The C–Cl Bonds in α-2,4,6-tris(trichloromethyl)-1,3,5-trioxane, α-Parachloral, $(Cl_3CCHO)_3$. A ^{35}Cl-NQR Single Crystal Study

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By single crystal ^{35}Cl-NQR Zeeman spectroscopy, the five independent ^{35}Cl nuclear quadrupole coupling tensors in α-parachloral, $(Cl_3CCHO)_3$, have been studied at 24 ± 2 °C. The directions of the electric field gradient (EFG) tensor components have been determined. The principal axes Φ_{zz} are within ± 0.8° parallel to the C-Cl bond directions found by X-ray diffraction. Very small asymmetry parameters in the range $0.002 \leqq \eta \leqq 0.046$ are characteristic for the EFG tensors of chlorine atoms bound to carbon atoms in aliphatic systems. The five nuclear quadrupole coupling constants are in the range $76.752 \leqq e^2 q Q h^{-1}/\mathrm{MHz} \leqq 78.155$. The orientation of the principal axes Φ_{xx} and Φ_{yy} can be correlated to the molecular structure.

Introduction

Todays major method of determining the electron density distribution in solids is the combination of X-ray diffraction and neutron diffraction. Therefrom bond lengths, bond angles, density distributions, $\varrho(x, y, z)$, and other molecular parameters in the crystalline state are obtained. An independent way to support and/or check the results from the diffraction experiments is the measurement of the electric field gradient (EFG) at the site of an appropriate nucleus within the solid by means of nuclear quadrupole resonance (NQR) [1].

The nuclear quadrupole interaction energy is usually measured in MHz and expressed as $e^2 \Phi_{zz} Q h^{-1} \equiv e^2 q Q h^{-1}$. For a nuclear spin with spin quantum number $I = 3/2$, such as ^{35}Cl, ^{37}Cl, the resonance frequency is given by

$$\nu = \frac{e^2 q Q h^{-1}}{2} \left(1 + \frac{\eta^2}{3}\right)^{1/2},$$

where η is the asymmetry parameter

$$\eta = (\Phi_{xx} - \Phi_{yy})/\Phi_{zz}\,;$$
$$|\Phi_{zz}| \geqq |\Phi_{yy}| \geqq |\Phi_{xx}|\,; \quad \sum_i \Phi_{ii} = 0\,. \qquad (1)$$

Zeeman-split NQR spectroscopy, in which a weak magnetic field is applied to a single crystal, allows the determination of the three principal components of EFG tensor (EFGT), Φ_{xx}, Φ_{yy}, Φ_{zz}, and their orientation with respect to the crystal axes [2].

Although the orientation of the EFGT can be, in principle, determined by Zeeman NQR spectroscopy of single crystals, the location of Φ_{xx} and Φ_{yy} is quite difficult for small η, unless the accuracy in the measurement of angles in the Zeeman NQR experiment is considerably high. By use of a NQR Zeeman goniometer with 4π-geometry [3] the ^{35}Cl-NQR Zeeman spectrum of a single crystal of trichloroethylidene trichlorolactic ester (Chloralide), $Cl_3CCHOCOCHOCCl_3$, was investigated. It was found that the principal axes Φ_{zz} at the sites of the six crystallographically independent chlorines are within ± 0.5° parallel to the C–Cl bond direction determined by X-ray diffraction, and the orientations of Φ_{xx} and Φ_{yy} were explained as due to intramolecular interactions [4]. In literature, a few more ^{35}Cl-NQR Zeeman studies on CCl_3 groups have been reported [5–7]. However, the discussion in these studies is restricted mainly to the properties of Φ_{zz}.

In studying derivatives of Chloral, Cl_3CCHO, the ^{35}Cl NQR spectrum of polycrystalline α-parachloral (cyclic trimer of Chloral)*, $(Cl_3CCHO)_3$, has been investigated [8]. The crystal structure of this material was reported by Hay and Mackay [9]. α-para-

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* α-2,4,6-tris(trichloromethyl)-1,3,5-trioxane.

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chloral crystallizes in the orthorhombic space group D_{2h}^{16}-Pnma, with $Z = 4$ formula units in the unit cell. Five ^{35}Cl-NQR lines are obtained at temperatures $77 \leqq T/\mathrm{K} \leqq 370$, in agreement with the crystal structure. By spin-echo double resonance (SEDOR) experiments it was possible to sort the five ^{35}Cl-NQR frequencies of the α-parachloral molecule into two groups [8].

Besides α-parachloral there is an isomeric compound, β-parachloral, which forms monoclinic crystals, space group C_{2h}^5–$P2_1/c$. The main difference of the isomeres is in the molecular structure. In α-parachloral the trioxane ring is of boat form, with considerable distortion from a regular form, and in β-parachloral the ring adopts the chair conformation. The ^{35}Cl NQR spectrum of β-parachloral is composed of 9 lines in agreement with the crystal structure [9], and by SEDOR experiments the spectrum has been sorted out according to the three CCl_3 groups of the molecule [8]. Up to now, no single crystal large enough to do ^{35}Cl Zeeman split NQR spectroscopy could be grown.

In this paper we report single crystal ^{35}Cl NQR Zeeman experiments of α-parachloral.

Experimental

The synthesis of α-parachloral is described elsewhere [8, 10]. After purification of the material by recrystallization, a single crystal of ca. $(20 \times 30 \times 10)$ mm^3 was grown from ethanolic solution by slow evaporation of the solvent at room temperature. Dominant faces of the large prismatic crystal were (010), (111), and (101) (see below). Single crystals of the compound have also been grown by Chattaway and Kellett [10] from ethanolic solution. They reported that the crystal is orthorhombic with faces (001), (111), and (110). For the axial ratios they found

$$a_0 : b_0 : c_0 = 0.8801 : 1 : 1.4505 .$$

The X-ray work of Hay and Mackay [9] shows that α-parachloral crystallizes with the orthorhombic space group D_{2h}^{16}-Pnma and the axial ratios are

$$a : b : c = 1 : 1.4474 : 0.8813 .$$

With the transformation, $a_0 \rightarrow c$, $b_0 \rightarrow a$, $c_0 \rightarrow b$, the setting of Chattaway and Kellett coincides well with that of Hay and Mackay. Since the single crystal used in the present work exhibited the same form as reported by Chattaway and Kellett, we found that the well developed faces are (010), (111), and (101) in the crystal coordinate system a, b, c, setting Pnma.

A Fourier transform (FT) NQR spectrometer was used for the registration of the ^{35}Cl-NQR spectrum at room temperature (24 + 2 °C). To determine the orientation of the EFGTs the zero splitting cone method was applied.

