UDC 547.233-31+547.821-31 : 543.422.4

78. Hideyo Shindo*1 and Bunsuke Umezawa*2 : Infrared Absorption Spectra of Aldonitrones. I. Infrared Spectra of Benzaldehyde N-Methyl and N-Phenyl Nitrones.

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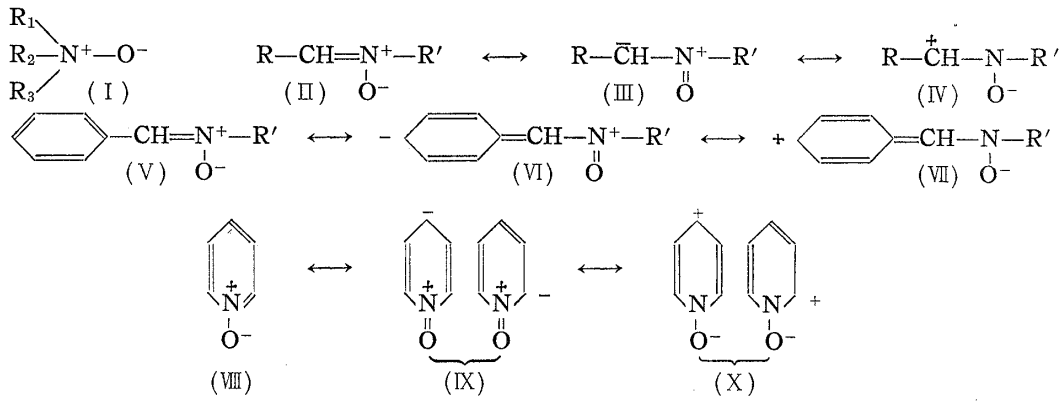
In ordinary aliphatic amine N-oxides (I), the N-O bond constitutes almost a pure co-ordinate linkage and there is little or no possibility for resonance. In aldonitrones (II), however, there are some possibilities for resonance as illustrated in the possible electronic structures, III and IV. In particular, in aldonitrones, where R is an aryl group, there are increased possibilities for resonance owing to conjugation with the aryl ring, as illustrated in V～VII. On the other hand, in heteroaromatic N-oxides such as pyridine N-oxide (VIII) it has been established from many chemical[1,2] and physico-chemical studies[3~5] that the contribution of the electronic structures as IX and X is very great in the resonance system and the N-O bond has a considerable double bond character. Therefore, it may be expected that the N-O bond in aldonitrones has just the intermediate properties of those in aliphatic and heteroaromatic N-oxides.



One of the present authors[3,6] previously investigated the infrared spectra of hetero-aromatic N-oxides and found that their N-O stretching vibrations appeared as a strong absorption in the region of 1350 and 1190 cm^{-1}, the frequencies varying within this range depending upon the electronic nature of the ring substituents. This absorption region is considerably higher frequencies than that of the N-O frequencies in aliphatic amine N-oxides (970～940 cm^{-1}),[7] indicating that the N-O bond in heteroaromatic N-oxides has a considerable double bond character according to a large contribution of the resonance structures of the type IX.

The present series of works were undertaken to make clear the nature of the N-O bond in aldonitrones by mean of infrared spectroscopy and to find its correlation to their reactivities.[8] In the present paper, the infrared spectra of benzaldehyde N-methyl and

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1) E. Ochiai : J. Org. Chem., **18**, 534 (1953).
2) A.R. Katritzky : Quart. Revs., **10**, 395 (1956).
3) H. Shindo : This Bulletin, **4**, 460 (1956), **6**, 117 (1958).
4) A.R. Katritzky, E.W. Randall, L.E. Sutton : J. Chem. Soc., **1957**, 1769.
5) T. Kubota : J. Chem. Soc. Japan, **80**, 578 (1959).
6) H. Shindo : This Bulletin, 8, 33, 845 (1960).
7) R. Mathis-Noel, R. Wolf, F. Gallais : Compt. rend., **242**, 1873 (1956).
8) B. Umezawa : This Bulletin, 8, 698, 967 (1960).

N-phenyl nitrones and their corresponding imines, which were chosen as the basic compounds of the series where R is an aryl and R′ is an alkyl or an aryl groups, were determined and the N-O stretching and other characteristic frequencies were assigned and discussed.

The infrared spectra of aldonitrones have ever been described in several cases on their C=N[9] and N-O[10] stretching frequencies, but any detailed assignment or discussion has not yet been made.

Results and Discussion

The infrared spectra of benzaldehyde N-methyl and N-phenyl nitrones and their corresponding imines are shown in Fig. 1.

