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ASYMMETRY PARAMETERS OF THE ELECTRIC FIELD GRADIENT AT THE ^{35}Cl NUCLEI OF (3-CHLOROPROPYL)TRICHLOROSTANNANE

V.P. FESHIN *, G.V. DOLGUSHIN, M.G. VORONKOV,

Irkutsk Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, 664033, Irkutsk (USSR)

Ju.E. SAPOZHNIKOV, Ja.B. JASMAN,

All-Union Research Technological Institute of Herbicides, 450029, Ufa (USSR)

and V.I. SHIRJAEV

State Research Institute of Chemistry and Technology of Elementoorganic Compounds, 111123, Moscow (USSR)

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Summary

Asymmetry parameters for the electric field gradient at the ^{35}Cl nuclei of polycrystalline $Cl(CH_2)_3SnCl_3$ have been measured at 77 K. They are in agreement with a trigonal-bipyramidal structure for the molecule. The electron distribution of the axial chlorine atom in the $SnCl_3$ group is almost axially symmetric whereas that of the two equatorial atoms and the chlorine atom in the $Cl(CH_2)_3$ group deviate noticeably from the axial symmetry. The deviation is mainly due to the interaction of the lone electron pair of the corresponding chlorine atom with the central tin atom.

Introduction

The X-ray data [1] indicate a distorted trigonal-bipyramidal structure for the (3-chloropropyl)trichlorostannane molecule with the Cl(1), Cl(2) and C(1) atoms in the equatorial positions and the Cl(3) and Cl(4) atoms in the axial position (Fig. 1). This structure is caused by the intramolecular interaction between the unbridged tin and chlorine atoms and agrees with the ^{35}Cl NQR spectrum of the compounds studied [1,2]. The lowest frequency line in the spectrum (Table 1) belongs to the axial Cl(3) atom and the two high frequency lines of the spectrum triplet (20.352 and 20.160 MHz) correspond to the equatorial Cl(1) and Cl(2) atoms. The NQR frequency of the chlorine atom in the 3-chloropropyl group (31.750 MHz) is essentially lower then that for other compounds of the $Cl(CH_2)_nX$ series with $n \geqslant 3$

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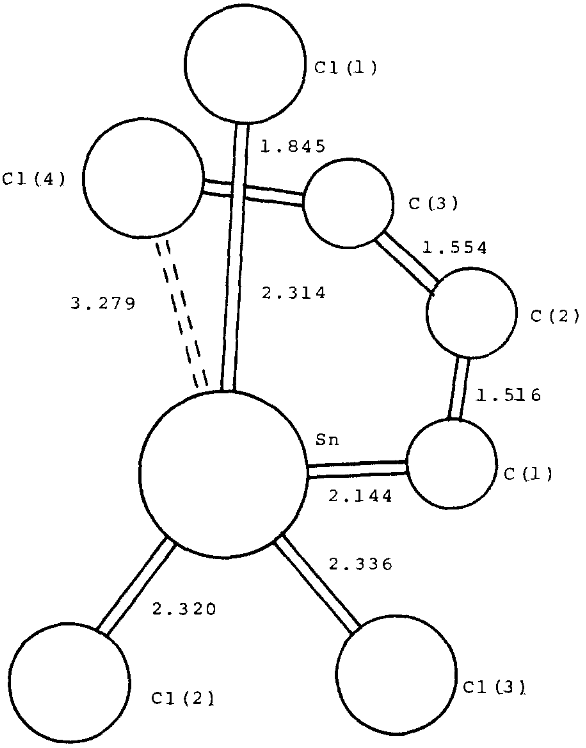

Fig. 1. Molecular structure of $ClCH_2CH_2CH_2SnCl_3$.

($\nu^{77} \approx 33.1$ MHz [1–3]). This was attributed to the interaction of the Cl(4) lone electron pair with the tin atom and C–Cl bond polarisation by partial positive charge at the tin atom directly through the field [1]. To investigate in more detail the intramolecular interaction of atoms in the (3-chloropropyl)trichlorostannane the asymmetry parameters of the electric field gradient (η) at the ^{35}Cl nuclei in this compound have been measured at 77 K (Table 1). The η value describes the deviation of the electron density distribution of the reference atom (chlorine in this case) from axial symmetry: $\eta = (q_{xx} - q_{yy})/q_{zz}$, where q_{xx}, q_{yy}, q_{zz} are the components of the electric field gradient along the X, Y and Z axes, respectively (the Z axis is directed along the M–Cl bond) (see, for example ref. 4). This information about the space distribution electron density of the reference atom permits investigation of both regularities of mutual influence of atoms in organic and organometallic

TABLE 1

THE ^{35}Cl NQR FREQUENCIES AT 77 K (ν^{77}) [1,2] AND THE ASYMMETRY PARAMETERS (η) OF THE ELECTRIC FIELD GRADIENT AT ^{35}Cl NUCLEI OF (3-CHLOROPROPYL)TRICHLOROSTANNANE

ν (MHz)	31.750	20.352	20.160	19.668
η (%)	8.7±2.0	6.3±1.0	10.7±1.0	0.4±1.0

molecules and, in a few cases, the mechanism of this influence (see, for example, refs. 5–7).

Experimental

(3-Chloropropyl)trichlorostannane was prepared from 1,3-dichloropropane and $SnCl_2$ by heating to 180–190°C in an autoclave [8].

The η value of the ^{35}Cl nuclei in the polycrystalline compound studied was measured at 77 K from the pulsation spectrum of the quadrupole spin echo envelope in an external constant magnetic field at 30–80 A/m^2. The pulsation spectrum was obtained from the experimental interferogramme using the fast Fourier transform program on the BNC-12 computer [9]. The improved impulse NQR spectrometer, ISSH-1-12 produced by SKB IRE AN SSSR, was used to obtain the interferogramme. The relative error of η estimation was determined on the 95% level of the corresponding pulsation spectrum amplitude.

