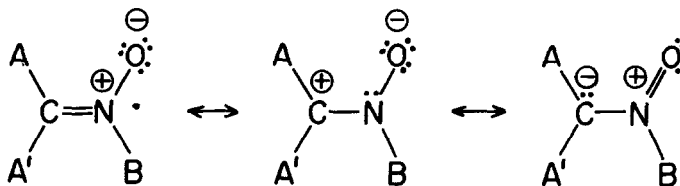# THE NMR SPECTRA AND MOLECULAR GEOMETRY OF NITRONES

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Nitrones have been recognized as having the following resonance structure (1,2):

When A, A', or B is a mesomeric substituent, the nitrone group (=C=NO-) will, of course, interact mesomerically with the substituent and thereby will probably exert an electron-attracting effect on the latter. With the view of obtaining information on the electronic structure and molecular geometry of nitrones which have one or two benzene rings in conjugation with the nitrone group, we measured the proton magnetic resonance spectra of the following aldonitrones (A-CH=NO-B) in $CDCl_3$ (concentration: about 120 mg in 1 ml of solvent) at room temperature, using a Japan Electron Optics Laboratory spectrometer Model JNM-4H-100 (100 Mc) and tetramethylsilane as an internal reference: α-methyl-N-cyclohexylnitrone (I), α-phenyl-N-methylnitrone (II), α,N-diphenylnitrone (III), and its derivatives having one or two methyl substituents on one of the benzene nuclei (IV-VII).
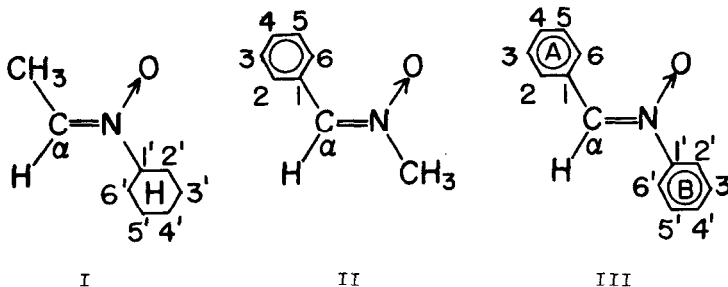
The results are summarized in TABLE I. The electronic absorption spectra of these nitrones were also measured. The data on the longest wavelength π-π* band (referred to hereafter as the A band) are shown in TABLE II.

TABLE I

The τ Values of Proton Signals of Nitrones in $CDCl_3$*

| Nitrone | Position of Protones | | | | | |
	α	2,6	3,4,5	2',6'	3',4',5'	Methyl
I	3.10(q)			(1') 6.72	(2'-6') 8.00-8.73	7.97(d)
II	2.63	1.72-1.84	2.55-2.63			6.14
III	2.12	1.58-1.69	2.54-2.64	2.22-2.44	2.54-2.64	
4-Methyl-III (IV)	2.16	1.73(d)	2.77(d)	2.20-2.31	2.55-2.65	7.61
4'-Methyl-III (V)	2.14	1.58-1.68	2.58-2.65	2.39(d)	2.84(d)	7.71
2,4-Dimethyl-III (VI)	2.00	(6) 0.70(d)	(3) (5) 2.98;2.89(d)	2.26-2.35	2.55-2.64	7.71;7.67
2',4'-Dimethyl-III (VII)	2.45	1.60-1.70	2.54-2.64	(6') 2.76(d)	(3') (5') 2.94;2.99(d)	7.71;7.68

*When a signal is doublet (indicated by letter d) or quartet (indicated by letter q), the τ value at its center is shown.

TABLE II

The Longest Wavelength π-π* Absorption Band of Nitrones

| Nitrone | In Cyclohexane | | In Ethanol | |
	λ_{max}, mμ	ϵ_{max} x 10^{-3}	λ_{max}, mμ	ϵ_{max} x 10^{-3}
I	244	6	236	7
II	299	19	292	19
III	320	19	315	21
IV	327	19	319	23
V	322	20	315	21
VI	329	19	325	21
VII	307	22	300	21

The following facts are noteworthy.

1) The α-proton τ values (τ_α) of nitrones I, II, and III-V are lower by 0.8-1.1 than those of correspondingly substituted ethylenes, that is, those of 1,2-dialkyl-ethylenes (4.22-4.27), styrene (3.4), and trans-stilbene (2.90), respectively.

2) The N-methyl proton signal of II is at lower field than the α-methyl proton signal of I by as much as 1.83 ppm. Even when the shift due to the possible deshielding effect of the phenyl group in II has been subtracted, the former is still at lower field than the latter.

3) The signals of meta and para ring protons in phenyl groups having no methyl substituent are unresolved and appear in the region of τ = 2.55-2.64. These values are near to, or slightly smaller than, the τ value of the benzene proton signal (2.63). In phenyl groups having one or two methyl substituents, when the possible substituent shielding effect of the methyl groups, which is taken to be 0.10 ppm for one meta methyl group and 0.17 ppm for one ortho or para methyl group, has been subtracted, the τ values of the meta ring protons fall to the same region. These facts suggest that the electron-attracting effect of the nitrone group on benzene rings in conjugation with it is comparatively small.