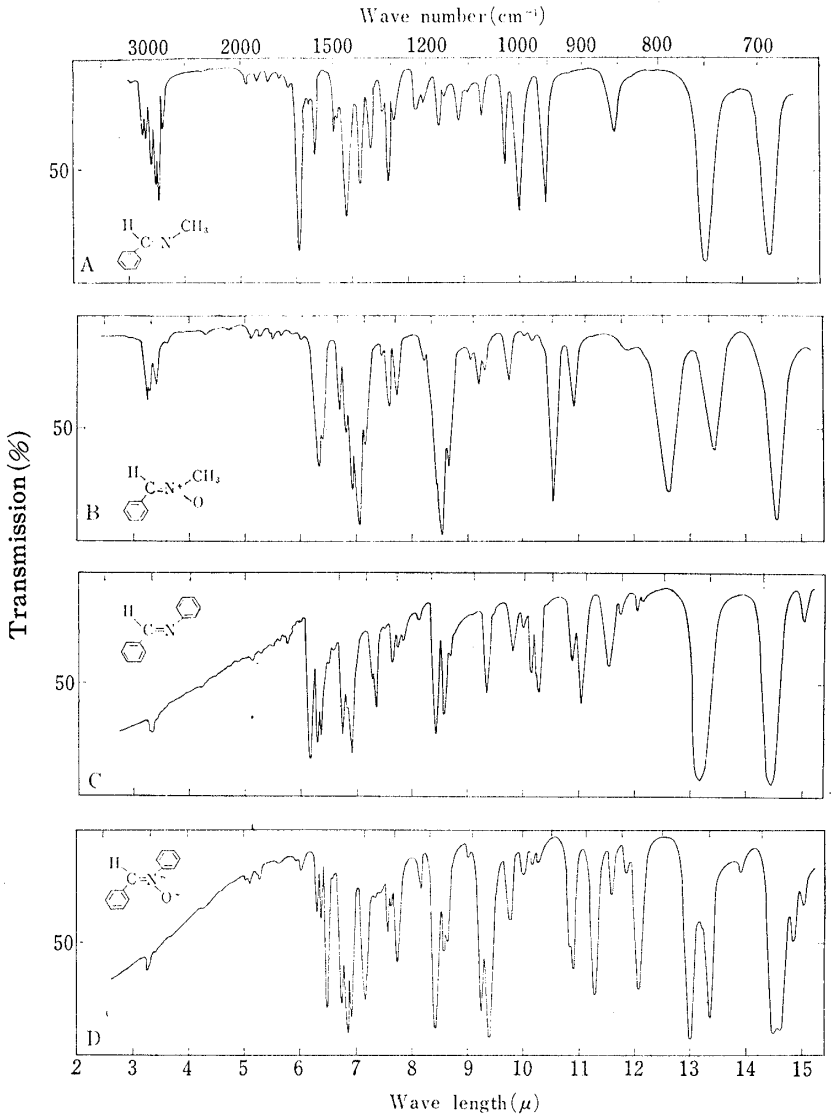
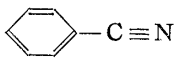
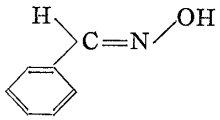
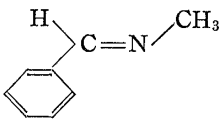
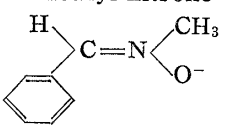


Fig. 1. Infrared Absorption Spectra of (A) Benzylidene Methylimine, (B) Benzaldehyde N-Methyl Nitrone (5.0% solution in CCl_4 and CS_2, cell thickness : 0.2 mm.), (C) Benzyliden Phenylimine, and (D) Benzaldehyde N-Phenyl Nitrone (Nujol and Hexachlorobutadiene Mull).

9) a) R. Bonnett, *et al.* : J. Chem. Soc., **1959**, 2094, 2102; R.F.C. Brown, *et al.* : *Ibid.*, **1959**, 2109, 2116. b) H. Krimm : Chem. Ber., **92**, 1057 (1958).
10) J. Thesing, W. Sirrenberg : Chem. Ber., **92**, 1748 (1959).

From the reason described above, the N-O stretching vibration of aldonitrones may be expected to absorb strongly somewhere between the N-O frequencies of heteroaromatic and aliphatic amine N-oxides, *i.e.*, between 1200 and 950 cm^{-1}. In fact, as can be seen in Fig. 1, N-methyl and N-phenyl nitrones show very strong absorptions at 1172 and 1067 cm^{-1}, respectively, which are absent in the spectra of the corresponding imines. From the following three considerations, these bands were assigned to their N-O stretching frequencies : i) Comparison with the spectra of related compounds and assignment of the

Table I. Observed Maxima and the Assignment for Benzaldehyde N-Methyl Nitrone and the Related Compounds in the 1700~650 cm^{-1} Region[a]

Benzonitrile 	α-Benzaldoxime 	Benzylidene methylimine 	Benzaldehyde N-methyl nitrone[b] 	Assignment[c]
—	1634 w	**1656 s**	**1587 ms**	**C=N stretching**
1602 m	1603 vw	1603 w		Ring (A_1, 8a)
1582 w	1580 w	1582 ms	1569 m	Ring (B_1, 8b)
1495 s	1495 ms	1498 m	1494 m	Ring (A_1, 19a)
—	—	1486 sh	1470 m	CH_3 deg. deformation
1450 s	1452 ms	1451 s	1449 ms	Ring (B_1, 19b)
—	1403 m	**1366 m**	**1419 vs**	**CH in-plane bending**
—	—	1403 ms	1397 m	CH_3 sym. deformation
1387 w		1323 w	1335 w	Ring (B_1, 14) and
1333 w	1315 m	1309 ms	1321 m	Overtone
1285 m	1287 m	1290 m	1296 m	Overtone (6a+10b)
—	1258 s[d]	—	—	OH in-plane bending
—	—	1225 m	1220 w	
1190 w	1208 w	1208 w	1189 sh	H bending (A_1, 9a, B_1, 3)
1176 m	1174 m	1169 m	1181 sh	Ph-C stretching
—	—	—	**1172 vs**	**N-O stretching**
1161 w	1156 vw	1156 w	1157 sh	H bending (B_1, 15)
—	—	1123 m	1085 m	CH_3 rocking
1095 w	1100 w	1101 wv	1101 w	Overtone
1070 m	1073 m	1073 m	1073 m	H bending (A_1, 18a, B_1, 18b)
1027 ms	1028 w	1027 ms	1028 m	Ring (A_1, 1)
1000 w			996 vw, 984 vw	Ring (A_1, 12)
—	—	**1001 s**	**949 s**	**C-N stretching**
923 ms	910 sh	956 ms	917 m	H bending (B_2, 5)
—	946 vs[d]	—	—	N-O stretching[e]
—	867 s	**857 ms**	**794 s**	**CH out-of-plane bending**
818 w	837 w		838 vw	H bending (A_2, 10a)
754 vs	752 vs	750 vs	745 s	H bending (B_2, 10b)
685 vs	689 vs	690 vs	687 vs	Ring (B_2, 4)

a) In CS_2(1400~650 cm^{-1}) and CCl_4(1700~1400 cm^{-1}), 2.0 or 20.0% solution, cell thicknes : 1.0 or 0.1 mm.
vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; vw, very weak.

