The Electronic Spectra of Nitrones and the Solvent Effect on Them[*1]

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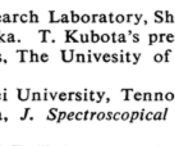
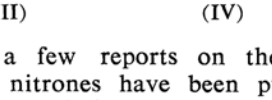
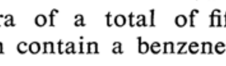
The spectroscopic behavior and the electronic states of such heterocyclic *N*-oxides as pyridine and quinoline *N*-oxides have been reported by the present authors[1-3] and by other workers.[4] Nitrone, the general formula of which can be expressed as I, may also be considered to be a kind of conjugated tertiary amine *N*-oxide. If the oxygen atom in I shows considerable resonance interaction with the rest of the molecule, a spectroscopic behavior similar to that of heterocyclic *N*-oxides may be expected for nitrones. For example, in aldonitrones, where R_1 and R_2 in I are an aryl group and a hydrogen atom respectively, the above-mentioned resonance structure may be written as II–IV.



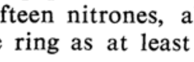
(I)



(II)



(III)



(IV)

Although a few reports on the electronic spectra of nitrones have been published by several workers,[5-7] a detailed spectroscopic investigation from the above view-point has not been made. For this paper, the electronic spectra of a total of fifteen nitrones, all of which contain a benzene ring as at least one

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[*3] Osaka Gakugei University, Tennoji-ku, Osaka.

1) See T. Kubota, *J. Spectroscopical Soc. Japan*, **10**, 83 (1962).

2) Y. Matsui and T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 985 (1962).

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

4) N. Hata and I. Tanaka, *J. Chem. Phys.*, **36**, 2072 (1962).

5) O. H. Wheeler and P. H. Gore, *J. Am. Chem. Soc.*, **78**, 3363 (1956).

6) B. W. Langley, B. Lythgoe and N. V. Riggs, *J. Chem. Soc.*, **1951**, 2309; **1952**, 4191.

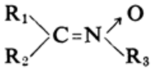
7) P. Brocklehurst, *Tetrahedron*, **18**, 299 (1962).

substituent of R_1, R_2 and R_3 in I, and such related compounds as anils and oximes, have been extensively examined in various solvents. The results thus obtained will be compared with the findings on spectroscopic behavior obtained previously on heterocyclic *N*-oxides. In addition, the configurations of the typical nitrones were also assumed from the measurement of the dipole moments and from their reactivities.[8)]

Experimental

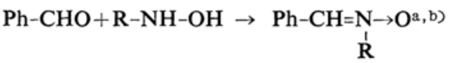
Measurement.—The ultraviolet absorption spectra were measured with a Hitachi recording spectrophotometer, model EPS-2 at 23°C and at a slow scanning speed, using matched quartz cells with a 1 cm. light path. The infrared spectra were measured with a Perkin-Elmer 12-C recording spectrometer provided with LiF optics and with a Nippon-Bunko DS-201-B recording spectrometer with NaCl optics. Special care was taken in the region of the OH-stretching frequency. The dipole moments were measured at 25°C in benzene or dioxane. The dielectric constants of dilute solutions were measured by the heterodyne beat method, using a platinum cell.[9)] The experiments were made for concentrations lower than 1%, a good linear relationship between the dielectric constants and the weight fractions of a sample being obtained within the range of experimental error. From

TABLE I. THE ELEMENTARY ANALYSIS, MELTING POINTS, SYNTHETIC METHODS, AND THE NUMBERING OF NITRONES



No.	Formula R₁	R₂	R₃	m. p. °C	C, % Calcd.	C, % Obs.	H, % Calcd.	H, % Obs.	N, % Calcd.	N, % Obs.	Synthetic method
1	Ph	H	CH_3	83.5～84.0	71.09	71.24	6.71	6.93	10.36	10.20	A
2**	Ph	H	CH_2-Ph	82 ～83	79.59	79.59	6.20	6.36	6.63	6.93	B
3	*p*-CH_3-Ph	H	CH_3	120.5	72.45	72.39	7.43	7.46	9.39	9.32	A
4*	*p*-Cl-Ph	H	CH_3	135	56.65	56.60	4.75	4.76	8.26	8.09	A
5	*p*-NO_2-Ph	H	CH_3	207～208	53.33	53.27	4.48	4.71	15.44	15.40	A
6	Ph	H	Ph	113～113.5	79.16	79.34	5.62	5.78	7.10	6.83	A
7	*p*-CH_3O-Ph	H	Ph	117～118	73.99	74.22	5.77	5.99	6.16	6.20	A
8	*p*-NO_2-Ph	H	Ph	182～183	64.46	64.46	4.16	4.27	11.57	11.63	A
9*	Ph	H	*p*-Cl-Ph	174	67.39	67.36	4.35	4.46	6.05	6.07	A
10	Ph	H	*o*-CH_3-Ph	118～119.5	79.59	79.72	6.20	6.25	6.63	6.65	A
11	Ph	H	*m*-CH_3-Ph	93～94	79.59	79.62	6.20	6.42	6.63	6.54	A
12	Ph	H	*p*-CH_3-Ph	123～124	79.59	79.71	6.20	6.20	6.63	6.56	A
13**	CH_3	Ph	CH_3	118～119	72.45	72.17	7.43	7.47	9.39	9.56	A′
14	Ph	Ph	CH_3	106.5～108.0	79.59	79.61	6.20	6.14	6.63	6.93	C
15	Ph	Ph	Ph	221～222	83.45	83.82	5.53	5.79	5.13	5.08	D

A:

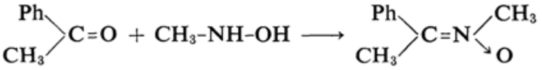


$\text{Ph-CHO} + \text{R-NH-OH} \rightarrow \text{Ph-CH}{=}\underset{\displaystyle R}{\text{N}}{\rightarrow}\text{O}$[a, b)]

a) O. H. Wheeler and P. H. Gore, *J. Am. Chem. Soc.*, **78**, 3363 (1956).

b) O. L. Brady and F. P. Dunn, *J. Chem. Soc.*, **1926**, 2411.