The crystal was fixed to a nonmagnetic goniometer head, optically adjusted on an optical two circle goniometer, and transfered to the 4π-Zeeman goniometer. In Fig. 1 the orientation of the crystal axes with respect to the laboratory coordinate system is shown. We call the laboratory system X_c, Y_c, Z_c, which is colinear to the 4π-Zeeman goniometer system. The crystal was set on the goniometer head in such a way that $\boldsymbol{b} \parallel \boldsymbol{Z}_c$. The orientation of the $\boldsymbol{a}$ and $\boldsymbol{c}$ axes in the plane (X_c, Y_c) was determined as shown in Figure 1. The principal axes system of EFGT is given by x, y, z throughout this paper.

The theory of NQR Zeeman spectroscopy was developed by Dean [11] who solved for spin $I = 3/2$ the problem exactly. In this case, e.g., ^{35}Cl, the different energy levels of the nucleus under the influence of an electric field gradient and a weak magnetic field are

$$E_{m,\pm} = 3A\zeta \pm \frac{h\Omega}{4\pi}\left[a_m^2 \cos^2\vartheta + (b_m^2 + c_m^2 + 2b_m c_m \cos 2\varphi)\sin^2\vartheta\right]^{1/2} . \quad (2a)$$

$$A = \frac{e^2 \Phi_{zz} Q}{4I(2I-1)}; \quad \Omega = \gamma B_0; \quad \zeta = \left(1 + \frac{\eta^2}{3}\right)^{1/2} . \quad (2b)$$

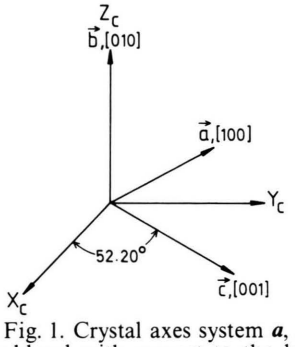


Fig. 1. Crystal axes system $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ of orthorhombic α-parachloral with respect to the laboratory coordinate system. The angle between X_c and the axis $\boldsymbol{c}$ is 52.20 °.

$$a_{1/2} = -1 + 2\zeta^{-1}; \quad a_{3/2} = -1 - 2\zeta^{-1}; \qquad (2c)$$
$$b_{1/2} = 1 + \zeta^{-1}; \quad b_{3/2} = 1 - \zeta^{-1};$$
$$-c_{1/2} = c_{3/2} = \eta\zeta^{-1}; \quad m = \tfrac{1}{2}, \tfrac{3}{2}.$$

Here γ is the gyromagnetic ratio of the nucleus, B_0 the applied magnetic field, h Planck's constant, I the nuclear spin quantum number, and m the magnetic quantum number.

Out of the four transitions,

$$\omega = \omega_0 (m_1 \rightleftharpoons m_2) \pm \frac{\Omega}{2} ([m_1] \pm [m_2]), \qquad (3)$$

where $[m]$ is given as the square root of the bracket in (2a), the pair with the smaller splitting

$$\left(\omega = \omega_0 \pm \frac{\Omega}{2} ([m_1] - [m_2])\right)$$

is called α-pair. Obviously, it merges at orientations of $\boldsymbol{B}_0$ for which $[m_1] = [m_2]$. For one EFGT, these special vectors $\boldsymbol{B}_0$ form a cone around Φ_{zz}, the "zero splitting cone" which has rotational symmetry for $\eta = 0$. With respect to the coordinate system X_c, Y_c, Z_c the polar and azimuthal angles for the vectors $\boldsymbol{B}_0$ positioned on a zero cone are called ϑ_0 and φ_0 throughout this paper.

After finding 18 combinations of ϑ_0, φ_0 for one of the zero splitting cones of the resonance line at 38.379 MHz (corresponding to $Cl^{(1,3)}$) a preliminary orientation of Φ_{zz} ($Cl^{(1,3)}$) has been calculated by a least squares procedure. Assuming that the principal z axis coincides with C–Cl direction and $\eta = 0$, the orientation of the crystal axes system with respect to X_c, Y_c, Z_c, and the whole set of zero splitting cones for all Cl-atoms could be calculated from the known crystal data. These cones were checked and refined experimentally. In this way all five basic cones for the five crystallographically inequivalent Cl-atoms of one molecule and 13 symmetry related cones were determined. Since the zero splitting cones reflect the symmetry elements of the unit cell, a precise determination of the crystal orientation with respect to the coil system of the Zeeman goniometer could be performed afterwards.

Results

As expected from the crystal structure and the ^{35}Cl-NQR powder spectrum of α-parachloral, five independent zero splitting cones were observed. The assignment of the five lines to two different CCl_3 groups within a molecule, based on SEDOR experiments, was confirmed. According to the crystal structure, a total of 36 ^{35}Cl-NQR tensors could be observed. Since the crystal structure is centrosymmetric, the number reduces to 18 (the direction x, y, z of the NQR tensor in the crystal is indistinguishable from direction $\bar{x}$, $\bar{y}$, $\bar{z}$). With the method applied here, by inverting the field vector $\boldsymbol{B}_0$ into $(-\boldsymbol{B}_0)$, one can find the two cones related by the inversion center. With each cone, its inverted counterpart was also studied by a few combinations ϑ_0, φ_0 to improve and check the accuracy of the angles. The results showed that the measurements of both ϑ_0 and φ_0 are accurate at least to $\pm 0.2°$.

