171. Nuclear Quadrupole Resonance and Stereochemistry II. Vicinal *cis*- and *trans*-Dichloro Derivatives of Carbocyclic Systems

by **Ziba Ardalan** and **Edwin A. C. Lucken**
Département de Chimie Physique, Section de Chimie de l'Université de Genève
30, quai de l'Ecole de Médecine, 1211 Genève 3

and

S. Masson
Département de chimie, Université de Caen, Caen 14, France

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Summary. The ^{35}Cl quadrupole resonance frequencies of sets of isomeric vicinal dichloro derivatives of carbocyclic molecules are presented. In all cases except one – *cis*- and *trans*-1,2-dichloro-acenaphthene – the configuration has only a small effect on the resonance frequency. This implies that the frequency-differences in cyclic α-chloroethers reported in Part I of this series [1] are indeed due to a specific interaction with the oxygen atom. The difference between the acenaphthenes may be due to hyperconjugation between the C-Cl bond and the aromatic system.

In the first paper in this series [1] it was shown that the ^{35}Cl NQR frequency of cyclic α-chloro ethers depends very markedly on the configuration, (axial or equatorial) of the carbon-chlorine bond. Most of the compounds whose quadrupole resonance spectra were reported therein contained either vicinal dichloro groups or a polar substituent in a vicinal position with respect to the nucleus under study so that at least a part of the effects reported in [1] could arise from the relative positions of the two vicinal groups. In this paper we report the ^{35}Cl NQR frequencies of a number of 1,2-dichloro derivatives of carbocyclic systems of known configuration and in the light of these and of other previously reported results, attempt to estimate the magnitude of such an effect.

Experimental. *Instrumentation,* see [1].

Preparation: trans- (I) and cis-*dichlorocycloheptane* (II) [2], trans- (III) and cis-*dichlorocyclooctane* (IV) [3], exo, exo-*2,3-dichloro*-exo, exo-*5,6-dimethoxycarbonyl-bicyclo[1.2.2]heptane* [4] (V), exo, endo-*2,3-dichloro*-exo, exo-*5,6-dimethoxycarbonyl-bicyclo[1.2.2]heptane* (VI), [4], exo, exo-*2,3-dichloro*-endo, endo-*5,6-dimethoxycarbonyl-bicyclo[1.2.2]heptane* (VII) [4], exo, exo-*2,3-dichloro*-endo, endo-*5,6-dicarboxy-bicyclo[1.2.2]heptane* (VIII) [4], exo, exo-*2,3-dichloro-bicyclo[1.2.2]heptane* (IX), exo, exo-*3,5-dichloro-tricyclo*$[2.2.1.0^{2,6}]$*heptane* (XIV) [5], trans-*9,10-dichloro-decalin* (XX) [5], d,l-*1,2-dichlorosuccinic anhydride* (XIV) [6], trans- and cis-*1,2-dichlorobenzocyclobutene* (XV & XVI) [7], trans- and cis-*1,2-dichloroacenaphthene* (XVII & XVIII) [8] were prepared by previously published methods, *meso* dichlorosuccinic acid (VIII) was a commercial product and the *d,l* acid (XII) was prepared from XIV by hydrolysis.

We thank Dr. *C.A. de Meij* for kindly supplying the 1e, 2e, 3e, 4e, 5e, 6e-hexachlorophenylcyclohexane (X) [9] and 1a, 2a, 3e, 4e, 5e, 6e-hexachlorophenylcyclohexane (XI) [9] and Dr. *Kalvoda* of CIBA-GEIGY, Basel for the four steroids: *3β-acetoxy-5,6β-dichloro-5α-androstane-17-one* (XXI), *3β-acetoxy-5-chloro-6β-hydroxy-5α-androstane-17-one* (XXII), *3β-acetoxy-5-chloro-6β,19-epoxy-5α-androstane-17-one* (XXIII) and *6α-chloro-4-ene-androstane-3,17-dione* (XXIV).

Results and Discussion. – Table 1 shows the ^{35}Cl NQR. frequencies of the various dichloro compounds I–XXIV. It is unfortunate that we have been unable, despite repeated efforts, to obtain any resonances from either *cis*- or *trans*-1,2-dichlorocyclohexane which would have been the ideal system with which to compare the dioxanes and tetrahydropyran derivatives. It is further regrettable that the crystal structures of only three of these compounds X [10]; XVI [11] and XVIII [12] have been determined. In agreement with this the six resonance frequencies of X and the two resonances of XVI show that these molecules have lost their plane of symmetry on crystallisation.

