses of the solvent effect led to the result of the decreasing dipole moment at π - π^* state. (3) The hydrogen-bonding ability of the nitrile *N*-oxides was found to be weak from experiments on three-component systems and from analyses of the above solvent effect. (4) The electronic structures of the nitrile *N*-oxides were discussed on the basis of the above-mentioned findings and the measurements of the infrared spectra. It was suggested that the interaction of oxygen $2p\pi$ electrons with the rest of the π -electron system should be taken into consideration.

The electronic spectra and the electronic states of such aliphatic and aromatic tertiary amine *N*-oxides as trimethylamineoxide, pyridineoxide, and benzylidene methylamineoxide have been of current interest from the experimental and theoretical points of view in connection with their chemical, especially, their photochemical, reactions, and in connection with charge transfer-type complexes.¹⁾ In addition to the above tertiary amine *N*-oxides, there is another kind of tertiary amineoxides, the so-called nitrile *N*-oxides. The structure of fulminic acid, $H-C\equiv N\rightarrow O$, the simplest compound of the nitrile *N*-oxides, has recently been examined in the vapor state by the method of infrared (IR) spectroscopy.²⁾

The resonance forms shown below were suggested by the fact that the IR spectra of fulminic acid and nitrous oxide, $N\equiv N\rightarrow O$, are quite similar to each other :



However, the electronic spectra of nitrile *N*-oxides have scarcely at all been reported on hitherto, so no discussion has been made of the relationship between the spectra and the electronic structure of nitrile *N*-oxides. In this paper we will report on the electronic spectra and their solvent effect for some nitrile *N*-oxides whose general form will be written as in (III), where Ar means an aromatic ring, such as substituted benzenes or anthracene :

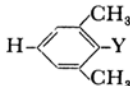
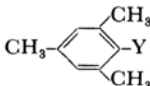
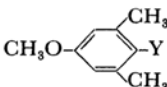
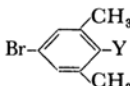
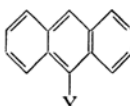
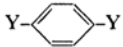
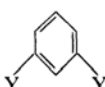


The results thus obtained will be compared with the spectra of the corresponding nitriles and with the findings on the spectral behavior of the other kinds of aromatic tertiary amine *N*-oxides reported on previously.¹⁾

1) a) T. Kubota, M. Yamakawa and I. Tanaka, *J. Mol. Spectroscopy*, **20**, 226 (1966). b) T. Kubota, *J. Am. Chem. Soc.*, **88**, 211 (1966). c) T. Kubota, H. Miyazaki and Y. Mori, *This Bulletin*, **40**, 245 (1967). d) K. Koyano and I. Tanaka, *J. Phys. Chem.*, **69**, 2545 (1965). e) M. Ishikawa, S. Yamada, H. Hotta and C. Kaneko, *Chem. Pharm. Bull. (Tokyo)*, **14**, 1102 (1966). f) N. Kataoka, A. Imamura, Y. Kawazoe, G. Chihara and C. Nagata, *ibid.*, **14**, 1171 (1966), and many other papers cited in these references.

2) W. Beck and K. Feldl, *Angew. Chem. Intern. Ed.*, **5**, 722 (1966).

TABLE 1. AROMATIC NITRILE *N*-OXIDES AND THEIR CORRESPONDING NITRILES STUDIED, WITH THEIR MELTING POINTS AND INFRARED ABSORPTION BANDS^{a)} ASSIGNED TO THE STRETCHING VIBRATION OF C≡N AND N→O BONDS^{b)}

Compound	Y	Mp, °C	$\tilde{\nu}_{\text{C}\equiv\text{N}}$, cm ⁻¹	$\tilde{\nu}_{\text{N}\rightarrow\text{O}}$, cm ⁻¹
	$\begin{cases} \text{C}\equiv\text{N} \\ \text{C}\equiv\text{N}\rightarrow\text{O} \end{cases}$	$\begin{matrix} 88.5-89.0 \\ 79.5-81.0 \end{matrix}$	$\begin{matrix} 2222 \\ 2288 \end{matrix}$	$\begin{matrix} - \\ 1349 \end{matrix}$
	$\begin{cases} \text{C}\equiv\text{N} \\ \text{C}\equiv\text{N}\rightarrow\text{O} \end{cases}$	$\begin{matrix} 50.0-51.5 \\ 110.0 \end{matrix}$	$\begin{matrix} 2221 \\ 2289 \end{matrix}$	$\begin{matrix} - \\ 1355 \end{matrix}$
	$\begin{cases} \text{C}\equiv\text{N} \\ \text{C}\equiv\text{N}\rightarrow\text{O} \end{cases}$	$\begin{matrix} 70.0-71.5 \\ 69.0-71.0 \end{matrix}$	$\begin{matrix} 2219 \\ 2290 \end{matrix}$	$\begin{matrix} - \\ 1351 \end{matrix}$
	$\begin{cases} \text{C}\equiv\text{N} \\ \text{C}\equiv\text{N}\rightarrow\text{O} \end{cases}$	$\begin{matrix} 69.0-70.0 \\ 100.0-101.5 \end{matrix}$	$\begin{matrix} 2223 \\ 2289 \end{matrix}$	$\begin{matrix} - \\ 1355 \end{matrix}$
	$\begin{cases} \text{C}\equiv\text{N} \\ \text{C}\equiv\text{N}\rightarrow\text{O} \end{cases}$	$\begin{matrix} 179.0-179.5 \\ 128.5-129.5 \end{matrix}$	$\begin{matrix} 2218 \\ 2286 \end{matrix}$	$\begin{matrix} - \\ 1382 \end{matrix}$
	$\begin{cases} \text{C}\equiv\text{N} \\ \text{C}\equiv\text{N}\rightarrow\text{O} \end{cases}$	$\begin{matrix} 225.5-226.0 \\ >260 \text{ (decomp.)} \end{matrix}$	$\begin{matrix} 2234 \\ 2283^{\text{c)}$	
	$\begin{cases} \text{C}\equiv\text{N} \\ \text{C}\equiv\text{N}\rightarrow\text{O}^{\text{d)}$	$\begin{matrix} 163.0 \\ \sim 198 \text{ (decomp.)} \end{matrix}$	$\begin{matrix} 2237 \\ 2300^{\text{c)}$	

a) All the data were recorded in CCl₄ unless otherwise noted.

b) See text for discussion of these assignments.

c) These data were obtained by Nujol mull method.

d) This compound is not so stable, so that the purity is less than that of the other compounds. The value $\sim 198^\circ\text{C}$ would be for the furoxan produced by heating.