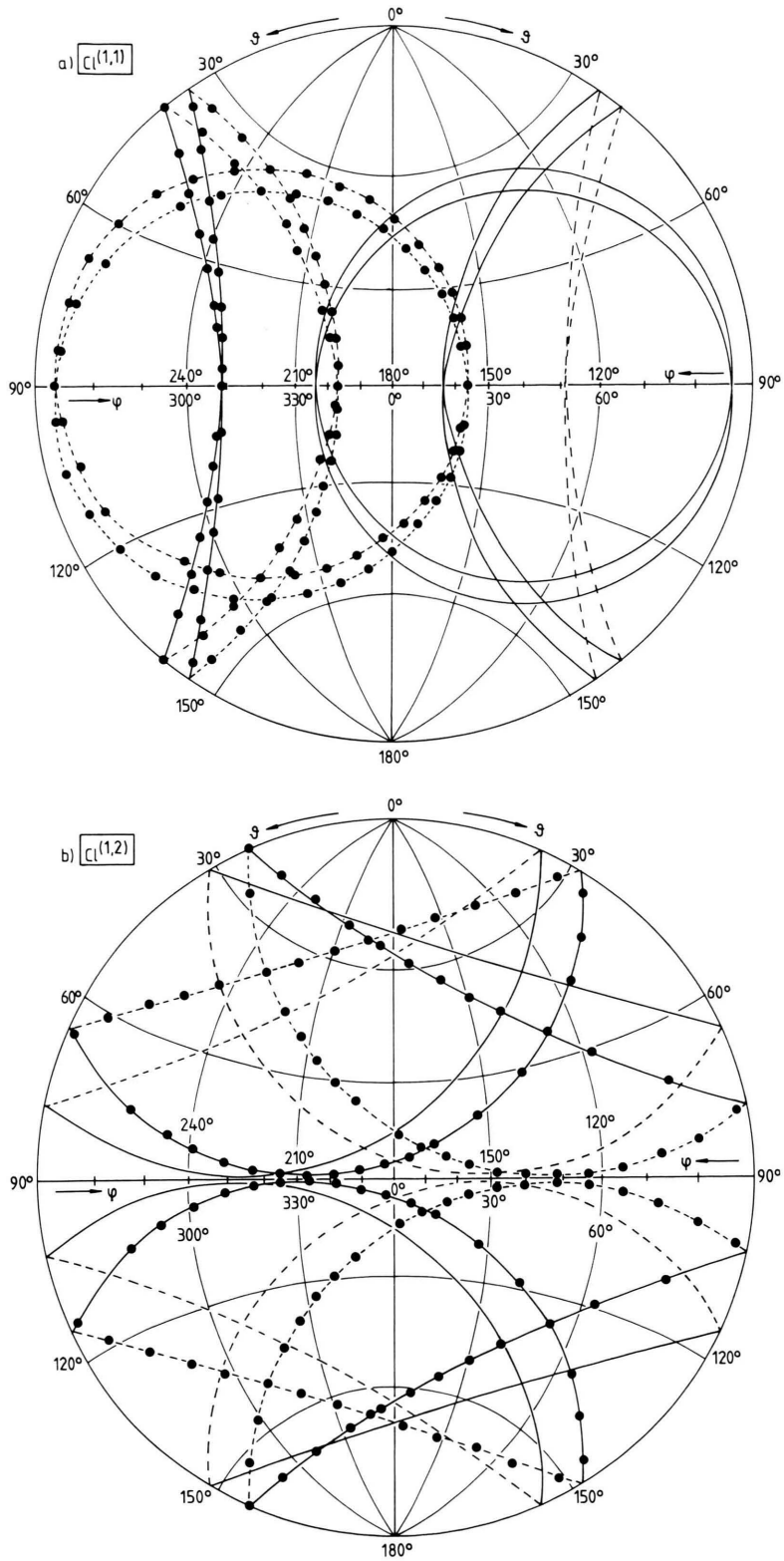
The zero splitting cones of the ^{35}Cl-NQR tensors in α-parachloral are shown in stereographic projection in Figs. 2a – 2e. From the zero splitting cones (sets of ϑ_0 and φ_0) the nuclear quadrupole coupling constants, the asymmetry parameters, and the direction cosines of the ^{35}Cl-NQR tensors with respect to the crystal axes system were determined analytically.

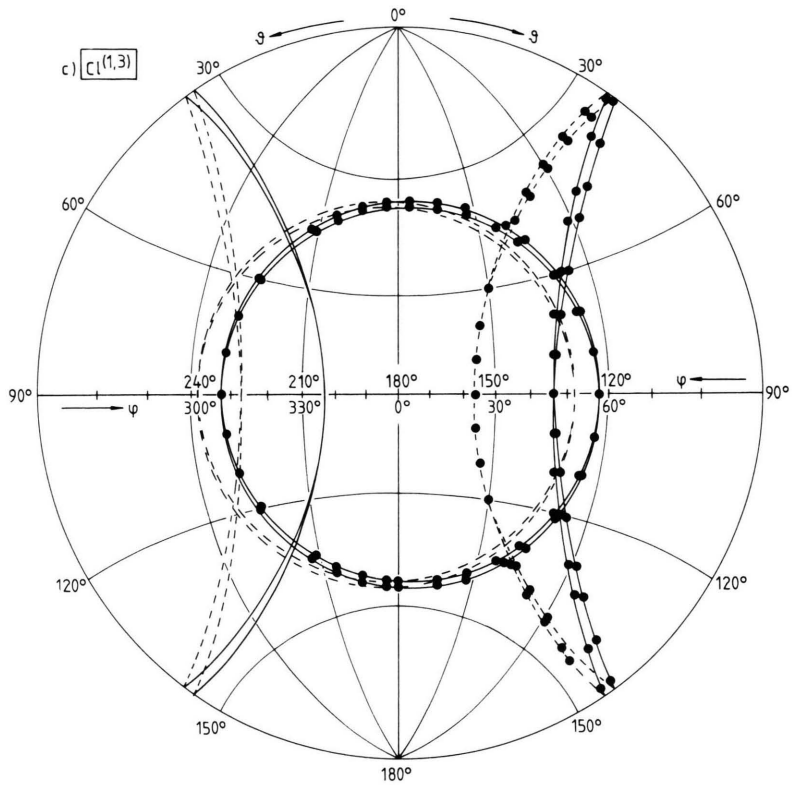
The results are summarized in Tables 1 and 2. Table 1 gives the scalar parameters found from the

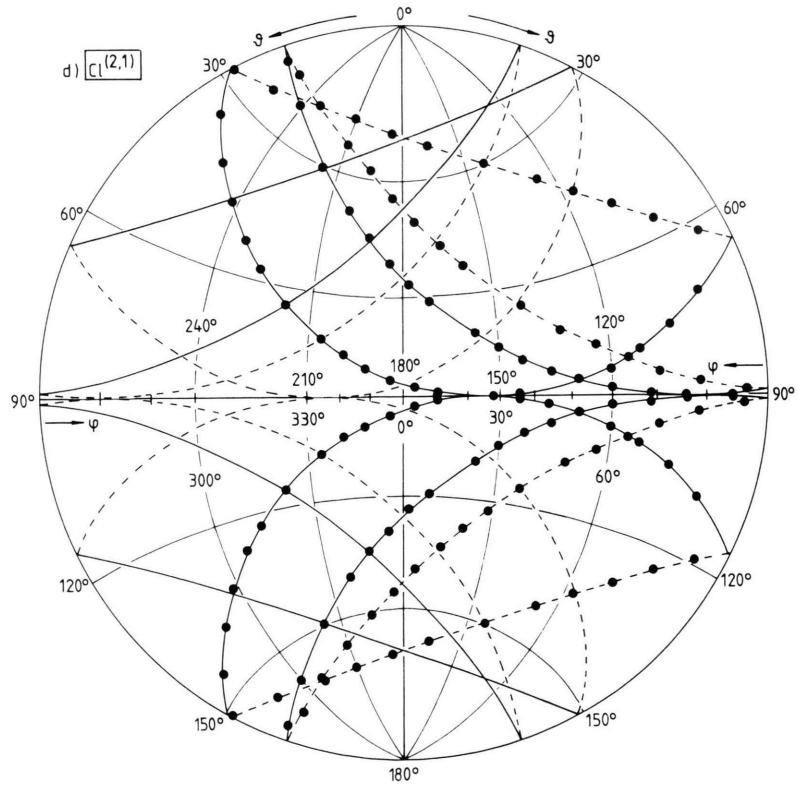
Table 1. The ^{35}Cl-NQR frequencies, the nuclear quadrupole coupling constants e^2qQh^{-1}, and asymmetry parameters η of α-2,4,6-tris(trichloromethyl)-1,3,5-trioxane, $(Cl_3CCHO)_3$. Additionally, the coordinates of the Cl atoms in the unit cell of the compound are listed (see also Figures 3, 4).