b) Aldonitrones have generally trans configuration. c.f. L.E. Sutton *et al.* : J. Chem. Soc., **1931**, 2190, J. Thesing *et al.* : Chem. Ber., **91**, 1978 (1958).
The configuration of the corresponding imines has not yet been established, but can be assumed to be also trans from the steric view-point.

c) In parentheses, assignment is given by analogy with that for benzonitrile, assuming C_{2v} symmetry for Ph-C group in these compounds.
The characteristic frequencies for the nitrone and the imine are shown in bold-faced type.

d) In concentrated solution, additional strong bands are shown at 1302 and 969 cm^{-1}, respectively, corresponding to the OH and the N-O frequencies of associated molecules, which diminish in their intensities on dilution.

e) c.f. A. Palm, H. Werbin : Can. J. Chem., **32**, 858 (1954).

absorptions originating in mono-substituted benzene rings, which are known to be fairly constant in their positions irrespective of the kind of substituents.[11] ii) The solvent effect of methanol and water, which is expected to cause a marked change in their electronic state through hydrogen bond formation. iii) Observation of the change in their spectra on irradiation of ultra-violet light, which is known to cause a photo-chemical reaction.[12]

Benzaldehyde N-Methyl Nitrone——The observed maxima for benzaldehyde N-methyl nitrone and the corresponding imine in the 1700~650 cm^{-1} region are shown in Table I, in comparison with those for benzonitrile and benzaldoxime. Comparison of the maxima revealed that most of the absorptions due to a phenyl ring showed a good correspondence in their frequencies and intensities through these four compounds, and they were easily selected out and assigned by analogy with the assignment of benzonitrile made by Bak *et al*,[13] as shown in the Table. In this case, benzonitrile is the most suitable as a standard for monosubstituted benzenes since it does not contain any fundamental originating in the C≡N group in the 2000~650 cm^{-1} region. Ph-C stretching frequencies were also assigned by analogy with the assignment of 1176 cm^{-1} band in benzonitrile. As the hydrogen out-of-plane bending frequencies corresponding to the 923 cm^{-1} band in benzonitrile (ν_5), the bands at 956 and 917 cm^{-1} in the nitrone and the imine, respectively, were chosen from the interpretation of their combination bands ($\nu_5+\nu_{10b}$)[14] observed weakly near 1700 cm^{-1}, as shown below.

	Benzonitrile	Benzylidene methylimine	Benzaldehyde N-methyl nitrone
Combination (obs.)	1675 w	1710 v w	1657 w
$\nu_{10b}+\nu_5$	754+923 =1677	750+956 =1706	745+917 =1662

Three deformation frequencies expected for a methyl group were also reasonably assigned as shown in the Table, by comparison of the spectra of these and other related compounds.

For the $-CH=N^{+}(O^{-})-C$ group in aldonitrones, the following five characteristic vibration frequencies are expected to occur in this region : C=N, N-O and C-N stretching and CH in-plane and out-of-plane bending frequencies. Other skeletal deformation modes are expected to absorb roughly in the region below 600 cm^{-1}.

The band at 1585 cm^{-1} in the nitrone can be attributed to the C=N stretching frequency, rather than a phenyl ring vibration, corresponding to the band at 1656 cm^{-1} in the imine, and this assignment was confirmed by the study of solvent effect, as will be described later. Such a large shift of this frequency to a lower frequency has been described[9] also in aliphatic nitrones and is considered to be characteristic for nitrones as compared with the corresponding imines.

The bands at 1419 and 794 cm^{-1} in the nitrone are assigned to the CH in-plane and out-of-plane bending frequencies, respectively, since they have the corresponding bands both in the imine and the oxime, but not in the nitrile. It is reasonable to assign the band near 1400 cm^{-1} to the CH in-plane bending mode in -CH=N- systems, since C-deuterated oximes show a new moderate strength band attributable to the CD in-plane

11) R. R. Randle, D. H. Whiffen : "The Characteristic Vibration Frequencies of Substituted Benzene" Inst. Petroleum, London (1955).
12) M. J. Kamlet, L. A. Kaplan : J. Org. Chem.. **22**, 576 (1957).
13) B. Bak, J. T. Nielsen : Z. Elektrochem., **64**, 560 (1960).
14) D. H. Whiffen : Spectrochim. Acta., **7**, 253 (1955); Y. Kakiuchi : J. Chem. Soc. Japan, **80**, 28 (1959).

bending mode at about 1040 cm^{-1}.*[3,15] This frequency could be differenciated from the CH_3 degenerate deformation by comparison with the spectra of the corresponding N-phenyl derivatives which show this frequency at 1368 and 1398 cm^{-1} in the imine and the nitrone, respectively. This band is particularly strong and characteristic in the nitrone, but that this band does not relate to any N-O mode in its origin was confirmed by the experiment of irradiation of ultra-violet light, as will be described later.

The very strong absorption at 1172 cm^{-1} in the nitrone is absent in other three compounds and is clearly assigned to the N-O stretching frequency. Then, the only remained strong band at 949 cm^{-1} in the nitrone must be ascribed to the C-N stretching frequency which may correspond to the strong band at 1001 cm^{-1} in the imine. This assignment is reasonable in the positions, since the same mode in nitroso-[16] and nitro-[17] methanes have been assigned to the bands at 914 and 842 cm^{-1}, respectively.