Experimental

Measurement. The ultraviolet (UV) absorption spectra were recorded with a Beckman DK-2A far UV spectrophotometer set in a well air-conditioned room adjusted to $\sim 25^\circ\text{C}$, matched quartz cells with a 1 cm light path being used. The recording in the far UV region was carried out by replacing the air in the spectrometer with dry nitrogen gas and by using thin, sandwich-type, 0.01 cm cells with super silica windows. The infrared (IR) spectra were measured with a Nihon Bunko Model DS-201-B recording spectrometer equipped with NaCl optics.

Solvents. Twelve kinds of solvents were used. Except for *n*-heptane and water, all the solvents purchased from Merck, Eastman, or the Dojindo Co., Ltd., were of spectrograde quality and were subjected to rectifying distillation using an efficient column after sufficient drying of the solvents. Phillips pure-grade (99 mol% minimum) *n*-heptane was shaken with concentrated H₂SO₄ and fuming H₂SO₄, then with water, with diluted NaOH, and again with water. After distillation it was dried over sodium wire, and again distilled using an efficient

column, the distillate being collected through a chromatographic tube packed with active alumina. Once-distilled water was mixed with a suitable amount of KMnO₄ and NaOH, and then distilled to collect the middle portion. All the organic solvents used are given below with their numbering, refractive index, n_D , and dielectric constant, D , in that order:³⁾ *n*-heptane (1), 1.388, 1.924; carbon tetrachloride (2), 1.463, 2.238; carbon disulfide (3), 1.632, 2.641; benzene (4), 1.501, 2.284; dichloromethane (5), 1.424, 9.08; dimethylformamide (6), 1.427, 36.7; acetonitrile (7), 1.344, 37.5; methanol (8), 1.327, 32.63; cyclohexane (9), 1.426, 2.023; isooctane (10), 1.391, 1.940; ethyl ether (11), 1.353, 4.335.

Materials. According to Grundmann's method,⁴⁾ 2,4,6-trimethylbenzonitrile *N*-oxide (TMBNO), 2,6-dimethylbenzonitrile *N*-oxide (DMBNO), and 9-an-

3) The values of n_D and D were taken from the book: A. Weissberger and E. S. Proskauer, "Organic Solvents," 2nd Ed., Interscience Publishers, New York (1955).

4) a) C. Grundmann and J. M. Dean, *Angew. Chem. Intern. Ed.*, **3**, 585 (1964). b) C. Grundmann and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965). c) C. Grundmann and H. D. Frommelt, *ibid.*, **30**, 2077 (1965).

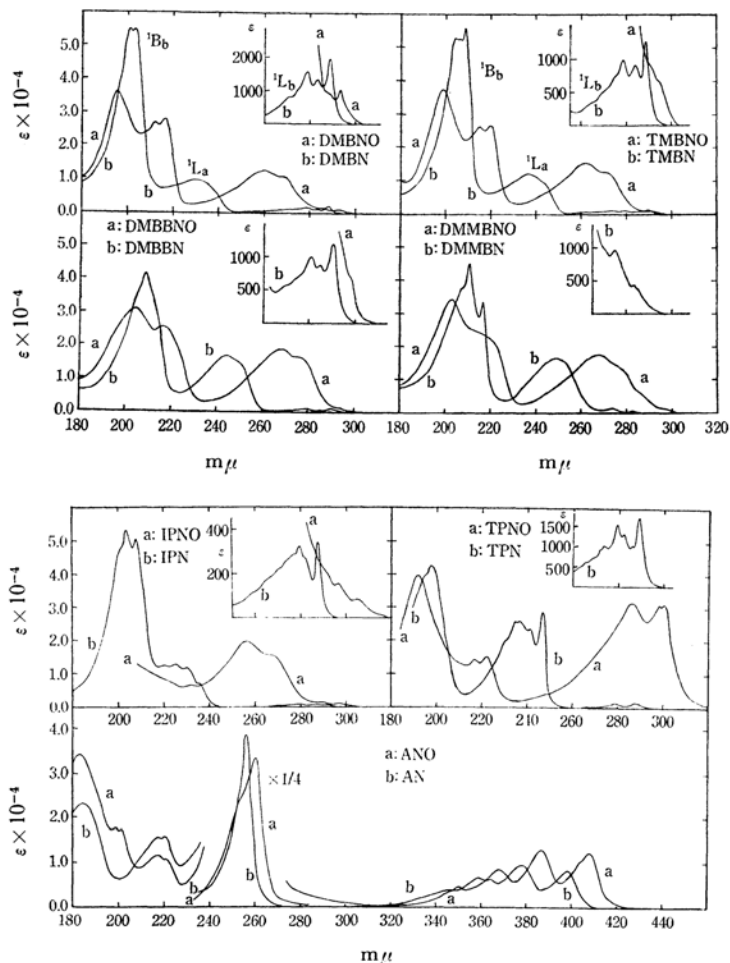


Fig. 1. The electronic spectra of aromatic nitrile *N*-oxides and the corresponding nitriles in *n*-heptane. The solubility of IPNO, TPNO, and TPN in *n*-heptane was very small, so that the spectra of these compounds were recorded with a respective saturated solution. The absorption intensities of IPNO, TPNO, and TPN were, respectively, estimated from the spectra of TMBNO in *n*-heptane, of TPNO in CH_3CN , and of TPN in CH_3CN . See text for an abbreviation of each compound.