Atom	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$	$\frac{\nu(^{35}\mathrm{Cl})^{a}}{\mathrm{MHz}}$	$\frac{e^2qQh^{-1}(^{35}\mathrm{Cl})^{b}}{\mathrm{MHz}}$	$\eta(^{35}\mathrm{Cl})^{b}$
$Cl^{(1,1)}$	0.7789(4)	0.1020(2)	0.6469(3)	38.776(3)	77.525(6)	0.0459(20)
$Cl^{(1,2)}$	0.6287(3)	0.0027(2)	0.8422(4)	39.082(3)	78.155(6)	0.0260(30)
$Cl^{(1,3)}$	0.8435(3)	0.0984(2)	0.9441(4)	38.379(3)	76.752(6)	0.0215(25)
$Cl^{(2,1)}$	0.5856(3)	0.1570(2)	1.2966(3)	39.028(3)	78.050(6)	0.0204(35)
$Cl^{(2,2)}$	0.3830(3)	0.2500	1.1665(4)	38.951(3)	77.902(6)	0.0016(10)

[a] At 25 °C. [b] At 24 ± 2 °C.


a) Cl(1,1)
b) Cl(1,2)
ϑ
φ
0°
30°
60°
90°
120°
150°
180°
210°
240°
300°
330°


c) Cl(1,3)
0°
30°
60°
90°
120°
150°
180°
240°
210°
300°
330°
φ


d) Cl(2,1)
0°
30°
60°
90°
120°
150°
180°
240°
210°
300°
330°
φ

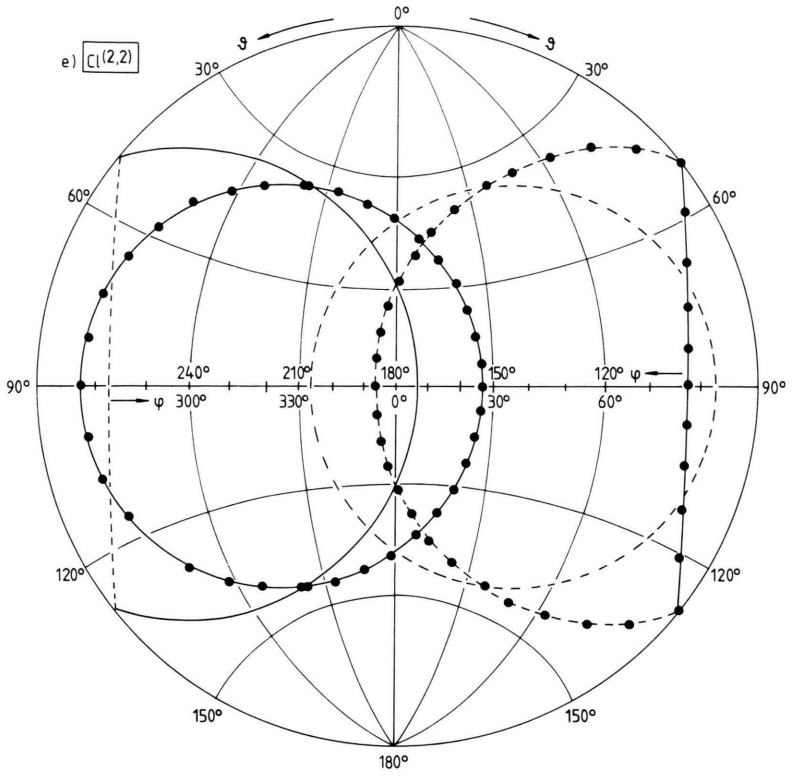


Fig. 2. Stereographic projections of the $Cl^{(j)}$ NQR zero splitting cones. The curves are fitted to the experimental points (●). Fully drawn lines: $270° \leqq \varphi \leqq 90°$. Dotted lines: $90° \leqq \varphi \leqq 270°$. The point $\vartheta = 0°$ of the stereographic projection marks the crystal axis ***b*** and the crystal axis ***c*** is determined by $\vartheta = 90°$, $\varphi = 52.20°$ (see also Figure 1).

^{35}Cl NQR experiments: ν (^{35}Cl) at 25 °C, e^2qQh^{-1} (^{35}Cl) at (24 ± 2) °C, and η (^{35}Cl) at (24 ± 2) °C. In Table 2 the direction cosines of the three principal axes for each of the ^{35}Cl EFG tensors are given with respect to the orthogonal crystal axes system, *a*, *b*, *c*. There, for example (*j*) in $\Phi_{xx}^{(j)}$ runs from (1, 1) to (2, 2); $\lambda^{(j)} = \pm 0.91954$ is cos ($\Phi_{xx}^{(1,1)}$, [100]), $\mu^{(j)} = \mp 0.19561$ is cos ($\Phi_{xx}^{(1,1)}$, [010]), etc. Additionally the direction cosines of the corresponding C–Cl bonds $r(C^{(k)}–Cl^{(j)})$ as found from X-ray diffractions studies [9] are shown. Here $\lambda^{(j)} = 0.3603$ is cos ($r(C^{(1)}–Cl^{(1,1)})$, [100]) etc. The small asymmetry parameters observed are accurate at least to $= \pm 0.004$, see Table 1. The orientation of the principal axes $\Phi_{zz}^{(j)}$ can be given to ± 0.1 °. The directions of Φ_{xx} and Φ_{yy} are reliable to ± 4 ° up to ± 30 °, depending on the magnitude of η.