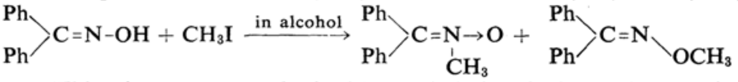
A′:



This method will be reported by Y. Mori.

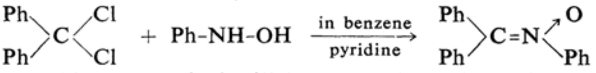
B: A. C. Cope and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **72**, 4896 (1950).

C:



(This nitrone was synthesized by methylating the benzophenonoxime with methyl iodide): c. f. L. Alessandri, *Atti della Reale Accademia dei Lincei* 5, **23**, II. 134 (1914).

D:



This new method will be reported by Y. Mori.

*: The elementary analysis for chlorine

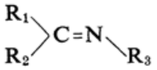
	Calcd.	Obs.
4)	20.90	20.87
9)	15.30	15.36

**: This configuration is not certain but is most probable.

[8)] The report on the chemical reactivities will be published shortly in the *Jounral of the Chemical Society of Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), by Mori et al.

[9)] Y. Kurita and M. Kubo, *J. Am. Chem. Soc.*, **79**, 5460 (1957).

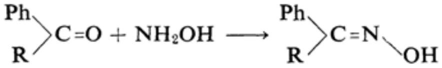
TABLE II. THE ELEMENTARY ANALYSIS, MELTING POINTS, SYNTHETIC METHODS, AND THE NUMBERING OF THE RELATED COMPOUNDS OF NITRONE



$$\begin{matrix}R_1\\R_2\end{matrix}\!\!>\!C{=}N\diagdown R_3$$

No.	Formula			m. p., °C	C, %		H, %		N, %		Synthetic method
	R_1	R_2	R_3		Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	
16	C_6H_{11}	CH_3	OH	60	68.04	68.51	10.71	10.79	9.92	9.93	E
17	Ph	H	OH	35.5							E
18	Ph	CH_3	OH	58	71.09	70.69	6.71	6.70	10.36	10.46	E
19	Ph	Ph	OH	144	79.16	79.21	5.62	5.76	7.10	7.12	E
20*	*p*-Cl-Ph	H	OH	110	54.04	54.01	3.89	4.05	9.00	8.82	E
21*	H	*p*-Cl-Ph	OH	142	54.04	53.52	3.89	3.97	9.00	9.10	E
22	Ph	H	OCH_3	101∼102/ 38 mmHg							C
23	Ph	H	OCH_3	60∼61	79.59	79.41	6.20	6.39	6.63	6.69	C
24	Ph	H	CH_3	76∼76.5/ 18 mmHg							F
25	Ph	Ph	Ph	52	86.15	86.44	6.12	5.92	7.73	7.74	F
26	Ph	Ph	Ph	113∼113.5	88.68	88.69	5.87	5.90	5.44	5.82	F

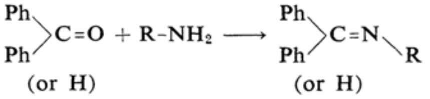
E:



$$\begin{matrix}Ph\\R\end{matrix}\!\!>\!C{=}O + NH_2OH \longrightarrow \begin{matrix}Ph\\R\end{matrix}\!\!>\!C{=}N\diagdown OH$$

(by the usual method)

F:



$$\begin{matrix}Ph\\Ph\\\text{(or H)}\end{matrix}\!\!>\!C{=}O + R\text{-}NH_2 \longrightarrow \begin{matrix}Ph\\Ph\\\text{(or H)}\end{matrix}\!\!>\!C{=}N\diagdown R$$

(by the usual method. c. f. G. Reddelien, *Ber.*, **42**, 4759 (1909))

*: The elementary analysis for chlorine

	Calcd.	Obs.
20)	22.79	22.74
21)	22.79	23.20

the slope of this straight line, the molar polarization of the solute was calculated by a method similar to that of Halverstadt-Kumlar.[10] The deformation polarization of nitrones was assumed to be 1.05 times the molar refraction estimated as the sum of the bond refractions.

Materials.—The solvents were purified by the method recommended by Weissberger and Proskauer;[11] special care was taken to remove contaminating water from the organic solvents. The synthetic method, microanalytical data, estimated configurations and physical properties of the nitrones and the related compounds are shown in Tables I and II, together with the numbering of the samples.

Results and Discussion

On the Electronic Spectra of Nitrones.—Figures 1 and 2 give the absorption spectra of nitrones and the related compounds in nonpolar solvents, while Table III lists the absorption maxima and the intensities of the compounds measured in various solvents. As may clearly be seen in Fig. 1, nitrones apparently show a characteristic strong π-π^* band in the region of 280∼370 mμ as well as one or two additional bands with a relatively low intensity in the region of 200∼260 mμ, the positions of which bands are dependent upon the kind of substituent. The molecular extinction coefficient (ε) of the former is about 20000. With regard to the examination of the character of the spectra of nitrones, a comparison of the spectra of the corresponding anils, oximes, etc., with those of nitrones would seem to be very important and interesting. Detailed investigations of the electronic spectra of anil-type compounds were carried out by Ebara,[12] by Brocklehurst,[7] and by other workers,[13-15] with results consistent with ours (see Fig. 2).