thronitrile *N*-oxide (ANO) were prepared by the reaction of the corresponding aldoxime with NaOBr at a low temperature, and then recrystallized several times with methanol or ether (TMBNO), with an ethyl ether-petroleum ether mixture (DMBNO), and with methanol (ANO). Terephthalonitrile di-*N*-oxide (TPNO) and isophthalonitrile di-*N*-oxide (IPNO) were synthesized by mixing a methanol solution of triethylamine with that of the corresponding dihydroxamic chloride⁵⁾ purified from aqueous methanol. This reaction proceeded smoothly and quantitatively, the di-*N*-oxides being precipitated. The above-mentioned dihydroxamic chloride was obtained by passing Cl_2 gas through a suspended CCl_4 solution of the corresponding oximes.⁵⁾ 2,6-Dimethyl-4-methoxybenzonitrile *N*-oxide

(DMMBNO) and 2,6-dimethyl-4-bromobenzonitrile *N*-oxide (DMBBNO) have not been prepared hitherto. However, these compounds could be synthesized by the same method as that recommended by Grundmann⁴⁾ mentioned above.

2,6-Dimethyl-4-methoxybenzaloxime (unknown compound) was obtained from the condensation reaction of the aldehyde and hydroxylamine: mp 120–123°C. 2,6-Dimethyl-4-bromobenzaloxime (unknown compound), mp 114–116°C, which is needed in preparing the corresponding nitrile *N*-oxide, was synthesized by the reaction of hydroxylamine with 2,6-dimethyl-4-bromobenzaldehyde (unknown compound), the latter being prepared by applying the Beech method⁶⁾ to 2,6-dimethyl-4-bromoaniline and being purified by repeated recrystallizations from ether: mp 63–65°C.

The corresponding nitriles of TMBNO, DMBNO,

5) a) Y. Iwakura, M. Akiyama and K. Nagakubo, *This Bulletin*, **37**, 767 (1964). b) Y. Iwakura, M. Akiyama and S. Shiraishi, *ibid.*, **38**, 335 (1965).

6) W. F. Beech, *J. Chem. Soc.*, **1954**, 1297.

TABLE 2. ABSORPTION MAXIMA ($m\mu$) AND INTENSITIES (ϵ) OF THE ELECTRONIC SPECTRA OF AROMATIC NITRILE *N*-OXIDES AND THEIR CORRESPONDING NITRILES IN SOME SOLVENTS

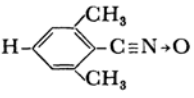
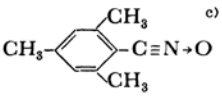
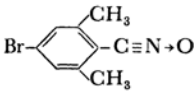
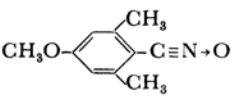
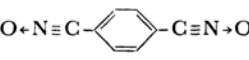
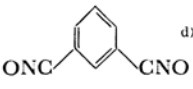
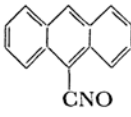
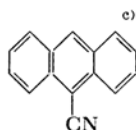
		<i>n</i> -Heptane		CCl_4		CH_3CN		CH_3OH		$H_2O^{b)}$ λ_{max}
		λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	
	I	293.5 228 ^{a)}	968 970	294.5 290 ^{a)}	1070 1100	293.5 288.5 ^{a)} 282.3	1230 1200 1520	293.8 289 ^{a)} 282.5	1260 1100 1520	293.3 283.3
	II	267.4 ^{a)} 259.7	11100 12700	268.2 ^{a)} 260.6	12200 13700	263.6 ^{a)} 255.4	11200 13000	263 ^{a)} 255.3	11000 12900	250.8
	III	216.2 211.6	27900 26800			208.8	30100	210.2	28500	206.7
	IV	195.2	36100			195.0	34500	194.6	35500	193.8
	I	294.2 ^{a)}	667	295.0 ^{a)}	803	293.7 288.9 ^{a)}	863 970	294.2 289.4 ^{a)}	970 1040	293.5
	II	269.8 ^{a)} 262.7	12800 15000	271.1 ^{a)} 263.9	14200 15900	266.6 ^{a)} 258.7	12800 15000	267.4 ^{a)} 258.7	13100 15600	256.0
	III	219.9 214.7	26900 26100			217.3 213.0	24300 21300	217.1 213.5	26300 26600	212.0
	IV	198.4	37300			197.4	33300	197.9	34400	196.3
	I	293.2 ^{a)}	1350	295 ^{a)}	1300	295.6	1030	295.7	1030	294.9
	II	274.6 ^{a)} 268.0	16400 19000	277.4 ^{a)} 268.7	17900 20600	271.4 ^{a)} 264.0	17100 19400	271.8 ^{a)} 264.4	16800 19200	260.3
	III	216.3	25700			214.3	26100	214.4	26700	212 ^{a)}
	IV	204.3	31000			203.0	31600	203.5	31400	203.8
	II	267.9	17900	270.2	17900	266.4	18800	266.9	19300	263.7
	III	213.7 ^{a)}	24700			215.7	23900	216.0	24200	214.8
	IV	202.5	34400			201.9	31500	201.7	31500	199.5
	I	300.7 298.2 285.8		301.4 286.6		290.5 279.4 218.1	29200 30000 15500	292.1 280.1 219.3	30800 30100 15400	286.8 275.7 210.3 ^{a)}
	II	222.2 216.8				213.9	15800	214.7	15400	
	III	191.5				189.0	41100	189.4	40600	
	I	306.2 296.9				300.7 ^{a)} 291.3 ^{a)}		302.7 ^{a)} 292.6 ^{a)}		
	II	268.0 ^{a)} 255.8				261 ^{a)} 247.4		262 ^{a)} 249.0		
	III	231.8				217.2 (211.5)		212.2 ^{a)}		
	I	408.3 386.5 367.3 350.0	12100 12900 8510 4080	411.9 389.8 369.5 352.4 ^{a)}	10600 11700 7840 3760	408.1 386.9 367.1 350.0 ^{a)}	9230 10900 7870 3940	407.8 386.7 366.9 349.9	9470 11300 8330 4160	408.6 386.2 366.0 347.3
	II	259.7	134000	260.4	91300	258.3	133000	257.8	132000	257.7
	III	221.0 217.4	10500 11400			220.8 217.6	11600 12100	220.7 217.3	12100 12600	217 ^{a)}
	IV	201.3 198.6	16600 16700			198 ^{a)}	15300	199 ^{a)}	15000	
	V	182.9	34400							