Discussion

From the basic theory of nuclear electric quadrupole interactions in solids, by simple arguments one can show that the coupling constants e^2qQh^{-1} should be proportional to r^{-3}, r being the bond distance $C^{(k)}–Cl^{(j)}$. In case of chloralide it was shown [4] that there is a tendency for $e^2qQh^{-1} \sim r^{-3}$. It was pointed out that the determination of bond lengths C–Cl which are known for chloralide to ± 0.4 pm [12] are too inaccurate to draw quantitative conclusions, particularly about the relation: Bond lengths determined from X-ray crystallography and charge distribution, or, molecular and lattice dynamics and charge distribution within the bond. For the compound α-2,4,6-tris(trichloromethyl)-1,3,5-trioxane the lengths of the bonds $C^{(h)}–Cl^{(j)}$ are known to ± 1.0 pm and therefore even a qualitative discussion $r(C^{(h)}–Cl^{(j)}) \leftrightarrow e^2qQh^{-1}(Cl^{(j)})$ is not possible. It is interesting to note that in trichloroethylidene trichlorolactic ester (Chloralide) the 6 crystallographically inequivalent bond distances $r(C^{(k)}–Cl^{(j)})$ are between 175.8 pm and 176.5 pm ($\Delta_{max} = 0.7$ pm) [12] whereas in α-chloral the distances $r(C^{(h)}\text{-}Cl^{(j)})$ are found between 173 pm and 178 pm ($\Delta_{max} = 5$ pm) [9].

As listed in Table 1, the asymmetry parameters η are very small, $0.002 \leqq \eta \leqq 0.046$, which values are comparable with those found for chloralide [4], and those reported for other trichloromethyl derivatives [5–7]. One may expect such small asymmetry parameters for chlorine atoms bonded to carbon within an aliphatic group, such as CCl_3. Thus, at least for this group, the usual procedure in ^{35}Cl-NQR spectroscopy, to neglect the influence of η on the frequency and to set $e^2 q Q/h = 2\nu$ is safe in first approximation.

To facilitate the discussion, the projection of the unit cell of α-parachloral onto the (100) plane is shown in Figure 3. Also a molecule viewed along the *a*-axis is shown in Figure 4. The numbering of the atoms given in this figure is used throughout this paper.

First we compare the orientation of the principal axes $\Phi_{zz}^{(j)}$ of the ^{35}Cl EFGT with the corresponding $C^{(k)}-Cl^{(j)}$ bond directions. The data given in Table 2 show that the orientation of the EFGT is primarily determined by the bond between Cl and C. The angles between the bond direction and Φ_{zz} do not exceed 0.8°. Since the error in the bond angles from the X-ray diffraction data [9] is ± 0.7°, and that of the direction of $\Phi_{zz}^{(j)}$ with respect to the crystal axes is ± 0.1°, it is quite safe to say that, in aliphatic C–Cl bonds, the bond direction coincides with the axis Φ_{zz} of the corresponding ^{35}Cl EFGT.

A comparison of bond angle $\measuredangle (Cl^{(j)}-C^{(k)}-Cl^{(l)})$ and $\measuredangle (\Phi_{zz}^{(j)}, \Phi_{zz}^{(l)})$ supports this above conclusion (see Table 3); the difference between the bond angle $\measuredangle (Cl^{(j)}-C^{(k)}-Cl^{(l)})$ and the corresponding angle of the EFGTs' $\measuredangle (\Phi_{zz}^{(j)}, \Phi_{zz}^{(l)})$ is quite small and never exceeds 0.7°.

In Fig. 5 we show the orientations of the ^{35}Cl EFGT for the Cl-atoms bonded to $C^{(1,1)}$ with respect to the plane $C^{(1)}-C^{(1,1)}-Cl^{(j)}$. In Fig. 6 the corresponding relations for the second group CCl_3, Cl-atoms bonded to $Cl^{(2,1)}$ are given, now with respect to the plane $C^{(2)}-C^{(2,1)}-Cl^{(j)}$.

An interesting result in the present study is the orientation of the EFGT axes $\Phi_{xx}^{(j)}$ and $\Phi_{yy}^{(j)}$ within the molecule. For the discussion it is convenient to consider the two crystallographically inequivalent

Table 2. Direction cosines of the three main axes of the EFG tensors with respect to the crystal axes ***a***, ***b***, ***c***. Additionally the direction cosines of the corresponding C–Cl bond vectors as found from the x-ray work [9] are given within the same coordinate system.

Atom	$\lambda^{(j)}$	$\mu^{(j)}$	$\nu^{(j)}$
		$\Phi_{xx}^{(j)}$	
$Cl^{(1,1)}$	± 0.91954	∓ 0.19561	± 0.34087
$Cl^{(1,2)}$	± 0.79292	∓ 0.48344	± 0.37104
$Cl^{(1,3)}$	∓ 0.39587	∓ 0.80074	± 0.44963
$Cl^{(2,1)}$	± 0.96779	± 0.22461	∓ 0.11338
$Cl^{(2,2)}$	0	± 1	0
		$\Phi_{yy}^{(j)}$	
$Cl^{(1,1)}$	∓ 0.16849	∓ 0.97983	∓ 0.10766
$Cl^{(1,2)}$	∓ 0.25596	± 0.28836	± 0.92267
$Cl^{(1,3)}$	± 0.51608	∓ 0.59889	∓ 0.61222
$Cl^{(2,1)}$	∓ 0.02601	± 0.53759	± 0.84282
$Cl^{(2,2)}$	± 0.17227	0	∓ 0.98505
		$\Phi_{zz}^{(j)}$	
$Cl^{(1,1)}$	± 0.35510	± 0.04152	∓ 0.93390
$Cl^{(1,2)}$	∓ 0.55311	∓ 0.82650	± 0.10487
$Cl^{(1,3)}$	± 0.75949	∓ 0.00960	± 0.65037
$Cl^{(2,1)}$	± 0.25038	∓ 0.81270	± 0.52613
$Cl^{(2,2)}$	∓ 0.98505	0	∓ 0.17228
		$r(C^{(k)}-Cl^{(j)})$	
$Cl^{(1,1)}$	0.3603	0.0297	− 0.9324
$Cl^{(1,2)}$	− 0.5427	− 0.8334	0.1042
$Cl^{(1,3)}$	0.7576	− 0.0018	0.6527
$Cl^{(2,1)}$	0.2567	− 0.8130	0.5227
$Cl^{(2,2)}$	− 0.9849	0	− 0.1729

Table 3. X-ray crystallographic bond angles $\measuredangle (Cl^{(j)}-C^{(k)}-Cl^{(l)})$, and ^{35}Cl EFG principal axes angles $\measuredangle (\Phi_{zz}^{(j)}, \Phi_{zz}^{(l)})$ in α-parachloral.