The spectra of compounds 17–24, which are oxime or anil-type compounds with no benzene ring on the *N*-atom, apparently consist of a rather weak band with vibronic structures at the longest wavelength region, a strong band continuing from the above weak band, and a strong band in the 200∼230 mμ region. Each of these spectra is essentially similar to

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[10] I. F. Halverstadt and W. D. Kumler, ibid., **64**, 2988 (1942).

[11] A. Weissberger and E. P. Proskauer, "Organic Solvents," 2nd Edition, Interscience Pub., Inc., New York (1955).

[12] N. Ebara, This Bulletin, **33**, 534 (1960); **34**, 1151 (1961).

[13] C. Wiegand and E. Merkel, *Ann.*, **550**, 175 (1942).

[14] H. Zollinger, "Azo and Diazo Chemistry," Interscience Pub., Inc., New York & London (1961), p. 316.

[15] M. B. Robin and W. T. Simpson, *J. Chem. Phys.*, **36**, 580 (1962).

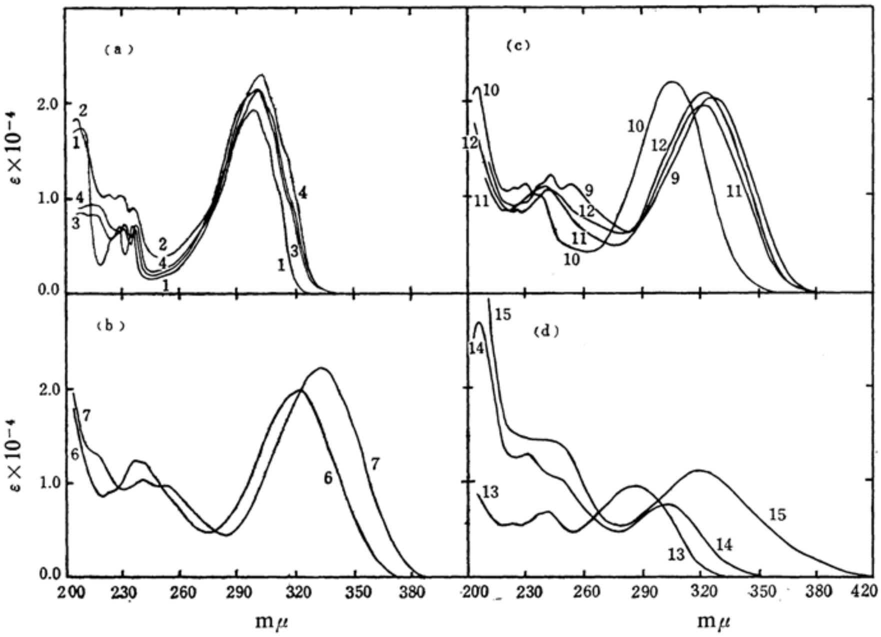

Fig. 1. The spectra of nitrones in *n*-heptane.
(The numbering of each curve is the same as that in Tables I and II.)

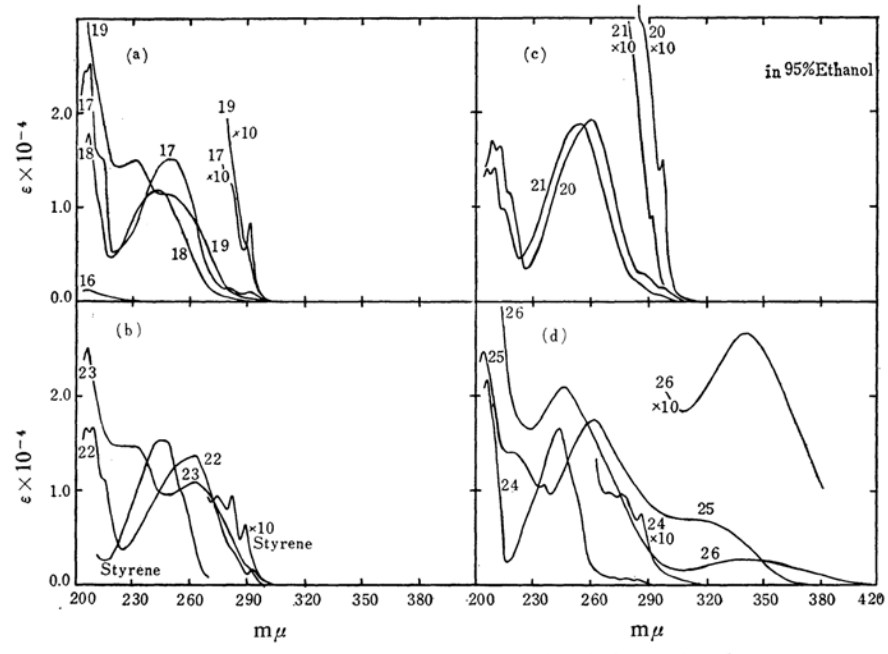

Fig. 2. Spectra of the related compounds of nitrone in *n*-heptane.
(The numbering of each curve is the same as that in Tables I and II.)

that of styrene, which is shown in Fig. 2 and the electronic state of which has been analyzed theoretically and experimentally by workers.[16-19] On the basis of these investigations, these absorption bands may reasonably be assigned to the ^1L_b, ^1L_a, and ^1B_b bands, according to

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16) J. F. Music and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5256 (1950).

