

Remarkable Deshielding Effects in the ^1H Nuclear Magnetic Resonance Spectra of Cyclic Amine *N*-Carbodithioic Acid Salts

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It is well known that the conversion of amines into acyl derivatives causes the α -hydrogen atoms to be deshielded in the ^1H n.m.r. spectrum. Thus acylation of piperidines^{1,2} causes a deshielding of the axial 2,6-hydrogen atoms by about 0.2 p.p.m. and of the equatorial 2,6-hydrogen atoms by about 1.1 p.p.m., increasing to 1.5 to 1.7 p.p.m. when

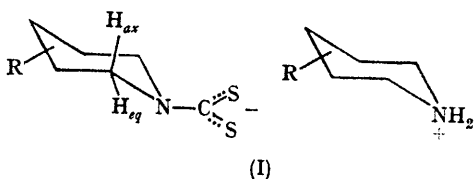
conditions of slow rotation about the N-C(O) bond allow observation of signals in individual rotational isomers.

We now report that exceptionally strong deshielding effects occur in the anions of the cyclic amine *N*-carbodithioic acid salts (I). Typical examples are given in the Table, which shows that

TABLE

Chemical shifts (τ values) of protons α - to nitrogen in cyclic amines and derived salts (I)

Cyclic amine	Chemical shifts (CDCl ₃ ; 60 Mc./sec.)			
	Amine		Anion of salt (I)	
	Axial	Equatorial	Axial	Equatorial
4-t-Butylpiperidine	7.43	6.87	7.15	4.15
4-Methylpiperidine	7.40	6.91	6.95	4.22
<i>cis</i> -3,5-Dimethylpiperidine	7.90	7.00	7.60 \pm 0.1	4.20
<i>cis</i> -2,6-Dimethylmorpholine	7.62	7.20	7.34	4.35
Piperidine	\longleftrightarrow 7.24 ^a \longleftrightarrow		\longleftrightarrow 5.60 ^a \longleftrightarrow	

^a Averaged chemical shift for axial and equatorial protons.

the 2,6-equatorial hydrogens of the anions of (I) give signals at about τ 4.15—4.35, the conversion from the free base having caused a deshielding of 2.7—2.8 p.p.m. As the 2,6-axial hydrogens are only deshielded by 0.2—0.3 p.p.m., the chemical-shift difference between equatorial and axial α -hydrogen atoms is extremely high in the anions of (I), reaching about 3.4 p.p.m. in the case of *cis*-3,5-dimethylpiperidine. It appears from these results

that the CS₂⁻ group is a valuable conformational probe.

The signals for the 2,6-hydrogens in the cations of (I) occur at τ 6.1—6.3 (equatorial) and τ 7.2—7.4 (axial). In general, the signals due to the 2,6 axial hydrogens in anion and cation were distinguished by spin-decoupling, but complications due to the cation may also be eliminated by conversion of the salts (I) into the corresponding sodium salts.

The amine salts (I) are rapidly and quantitatively formed from the secondary amine and carbon disulphide. For small quantities of amine, the reaction is conveniently performed in the n.m.r. sample tube, using CDCl₃ as solvent.

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¹ H. O. House, B. A. Tefertiller, and C. G. Pitt, *J. Org. Chem.*, 1966, **31**, 1073.² D. M. Lynch and W. Cole, *J. Org. Chem.*, 1966, **31**, 3337.