$\measuredangle (\Phi_{zz}^{(j)}, \Phi_{zz}^{(l)})$	angle / degree	$\measuredangle (Cl^{(j)}-C^{(k)}-Cl^{(l)})$	angle / degree
$\measuredangle (\Phi_{zz}^{(1,1)}, \Phi_{zz}^{(1,2)})$	109.18	$\measuredangle (Cl^{(1,1)}-C^{(1,1)}-Cl^{(1,2)})$	108.5(6)
$\measuredangle (\Phi_{zz}^{(1,1)}, \Phi_{zz}^{(1,3)})$	109.75	$\measuredangle (Cl^{(1,1)}-C^{(1,1)}-Cl^{(1,3)})$	109.6(7)
$\measuredangle (\Phi_{zz}^{(1,2)}, \Phi_{zz}^{(1,3)})$	110.11	$\measuredangle (Cl^{(1,2)}-C^{(1,1)}-Cl^{(1,3)})$	110.0(6)
$\measuredangle (\Phi_{zz}^{(2,1)}, \Phi_{zz}^{(2,2)})$	109.75	$\measuredangle (Cl^{(2,1)}-C^{(2,1)}-Cl^{(2,2)})$	110.1(6)
$\measuredangle (\Phi_{zz}^{(2,1)}, \Phi_{zz}^{(2,1')})$	108.72	$\measuredangle (Cl^{(2,1)}-C^{(2,1)}-Cl^{(2,1')})$	108.8(6)

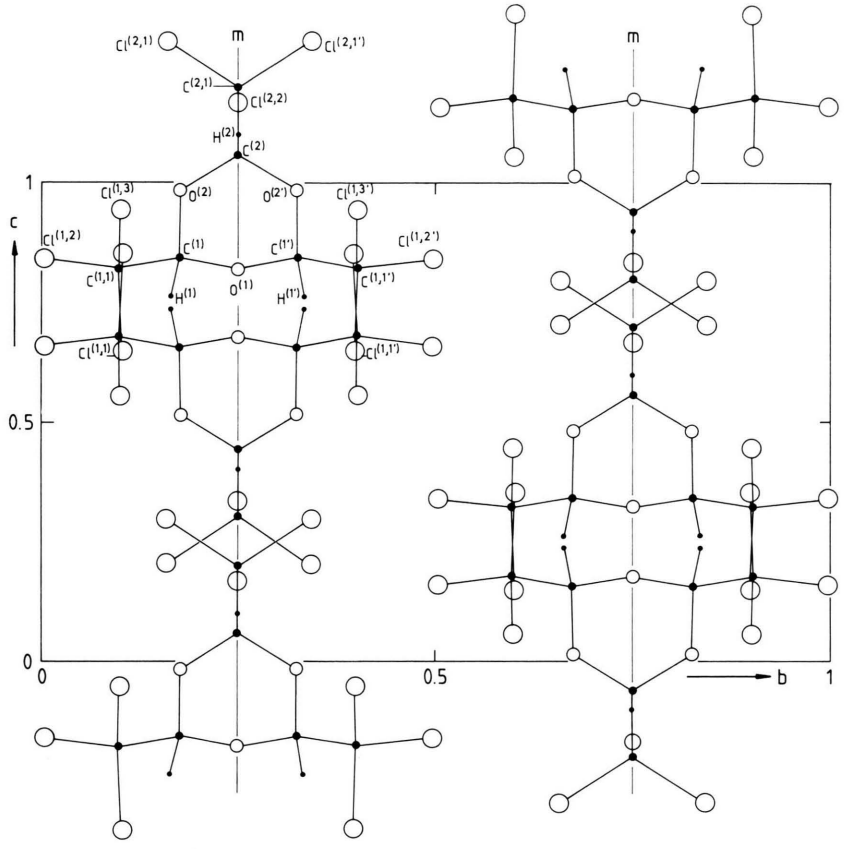


Fig. 3. Projection of the structure of α-parachloral along [100] on the plane (100). The molecule at the upper left corner is the one for which the relative coordinates x/a, y/b, z/c are given in Table 1.

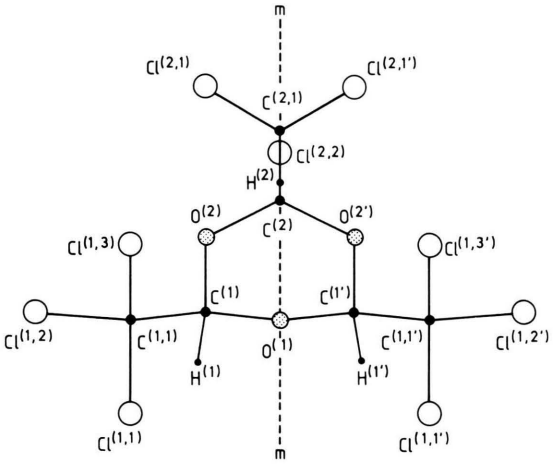
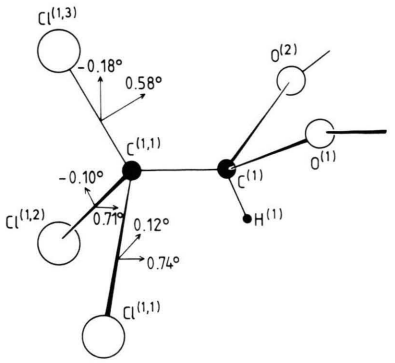


Fig. 4. Molecule of α-parachloral with the numbering of the atoms used throughout this paper.