17) W. W. Robertson, J. F. Music and F. A. Matsen, ibid., **72**, 5260 (1950).

18) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **68**, 601 (1955).

19) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

TABLE III. THE $\varepsilon_{\max}$*1 AND THE $\lambda_{\max}$*1 OF NITRONES AND THEIR RELATED COMPOUNDS IN VARIOUS SOLVENTS

Nitrones

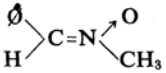
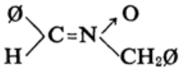
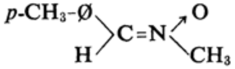
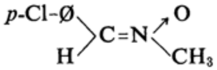
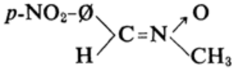
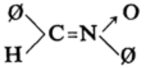
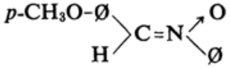
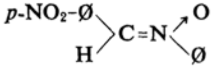
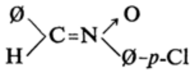
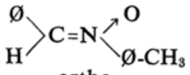
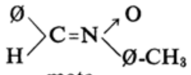
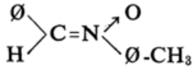
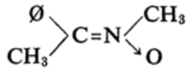
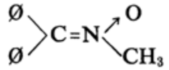
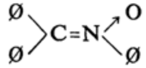
No.	Compound	CCl_4		n-Heptane		EtOH		MeOH		H_2O	
		$\lambda_{\max}$	$\varepsilon_{\max}$	$\lambda_{\max}$	$\varepsilon_{\max}$	$\lambda_{\max}$	$\varepsilon_{\max}$	$\lambda_{\max}$	$\varepsilon_{\max}$	$\lambda_{\max}$	$\varepsilon_{\max}$
1				207.5	17490	206.8	9510	207.0	8310	203.9	10370
				229.2	7390	223.2	8700	222.3	7780	218.3	9180
				235.8	7380						
		300.9	19890	298.3	19330	291.6	21150	290.0	19250	286.0	18570
2*2				205.5	18170	206.8	17800	207.2	16750	202.8	20330
				222.6	10470						
				229.4	10470	223.2	10400	221.7	9970		
				236.7	8910						
		304.0	20110	300.7	21710	295.5	21560	295.0	20950	291.4	21420
3				215.8	8210	208.0	9270	207.6	8150		
				224.0	6020	225.8	8980	218.3	6840	217.8	8230
				230.9	7470	231.7	7820	224.7	8340	222.3	9360
				238.0	7070			230.3	7070	227.7	7580
		304.0	22080	300.5	21830	295.8	24650	295.2	22880	292.3	22800
4				216.7	9510	208.2	9270	207.5	9480		
				223.8	7310	226.6	7610	225.7	7910	222.3	9520
				231.0	7520	233.6	7040	232.3	7260	229.0	7890
				237.9	7430						
		305.1	23280	302.9	23140	298.0	22650	296.8	22980	294.0	22980
5				247.2	—	247.0	10400	247.2	10170	247.8	9500
		348.6	—	345.2	—	339.9	15810	336.6	15570	328.3	15230
6				238.0	12320	231.8	10680	230.2	9930	202.2	19980
										225.8	10340
				243.0	12120						
		324.9	19630	322.6	19900	315.5	20180	313.0	19210	308.0	21420
7				241.4	10410	238.3	11630	237.6	11710	231.6	10200
				254.0	9770						
		339.0	22900	336.0	22050	332.0	26700	330.5	28200	325.0	25000
8				246.4	—						
				253.6	—	245.0	9140	244.4	9290		
				266.0	—	265.4	9660	263.2	10000	268.6	—
		365.0	20830	361.0	—	356.0	19550	353.5	20420	341.0	—

TABLE III (continued)

Nitrones (continued)

No.	Compound	CCl$_4$		n-Heptane		EtOH		MeOH		H$_2$O	
		λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
9				243.9	12210						
				253.8	11250	234.4	10750				
		328.0	21400	327.5	20120	320.5	22350				
10	 ortho			205.6	21200	207.2	17560	207.2	17250	202.3	20350
				226.0	11080	225.7	10290	224.5	10070		
				231.2	11490						
				238.0	10380						
		311.0	20750	307.4	22000	300.5	21770	299.0	21590	295.6	20800
11	 meta			212.3	10740	207.5	18100			203.8	21730
				241.7	11670	233.0	10250			222.6	9560
		324.9	19850	323.3	19650	315.4	20600			308.7	20800
12	 para			205.0	17100	206.0	13960	206.6	14600		
				226.4	9060	233.7	9800	232.0	10230		
				242.6	11240						
		326.0	21450	324.0	20930	317.2	22010	315.3	23600		
13*2						210.8	8220	208.7	8430	207.7	10350
				221.0	5640						
				237.1	6700						
				240.7	6840						
		286.2	11040	286.6	9470	260.5	11690	258.0	11030	253.8	12000
14				206.8	26870	208.0	23580			205.5	—
				231.8	13060	233.7	14130			230.6	—
		307.8	7780	303.9	7570	293.1	6950			282.0	—
15				206.1	33060	210.5	20680	207.6	28770	203.3	—
				234.6	14530	233.7	15810	232.9	15400	231.7	—
		324.0	11270	320.0	11240	312.2	10800	310.5	10780	310.0	—

*1 : ε_{max} and λ_{max} in the region less than 215 mμ are a little ambiguous because of the limitation in the apparatus.

*2 : This configuration is not certain but is most probable.