It was previously found[3,18] that the N-O stretching frequencies in pyridine N-oxides exhibited a marked shift to a lower frequency (50~20 cm^{-1}) in a solvent capable of hydrogen bond formation and it was considered that the hydrogen bond formation of the N-oxide linkage prevented the contribution of the resonance structures as IX and the resultant decrease in the double bond character of the N-O bond caused a displacement of its stretching frequency to a lower frequency. Therefore, assuming that the contribution of the electronic structures as VI is also operating in the resonance system of aldonitrones, their N-O stretching frequencies should show a similar shift in a solvent capable of hydrogen bond formation. As shown in Table II, indeed, the strong band at 1172 cm^{-1} of the nitrone showed a marked shift to a lower frequency in a solvent containing methanol and, more distinctly, in water. This can be explained also in terms of the

Table II. Solvent Effects of Methanol and Water on the Absorptions of Benzaldehyde N-Methyl Nitrone in the 1700~900 cm^{-1} Region

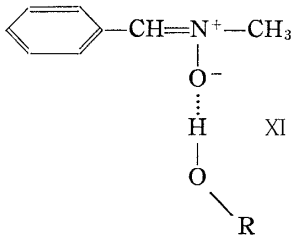
Observed Maxima (cm^{-1})					Assignment
in CCl_4	in 10% CH_3OH/CCl_4		in H_2O or D_2O		
1587 ms	1601	+14	1609 m	+22	C=N stretching
1569 m	1570				
1494 m	1494		1494 m		
1470 m	1470				
1449 ms	1450		1449 ms		
1419 vs	1416	− 3	1411 s	− 8	CH in-plane bending
1397 m	1400	+ 3	1406 sh	+ 9	CH_3 sym. deformation
1321 m	1321		1323 m		
1296 m	1296		1297 m		
1220 w	1220		1220 w		
1181 sh	1181		1180 sh		Ph-C stretching
1172 vs	1164	− 8	1152 s	−20	N-O stretching
1157 sh	1156[a]				
1085 m	1091	+ 6	1094 w	+ 9	CH_3 rocking
1073 w	1073		1074 w		
1028 m			1028 w		
949 vs	944	− 5	936 ms	−13	C-N stretching
917 m	922	+ 5			

a) The intensity was largely increased.

*3 The 1258 cm^{-1} band in benzaldoxime is attributed to the OH in-plane bending frequency from the increase in its intensity on dilution, as indicated in Table I.

15) Y. Matsui: Private Communication.
16) W. Lüttke: Z. Elektrochem., **61**, 302 (1957).
17) D.C. Smith, C.Y. Pan, J.R. Nielsen: J. Chem. Phys., **18**, 7060 (1950).
18) H. Shindo: This Bulletin, **7**, 791 (1959).

decrease in the double bond character of the N-O bond as the result of inhibition in the contribution of resonance structures as VI through hydrogen bond formation like XI.



XI

While, the C-N stretching frequency at 949 cm^{-1} also showed an appreciable shift to a lower frequency and this seems to indicate that this band also involves some contribution of the N-O stretching mode through a mechanical coupling. Although the occurrence of such a coupling is very probable in this system, the extent of coupling is considered to be only small in this case, because the frequency difference of the two absorptions is too large.

On the other hand, the band at 1587 cm^{-1} which was ascribed to the C=N stretching frequency showed a marked shift to a higher frequency. This behavior is that expected for this mode, because inhibition in the contribution of resonance structures as VI through hydrogen bond formation may result in an increase of the double bond character of the C=N bond and in a consequential shift of its stretching frequency to a higher frequency. Reversely, therefore, the large shift of this frequency to a lower frequency as compared with that of the imine (1656 cm^{-1}) can be attributed to a large contribution of resonance structures as VI to the electronic state of the nitrone.

As shown in Table II, it was also noted that the =CH and CH_3 deformation frequencies showed an appreciable shift, possibly corresponding to a large change in the electronic state of the nitrone through hydrogen bond formation. All other absorptions which are ascribed to the benzene vibrations did not show any appreciable shift.

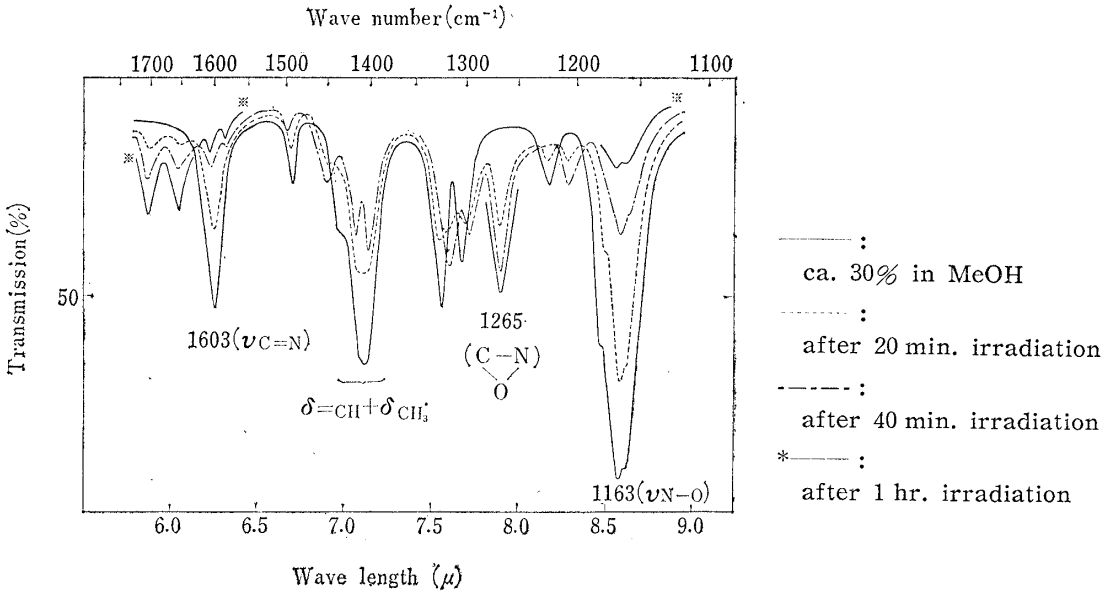
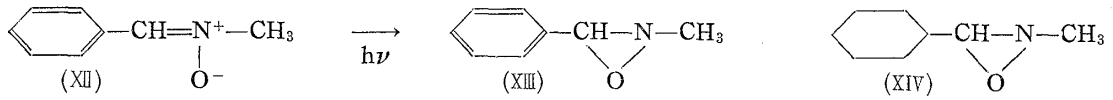