The measurements on the hexachlorophenylcyclohexanes extend those already available for the hexachlorocyclohexanes themselves. These have been the object of extensive studies which have allowed the assignment of the resonance frequencies to individual chlorine atoms [13]–[16]. The assignments are not absolutely certain but they seem to indicate that on the whole axial chlorine substituents have their resonance frequencies about 0.5 MHz lower than the corresponding equatorial ones. It does not appear to be possible to narrow down the range by taking into account such things as the relative orientation of the nearest neighbours. Although no experimental attempt was made to assign the resonance frequencies in the case of the hexachlorophenylcyclohexanes the difference between X, where all the chlorine atoms are in the equatorial configuration, and XI where two chlorine atoms have gone over to the axial one supports this conclusion. However, it must be stressed that this difference is of the same order of magnitude as the frequency shifts brought about by intermolecular field-gradients.

Turning now to the seven and eight membered rings the total spread in frequencies for I and II is only 0.77 MHz and for II and IV even less, 0.23 MHz. Even though the geometry of these rings is unknown the dihedral angle between the C–Cl bonds is certainly different and almost certainly smaller in the *cis* than the *trans* derivatives. Again in the dichlorosuccinic acids the crystal structure of neither is known but the resonance frequencies have a spread of only 0.39 MHz. However, the large difference between the frequency of XII and the corresponding anhydride XIV where the two chlorine atoms are necessarily *trans* to each other may be in part due to a conformational change.

Although once again the crystal structures are unknown the derivatives of [1.2.2]bicycloheptane have a molecular skeleton of sufficient rigiditiy for it to be possible to estimate the relative orientation of the chlorine atoms with fair certainty. In V they are no doubt essentially in the eclipsed configuration while in the *trans* compound VI the chlorine atoms eclipse the corresponding hydrogen atoms. In V the two chlorine atoms are probably but not necessarily equivalent in the free molecule in which case the two frequencies differing by 0.1 MHz must be ascribed to inequivalence induced by crystallisation; in VI however the two chlorine atoms are inequivalent even in the free molecule and this inequivalence with respect to the methylene bridge produces a change of only 0.28 MHz while the difference in the average frequencies of V and VI is only 0.75 MHz. It would be interesting to determine the effect of *exo* or *endo* configuration directly by comparing corresponding *exo* and *endo-cis* dichlorides or the *exo* and *endo* chlorides but we have not so far been successful in observing resonances in appropriate sets of compounds. However, the effects which we do observe here are comparable with those produced by a configurational change a more remote part of the molecule (compare V with VII and VII with VIII) and by a change in crystal structure structure of the same molecule (*e.g. p*-dichlorobenzene [17] at 77 K; α-phase 34.775 MHz, β-phase 34.760 MHz γ-phase 35.208 MHz).

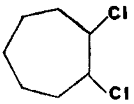
Compounds XV, XVI, XVII and XVIII are, with the dichlorosuccinic acids XII, XIII and anhydride XIV, examples of molecules in which the C–Cl bond is adjacent to an unsaturated system. The frequency difference between XV and XVI is comparable with those observed previously but XVII and XVIII differ by 2.4 MHz. The crystal structure of the latter compound has recently been determined and shows that the C_8-C_1-Cl fragment lies in a plane which is almost perpendicular to the aromatic plane [12]. The structure of the *cis* isomer is unknown but repulsion between the two neighbouring chlorine atoms would in this case presumably force the C_8-C_1-Cl plane to be more nearly parallel to the aromatic plane. An explanation of the frequency difference may then lie in an electron-releasing hyperconjugation which would of course be at its maximum for the *trans* isomer, XVIII. However, this point will be taken up in a later paper in this series in which such hyperconjugation will be discussed specifically.

Also included in Table 1 are the results for compounds XIX–XXIV which do not make up sets of isomers. It is interesting to note that although the resonance frequency of a chlorine linked to a tertiary carbon atom is in general lower than that attached to a secondary carbon atom (see for example XXI) the resonance frequency of XX is similar to that of compounds I–IV.

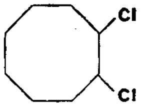
The similarity of the frequencies of the 5 α chlorine atom in XXI, XXII and XXIII shows that the effect of a *trans* RO group is similar to that of a *trans* Cl group. XXIV is the only one of these four compounds having an equatorial chlorine substituent; the structures of XXI and XXIV are however too different for the frequencies of the 6α and the 6β chlorine atoms to be compared in the present context. All these observations strongly indicate that in the absence of a neighbouring heteroatom or conjugating group the relative configuration of two C–Cl bonds affects

Table 1. ^{35}Cl *NQR resonance frequencies (MHz at 77 K) of vicinal dichloro compounds*