TABLE 2 (Continued)

		<i>n</i> -Heptane		CCl ₄		CH ₃ CN		CH ₃ OH		H ₂ O ^{b)}
		λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}
	I	288.2	1910	289.7	1910	289.7	1910	289.2	1960	290.2
		283.3	1350	285.0	1460	285.1	1610			
		278.5	1540	280.2	1660	280.3	1780	280.4	1810	282.0
		274.0 ^{a)}	1020							
	II	229.8	9600			231.4	9660	231.5	10100	232.1
	III	203.2	55400			203.0	50400	202.8	52300	200.1
	I	288.3	1270	289.6	1380	289.4	1480	289.0	1520	289.9
		284.0	922	285.4	1040	285.9	1210			
		278.3	999	279.7	1130	279.5	1300	279.6	1350	280.7
	II	236.3	12300			238.3	13000	238.7	13400	240.6
	III	208.5	56100			205.6	54600	208.2	51000	205.7
		204.0	53100					205.7	51900	
	I	290.1	1200	291.2	1340	291.0	1570	291.0	1540	291.9
		284.7	845	285.4 ^{a)}	971					
		280.0	1020	281.3	1160	281.2	1380	281.4	1370	282.3
	II	244.1	17000	248.4	16300	244.3	16800	245.0	17000	246.5
	III	208.2	41600			208.1	40800	208.3	41900	208.4
	I	286.5 ^{a)}	300							
		283.2	436	283.8 ^{a)}	573	282.5 ^{a)}	560	283 ^{a)}	640	282.5
		274.9	954	275.3 ^{a)}	1390	274.6 ^{a)}	1600	275 ^{a)}	2000	275 ^{a)}
		270.5 ^{a)}	950							
	II	248.9	16500	252.4	16900	252.1	16900	252.6	17600	252.6
	III	216.1	34000			216.8	26700	216.9	27100	
		210.4	45100			210.6	40100	211.2	36600	210.3
		207 ^{a)}	38000			207.1	40100	207 ^{a)}	34000	
	I	288.8		290.0	1510	290.5	1640	290.4	1700	291.8
		286.0		287.3 ^{a)}	1020					
		282.3		283.0 ^{a)}	1170					
		279.5		280.6	1410	281.4	1640	281.4	1690	283.0
		276.9								
		273.7		274.7	920					
		271.3		272.6 ^{a)}	835					
		265.8 ^{a)}								
		246.3				246.2	29000	246.3	26900	247.0
		241.2				241.1	22200	240.9	21800	241.6 ^{a)}
	II	236.8				236.8	24100	236.8	23700	237.8
		234.9				234.4	23900			235.1
		230.8 ^{a)}				230.8 ^{a)}	18200			230.8
	III	197.6				196.6	43300	196.6	38800	195.7
	I	287.6	347	288.1	430	287.6	507	287.7	526	287.9
		279.6	330	280.0	394	279.6	482	279.8	498	280.0
		277.3	297	277.7	343					
				273.0	300	272.3	358	272.5	371	272.6
	II	235.1	7050			235.4	6250	235.4 ^{a)}	6870	236.1 ^{a)}
		229.6	11600			229.6	11000	229.6 ^{a)}	11700	230.5 ^{a)}
		224.9	12700			225.3	12100	225.5	13000	226.3
	II	219.5	12400			220.3	11600	220.2	12700	221.1

TABLE 2 (Continued)

	<i>n</i> -Heptane		CCl ₄		CH ₃ CN		CH ₃ OH		H ₂ O ^{b)} λ_{max}
	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	
III	207.8	50900			207.4	57400	207.5	55800	208.3
	203.8	53300			203.8	56700	204.2	56200	204.7
I	398.8	8340	402.8	7570	402.0	6160	402.5	5240	403.3
	378.0	9550	381.6	8990	381.7	7980	382.5	7160	384.1
	363.8	6620	365.0	7360	364.2	7730	364.9	7160	363.0
	359.1	6860							
	346.5	4010	347.7	3980	346.9	4120	347.6	3320	345.7
II	255.8	155000	258.8	115000	255.3	166000	254.9	142000	255.8
III					227.7	12400	228.3	9780	227.2 ^{a)}
	220.7	15600			220.5	19300	220.3	17300	220.5
	217.3	15500			217.7	18800	217.3	16800	217.5 ^{a)}
IV	184.0	23300			184.4	20400			



a) Shoulder type band.

b) The ϵ values could not be determined in water because of too small solubility of all the samples used.

c) The absorption peaks of these compounds were also measured in some other solvents to study the solvent effect on absorption bands by applying Eq. (1) (see text). For bands I and II of 2, 4, 6-trimethylbenzonitrile *N*-oxide the observed values are respectively: —, 264.7 $m\mu$ (3); 295.1, — (4); 294.8, 260.5 (5); 295.1, 260.8 (6). The values of 387.6 (3), 383.4 (4), 384.2 (5), 385.8 (6), 380.3 (9), 377.8 (10), 379.6 (11) were got for band I of 9-anthronitrile. Here the number written in parentheses stands for the solvent used (see Experimental section in text).

d) ϵ values could not be given because of small solubility in solvents employed.

