Nuclear Quadrupole Resonance and Stereochemistry. Part 6. Transmission of Substituent Effects through a Double Bond

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The ^{35}Cl quadrupole resonance frequencies of a variety of pairs of *cis–trans*-isomers of chloroethylenes and of bridged bicyclic chloroethylenes are reported. The results show that *cis*-substituents produce small but significantly greater frequency shifts than do *trans*-substituents.

IN previous papers in this series [1] we have been concerned with the effect of stereochemistry on the ^{35}Cl quadrupole resonance frequencies of saturated organochlorine compounds. Here we report the resonance frequency of compounds which are all essentially vinyl chlorides.

EXPERIMENTAL

All compounds other than those specifically mentioned here were commercially available and repurified before measurement. Phenyl ββ′-dichlorovinyl ketone (I),[2] 3-chlorobicyclo[3.2.1]oct-2-ene (IV),[3] 3,4-dichlorobicyclo[3.2.1]oct-2-ene (V),[3] 3,4-dichloro-2-methylbicyclo[3.2.1]oct-2-ene (VI),[4] 3,4-dichloro-2-phenylbicyclo[3.2.1]oct-2-ene (VII),[4] 2,3,4-trichlorobicyclo[3.2.1]oct-2-ene (VIII),[5] 2,3,4-trichlorobicyclo[4.2.1]non-3-ene (IX),[6] 2,3,4,5-tetrachlorobicyclo-[4,2.1]non-3-ene (X),[6] 5α,6β-dichlorocholesteryl 3β-benzoate (XI),[7] 5α,6α-dichlorocholesteryl 3β-benzoate (XII),[8] were prepared by published methods. We thank Dr. Y. Amiel of the Weizmann Institute for a loan of samples of *cis*- and *trans*-α-chloro-β-(phenylsulphonyl)styrene and Professor J. Tronchet of the Department of Pharmacy, University of Geneva, for the two chloro-sugars (II) and (III).

RESULTS AND DISCUSSION

Table 1 shows the pure quadrupole resonance frequencies of pairs of *cis–trans*-isomers of substituted vinyl chlorides. In all cases the frequency of the isomer in which the polar substituent (Cl, CO_2H, SO_2Ph) is *cis* to the chlorine atom is higher than that in which it is *trans*, although with only one exception this difference is less than one MHz and in one case quite insignificant. The exception is *cis*- and *trans*-1,2-dichlorostyrene for which the *cis*-dichloro-isomer shows two distinct resonances at 35.692 and 37.790 MHz whereas the *trans* isomer has two closely-spaced resonances at 35.68 and 35.81 MHz respectively. The assignment of the very different frequencies in the *cis*-isomer is uncertain but it is, nevertheless, likely that the higher of the two corresponds to the chlorine atom closest to the phenyl group, since the lower frequency is similar to that of *cis*-dichloroethylene. Whatever the correct assignment is, it is certain that one of the ^{35}Cl resonance frequencies changes by at least 1.98 MHz when the configuration changes from *cis* to *trans*. There is no obvious explanation for the magnitude of this shift which the relatively unshifted set of resonances for *cis*-dichlorostilbene makes even more surprising and this once more serves to emphasise the fact that in studying electronic structure by pure quadrupole resonance it is usually necessary to study series of compounds in order to eliminate adventitious solid-state effects.

The conclusion that, at least for the types of substituent studied here, the quadrupole resonance frequency of the ^{35}Cl nucleus is only slightly affected by whether it is in the *cis*- or *trans*-position, is reinforced by the data for the two *gem*-dichloroethylenes (I) and (II) shown in Table 2. The direction of the effect is, however, quite consistently in favour of a polar *cis*-substituent increasing the frequency more than the corresponding *trans*-substituent. This may be due to a direct ' through-space ' interaction between the carbon–chlorine bond and the substituent. For the carboxy group, where we have two sets of data and where the molecules are relatively uncomplicated, the frequency shift on replacing the hydrogen atom in the *cis*-position by the substituents is 1.85 MHz in chloroacrylic acid (ν_Q of CH_2=CHCl 33.411 MHz [9]) and 2.35 MHz in crotonic acid [ν_Q of CH_2=$C(CH_3)Cl$ 32.629 MHz [10]]. Thus the geometric effect is a little more than one third the maximum effect. For the chloro-substituent which is less well documented the shift on addition of a *cis*-substituent is 1.45 MHz so that the geometric effect is roughly one quarter of the total.

Also shown in Table 2 are the results for series of bridged bicyclic chloroethylenes.