Fig. 2. Change in the Infrared Spectrum of Benzaldehyde N-Methyl Nitrone on Irradiation of Ultra-violet Light

As shown in Fig. 2, the infrared spectrum of the nitrone in methanol showed a striking change on irradiation of ultra-violet light (2536 A). Both the N-O and the C=N stretching absorptions at 1163 and 1603 cm^{-1} in methanol markedly diminished in their intensities and on enough irradiation almost completely disappeared, while a new prominent absorption appeared at 1265 cm^{-1}. These spectral change can be reasonably explained by assuming that there takes place a photochemical conversion of the nitrone to the corresponding isonitrone XIII, as suggested by Kamlet *et al.*[12] The band at 1265 cm^{-1} is considered to be a characteristic absorption for the oxaziridine ring, since an epoxide ring[19] has a characteristic absorption near 1265 cm^{-1} and the compound XIV[20] shows also a strong absorption at 1259 cm^{-1}. The band at 1404 cm^{-1} in methanol, which is splitted into two bands at 1419 and 1397 cm^{-1} in carbon tetrachloride, remains as two separated bands till the last stage of this conversion, confirming the assignment of CH and CH_3 deformation frequencies to these bands.



After about forty minutes' irradiation, two new weak bands appeared at 1702 and 1653 cm^{-1}. These positions coincide with the carbonyl frequencies of benzaldehyde and N-methyl benzamide, respectively, and these may be products in a secondary change of XIII.

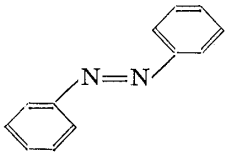
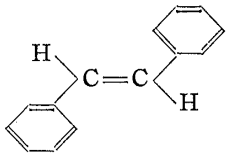
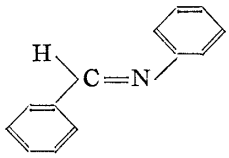
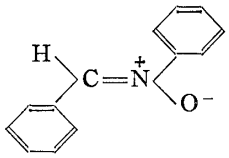
Benzaldehyde N-Phenyl Nitrone——The observed maxima for benzaldehyde N-phenyl nitrone and the corresponding imine in the 1700~650 cm^{-1} region are shown in Table III, in comparison with those for trans azo-benzene and trans stilbene. The infrared spectra of the latter two reference compounds have been analyzed by Mecke *et al.*,[21] Maier *et al.*,[22] and Kübler *et al.*,[23] although some discrepancies are found between their detailed assignment. Thus, in the same way as in the N-methyl nitrone, the absorptions originating in monosubstituted benzene rings could be selected out and the approximate assignment was made as shown in the Table. In the N-phenyl nitrone these absorption are somewhat complex as compared with those in the N-methyl nitrone and in some cases, particularly in the out-of-plane vibrations, the doublet was attributed to one vibrational mode. This, however, seems to be reasonable, because the presence of two unequivalent benzene rings in a molecule may cause a mechanical coupling between the same vibrations in the two rings.

From a comparison of these spectra, the C=N stretching frequencies are clearly assigned to the strong bands at 1548 and 1629 cm^{-1} in the nitrone and the imine, respectively, the former showing a characteristic large shift to a lower frequency than the latter. The CH in-plane and out-of-plane bending frequencies are also reasonably assigned as shown in the Table, their positions and intensities being in good agreement with those in the N-methyl nitrone.

The C-N stretching frequency in the N-phenyl derivatives is expected to be higher than that in the N-methyl derivatives, i.e. the 1000 cm^{-1} region, because the C-N bond in question must have more double bond character than that in the latter. It has been clarified, recently, that a medium strength band at 1219 cm^{-1} and a very weak band at 812 cm^{-1} in trans azobenzene are attributable to the bands of Ph-N character, from the study using ^{15}N-compound by Kübler *et al.*[23] Therefore, the strong bands at 1191 and

19) W. A. Patterson : Anal. Chem., **26**, 823 (1954).
20) Ref. 9b) and D. M. S. Card No. 3913.
21) R. Mecke, E. Greinacher : Z. Elektrochem., **61**, 530 (1957).
22) W. Maier, G. Englert : *Ibid.*, **62**, 1020 (1958).
23) R. Kübler, W. Lüttke, S. Weckherlin : *Ibid.*, **64**, 650 (1960).

