Conformational Studies of Chlorotetrahydropyrans by Nuclear Quadrupole Resonance Spectroscopy

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Summary A ^{35}Cl nuclear quadrupole resonance study of 2,2,3,3-tetrachlorotetrahydropyran (I) at 77 K has revealed an anomeric shift of *ca.* 2·4 MHz between the chlorine atoms in the 2-position; in 2,3,3-trichlorotetrahydropyran (II), similar arguments show that the 2-chlorine takes up an axial position in the solid state.

Relatively few examples of conformational shifts of n.q.r. frequencies have been reported in the literature. Lucken and his collaborators have advanced theoretical reasons for their existence and have reviewed the experimental evidence,[1,2] and there are two other reports, on the acetylated glycopyranosyl chlorides[3] and the phosphonitrilic chlorides.[4] We report a further well substantiated case of such shifts in the chlorotetrahydropyrans. The ^{35}Cl n.q.r. frequencies of two such molecules at 77 K are given in the Table. 2,2,3,3-Tetrachlorotetrahydropyran (I) was prepared by chlorination of 2,3-dichloro-5,6-dihydro-4*H*-pyran[5] in CCl_4 solution at −10 °C; the preparation of 2,3,3-trichlorotetrahydropyran (II) has been reported elsewhere.[6] The assignment of frequencies is based on the analysis of Guibé *et al.*;[3] although compound (I) appears to contain two molecules in the crystalline asymmetric unit, there is a clear indication of an anomeric shift of *ca.* 2·4 MHz between O–C–Cl_{ax} and O–C–Cl_{eq}, compared to *ca.* 2 MHz in peracetylated glycopyranosyl chlorides.[3] The axial chlorine is assigned the lower frequency, in conformity with the conclusions of Guibé *et al.*[3] and Ardalan and Lucken for tetrachlorodioxans.[2] In molecules where conformational shifts are unlikely to be large, replacement of –CCl_2– by –CHCl– lowers the ^{35}Cl frequency by 2—3·4 MHz, depending on the other carbon substituents; thus the mean ^{35}Cl frequencies in $Me[CH_2]_2CHCl_2$ and $(-CH_2CH_2Cl)_2$ at 77 K differ by 2·32 MHz.[7] It therefore follows that the 2-chlorine atom in (II) is almost certainly in the axial position, which is the first reliable spectroscopic evidence for the conformation of this molecule. This conclusion is consistent with the observation by Ardalan and Lucken[2] of a ^{35}Cl n.q.r. frequency at 77 K of 29·939 MHz in 2-chlorotetrahydropyran, from which they assigned an axial position to the 2-chlorine atom. Thus the axial ^{35}Cl n.q.r. frequencies drop by a mean value of 3·01 MHz on going from (I) to (II), and by a further 3·03 MHz on going from (II) to 2-chlorotetrahydropyran. Unfortunately, we have failed to find a signal from the 3-chloro-isomer, although it has been reported to be largely equatorial in CCl_4 solution.[8]

TABLE. ^{35}Cl N.q.r. frequencies (MHz) in chlorotetrahydropyrans at 77 K (approximate signal-to-noise ratios in parentheses).

Molecule	Cl $-O-C-Cl_{ax}$	Cl $O-C-Cl_{eq}$	$-CCl_2-$	
(I)	35·897(12)	38·300(8)	38·495(10)	39·017(10)
	36·052(12)	38·434(8)	38·576(12)	39·139(10)
(II)	32·952(15)	—	36·691(15)	37·186(15)

The assignments of the $O-C-Cl_{eq}$ and $-CCl_2-$ frequencies for (I) are somewhat uncertain, and are largely based on a measurement of the temperature dependence of their frequencies.

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