Compound (IV) may be considered as the parent of this series and the addition of an α-chloro-substituent (V) increases the resonance frequency as expected by *ca.* 1 MHz. Compounds (VI) and (VII) show that the presence of a *cis*-methyl or -phenyl substituent has little effect on the resonance frequency while a *cis*-chloro-substituent (VIII) increases it by 1 MHz, in agreement with the results of Table 1. The high frequencies of compound (IX), where the ring-size has been increased by one methylene unit appear anomalous, especially in view of the more normal pattern exhibited by the corresponding symmetrical tetrachloro-derivative (X).

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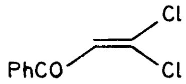
TABLE 1

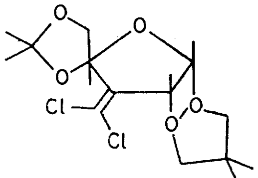
^{35}Cl Quadrupole resonance frequencies of *cis*- and *trans*-chloroethylenes (MHz at 77 K)

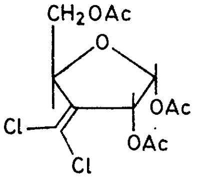
X	Y	Z	(Y-*cis*) X\=/Y Cl/ \Z	(Y-*trans*) X\=/Y Cl/ \Z	
H	Cl	H	34.837, 34.894	34.497	+0.36
H	CO$_2$H	H	35.261	34.315, 34.337	+0.94
Me	CO$_2$H	H	34.980	34.250	+0.73
Ph	PhSO$_2$	H	35.847, 37.765 35.920, 36.076	34.964	+0.89
Ph	Cl	H	35.692	35.68	−0.01
H	Cl	C$_6$H$_5$	37.790	35.81	+1.98
Ph	Cl	C$_6$H$_5$	35.49, 35.63 35.68, 35.74		

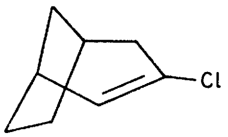
TABLE 2

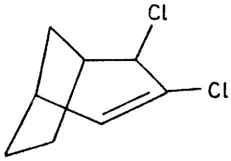
^{35}Cl N.q.r. frequencies (MHz) of substituted vinyl chlorides at 77 K

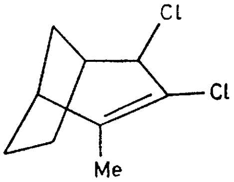

(I)
37·46. 37·51

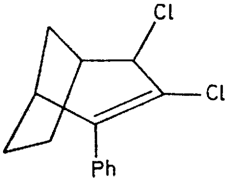

(II)
36·959, 37·136

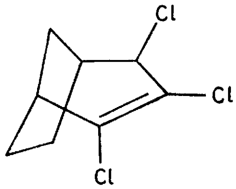

(III)
36·721, 37·399

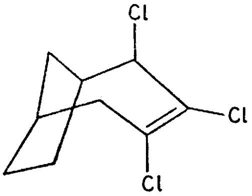

(IV)
33·175

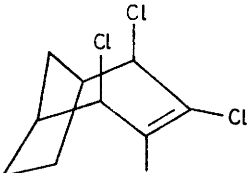

(V)
33·4, 34·3

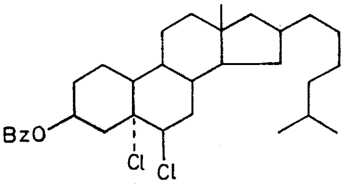

(VI)
33·1, 34·4

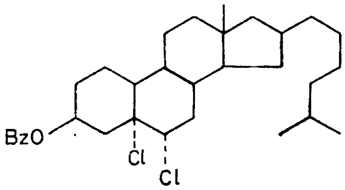

(VII)
33·550, 33·625, 34·400, 34·475


(VIII)
34·075, 35·100, 35·400


(IX)
33·100, 36·725, 36·800


(X)
34·500, 34·725, 36·225, 36·375


(XI)
33·450, 34·354


(XII)
33·513, 34·029

The two final compounds (XI) and (XII) in this Table more properly belong to Part 3 of this series but the results have only recently been obtained. They fully substantiate the conclusions of that paper that the *cis*-*trans*-nature of 1,2-dichloro-compounds in cyclic saturated molecules has little effect on the resonance frequency. The present results show that the corresponding effect concerned with *cis*–*trans*-isomerism about a double bond, even when the substituent is a relatively active one such as Cl, COR, or SO$_2$R, is not usually very great but that *cis*-substituents produce significantly greater effects than *trans*-substituents.

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