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NITROGEN-15 MAGNETIC RESONANCE SPECTROSCOPY. IV. CONFIGURATIONAL ASSIGNMENTS IN ALKYL NITRITES

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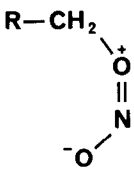
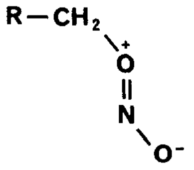
Evidence for rotational isomerism in alkyl nitrites has been provided by infrared and ultraviolet spectroscopy (1), dipole moment measurements (2), and nuclear magnetic resonance studies (3). The potential energy barrier for rotation about the -O-N bond has been shown to be 6-10 kcal (4), and at low temperatures where the frequency of rotation is sufficiently retarded, separate resonances for the cis (I) and trans (II) configurational isomers can readily be observed in the nmr spectrum.



I



II

The low-temperature chloroform spectrum of benzyl nitrite-^{14}N presented in Figure 1 exhibits a low field singlet at δ6.03 ppm and a high field singlet at δ4.93 ppm in the ratio 2:1 respectively. Early investigators (3,5) assigned the low field resonance to the α-methylene protons of the cis- isomer and the high field resonance to the corresponding protons of the trans- isomer.[1] In a more recent investigation, Brown and Hollis (6), on the basis of steric considerations have reversed these assignments. The purpose of this communication is to present evidence in support of the conclusions of these latter workers.

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[1] For a summary of inconsistent assignments made by different methods, see P. Gray and M. J. Pearson, Trans. Faraday Soc., 59, 347 (1963).

Previous studies in these laboratories have shown that configurational assignments in N-nitrosamines (7), N-nitrosohydrazines (8), and N-nitrosohydroxylamines (9) could be related to the magnitude of the ^{15}N-N-C-H coupling in the corresponding ^{15}N-nitroso labeled compounds. In all cases, the trans-α-protons have been found to be more strongly coupled (2-3 cps) to the ^{15}N atom than the corresponding cis-α-protons (~0 cps).

A series of ^{15}N-labeled alkyl nitrites having an isotopic enrichment of 99% was prepared and their nmr spectra were investigated. The chemical shift values for the α-protons and the equilibrium isomer ratios for the several alkyl nitrites studied are summarized in Table I.

Table I

Chemical Shift Values and Equilibrium Ratios in Cis- and Trans-Alkyl Nitrites[a,b]

R-ONO	Trans	Cis	$\frac{\text{Trans}}{\text{Cis}}$
$PhC\underline{H}_2$	6.03	4.93	2.0
$Ph(CH_3)C\underline{H}$	6.48	5.60	4.9
$Ph(CH_2CH_3)C\underline{H}$	6.42	5.53	6.5
$PhCH_2C\underline{H}_2$	5.20	4.08	2.4
$(CH_3)_3CCH_2C\underline{H}_2$	5.22	4.08	1.4

[a] Spectra were determined in $CDCl_3$ solution using a Varian A-60 spectrometer and chemical shifts are reported in ppm from internal TMS. [b] Measurements made at -75°.

These data indicate that the equilibrium isomer ratio is sensitive to substitution at the α-carbon atom. In agreement with Brown and Hollis (6), the assignment of the larger low field signal to the trans-α-protons is reasonable and furthermore is in accord with the expected greater stability of the trans-configuration due to the lesser lone pair - lone pair repulsions (10).

In Table II, there are presented the average ^{15}N-O-C-H coupling constants observed at room temperature and the individual cis and trans ^{15}N-O-C-H coupling constants observed at low temperatures. The temperature-dependent spectrum of benzyl nitrite-^{15}N is also illustrated in Figure 1.

Figure 1

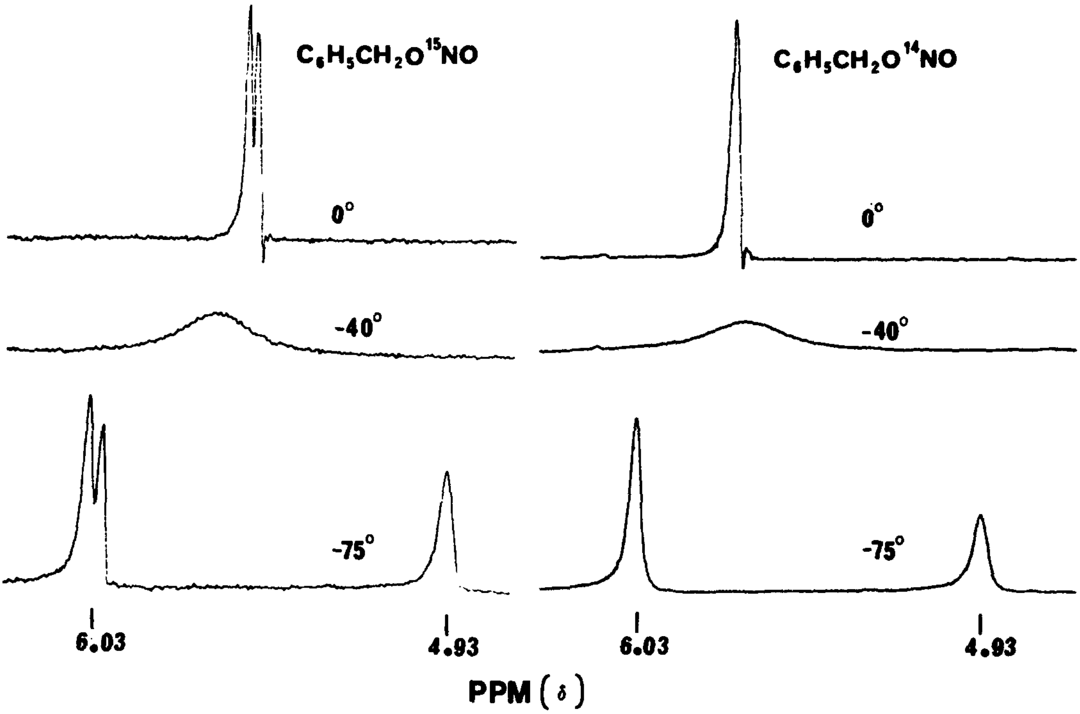

Figure 1. Temperature-dependent 60-Mc spectra of benzyl nitrite isotopomers.

Table II

Coupling Constants in Alkyl Nitrites-^{15}N [a,b]

	$J_{^{15}NOCH}$		
	+37°C	-75°C	
$R\text{-}O^{15}NO$	average	trans	cis
$PhC\underline{H}_2$	1.7	2.4	0
$PhCH_2C\underline{H}_2$	1.8	2.3	0
$Ph(CH_3)C\underline{H}$	1.9	2.4	0
$Ph(CH_2CH_3)C\underline{H}$	2.1	2.1	0
$(CH_3)_3CCH_2C\underline{H}_2$	1.7	2.4	0

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[a] All constants expressed in cps. [b] The uncertainty is ±0.2 cps.

Consistent with our previous findings for ^{15}N-N-C-H coupling in N-nitroso compounds, the ^{15}N-O-C-H coupling in alkyl nitrites is similarly configuration dependent. In each case, the low field α-proton resonance shows stronger coupling ($\sim$ 2.4 cps) to the ^{15}N-atom than does the high field signal ($\sim$ 0 cps). These observations lend support to the assignment of the low field resonance to the α-protons oriented trans to the nitroso oxygen atom. The use of coupling constants in these systems provides a valuable complement to chemical shifts and isomer ratios as a means of assigning configurations.

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