TABLE III. Observed Maxima and the Assignment for Benzaldehyde N-Phenyl Nitrone and the Related Compounds in the 1700~650 cm^{-1} Region[a]

trans-Azobenzene	*trans*-Stilbene	Benzylidene phenylimine	Benzaldehyde N-phenyl nitrone[b]	Assignment[c]
				
—	—	**1629 s**	—	**C=N stretching**
(1601)[d]	1599 m	1592 s	1592 m	Ring, A_1
1584 m	1578 w	1580 s	1575 m	Ring, B_1
—	—	—	**1548 s**	**C=N stretching**
1486 s	1497 s	1487 ms	1487 s	Ring, A_1
1456 s	1453 s	1453 s	1464 s 1447 s	Ring, B_1
—	1331 w	**1368 m**	**1398 s**	**CH in-plane bending**
1397 w	1389 w	1314 m	1324 m	
1297 ms	1298 w	1297 w	1296 ms	Ring, B_1
—	1219 w	1238 vw	1229 m	Ph-C stretching
1219 m	—	**1192 s**	**1191 s**	**Ph-N stretching**
1156 m	1179 vw	1171 ms	1170 m	H bending, A_1
1150 m	1155 m	1156 w	1160 m	H bending, B_1
1071 ms	1072 ms	1073 ms	1082 s	H bending, B_1
—	—	—	**1067 vs**	**N-O stretching**
1019 ms	1029 m	1022 m	1025 m	H bending, A_1
999 m	1001 w	1001 w	1000 w	Ring, A_1
984 w	984 m	988 m 975 ms	985 m 974 w	H bending, A_2
—	963 s	—	—	CH out-of-plane bending
925 s	909 m	924 m 907 ms	924 sh 919 ms	H bending, B_2
—	—	**869 ms**	**887 ms**	**CH out-of-plane bending**
849 w	846 w	853 w	864 m	H bending, A_2
812 vw	—	833 w	845 w	Ph-N vibration
—	—	—	829 ms	
775 vs	764 vs	759 vs	770 s 750 s	H bending, B_2
688 vs	691 vs	692 vs	691 s 686 s	Ring, B_2

a) Nujol and Hexachlorobutadiene Mull.
vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; vw, very weak.
b) The same as b) in Table I.
c) Symmetry class of the vibrations is indicated by analogy with those given for *trans* azobenzene (ref. 23).
The characteristic frequencies for the nitrone and the imine are shown in bold-faced type.
d) Raman datum.

1192 cm^{-1} in the nitrone and the imine, respectively, are reasonably assigned to the band concerning mainly to the C-N stretching mode.*4 The weak bands at 845 and 833 cm^{-1} in the nitrone and the imine, respectively, are also ascribed to the bands involving some Ph-N character, corresponding to the band at 812 cm^{-1} in *trans* azobenzene.*5 In a similar way, Lüttke[16] has considered the two bands at 1110 and 810 cm^{-1} and 1109 and 851 cm^{-1} in nitroso- and nitrobenzenes, respectively, as the Ph-N stretching mode.

Thus, the very strong absorption at 1067 cm^{-1} in the nitrone, which is absent in the imine, is clearly assigned to the N-O stretching frequency. It is noted, however, that

*4 More correctly, the two bands near 1190 and 1230 cm^{-1} must be considered to be coupled Ph-N and Ph-C stretching frequencies.
*5 The C-N stretching motion is requires from two different modes of the phenyl vibration.

a phenyl hydrogen in-plane bending frequency which appears in all other compounds (see also Table I) at a very constant position of $1072\pm2\,cm^{-1}$ is shown in the nitrone at an appreciably higher frequency of $1082\,cm^{-1}$ with enhanced intensity. This fact might indicate that this vibration is interacting with the N-O stretching vibration to a considerable extent, and, indeed, the average frequency of these two vibrations amounts to $1074\,cm^{-1}$ which coincides with the normal frequency of the former vibration. Therefore, these two absorptions must be considered to be a coupled N-O stretching frequency.

The origin of the band at $829\,cm^{-1}$ in the nitrone which is absent in any other compounds cannot be explained, but it is probable that this may be the Ph-N vibration corresponding to the $812\,cm^{-1}$ band in *trans* azobenzene enhanced in its intensity for some reason.

These assignment could be confirmed by the study of the solvent effects of methanol and water, as shown in Table IV. Both of the two bands at 1088 and 1071 cm^{-1} in carbon

Table IV. Solvent Effects of Methanol and Water on the Absorption Bands of Benzaldehyde N-Phenyl Nitorone in the 1700~900 cm^{-1} Region

Observed Maxima (cm^{-1}) in CCl_4	in 10% MeOH/CCl_4		in D_2O+MeOH (1:2)[a]		Assignment
1595 m	1596		1597		
1575 m	1578		1578		
1548 ms	1554	+ 5	1563	+15	C=N stretching
1490 ms	1490		1488		
1463 s	1462				
1448 ms	1447				
1408 s	1403	− 5	1397	−11	CH in-plane bending
1323 m	1325		1326		
1297 m	1297		1296		
1190 s	1190		1189		C-N stretching
1105 m	1103				
1088 ms	1081	− 7	1078	−10	N-O stretching
1071 s	1066	− 5	1058	−13	
918 m	919				
890 m	888				

a) The mixed solvent was used, since the sample was not very soluble in water.

tetrachloride showed a marked shift to a lower frequency of approximately the same magnitude, indicating that the N-O stretching mode contributes to these two absorptions to the same extent and these two bands must be attributed to a coupled N-O stretching frequency. That the Ph-N stretching frequency at $1190\,cm^{-1}$ did not show any appreciable shift indicates the lack of coupling with the N-O stretching mode. In the same way as in the N-methyl nitrone, the C=N stretching frequency at $1548\,cm^{-1}$ showed a marked shift to a higher frequency and the CH in-plane bending frequency at $1408\,cm^{-1}$ showed also an appreciable shift to a lower frequency.

These behaviors of the characteristic frequencies are reasonably interpreted in the same way as in the N-methyl nitrone, in terms of inhibition in the contribution of resonance structures as VI through hydrogen bond formation.

As shown in Fig. 3, the spectrum of the N-phenyl nitrone in methanol also exhibited a striking change on irradiation of ultra-violet light, but the change occurred much more rapidly and in much more complex manner than that observed in the N-methyl nitrone. Both the N-O and the C=N stretching frequencies at $1063\,cm^{-1}$ (with a shoulder at 1078 cm^{-1}) and $1562\,cm^{-1}$ in methanol, respectively, almost completely disappeared and the Ph-N stretching frequency at $1190\,cm^{-1}$ also showed a marked decrease in its intensity.*6

*6 That this band does not perfectly disappear is reasonable, since the newly produced imine (XVII) has a strong absorption at the same position.