TABLE III (continued)
The related compounds of nitrones

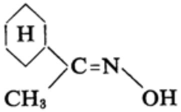
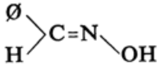
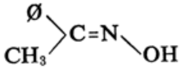
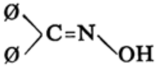
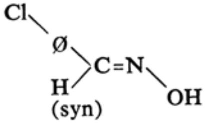
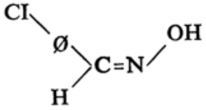
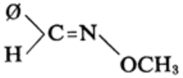
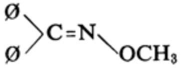
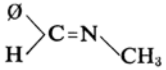
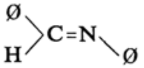
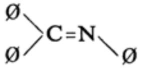
No.	Compound	CCl_4		*n*-Heptane		EtOH		MeOH		H_2O	
		λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
16				205.2	1380					206.4	2140
17				205.5	25170					204.7	24370
				208.3	25200						
				213.7	15370						
				250.2	15160					252.0	15290
				280.8	1269						
				291.2	821					291.2	1043
18				207.7	18060					205.0	18050
				244.0	11990					241.4	11210
19				205.0	33230						
				231.3	15130						
				248.0	11460						
20						207.8	17160[*3]				
						212.6	16520				
						218.4	11490				
						260.0	19240				
						297.4	1530				
21						206.6	14130[*3]				
						210.5	14100				
						253.3	18860				
						292.0	914				
22				207.3	16620	208.6	17170				
				211.3	16880	210.6	17520				
				216.8	11340						
				262.1	13890	261.0	14000				
				293.0	1609	293.0	1743				
23				206.9	25190	210.2	19300				
				232.0	14700	232.0	13990				
				263.0	11060	263.0	10810				

TABLE III (continued)

The related compounds of nitrones (continued)

No.	Compound	CCl$_4$		n-Heptane		EtOH		MeOH		H$_2$O	
		λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
24				205.5	21740	208.5	15430			204.6	16030
				244.0	16660	245.3	15930			250.0	14110
				269.1	999						
		278.0	1240	277.0	973	278.0	1330				
		288.0	893	286.9	751	286.8	884			280.7	1632
25				204.2	25430	206.7	20640				
				218.5	14080	218.0	14390				
				235.3	10770	235.0	9071				
				261.6	17480	263.0					
				310.0	7285	306.0					
26				206.5	38710	210.3	31140	208.4	32660		
				246.0	21120	246.0	19780	245.7	19840		
		344.0	2965	340.9	2639	333.0	2744	330.6	2779		

[3] : In 95% ethanol.

The absorption band of compound 21 shifts to more blue region than that of compound 20, because there is a little steric hindrance for which the benzene ring and the side chain are not in the same plane.[4]

[4] : B. Jersler, *Nature*, **180**, 1410 (1958); **166**, 741 (1950).

TABLE IV. THE RELATIONSHIP BETWEEN C_{CH_3OH} AND $(E-E_{NO})/C_{CH_3OH}$

C_{CH_3OH} mol./l.	E_{280}	$E-E_{NO}$	$(E-E_{NO})/C_{CH_3OH}$	E_{270}	$E-E_{NO}$	$(E-E_{NO})/C_{CH_3OH}$	E_{304}	$E_{NO}-E$	$(E_{NO}-E)/C_{CH_3OH}$
0.0000	0.506	—	—	0.279	—	—	0.720	—	—
0.05165	0.565	0.059	1.142	0.316	0.037	0.716	0.703	0.017	0.329
0.1033	0.593	0.087	0.842	0.340	0.061	0.591	0.670	0.050	0.484
0.1550	0.613	0.107	0.690	0.358	0.079	0.510	0.656	0.064	0.413
0.2066	0.636	0.130	0.629	0.380	0.101	0.489	0.647	0.073	0.353
0.2583	0.640	0.134	0.519	0.385	0.106	0.410	0.635	0.085	0.329
0.3099	0.652	0.146	0.471	0.396	0.117	0.378	0.631	0.089	0.287
0.4358	0.661	0.155	0.356	0.402	0.123	0.282	0.620	0.100	0.229
0.5448	0.674	0.168	0.308	0.420	0.141	0.259	0.615	0.105	0.193

Platt's notation and in the order given above, as Figs. 2a–2d show. In the case of the absorption spectra of nitrones, we could not explicitly find the band corresponding to ^1L_b, but it may be hidden below the strongest π-π^* band.[20] Moreover, in the case of oximes or anils, we could not obviously find the absorption band corresponding to those of nitrones appearing in the 200∼250 mμ region with relatively low intensity and fine structures. These facts clearly suggest that the difference in electronic structures between nitrones and anil-type compounds is fairly large, and that the resonance structures, for example as shown in II–IV, must be taken into consideration.

Recently, the abnormal electronic spectra of such anils as benzylidene aniline have been found by several authors[7,12] and have been discussed from the standpoint of steric hindrance by comparison with the spectra of stilbene or azobenzene. These authors concluded that benzylidene aniline has no planar structure and that two benzene rings are considerably twisted with regard to each other. Spectral curves similar to those obtained by previous authors were also recorded by us for the benzylidene aniline. As may be understood from Figs. 1a, 1b, 1c and 1d, however, in the case of *N*-phenyl benzaldoxime and its analogous nitrones distinctly different spectra from those of, for instance, the benzylidene aniline were observed. These spectra are analogous to those of nitrones with no benzene ring on the *N*-atom in molecules and show, at the longest wavelength region, the strongest π-π^* band, which depends on the nature of the substituent introduced in the benzene ring, as may be seen in Figs. 1a, 1b, and 1c and Table I. This character is similar to that of the spectra shown by normal nitrones, as has been mentioned before, where the steric hindrance may be inferred to be small. This fact indicates that the electronic structure of these nitrones differs considerably from that of, for instance, the benzylidene aniline and that these nitrones may be closely represented by a planar structure, although some steric hindrance may be inferred from the the molecular model shown in Fig. 3.[21]

