The Effect of Conformation on Nuclear Quadrupole Coupling Constants of α-Chloro-ethers

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Summary The difference in the bond length between axial and equatorial carbon–chlorine bonds in chlorodioxans is paralleled by a large change in the ^{35}Cl nuclear quadrupole coupling constant and both these effects are compatible with an orientation-dependent conjugative interaction between the oxygen atom and the carbon–chlorine bond.

(I)

IN a previous communication[1] the "anomalously" low ^{35}Cl nuclear quadrupole coupling constants of various fluoro- and methoxy-derivatives of methyl chloride were explained in terms of partial double bonding between the fluoro- or methoxy-groups and the central carbon atom which releases electrons to the carbon–chlorine σ-bond (I). This interaction gives rise to an increase in the ionic character, *i*, of the carbon–chlorine bond approximately related[2] to the ^{35}Cl quadrupole resonance frequency ν:

$$\nu/\nu_0 = 1 - i \qquad (1)$$

where ν_0, the resonance frequency for a pure covalent bond formed by the 2*p* orbital of chlorine, has the value 55 MHz.

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Although this was not brought out clearly at the time, such a mechanism implies that in the methoxy-derivatives the interaction might be expected to have a marked conformation-dependence since in the fragment H_3C–O–C– the plane defined by the oxygen atom and the two carbon atoms is the nodal plane of the only $2p$ orbital possessed by the oxygen atom which would be responsible for such a partial double bond. The Figure shows a projection along the carbon–oxygen bond in chloromethyl methyl ether the angle θ being the dihedral angle between the C^a–O–C^b plane and the Cl–O–C^b plane. The postulated partial double bond formation should be zero when $\theta = 0°$ and attain a maximum when $\theta = 90°$.

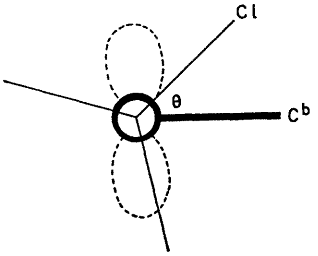

FIGURE. *Projection along the* C^a–O *bond in* $ClC^aH_2OC^bH_3$.

Altona[3] determined the crystal structure of various halogenated dioxan derivatives and noted marked differences in the carbon–chlorine bond lengths of the *cis*- and *trans*-2,3-dichlorodioxans. The relevant crystallographic data are shown in the Table.

Crystallographic data and ^{35}Cl *n.q.r. frequencies of dichlorodioxans*

Compound	C–Cl bond- length (Å)	Conformation of bond	θ	^{35}Cl n.q.r frequency (MHz at 77K)
trans-2,3-Dichlorodioxan	1·844 ± 0·014	*ax*	69·4	31·910
	1·833 ± 0·014	*ax*	71·6	32·983 ±0·001
cis-2,3-Dichlorodioxan	1·819 ± 0·008	*ax*	71·2	32·205 ±0·001
	1·781 ± 0·008	*eq*	180·0	34·990 ±0·001
trans-2,5-Dichlorodioxan	1·845 ± 0·006	*ax*	70·2	29·75 ±0·02

The equatorial C–Cl bond is clearly shorter than any of the four axial C–Cl bonds. The bond lengths which are anomalous are in fact the axial halogen bonds which are very significantly *longer* than the average value given by Sutton *et al.* for aliphatic C–Cl[4] (1·767 ± 0·005 Å). Altona suggested that the explanation lies in the double bonding postulated in ref. 1.

The ^{35}Cl quadrupole resonance frequencies for the three compounds in question are also shown in the Table. The number of distinct resonances is in each case in accord with the crystal structure,[3] the higher frequencies of *trans*-2,3-dichlorodioxan compared to the *trans*-2,5-derivative being due to the inductive effect of the adjacent chlorine atom. The frequency of the latter compound is comparable with that of chloromethyl methyl ether (30·181 MHz). Although these measurements have been made only on polycrystalline materials so that it has not been possible to make rigorously unambiguous assignments of the quadrupole resonance frequencies, there appears to be little real doubt that the higher frequency in *cis*-2,3-dichlorodioxan is to be assigned to the chlorine atom in the equatorial position. The difference in the two frequencies (2·78 MHz) is well outside the range of differences which can be attributed to mere physical effects (*ca.* 0·5 MHz) and must reflect very real differences in the electronic structures of the two carbon–halogen bonds. This difference is all the more striking when it is realised that the whole range, from carbon tetrachloride to the carbonyl chlorides, of quadrupole resonance frequencies for chlorine atoms attached to carbon atoms is some 11·0 MHz while the range of frequencies for compounds of the type RCH_2Cl is less than a half of this.[2] This increase of frequency is, of course, exactly what would be predicted upon the basis of the partial double-bond of ref. 1. To our knowledge this is the first time conformational changes have been associated with such significant differences in quadrupole coupling constants. We have also measured the resonance frequencies in 2,2,3,3-tetrachlorodithian (38·461 and 39·402 MHz at 77K). The double bond interaction would be expected to be much less significant for sulphur compounds[1] and the difference between the resonance frequencies of the axial and equatorial chlorine atoms is, in accordance with this expectation, much less marked.

Some part of the differences in quadrupole resonance frequencies must come from the different mutual interactions of the two chlorine atoms. A first attempt at measuring this effect by observation of the chlorine resonance frequencies in *cis*- and *trans*-1,2-dichlorocyclohexane was unsuccessful since, as is unfortunately too often the case in pure quadrupole resonance spectroscopy, no resonances could be observed in either of these compounds.

Single-crystal studies of the dioxan derivatives and related compounds which will lead to a determination of the directions of the field-gradient axes and hence unambiguous assignments of the quadrupole coupling constants to particular chlorine atoms are now being undertaken as also is a search for resonances in carbon analogues of these cyclic ethers.

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[3] C. Altona, Thesis, University of Leiden, 1964.

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