ANO, DMMBNO, and DMBBNO were easily obtained by one of two methods: deoxygenation from nitrile *N*-oxides by refluxing a benzene solution of nitrile *N*-oxides with $(CH_3O)_3P$,⁴⁾ or the dehydration of oximes with acetic anhydride.⁷⁾ The former method was applied to the syntheses of 2,4,6-trimethylbenzonitrile (TMBN), 2,6-dimethyl-4-methoxybenzonitrile (DM-MBN), and 2,6-dimethyl-4-bromobenzonitrile (DMB-BN). On the other hand, 9-anthronitrile (AN) and 2,6-dimethylbenzonitrile (DMBN) was prepared by the latter method. The physical constants of the nitrile *N*-oxides and nitriles prepared here are listed in Table 1; the purity of these compounds was carefully checked by elementary analyses and by UV, IR, and NMR spectroscopic measurements. Commercial (Tokyo Kasei Co., Ltd.) terephthal dinitrile (TPN) and isophthal dinitrile (IPN) were purified by the recrystallization from aqueous methanol for the former and by sublimating twice for the latter.

Results and Discussion

Comparison of the Electronic Spectra and Electronic States of Nitrile *N*-Oxides with Those of the Corresponding Nitriles. Figure 1 shows the electronic spectra in the *n*-heptane of the nitrile *N*-oxides studied, and also the corresponding nitriles for the sake of comparison, while Table 2 indicates the absorption maxima and intensity in various solvents.

From Fig. 1 and Table 2 it is clear that the electronic spectra of substituted benzonitrile *N*-oxides show quite different patterns from those of the corresponding nitriles. For example, TMBNO exhibits a strong π - π^* absorption band (262.7 $m\mu$) as well as an additional band with a relatively low intensity⁸⁾ (294.2 $m\mu$) in the wavelength region longer than 250 $m\mu$, but TMBN only absorbs the light with a weak intensity (288.3 $m\mu$ with $\epsilon=1270$) in the above region. The spectral differences mentioned above are generally found on the substituted benzonitrile *N*-oxides, although the band positions of π - π^* bands are dependent on the substituents. Similarly, a comparison of the electronic spectrum of ANO with those of AN and anthracene shows clearly that the bands of ANO occur at wavelengths longer than those of AN and anthracene.

Recently, experimental and theoretical studies of substituted benzonitriles have been carried out by several authors.⁹⁻¹¹⁾ Kimura and Nagakura^{11a,b)} concluded, from their far UV spectral measurements

8) We will here call the strong and weak bands A_1 and B_1 bands, respectively.

9) T. E. Peacock and P. T. Wilkinson, *Proc. Phys. Soc.*, **79**, 105 (1962).

10) H. E. Popkie and J. B. Moffat, *Can. J. Chem.*, **43**, 624 (1965); S. Iwata, J. Tanaka and S. Nagakura, *J. Am. Chem. Soc.*, **88**, 894 (1966).

11) a) K. Kimura and S. Nagakura, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 1 (1965).
b) K. Kimura and S. Nagakura, *Theor. Chim. Acta*, **3**, 164 (1965).

7) L. F. Fieser and J. L. Hartwell, *J. Am. Chem. Soc.*, **60**, 2555 (1938).

and from considerations based on the method of composite systems, that the intramolecular interaction between the benzene ring and the nitrile group is weak. This conclusion is in agreement with that reached by Peacock and Wilkinson.⁹⁾ It may be said that the near UV bands of benzonitrile, DMBN, and TMBN are to be assigned, according to the Platt notation,¹²⁾ as 1L_b , 1L_a and 1B_b in the order of increasing wave number, as is designated in Fig. 1. However, the fact that the electronic spectra of substituted benzonitrile *N*-oxides are considerably different from those of the corresponding nitriles leads to the conclusion that the *N*-oxidation of the nitrile group should alter the electronic structure of substituted benzonitriles considerably. In connection with this result, it should be noted that neither of the CH_3 groups occupying two ortho-positions in relation to the $\text{C}\equiv\text{N}\rightarrow\text{O}$ group in substituted benzonitrile *N*-oxides take part in the steric hindrance of the whole conjugated system. This is because the linear configuration of the $\text{>C-C}\equiv\text{N}\rightarrow\text{O}$ group can reasonably be expected,¹³⁾ as may be easily understood from Fig. 2. We will now suggest resonance forms such as IV—VII, which are illustrated below for a typical example, benzonitrile *N*-oxide.¹⁴⁾

Moreover, the π -conjugated systems of these nitrile *N*-oxides may also be written as in Fig. 3. Of the three oxygen lone-pair orbitals, p_x , p_y , and σ_n , p_x and p_y can enter into π -conjugation. Therefore, we may predict a greater decrease in the net electronic

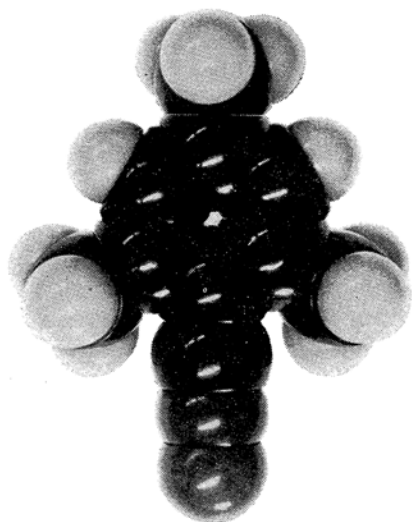


Fig. 2. The molecular model of 2,4,6-trimethylbenzonitrile *N*-oxide, showing no steric effect of methyl groups on $\text{C}\equiv\text{N}\rightarrow\text{O}$ bond.