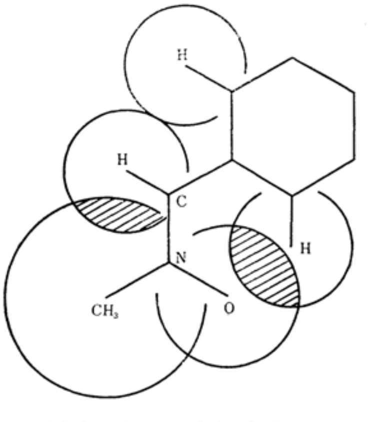


Fig. 3. Molecular model of *N*-methyl benzaldoxime.

Steric Effect on the Electronic Spectra of Nitrones.—It should be clearly noted in Fig. 1d that the intensity of the π-π^* band of *N*-methyl or *N*-phenyl benzophenonoxime is much lower than that of *N*-phenyl benzaldoxime. The same tendency can also be found in the spectra of *N*-methyl acetophenonoxime, the intensity of the π–π^* band of which is much lower than that of *N*-methyl benzaldoxime.

As an example, Fig. 4 shows the molecular model of *N*-methyl benzophenonoxime drawn by the aid of Pauling's van der Waals radii.[21] From this figure it is evident that these nitrones have a considerable steric hindrance for planar structure and that, as is often the case, such a steric hindrance is the main reason for the decrease in the intensity of the characteristic strong π-π^* band of nitrones because the resonance among such canonical structures as II–IV may be hindered by the steric hindrance. The spectroscopic behavior of *N*-methyl acetophenonoxime is of especial interest. This compound can be obtained only by the replacement of the side chain C–H group of *N*-methyl benzaldoxime by a C–CH_3 group.

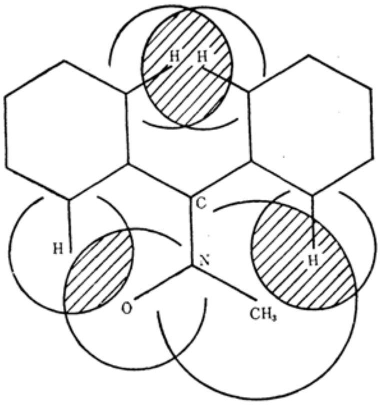


Fig. 4. Molecular model of *N*-methyl benzophenonoxime.

It is well known that the effect of methyl substitution on the electronic spectra of conjugated systems is rather small. Nevertheless, a serious difference was observed between the

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[20] Detailed theoretical calculation results on this point will be published in the next paper.

[21] L. Pauling, "The Nature of the Chemical Bond," 3rd Edition, Cornell University Press, New York (1956), p. 260. C–H, 1.08Å; C–C (aromatic), 1.40; C–C (–Ph), 1.43; C–CH_3, 1.52; C–N, 1.48; N→O, 1.33; C=N 1.32.

spectra of *N*-methyl benzaldoxime and those of *N*-methyl acetophenonoxime. Namely as may be seen in Figs. 1a and 1d, the intensity of the latter is very weak. It seems probable that the steric effect is the main reason for this, as may, for example, be seen in Fig. 5. In this molecule the configuration of the benzene part and the side chain part may depart more from the coplanar structure than from the structure of *N*-methyl benzaldoxime.[22]

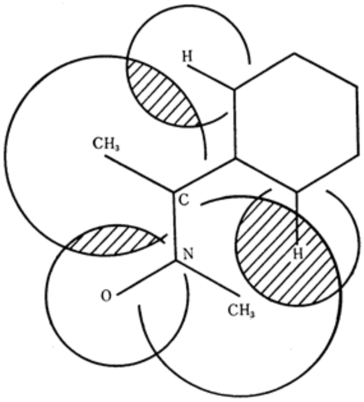
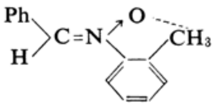


Fig. 5. Molecular model of *N*-methyl acetophenonoxime on the assumption of the "anti" form of phenyl group against N→O bond.

The fact that compound 10 absorbs light at a shorter wavelength than the π-π^* bands of compounds 11 and 12 may also be explained by considering the structure.



Solvent Effect on the Electronic Spectra of Nitrones and Their Related Compounds.—As may clearly be seen in Table I, the blue shift of the absorption bands of all nitrones is caused by the increasing polarity of those solvents which contain active hydrogen atoms which can form hydrogen bonds. This phenomenon is analogous to that discovered generally in heterocyclic *N*-oxides and may be considered to be due to the reason discussed in detail in our previous papers.[1,3] It is conceivable that hydrogen bonding, such as $\gg N \rightarrow O \cdots H$ (solvent), plays an important role in the blue shift phenomenon. In order to make a more detailed study concerning the contribution of the hydrogen-bonding effect, we made an experiment on three component systems (*N*-methyl benzaldoxime, methanol and *n*-heptane). The change in the spectra of *N*-methyl benzaldoxime upon the addition of methanol is shown in Fig. 6. The behavior