4) The B ring ortho proton ($H_{2'}$ and $H_{6'}$) signals of III-VI are at lower field than the meta and para ring proton signals, and the A ring ortho proton (H_2 and H_6) signals of II-V and VII are at further lower field. At first sight, this fact appears to be inconsistent with fact 2.

5) The τ value of the A ring ortho proton (H_6) signal of VI is extraordinarily low, being much lower even than the τ values of the A ring ortho proton signals of III-V. From this fact an explanation of fact 4 and information on the molecular geometry of VI are drawn, as follows.

The most preferred conformation of an α,N-diphenylnitrone having no substituent at ortho positions, such as III-V, is probably a planar or nearly planar conformation (3). From the fact that the values of λ_{max} and ϵ_{max} of the A band of VI are nearly equal to those of IV (see TABLE II), the most preferred conformation of VI is inferred to be similar to that of IV, that is, to be planar or nearly planar. On the other hand, a

scale model of VI shows that the 2-methyl group must be sterically hindered from
approaching the oxygen atom of the nitrone group. The most preferred conformation of VI
is, therefore, inferred to be a planar or nearly planar conformation in which the
6-proton is located near to the oxygen atom. Fact 5 gives a support to this inference.
Thus in such a conformation, the fractionally negatively charged oxygen atom of the
nitrone group will exert directly large deshielding effects (e.g., electric field, van
der Waals, and magnetic anisotropy effects) on the 6-proton. A few examples are known in
which the signal of a proton located near to an oxygen atom, especially a negatively
charged oxygen atom, appears at very low field (4,5).

If such a nitrone as III-V had a fixed planar or nearly planar conformation, the 2-
and 6-protons were not equivalent, and would show their signals at different τ values
(τ_2 and τ_6). The observed τ values of the 2- and 6-protons ($\tau_{2,6}$) of III-V are
considered to be approximately the means of τ_2 and τ_6. If the shift due to the
substituent shielding effect of a _meta_ methyl group is taken to be about 0.10 ppm, from
the observed value of τ_6 of VI the value of τ_6 of III is estimated at about 0.50 and
hence the value of τ_2 of III at about 2.76.

6) When the possible shift due to the substituent shielding effect of _meta_ methyl
groups has been subtracted, the value of $\tau_{2',6'}$ of V becomes about 2.29, and the value
of $\tau_{6'}$ of VII becomes 2.56. The former is nearly equal to the values of $\tau_{2',6'}$ of III
and IV; the latter is 0.27 higher than the former, and is slightly smaller than the τ
value of the benzene proton signal.

This fact suggests that in the most preferred conformation of VII the 6'-proton is
located far from the oxygen atom of the nitrone group. A scale model of VII shows that
coplanarity of ring B with the nitrone group is sterically hindered and that the steric
hindrance is probably smaller when the 2'-methyl group faces to the oxygen atom than when
it faces to the α-hydrogen atom. The electronic absorption spectral data of VII and
related nitrones (see TABLE II) probably indicates that in VII the B ring and the nitrone
group are not coplanar. Thus, the value of λ_{max} of the A band of VII is 15 mμ shorter
than that of V, and is 8 mμ longer than that of II. From these data the interplanar
angle (θ) between the B ring and the nitrone group in the most preferred conformation of

VII is estimated at about 53°, by use of simple MO method and of the assumption that the θ in the most preferred conformation of V is 0°.*

7) The value of τ_α of VII is about 0.3 higher than those of III-V, and is 0.18 lower than that of II. This fact is also thought to indicate that the θ in the most preferred conformation of VII is not 0°. In a planar conformation of III the shift of the α-proton signal due to the ring current in ring B is estimated at about - 0.54 (ppm) by use of the Johnson-Bovey table (6). This value is near to the differences of the τ_α values of III-V from that of II. On the basis of the assumptions that in the most preferred conformations of III-V the θ is about 0°, that the differences of the τ_α values of these compounds from that of II are mainly due to the effect of the ring current in ring B, and that the differences of the τ_α value of VII from those of III-V are mainly due to the difference in the ring current effect caused by rotation of ring B out of the nitrone group plane, the value of θ in the most preferred conformation of VII is estimated at about 55°

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*The estimation of θ was made by use of the following approximate equation, which is based on the second order perturbation theory (cf. H. Suzuki, Electronic Absorption Spectra and Geometry of Organic Molecules, Chapter 19. Academic Press, New York (1967)):

$$\frac{\nu_{max}(90°) - \nu_{max}(\theta)}{\nu_{max}(90°) - \nu_{max}(0°)} = \cos^2\theta$$

In this equation, $\nu_{max}(\theta)$ is the wave number of the absorption band maximum of the compound under consideration, and $\nu_{max}(90°)$ and $\nu_{max}(0°)$ are those of reference compounds in which θ is 90° and 0°, respectively. In the present case, the ν_{max} values of the A bands of II, V, and VII were taken as $\nu_{max}(90°)$, $\nu_{max}(0°)$, and $\nu_{max}(\theta)$, respectively.

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