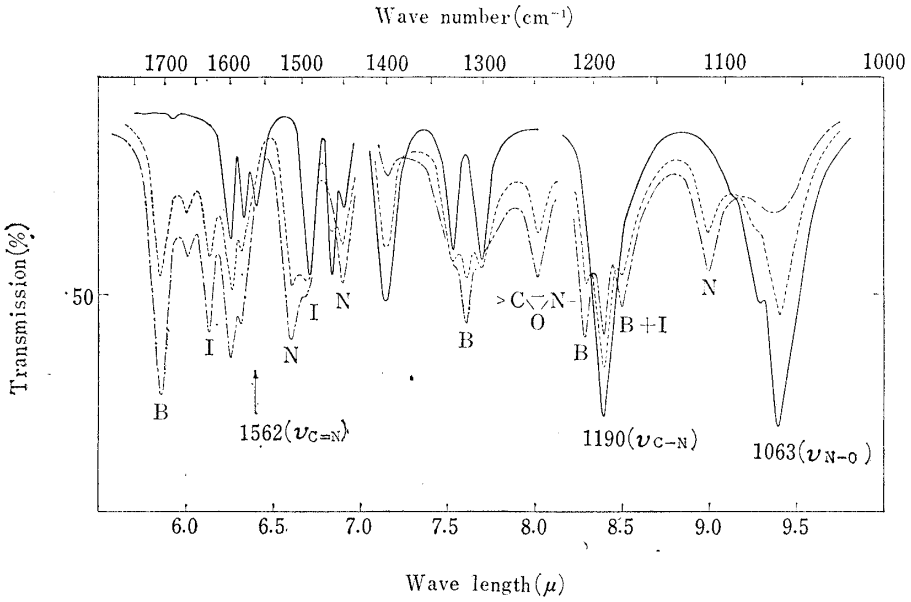


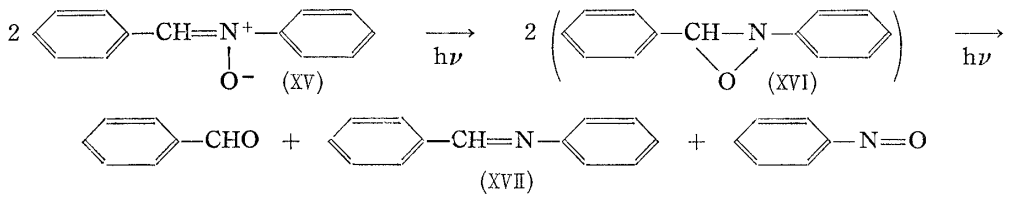
Fig. 3. Change in the Infrared Spectrum of Benzaldehyde N-Phenyl Nitrone on Irradiation of Ultra-violet Light

——— : ca. 30% in MeOH+$CHCl_3$(1:1)

·····: after 10 min. irradiation -·-·-·: after 30 min. irradiation

B : Benzaldehyde I : Benzylidene phenylimine N : Nitrosobenzene

On the other hand, there appeared a number of new bands, showing progressive increases in their intensities with increasing irradiation time. These new bands were analyzed by comparison with the spectra of reference compounds in the same solvent and the following compounds were identified; benzaldehyde (1705 s, 1312 m, 1203 m, 1168 cm^{-1}), benzylidene N-phenylimine (XVII) (1631 ms, 1493 m, 1190 ms, 1168 cm^{-1}), nitrosobenzene (1508 ms, 1445 m, 1111 m cm^{-1}) and a small amount of N-phenyl benzamide (1661 w cm^{-1}). The band appeared at 1247 cm^{-1} with a medium strength is considered to be an indication of the formation of the corresponding isonitrone (XVI). Accordingly, it can be anticipated that there takes place a photochemical conversion as shown below as a main reaction, where the isonitrone (XVI) once produced may be further decomposed rapidly by oxidation-reduction reaction between two molecules of the isonitrone.*[7]

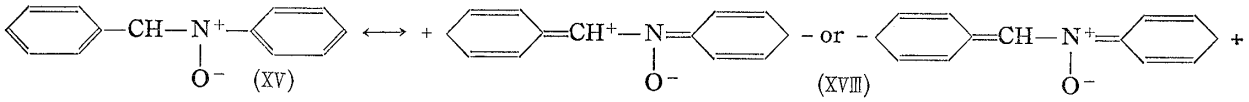


This reaction was almost completed by about thirty minutes' irradiation and it can be said that the N-phenyl nitrone is much more susceptible to photochemical reaction than the N-methyl nitrone, where its conversion to the isonitrone (XIII) was almost completed by about one hour's irradiation.

The Nature of the N-O Bond in Aldonitrones——From the foregoing results, it was made clear that the N-O stretching vibrations of benzaldehyde N-methyl and N-phenyl nitrones occur as a strong absorption at 1172 cm^{-1} and a strong doublet at 1088 and 1071 cm^{-1}, respectively, in non-polar solvents.

*[7] It has been reported (ref. 9b) that isonitrone has an active oxygen and can act as an oxidizing agent similar to peroxides.

Since the absorption frequency of the N-oxide function depends mainly on the bond force constant of the N-O linkage,[3,6,24] the observed frequency can be regarded as an approximate measure of the double bond character of the N-O bond. Therefore, the fact that both nitrones absorb in a frequency region higher than aliphatic amine N-oxides (970~940 cm^{-1}).[7] but lower than heteroaromatic amine N-oxides (1350~1190 cm^{-1}),[3,6] indicates that the N-oxide function in aldonitrones has some double bond character owing to the contribution of the resonance structures as VI in their electronic state. Furthermore, the fact that the N-methyl nitrone absorbs at a considerably higher frequency than the N-phenyl nitrone indicates that the contribution of the resonance structures as VI is much greater in the former than in the latter. This difference is considered to be due to the cross conjugated system of the latter compound where the contribution of the electronic structures as XVIII must be so great that it causes the resultant decrease in the contribution of the structures as VI in its resonance hybrid.