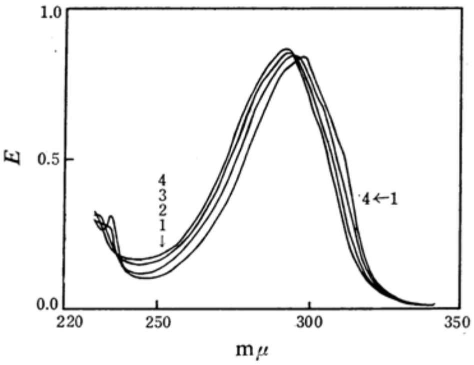


Fig. 6. The UV spectra of *N*-methyl benzaldoxime in *n*-heptane containing methanol.
Concentrations of methanol (mol./l.)
1 : 0.0000 2 : 0.1033 3 : 0.3099 4 : 0.5448
Concentration of *N*-methyl benzaldoxime: 4.217×10^{-5} mol./l.
Temp.: 26.8°C Light path: 1.0 cm.

of the spectra suggests that the equilibrium shown in Eq. 1 may exist.[27]

$$N \rightarrow O + HO\text{-}CH_3 \rightleftarrows N \rightarrow O \cdots HO\text{-}CH_3 \qquad (1)$$

This fact is also supported by the behavior of the OH-stretching band of methanol when nitrone is added, as is shown in Fig. 7. From Eq. 1, the following equation is obtained:

$$K = \frac{[C_{NO \cdots H}]}{[C_{NO} - C_{NO \cdots H}]\ [C_{CH_3OH} - C_{NO \cdots H}]} \qquad (2)$$

where C_{NO}, C_{CH_3OH} and $C_{NO \cdots H}$ are the concentrations of nitrone, methanol and the associated compound respectively. Under the experimental conditions shown in Fig. 6, $C_{CH_3OH} \gg C_{NO \cdots H}$. Then, Eq. 3 is easily obtained by appling the Lambert-Beeer law.

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[22] The configuration shown in Fig. 5 is also supported by the fact that mutual interaction like $\gg N\text{-}O \cdots H_3C$- can be expected. The interaction of this type has often been reported in the heterocyclic *N*-oxides, such as α-picoline *N*-oxide.[4,23-25] Furthermore, this structure is more reasonable from the stand-point of chemical reactivities.[26]

[23] N. Ikekawa and Y. Sato, *Pharm. Bull. Japan*, **2**, 400 (1954).

[24] T. Kubota, *J. Pharm. Soc. Japan*, **77**, 785 (1957).

[25] N. Hata, This Bulletin, **34**, 1440 (1961).

[26] Y. Mori, to be published.

[27] In this case, it was found that the fine structure at about 293.4 mμ disappeared rapidly upon the addition of a small amount of methanol, and no fine isosbestic point could be obtained. This shows some contribution from effects other than the hydrogen bonding. Howevor, it is clear that the shift due to the hydrogen-bonding effect is the largest. This fact is also supported by the behavior of the infrared spectra shown in Fig. 7.[27a]

[27a] See also footnote 3, and the following paper concerning the investigation of infrared spectra: H. Shindo and B. Umezawa, *Chem. Pharm. Bull.*, **10**, 492 (1962).

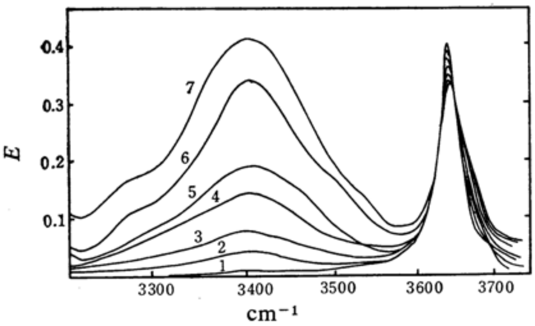


Fig. 7. The O–H stretching bands of methanol in carbon tetrachloride containing *N*-methyl benzaldoxime.
Concentration of *N*-methyl benzaldoxime ($\times 10^{-3}$ mol./l.)
1: 0.0000 2: 4.380 3: 9.510 4: 19.9
5: 27.6 6: 52.9 7: 79.4
Concentration of methanol: 0.0102 mol./l.
Temp.: 24.0°C Light path: 1.0 cm.

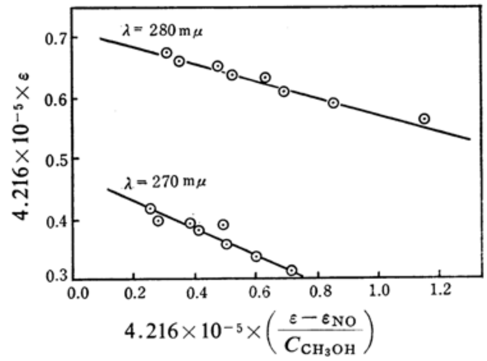


Fig. 8. The relationship between ε and $(\varepsilon - \varepsilon_{NO})/C_{CH_3OH}$ for *N*-methyl benzaldoxime.

$$\varepsilon = \frac{1}{K}\left(\frac{\varepsilon_{NO} - \varepsilon}{C_{CH_3OH}}\right) + \varepsilon_{NO\cdots H} \tag{3}$$

where ε is an apparent molecular extinction coefficient, and ε_{NO} and $\varepsilon_{NO\cdots H}$ are the molecular extinction coefficients of nitrone and the hydrogen-bonding compound respectively. The relations of Eq. 3 at various wavelengths are shown in Fig. 8 and Table IV. The averaged value of K is 5.6 l./mol., while the degree of blue shift caused by hydrogen bonding (1 : 1) is about 642 cm^{-1}. In addition, the degree of the red shift of the OH-stretching band resulting from this hydrogen bonding effect is about 238 cm^{-1}. In the case of *N*-methyl acetophenonoxime, its absorption bands shift largely to blue upon the addition of a small quantity of methanol, as is shown in Fig. 9, where no good isosbestic point could be obtained. The absorption bands of oximes and anils did not show such a large blue shift with the increasing polarity of solvents as was found for

