The CS_2^- Group as a Conformational Probe for Cyclic Amines: Nuclear Magnetic Resonance Study

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Summary The n.m.r. spectra of the *N*-carbodithioic acid sodium salts of piperidines having equatorial α-alkyl substituents indicate that conformational inversion of the piperidine ring occurs upon formation of these derivatives.

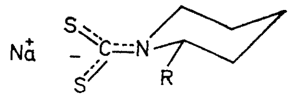
THE exceptionally strong deshielding of the equatorial 2,6-protons by the CS_2^- group in the *N*-carbodithioic acid salts of piperidines provides an excellent means of distinguishing between the equatorial and the axial protons.[1] However, we have found that the observation of this strong deshielding in the salts does not necessarily indicate that the deshielded proton has an equatorial orientation in the free base. A conformational inversion of the piperidine ring was found to occur upon formation of the *N*-carbodithioic acid salts of piperidines which contained α-alkyl equatorial substituents, thus reversing the axial–equatorial orientation of the ring protons.

Chemical shifts (*τ values*) *of α-protons* (60 *MHz*)

Compound	Amine[a] Axial	Amine[a] Equatorial	Salt[b] Axial	Salt[b] Equatorial
4-Methylpiperidine	7·40	6·91	6·82	4·63
2-Methylpiperidine	7·4 ± 0·1	6·90	6·85	4·07, 4·52
2-Ethylpiperidine	7·4 ± 0·1	6·90	6·83	4·1, 4·47
2-Propylpiperidine	7·4 ± 0·1	6·90	6·83	4·1, 4·4
cis-2,6-Dimethylpiperidine	7·44	—	—	4·20

[a] In $CDCl_3$, Me_4Si as internal standard.
[b] In D_2O, sodium 2,2-dimethyl-2-silapentane-5-sulphonate as internal standard.

The chemical shifts of the 2,6-protons in the free base and in the *N*-carbodithioic acid sodium salts of some substituted piperidines are shown in the Table. The signals due to the equatorial protons in the salts are found near τ 4, whereas those due to the axial protons are found near τ 7. It may be seen that there are two signals near τ 4 in the n.m.r. spectra of each piperidine salt which has one α-substituent. These peaks are due to the two equatorial protons, thus showing that the alkyl substituent is in the axial position. In the case of the *cis*-2,6-dimethylpiperidine the two α-protons are found at τ 4·2 indicating that the two protons are equatorial and the methyl groups have been forced into a 1,3-diaxial interaction with one another. The assignment of the axial or equatorial orientation to the 2,6-protons of the salts is verified by their splitting patterns. The axial protons appear as triplets (splitting of about 13 Hz; geminal and vicinal diaxial coupling) further split by *ca.* 3 Hz (vicinal axial–equatorial coupling). The equatorial protons show the expected splitting patterns with no vicinal coupling greater than 4 Hz.



FIGURE

This large steric interaction between the CS_2^- group and the equatorial alkyl substituent must be due to the partial double bond character of the C–N bond which places the CS_2^- group in an orientation which causes it nearly to eclipse the equatorial substituent (see Figure).

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[1] H. Booth and A. H. Bostock, *Chem. Comm.*, 1967, 637.