After all, it may be concluded that the double bond character of the N-O bond increases in the following sequence: trimethylamine N-oxide (952 cm^{-1}),[7] benzaldehyde N-phenyl nitrone (1088, 1071 cm^{-1}), benzaldehyde N-methyl nitrone (1172 cm^{-1}) and pyridine N-oxide (1265 cm^{-1}),[3] and more generally that aldonitrones*8 constitute a transitory group located between heteroaromatic and aliphatic amine N-oxides with respect to the nature of the N-O bond, the N-alkyl derivatives being closer to the former and the N-aryl derivatives to the latter.

This conclusion is in good agreement with that obtained from the study of their reactivities.[8] For example, the N-alkyl aldonitrones are not affected by sulfur dioxide, while the N-aryl aldonitrones are readily deoxygenated by the same reagent, and this shows that the former is similar to heteroaromatic amine N-oxides.

These results were confirmed by investigating the infrared spectra of aldonitrones with various substituents and this will be discussed more widely in relation of their reactitvities in a subsequent paper.

Experimental

Materials——Benzaldehyde N-methyl- (m.p. 81~82°)[25] and N-phenyl- (m.p. 112~113°)[26] nitrones were prepared by the condensation of benzaldehyde with methylhydroxylamine and phenylhydroxylamine, respectively. Benzylidene methyl- ($b.p_{34}$ 92~93°)[27] and phenyl- (m.p. 53°)[28] imines were prepared by the condensation of benzaldehyde with methylamine and aniline, respectively. All other compounds used for reference are commercialy available products. All samples were carefully purified by repeated recrystallization or distillation.

Method——Infrared spectra were measured with a Perkin-Elmer Model 21 double-beam spectrophotometer provided with NaCl prism. Conditions of measurement are described in Table I and III. Benzaldehyde N-phenyl nitrone and the related compounds were measured in the solid state, because this compound reacts with CS_2 during the measurement. The measurement in CCl_4 containing CH_3OH was made in a sealed cell with NaCl windows of 0.1 mm. thickness, and the absorptions due

*8 Discussion in this study concerns only aldonitrones involving conjugated systems i.e., those of type V.

24) It has been shown that a plot of the N-O stretching frequency against the N-O bond length gives a smooth curve. W. Lüttke: Elektrochem., **61**, 976 (1957).

25) O.L. Brady, F.P. Dunn, R.F. Goldstein: J. Chem. Soc., **1926**, 2386.

26) E. Beckmann: Chem. Ber., **27**, 1958 (1894).

27) Org. Syntheses, **34**, 64 (1954).

28) Org. Syntheses, Coll. Vol. **1**, 80 (1947).

to CH_3OH was extinguished by compensation of the same solvent. The measurement in H_2O or H_2O-CH_3OH mixture was made in a sealed cell with CaF_2 windows of 0.025 mm. thickness. D_2O (99.5%) was used to complement the 1600 cm^{-1} region. The photochemical reactions were investigated in a sealed cell with CaF_2 windows of 0.025 mm. thickness using ca. 30% solution in CH_3OH or CH_3OH-$CHCl_3$ mixture, depending upon the solubility of the sample. The irradiation of 2536 Å ultra-violet light was directly applied into the cell, followed by subsequent spectral measurements.

The authors express their deep gratitudes to Prof. M. Hamana of Kyushu University for his kind guidance, and to Mr. M. Matsui, Director of this laboratory, and to Dr. G. Sunagawa of this laboratory for their helpful encouragements.

Summary

The infrared spectra of benzaldehyde N-methyl and N-phenyl nitrones and the corresponding imines, as well as those of the related monosubstituted benzenes, were determined and the assignment was made for most of the vibrations in the 1700~650 cm^{-1} region and the characteristic frequencies for aldonitrones were discussed.

The N-O stretching frequencies were assigned to the strong absorption at 1172 cm^{-1} in the N-methyl and the strong doublet at 1088 and 1071 cm^{-1} (1082 and 1067 cm^{-1} as solid) in the N-phenyl nitrones, respectively. From these positions, it was concluded that these aldonitrones constitute a transitory group located between heteroaromatic and aliphatic amine N-oxides with respect to the nature of the N-oxide function, the N-methyl nitrone being closer to the former and the N-phenyl nitrone to the latter. The C=N stretching frequencies showed a large shift to a lower frequency in the nitrones as compared with those in the corresponding imines. Study of the solvent effect showed that the N-O and the C=N frequencies shifted markedly to a lower and a higher frequency, respectively, in a solvent capable of hydrogen bond formation. These results were discussed in terms of resonance contribution in the electronic state of the nitrones.

Photochemical reaction of these nitrones was investigated spectrophotometrically and their conversion products on irradiation of ultraviolet light were identified and discussed.

(Received March 30, 1961)

UDC 615.752.34-011 : 661.185

79. Hisashi Nogami, Shoji Awazu*1, and Noriyasu Nakajima*2 : Studies on Decomposition and Stabilization of Drugs in Solution. IX*3 Stabilization of Acetylsalicylic Acid in Aqueous Solution by Surface-active Agents.

(*Faculty of Pharmaceutical Sciences, University of Tokyo**4)

The authors reported previously[1] that the hydrolysis of Methantheline Bromide, a quaternary amine, is suppressed by sodium laurylsulfate (anionic surfactant). Methantheline Bromide is positively charged in aqueous solution and therefore, the present study was instituted in order to examine the effect of cationic, anionic, and nonionic surfactants on the suppression of the hydrolysis of the drug which exists in anionic and undissociated

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