CCl_3-groups separately. The one group, ($C^{(1)}$–$Cl^{(1,1;1,2;1,3)}$), is in itself asymmetric. We consider the EFG tensors of the Cl atoms with respect to the plane determined by ($H^{(1)}$–$C^{(1)}$–$C^{(1,1)}$). For this purpose the orientation of the EFGTs and the next neighbouring atoms are shown in a projection along the direction $C^{(1,1)}$–$C^{(1)}$ in Figure 7. Disregarding the atoms $C^{(2)}$ and $H^{(2)}$, the plane ($H^{(1)}$–$C^{(1)}$–$C^{(1,1)}$) is pseudo mirror plane with respect to $Cl^{(1,1)}$, $Cl^{(1,2)}$, and $Cl^{(1,3)}$. It can be seen from Fig. 7 that the orientation of the EFGT of $Cl^{(1,1)}$ and of $Cl^{(1,2)}$ in first approximation obeys this mirror plane. It is the influence of the oxygen atoms $O^{(1)}$ and $O^{(2)}$ which deforms the EFGTs in such a way that Φ_{yy} ($Cl^{(1,j)}$) is oriented towards the planes ($C^{(1,1)}$–$O^{(j)}$–$Cl^{(1,j)}$), $j=1,2$. The angles between the planes ($Cl^{(1,1)}$–$O^{(j)}$–$Cl^{(1,j)}$) and Φ_{yy} ($Cl^{(1,j)}$) are 15.3° ($j=1$) and 28.8° ($j=2$), respectively. The influence of $O^{(2)}$ on $Cl^{(1,2)}$ is somewhat weaker than that of $O^{(1)}$ on $Cl^{(1,1)}$, showing up by the smaller η and the less pronounced orientation of Φ_{yy} ($Cl^{(1,2)}$) with respect to the corresponding plane (C–O–Cl). This may be due to the fact that the intramolecular distance $O^{(2)}$–$Cl^{(1,2)}$ is appreciably larger (302 pm) than the distance $O^{(1)}$–$Cl^{(1,1)}$ (292 pm). A mutual influence of the Cl-atoms cannot be recognized. It should – in first approximation – lead to an additionally pseudo

α-Parachloral, $(Cl_3CCHO)_3$, T = 24 °C;

group $C^{(1,1)} - Cl^{(1,1;\,1,2;\,1,3)}$



plane ($C^{(1)} - C^{(1,1)} - Cl^{(1,1)}$); $e^2\Phi_{zz}Qh^{-1}(^{35}Cl^{(1,1)}) = 77.525$ MHz; $\eta(^{35}Cl^{(1,1)}) = 0.046$

($\Phi_{zz}^{(1,1)}$, plane): 0.12° ⊥ plane, 0.74° in plane

($\Phi_{xx}^{(1,1)}$, plane): 45° ± 4°; ($\Phi_{yy}^{(1,1)}$, plane): −45° ± 4°

plane ($C^{(1)} - C^{(1,1)} - Cl^{(1,2)}$); $e^2\Phi_{zz}Qh^{-1}(^{35}Cl^{(1,2)}) = 78.155$ MHz; $\eta(^{35}Cl^{(1,2)}) = 0.026$

($\Phi_{zz}^{(1,2)}$, plane): −0.10° ⊥ plane, 0.71° in plane

($\Phi_{xx}^{(1,2)}$, plane): 32° ± 13°; ($\Phi_{yy}^{(1,2)}$, plane): 58° ± 13°

plane ($C^{(1)} - C^{(1,1)} - Cl^{(1,3)}$); $e^2\Phi_{zz}Qh^{-1}(^{35}Cl^{(1,3)}) = 76.752$ MHz; $\eta(^{35}Cl^{(1,3)}) = 0.022$

($\Phi_{zz}^{(1,3)}$, plane): −0.18° ⊥ plane, 0.58° in plane

($\Phi_{xx}^{(1,3)}$, plane): −70° ± 8°; ($\Phi_{yy}^{(1,3)}$, plane): 20° ± 8°

Fig. 5. Orientation of the EFGTs of the group $C^{(1,1)}-Cl^{(1,1;\,1,2;\,1,3)}$ with respect to the plane $(C^{(1)}-C^{(1,1)}-Cl^{(j)})$. The signs of the angles refer to the upper signs of the directions cosines in Table 2.

threefold symmetry for the orientation of Φ_{xx} and Φ_{yy} of the three EFGTs, which has not been observed in any of the CCl_3 groups discussed here.

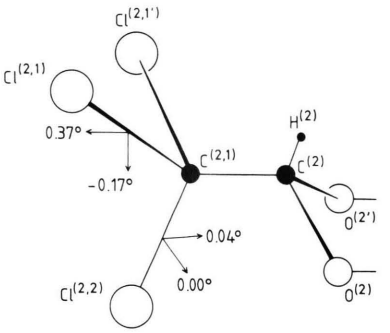
The asymmetry parameter of the EFGT ($Cl^{(1,3)}$) is even smaller than that of $Cl^{(1,2)}$. For $Cl^{(1,3)}$ the mirror symmetry is much more violated by the relatively close lieing atoms $C^{(2)}$ and $H^{(2)}$ (distance $Cl^{(1,3)}-C^{(2)} = 351$ pm, $Cl^{(1,3)}-H^{(2)} = 317$ pm). The influence of symmetry destroying atoms $H^{(2)}$ and $C^{(2)}$ is seen by the orientation of Φ_{yy}. Φ_{yy} ($Cl^{(1,3)}$) is almost in the plane $(C^{(1,1)}-O^{(2)}-H^{(2)})$ with a deviation of 4.4°.

The second group, $(C^{(2,1)}-Cl^{(2,1;\,2,1';\,2,2)})$ can be referred to the true mirror plane determined by the atomic plane $(H^{(2)}-C^{(2)}-Cl^{(2,1)})$. The asymmetry parameters are very small: 0.0204 for $Cl^{(2,1;\,2,1')}$; 0.0016 for $Cl^{(2,2)}$. Again the angle (plane $Cl^{(2,1)}-C^{(2,1)}-O^{(2)}$, $\Phi_{yy}(Cl^{(2,1)})$) is small 9.6°, showing the influence of the oxygen atom. This is seen in Figure 8. For $Cl^{(2,2)}$ there is no reason for further discussion of the orientation of the EFGT regarding the very small asymmetry parameter.

The results on α-parachloral can be compared with those found for Chloralide [4]. In the Chloralide molecule there are two crystallographically independent groups CCl_3. One of these groups, $C^{(4)}-Cl^{(4,5,6)}$, has an intramolecular nearest neighbourhood very similar to the group CCl_3 in α-parachloral; it is the configuration $Cl_3C-C(=O)(-O-)H$. Figure 9 shows a pseudo miror plane through $H^{(2)}$, $C^{(4)}$, $C^{(5)}$. Again the orientation of two of the ^{35}Cl EFGT, EFGT ($Cl^{(4)}$) and EFGT ($Cl^{(6)}$), is almost reflected by the pseudo mirror plane, and the influence of the neighbouring oxygen results in a similar way as

α-Parachloral, $(Cl_3CCHO)_3$, T = 24 °C;

group $C^{(2,1)} - Cl^{(2,1;\,2,1';\,2,2)}$



plane ($C^{(2)} - C^{(2,1)} - Cl^{(2,1)}$); $e^2\Phi_{zz}Qh^{-1}(^{35}Cl^{(2,1)}) = 78.050$ MHz; $\eta(^{35}Cl^{(2,1)}) = 0.020$