Results and discussion

The asymmetry parameters of the electric field gradient at the ^{35}Cl nuclei in the $SnCl_3$ group of (3-chloropropyl)trichlorostannane are in agreement with its trigonal-bipyramidal structure. The η value for the axial Cl(3) atom is equal to 0 within the measurement error. Therefore, the electron distribution of this atom is practically axially symmetric. The distribution for the equatorial Cl(1) and Cl(2) atoms deviates essentially from the axial symmetry. Their η values are considerably high (Table 1). This character of the electron density distribution of axial and equatorial chlorine atoms is observed also in other molecules having a trigonal-bipyramidal structure. For example, the electron density distribution of two chlorine atoms in the $(C_6H_5)_2PCl_3$ molecule is almost axially symmetric (their η values approach 0, $\eta = 2.5 \pm 1.5\%$) whereas that of the equatorial chlorine atom deviates considerably from the axial symmetry ($\eta = 28.5 \pm 2.0\%$) [5]. This deviation was explained by the interaction of the lone electron pair of the equatorial chlorine atoms with the p_z orbital of the central phosphorus atom [5]. An interaction of this type, between the Cl and Sn atoms, is evidently responsible for the essentially high η values of the equatorial chlorine atoms in (3-chloropropyl)trichlorostannane. However, the lesser η value for this molecule as compared with the chlorophosphoranes shows that in the former the interaction appears to be considerably weaker than in the latter [5].

Usually the electron distribution of the chlorine atom bridged with an sp^3 hybridized carbon atom is practically symmetric. However the considerably high η value for the chlorine atom in the $Cl(CH_2)_3$ group of $Cl(CH_2)_3SnCl_3$ indicates that its electron distribution deviates from axial symmetry. This deviation may be due to the interaction between unbridged Sn and Cl atoms in the (3-chloropropyl)-trichlorostannane molecule when the Sn...Cl distance (3.279 Å) is less than the sum of Van der Waals' radii (3.91 Å) according to the X-ray data [1]. It may be supposed that the Cl(4) lone electron pair is involved in this interaction which would give rise to the high value for this atom (Table 1). The interaction should be responsible for the lower ^{35}Cl NQR frequency because of a decrease in the lone electron pair (N_x or N_y) population: $\nu = f(\frac{1}{2}(N_x + N_y) - N_z)$ [1]. Hence, the anomalously low Cl(4) NQR frequency (see above) can be explained by the same interaction.

As shown earlier [6], a 1% increase in the asymmetry parameter of the electric field gradient at the ^{35}Cl nuclei decreases by 0.12 MHz, on average, the ^{35}Cl NQR frequency. Consequently, the asymmetry of the electron distribution of the chlorine atom in the 3-chloropropyl group of $Cl(CH_2)_3SnCl_3$ can decrease its NQR frequency by $8.7 \times 0.12 = 1.044$ MHz. In the absence of asymmetry the NQR frequency ($31.750 + 1.044 = 32.794$ MHz) should be close to these of compounds of the series $Cl(CH_2)_nX$ with $n \geqslant 3$ (see above). However, the alignment between NQR frequencies and the asymmetry parameters for the chlorine atoms in the trichlorostannyl group of $Cl(CH_2)_3SnCl_3$ indicates the absence of direct interconnection between these values. The chlorine atom in this group corresponding to the low frequency line in the NQR spectrum shows an approximately zero η value whereas a higher η value is observed for the chlorine atoms corresponding to higher NQR frequencies (Table 1). Consequently, the noticeable lower NQR frequency of one chlorine atom in the $SnCl_3$ group and the difference in its chlorines cannot be due to a different asymmetry of their electron distribution. The asymmetry of electron distribution evidently gives rise to a smaller decrease in NQR frequency of the equatorial chlorine atoms as compared with the axial one in both (3-chloropropyl)trichlorostannane and chlorophosphoranes [5] than the more ionic character of the axial Sn–Cl bond does.

An equation for estimating the asymmetry parameter of the electric field gradient at a bridging chlorine or bromine from the NQR frequencies of terminal (ν_T) and bridging (ν_B) halogen atoms in nontransition metal halides has been suggested in [10] $\eta \approx 1.8[(\nu_T/\nu_B) - 1]$. It has been assumed that the p orbitals of the bridging halogen atom are not hybridized and the bridging bond is formed by its lone electron pair, p_y. This equation enables estimation of the η value for the chlorine atom of the 3-chloropropyl group in $Cl(CH_2)_3SnCl_3$ under the assumption that it is a bridging atom, whereas in the absence of the $Cl \rightarrow Sn$ interaction it is a terminal one with the same ^{35}Cl NQR frequency as in other compounds of the $Cl(CH_2)_nX$ series with $n \geqslant 3$ (see above). The η value (7.2%) calculated in such a way is close to the experimental one (Table 1). This is in agreement with the high η value and the anomalously low NQR frequency of the chlorine atom in the 3-chloropropyl group of $Cl(CH_2)_3SnCl_3$ explained in terms of participation of its lone electron pair in the intramolecular $Cl \rightarrow Sn$ interaction. The more so, that the CClSn angle in the molecule is close to 90° [1,2] as is to be expected in the case of unhybridized chlorine p orbitals.

Evidently, the anomalously low NQR frequency of the chlorine atom in 3-chloropropyl group of $Cl(CH_2)_3SnCl_3$ and its high η value are mainly due to the interaction of the chlorine lone electron pair with the tin atom.

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