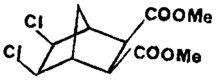
Compound	ν_Q (MH$_z$)	Compound	ν_Q (MH$_z$)
I	33,068; 33,439	XII	37,745; 37,866
II	32,946; 33,719	XIII	38,135
III	33,810	XIV	38,749; 39,187
IV	33,815; 34,040	XV	33,915; 33,958
V	35,234; 35,335	XVI	34,603; 34,730
VI	34,403; 34,689	XVII	33,323
VII	34,817; 34,888; 35,164; 35,164	XVIII	35,652; 35,836
VIII	34,977; 35,119	XIX	33,057; 33,163
IX	34,580	XX	33,279
X	36,886; 37,089; 37,287;	XXI	33,594; 34,520
	37,593; 37,593; 37,730	XXII	33,069
XI	36,000; 36,287; 36,407; 36,443;	XXIII	33,152
	36,732; 36,854; 36,891; 36,940;	XXIV	33,710
	37,143; 37,382; 37,456; 37,633		



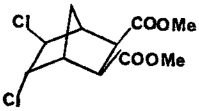
I = *trans*
II = *cis*



III = *trans*
IV = *cis*



V



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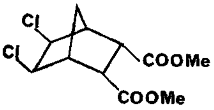
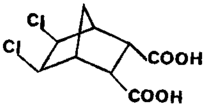
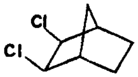


VII



VIII



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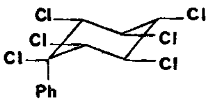
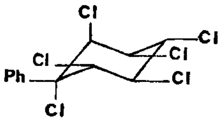
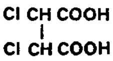


X

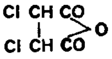


XI

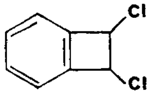


$$\begin{array}{l}\mathrm{Cl\,CH\,COOH}\\ \quad\;|\\ \mathrm{Cl\,CH\,COOH}\end{array}$$

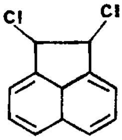
XII = dl
XIII = meso



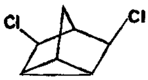
XIV = dl



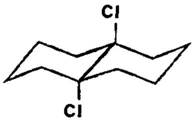
XV = *trans*
XVI = *cis*



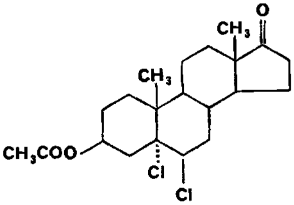
XVII = *trans*
XVIII = *cis*



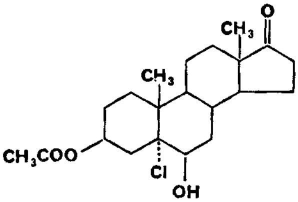
XIX



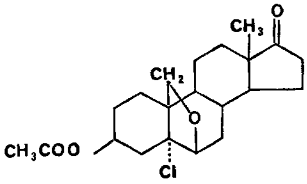
XX



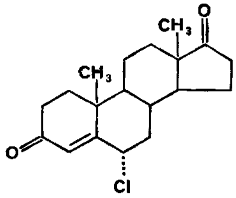
XXI



XXII



XXIII



XXIV

the ^{35}Cl resonance frequency by less than 0.8 MHz and hence confirms that the large difference between axial and equatorial chlorine atoms in α chloroethers reported in [1] arises from a specific interaction with the oxygen atom.

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172. Nuclear Quadrupole Resonance and Stereochemistry III. Trichloromethyl Derivatives

by **Ziba Ardalan** and **Edwin A. C. Lucken**

Département de Chimie Physique
Section de Chimie de l'Université de Genève
30, quai de l'Ecole de Médecine, 1211 Genève 4

(11. IV. 73)

Summary. ^{35}Cl nuclear quadrupole resonance frequencies are reported of the chlorine atoms in the trichloromethyl group of benzotrichlorides and trichloromethyl derivatives of heterocyclic molecules. They are compared with previously reported results for the same group attached to other planar conjugated radicals. In such compounds the three chlorine atoms cannot be equivalent and all the results are discussed from the point of view of possible orientation-dependant hyperconjugation between the C-Cl bonds and the conjugated moiety, particularly with reference to the marked effects observed in trichloromethyl ethers reported in part I of this series. In the benzotrichloride and indeed most of the compounds discussed such effects are small.

In part I of this series [1] it was shown that the ^{35}Cl resonance frequency of a cyclic α-chloro ether had a marked dependence on the axial or equatorial nature of the carbon-chlorine bond. In part II [2] it was shown that there was no such marked orientation-dependence in saturated carbocyclic systems and it may thus be concluded that the effect in the ethers is due to a specific interaction between the C–Cl bond and the oxygen atom. A model (no doubt much oversimplified), of such an