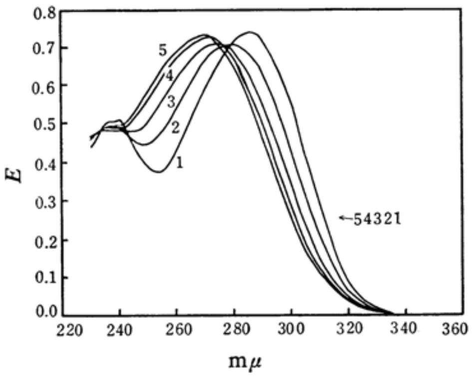
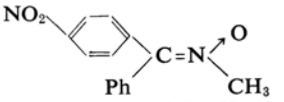


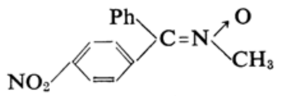
Fig. 9. The UV spectra of *N*-methyl acetophenonoxime in *n*-heptane containing methanol.
Concentrations of methanol (mol./l.)
1: 0.0000 2: 0.02596 3: 0.05192
4: 0.07788 5: 0.10384
Concentration of *N*-methyl acetophenonoxime: 1.184 mg./100 ml.
Temp.: 30°C Light path: 1.0 cm.

nitrones or heterocyclic *N*-oxides.[1] Generally, the solvent effect on the spectra of these compounds is very small. These results suggest that the blue shift is characteristic of conjugated *N*-oxides; this phenomenon was always observed in both heterocyclic *N*-oxides and nitrones. It seems that hydrogen bonding, such as N→O···H–O– (solvents), plays an important role in this phenomenon.[28]

On the Configuration of Nitrones.—Whether the conjugated system of nitrones is a syn or an anti form is very important for the analysis of these spectra, which has been described before and which will be discussed in the next paper more fully, and for the problem of the steric hindrance, which was discussed in the previous section. The configurations of nitrones are inferred from the methods of synthesis,[29] their reactivities,[29] and the measurement of the dipole moments which are



6.60 D. U.



1.09 D. U.

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[28] After we finished work on this paper, we learned of the paper by Kinko Shinzawa, of the Tokyo Institute of Technology, read at "The Symposium on Photochemistry" held by the Chemical Society of Japan, in Nagoya, October 17, 1962, in which she found that free nitrone (benzylidene aniline *N*-oxide) and hydrogen-bonded nitrone clearly show a different behavior in the quantum yield of the photochemical reaction.

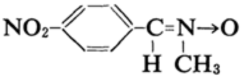
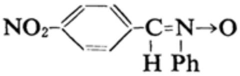
[29] Y. Mori, to be published.

TABLE V. THE DIPOLE MOMENTS OF COMPOUNDS 1, 5, AND 8*

Compound	α	β	$P_{2\infty}$, cc.	MR_D, cc.	μ, D.	Solvent
1	10.02	0.21	290.24	39.89	3.49	Benzene
5	26.88	0.30	835.5	45.56	6.20	Dioxane
8	20.98	0.31	886.58	65.31	6.32	Dioxane

*: In this Table, α and β denote the changes in the dielectric constant and in the density of the solutions with the weight fraction of the solute respectively, and other notations have their usual meaning.

shown in Table V. The dipole moments of the following compounds were measured by Taylar and Sutton.[30]

The dipole moment of the compound in which the nitrophenyl group is cis against the *N*-oxide group is 6.60 D. U., but that for the trans form is 1.09 D. U. The measured dipole moments of  and  are 6.20 D. U. and 6.32 D. U. respectively. Therefore, it may reasonably be considered that these configurations are the anti form, that is, that the nitrophenyl group is cis to the *N*-oxide group. The nitrone configurations shown in Table I have been decided on the basis of the reasonable assumption that the nitrones synthesized with the same method have the same configuration. This rule may be safely applied for compounds of this type.

It seems that these configurations give a reasonable explanation of the steric effect on the spectra of nitrones and for the reactivity of these compounds.[29]

Summary

The ultraviolet spectra of nitrones, the configurations of which were assumed from their dipole moments and chemical reactivities, and their related compounds have been measured in various solvents. The following results have been obtained:

(1) Nitrones show a characteristic strong π-π^* band in the 280~370 mμ region as well as one or two additional bands with a relatively low intensity in the 200~260 mμ region. The molecular extinction coefficient (ε) of the former is about 20000. The decrease in intensity of the π-π^* band is observed in the spectra of the sterically-hindered compounds.

(2) These bands always show a blue shifs with the increasing polarity of the solvent. The general rule of solvent effect on heterocyclic *N*-oxides applies also to nitrones, the conjugated *N*-oxide band of which has the same property as that of heterocyclic *N*-oxides.

(3) It has been confirmed by ultraviolet and infrared spectra that the formation of a hydrogen bond such as N→O···H (solvent) plays an important role in this blue shift phenomenon.

The authors wish to express their deep gratitude to Professor Emeritus Eiji Ochiai of The University of Tokyo for his kind guidance throughout the course of this work; to Professor Saburo Nagakura of the Institute for Solid State Physics, The University of Tokyo, for his valuable discussions and for reading the manuscript; to Dr. Ken'ichi Takeda, Director of this Research Laboratory, and Dr. Noboru Mataga of Osaka Municipal University for their valuable advice; to Dr. Haruyuki Watanabe of this Research Laboratory for the measurement of the dipole moments and for valuable advice, and to Mr. Mamoru Takasuka for the measurement of the infrared spectra.

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