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

13) Quite recently this prediction was confirmed by X-ray analyses of TMBNO, *etc.*; M. Shiro and H. Koyama, private communication.

14) It should be noted that benzonitrile *N*-oxide itself is not very stable at room temperature and gradually changes to furoxan (the dimer of benzonitrile *N*-oxide).

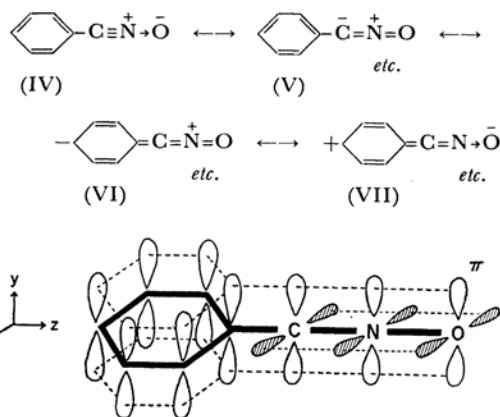


Fig. 3. Scheme of the two kinds (π and π^* systems) of π -resonance interaction of benzonitrile *N*-oxide.

charge on the oxygen atom of the nitrile *N*-oxide group than in the case of the other kinds of aromatic tertiary amine *N*-oxides, such as heterocyclic *N*-oxides and nitrones, where the *N*-atom is roughly in sp^2 hybridization. These circumstances seem to be characteristic of the nitrile *N*-oxide group; the predicted intermolecular interaction ability of nitrile *N*-oxides is weaker¹⁵⁾ than in the other kinds of *N*-oxides reported on hitherto, as will be discussed later.

The above considerations are also supported by the analyses of the IR spectra of substituted benzonitrile *N*-oxides. The infrared spectra of the *N*-oxides always showed two strong bands in the 2250—2300 cm^{-1} and 1330—1390 cm^{-1} regions (*cf.* Table 1). The former may doubtlessly be assigned to the $\text{C}\equiv\text{N}$ stretching band, $\tilde{\nu}_{\text{C}\equiv\text{N}}$. The character of the latter band was first studied by Califano *et al.*,¹⁶⁾ who assigned this band to the $\text{N}-\text{O}$ stretching band $\tilde{\nu}_{\text{N}-\text{O}}$ because there was no obvious band in the case of the corresponding nitriles, although the above two bands seemed to be coupled. The same interpretation has also been suggested by other authors;¹⁷⁾ the conclusion¹⁸⁾ is consistent with that reached for the $\text{H}-\text{C}\equiv\text{N}\rightarrow\text{O}$ molecule²⁾ mentioned at the beginning of this paper. Now we can conclude that the $\text{N}-\text{O}$ stretching band described above has

15) T. Kubota, M. Yamakawa, M. Takasuka, K. Iwatani, H. Akazawa and I. Tanaka, *J. Phys. Chem.*, in press.

16) S. Califano, R. Moccia, R. Scarpati and G. Speroni, *J. Chem. Phys.*, **26**, 1777 (1957).

17) R. H. Wiley and B. J. Wakefield, *J. Org. Chem.*, **25**, 546 (1960).

18) The following fact seems to support this conclusion. Our recent IR study of the 1:1 iodine complex of TMBNO in a CS_2 solvent showed that only the 1351 cm^{-1} band undergoes a lower frequency shift (15 cm^{-1}). This behavior is very similar to that of the $\tilde{\nu}_{\text{NO}}$ of pyridine *N*-oxide and its alkyl derivatives perturbed by the 1:1 iodine complex formation; T. Kubota, K. Ezumi, M. Yamakawa and Y. Matsui, to be published.

a much higher frequency than that ($\sim 940\text{ cm}^{-1}$) of aliphatic amine *N*-oxides¹⁹⁾ and is also higher than the $\bar{\nu}_{\text{NO}}$ (1264 cm^{-1}) of pyridine *N*-oxide.²⁰⁾ Considering the aforementioned facts, such resonance forms as IV—VII are reasonable.

Let us now consider the substituent effect on the electronic spectra of DMBN and DMBNO. When the substituents, CH_3 , Br, and OCH_3 , are introduced at the para-position in relation to the $\text{C}\equiv\text{N}$ or $\text{C}\equiv\text{N}\rightarrow\text{O}$ group (see Table 2), the red shifts of the strong band, ${}^1\text{L}_a$, of DMBN and of the strong band, A_1 , of DMBNO occur.²¹⁾ On the other hand, the shifts of the weak bands, ${}^1\text{L}_b$ for DMBN and B_1 for DMBNO, are both quite small. From the above similarity of the substituent effect on the strong and weak bands of DMBN and DMBNO, it may be thought that the transition moments of the B_1 and A_1 bands of these *N*-oxides are, respectively, in the same direction as the ${}^1\text{L}_b$ and ${}^1\text{L}_a$ bands of DMBN. In other words, the B_1 and ${}^1\text{L}_b$ bands may have the transition moment in the x direction in Fig. 3, but A_1 and ${}^1\text{L}_a$ bands may be polarized along the z axis. This conclusion agrees with that derived from the theoretical calculations.²²⁾

Solvent Effect on the Electronic Spectra of Nitrile *N*-Oxides and Related Compounds.

In a preceding section the electronic charge on the oxygen atom of the nitrile *N*-oxide group was predicted to be small in comparison with that of the other kinds of tertiary amine *N*-oxides. Thus, the intermolecular interaction ability, such as hydrogen bonding or iodine complex formation, of the nitrile *N*-oxides would be weak.¹⁵⁾ The following experiment on a three-component system supports this conclusion. Figure 4 shows the spectral behaviour of TMBNO in CH_2Cl_2 upon the addition of methanol.²³⁾ We see that the spectrum of TMBNO is

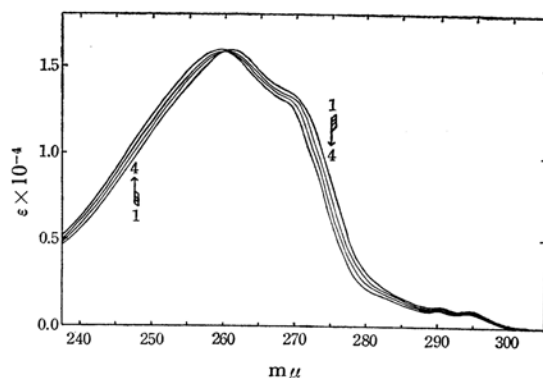


Fig. 4. The ultraviolet absorption spectra of 2,4,6-trimethylbenzonitrile *N*-oxide-methanol in CH_2Cl_2 (1 cm cell: 23.5°C). Curve 1 is for 4.99×10^{-5} mol/l of the *N*-oxide itself. The concentrations of methanol are 4.91, 9.82, and 19.65 mol/l for curves 2, 3, and 4, respectively.

quite insensitive to any added methanol and that much methanol is necessary to bring about the blue shift of the characteristic $\pi-\pi^*$ band, as has been generally observed with aromatic tertiary amine *N*-oxides.²⁴⁾ This means that the equilibrium constant, K , for the $\text{TMBNO} + \text{CH}_3\text{OH} \rightleftharpoons \text{TMBNO} \cdots \text{HOCH}_3$ system is quite small (less than 1 l/mol). No reliable K value was evaluated, because the self-association of methanol itself and the shift caused by solvent polarity, in addition to that due to the hydrogen-bonding effect, are not both neglected in such high alcohol concentrations as are shown in Fig. 4.

Results similar to the above were also found for such other nitrile *N*-oxides as TPNO (see Table 2), showing that the intermolecular interaction ability of nitrile *N*-oxides is weak, as had been predicted. However, it was observed that the substituted benzonitrile *N*-oxides undergo a blue shift of the strong $\pi-\pi^*$ band (A_1 band) in such solvents as acetonitrile, methanol, and water, although the shift is not very large (see Table 2). This result suggests that the dipole moment of the nitrile *N*-oxides decreases in the $\pi-\pi^*$ state, and that at the excited state an intramolecular charge transfer structure like VI may be more important than the other resonance structures.

To examine this assumption, we studied the effect of non-hydrogen bonding solvents on the $\pi-\pi^*$ band by applying the same theoretical and experimental treatments as have already been reported by us.²⁵⁾ The spectral shift induced by the solvents mentioned above is now written as Eq. (1),^{25,26)} where the

19) a) P. A. Giguere and D. Chin, *Can. J. Chem.*, **39**, 1214 (1961). b) D. Cook, *ibid.*, **41**, 1127 (1963). c) Y. Matsui and T. Kubota, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 985 (1962). d) Y. Kuroda and M. Kimura, *Spectrochimica Acta*, **22**, 47 (1966).

20) H. Shindo, *Chem. Pharm. Bull. (Tokyo)*, **7**, 791 (1959), etc.

21) The shift of the former is larger than that of the latter. This very interesting result may be ascribed to the difference in conjugated systems; for the nitrile compounds the main resonance forms are the intramolecular charge transfer from a substituent to the benzonitrile group, but in the case of nitrile *N*-oxides there are considered to be two kinds of resonance forms, with opposite directions of charge transfer, expressed VI and VII.

22) M. Yamakawa and T. Kubota, presented at the meeting of "Symposium on the Structures and the Electronic States of Molecules," sponsored by the Chemical Society of Japan, Osaka, October, 1966, to be published. The substituent effect on absorption bands in the far UV region will not be discussed here, because configuration interaction (CI) seems to play an especially important role in the interpretation of the electronic spectra in the above region.

23) Since the methanol of the concentrations indicated in Fig. 4 was not dissolved in *n*-heptane, we could not employ *n*-heptane as a solvent.

24) a) T. Kubota, M. Yamakawa and Y. Mori, *This Bulletin*, **36**, 1552 (1963). b) T. Kubota and H. Miyazaki, *Chem. Pharm. Bull. (Tokyo)*, **9**, 948 (1961), and many other references given therein.

25) T. Kubota and M. Yamakawa, *This Bulletin*, **35**, 555 (1962).

26) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

constant, C , is expressed as in Eq. (2):

$$\bar{\nu}_{\text{abs}} = \bar{\nu}_{\text{abs}}^0 + (A+B) \frac{n_D^2 - 1}{2n_D^2 + 1} + C \left[\frac{D-1}{D+2} - \frac{n_D^2 - 1}{n_D^2 + 2} \right] \quad (1)$$

$$C = \frac{2}{hc} \left[\frac{\vec{M}_{00}^u (\vec{M}_{00}^u - \vec{M}_{ii}^u)}{a^3} \right] \quad (2)$$

Here, each notation has the same meaning as that given in a previous paper,²⁵⁾ and the A , B , and C values are dependent only upon the solutes. The spectral data (see Table 2) recorded in seven kinds of solvents, the n_D and D values of which have been given in the "Experimental Section," were treated by the aid of the least-squares method. The values of $(A+B)$ and C thus obtained for the case of TMBNO were -3540 cm^{-1} and 763 cm^{-1} for the A_1 band and -2710 cm^{-1} and -54 cm^{-1} for the B_1 band. The relationship between observed $\bar{\nu}_{\text{abs}}$ values and their values calculated using the constants given above is depicted in Fig. 5. All the points fit a straight line, with a root mean-square deviation of 43 cm^{-1} for the A_1 band and 35 cm^{-1} for the B_1 band. The correlation between the two values is very good, the application of Eq. (1) being so fulfilled. The fact that the $(A+B)$ term shows a minus sign is reasonable, because in this term the A value, originating from the so-called dispersion interaction between solvent and solute, plays an important role and causes a red shift of the absorption bands.

However, it should be stressed that the C value is positive for the A_1 band but negative for the B_1 band of TMBNO. The former finding means that the dipole moment of TMBNO in the excited A_1 state decreases according to Eq. (2). This result is the same as is commonly derived from the study of the

non-hydrogen bonding solvent effect on the absorption spectra (intramolecular CT band) of pyridine N -oxide, *etc.* It may be deemed that the contribution of the intramolecular charge transfer configuration, written formally as the resonance structure (VI), will be larger in the $A_1 \pi-\pi^*$ state than in the ground state. Therefore, the decrease in the dipole moment occurs in the excited state,²⁷⁾ because the direction of the total dipole moment (4.38 D.U. for TMBNO in the ground state) in the A_1 and the ground states seems certainly to be the same. This outcome does not conflict with the finding that the transition moment of the above A_1 band is along the z axis (see Fig. 3), as has been discussed before.

Keeping in mind the above conclusion, it is valuable to point out that the 1L_a band of benzonitrile and TMBN, like the 1L_b band, more or less shows a red shift with an increase in the polarity of solvents, as may be seen in Table 2. This may be ascribed to the increasing dipole moment at the excited $\pi-\pi^*$ states, where intramolecular charge transfer from a benzene ring to a $C\equiv N$ group becomes larger than in the ground state.²⁸⁾ On the other hand, that the B_1 band of TMBNO has a very small C value, with a negative sign, indicates that the band is of a different nature from the A_1 band. It is now reasonable, on the basis of its intensity and its presumed direction of the transition dipole (x axis: see Fig. 3),²²⁾ to assign the band to the $\pi-\pi^*$ transition (1L_b) localized in the benzene ring, as was also discussed in a foregoing section.²⁹⁾

In the meantime we must remember the following obvious findings: the $\pi-\pi^*$ strong absorption bands of such aromatic tertiary amine N -oxides as N -heterocyclic amineoxides and nitrones, as well as the $n\rightarrow\sigma^*$ band of trimethylamineoxide, undergo a large blue shift in alcohols or water.^{1a,25)} The predicted value derived by using Eq. (1) was not at all sufficient to understand the above large blue shift.^{24,25)} The deviation from the expected value due to Eq. (1) was thus attributed to the short-range intermolecular interaction resulting mainly from hydrogen bonding. However, as may be seen

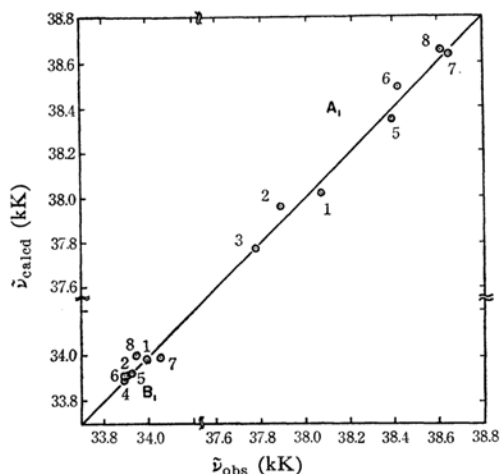


Fig. 5. Relationship between observed and calculated band maxima of 2,4,6-trimethylbenzonitrile N -oxide in various solvents. See chapter "Experimental" in text for the numbering of solvents used.

27) Supposing the cavity radius, a , to be $3.5\text{--}4 \text{ \AA}$, the decrease in dipole moment at the A_1 state comes out $0.7\text{--}1.1$ D.U.

28) This fact was also certified by the results of an experiment on the solvent effect on the 1L_a band ($378.0 \text{ m}\mu$) of AN. Using Eq. (1) and ten kinds of solvents, we got the values: $(A+B) = -9370 \text{ cm}^{-1}$, $C = -588 \text{ cm}^{-1}$, and the root mean-square deviation of 23 cm^{-1} . Assuming a cavity radius of $a = 3.5\text{--}4 \text{ \AA}$, the increasing dipole moment of $0.6\text{--}0.9$ D.U. was derived.

29) The assignment of this B_1 band to the $n-\pi^*$ transition is not reasonable, because it is well known that the $n-\pi^*$ band brings about a blue shift with an increase in the polarity of solvents: M. Ito, K. Inuzuka and S. Imanishi, *J. Am. Chem. Soc.*, **82**, 1317 (1960); A. Balasubramanian and C. N. R. Rao, *Spectrochim. Acta*, **18**, 1337 (1962); H. Baba, L. Goodman and P. C. Valenti, *J. Am. Chem. Soc.*, **88**, 5410 (1966).

in Fig. 5, the band positions of TMBNO in methanol fit the calculated values well. This finding shows that the hydrogen-bonding ability of this kind of nitrile *N*-oxides is weak, as has been discussed before and as has also been actually verified by the experiments on a three-component system.¹⁵⁾

The authors wish to express their thanks to Professor Saburo Nagakura of the Institute for Solid State Physics, the University of Tokyo, and to Professor Noboru Mataga of Osaka University for their discussions.