($\Phi_{zz}^{(2,1)}$, plane): −0.17° ⊥ plane, 0.37° in plane

($\Phi_{xx}^{(2,1)}$, plane): 50° ± 7°; ($\Phi_{yy}^{(2,1)}$, plane): 40° ± 7°

plane ($C^{(2)} - C^{(2,1)} - Cl^{(2,2)}$); $e^2\Phi_{zz}Qh^{-1}(^{35}Cl^{(2,2)}) = 77.902$ MHz; $\eta(^{35}Cl^{(2,2)}) = 0.002$

($\Phi_{zz}^{(2,2)}$, plane): 0.00° ⊥ plane, 0.04° in plane

($\Phi_{xx}^{(2,2)}$, plane): 90° ± 30°; ($\Phi_{yy}^{(2,2)}$, plane): 0° ± 30°

Fig. 6. Orientation of the EFGTs of the group $C^{(2,2)}-Cl^{(2,1;\,2,1';\,2,2)}$ with respect to the plane $(C^{(2)}-C^{(2,2)}-Cl^{(j)})$. The signs of the angles refer to the upper signs of the direction cosines in Table 2.

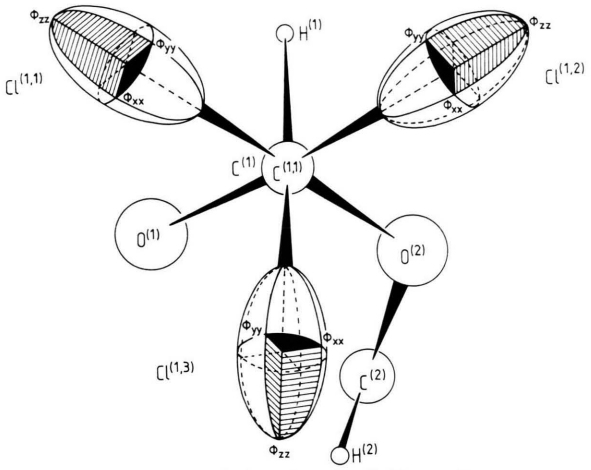


Fig. 7. Orientation of the electric field gradient tensors (EFGT) of $Cl^{(1,1)}$, $Cl^{(1,2)}$, and $Cl^{(1,3)}$ in α-parachloral with respect to the next neighbouring atoms. The EFGTs are drawn as projection of threedimensional ellipsoids in a similar way as usually done for thermal ellipsoids in X-ray crystallography. The projection is along $C^{(1,1)}-C^{(1)}$.

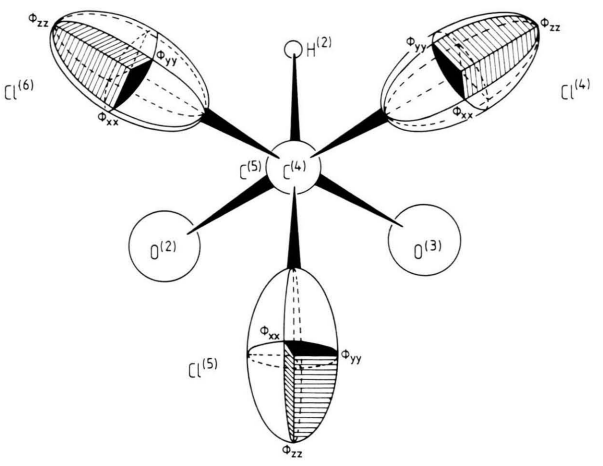


Fig. 9. Orientation of the EFGTs of $Cl^{(4)}$, $Cl^{(5)}$, and $Cl^{(6)}$ in Chloralide with respect to the next neighbouring atoms. The EFGTs are drawn as projection of threedimensional ellipsoids in a similar way as usually done for thermal ellipsoids in X-ray crystallography. The projection is along $C^{(4)}-C^{(5)}$.

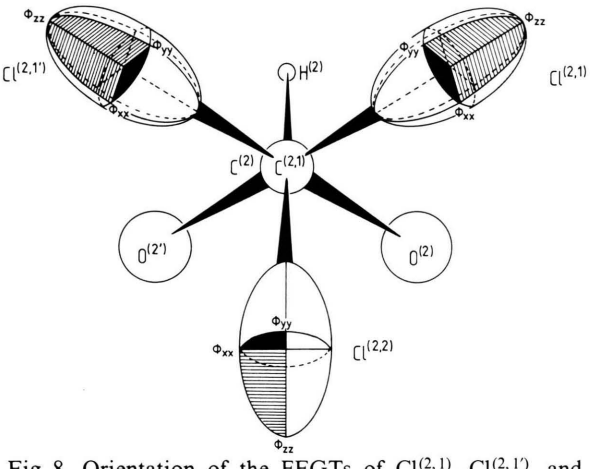


Fig. 8. Orientation of the EFGTs of $Cl^{(2,1)}$, $Cl^{(2,1')}$, and $Cl^{(2,2)}$ in α-parachloral with respect to the next neighbouring atoms. The EFGTs are drawn as projection of threedimensional ellipsoids in a similar way as usually done for thermal ellipsoids in X-ray crystallography. The projection is along $C^{(2,1)}-C^{(2)}$.

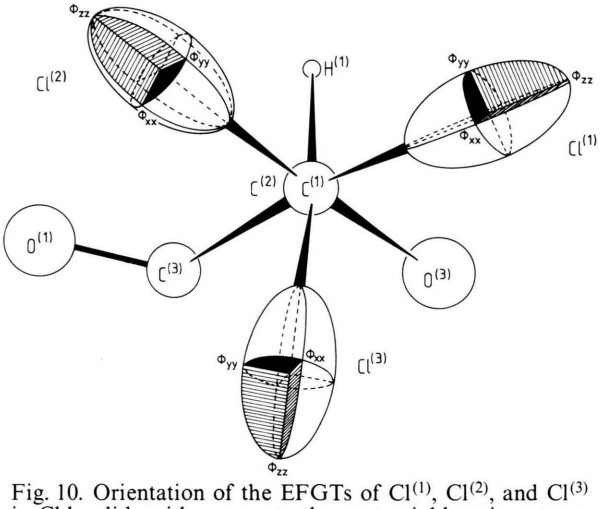


Fig. 10. Orientation of the EFGTs of $Cl^{(1)}$, $Cl^{(2)}$, and $Cl^{(3)}$ in Chloralide with respect to the next neighbouring atoms. The EFGTs are drawn as projection of threedimensional ellipsoids in a similar way as usually done for thermal ellipsoids in X-ray crystallography. The projection is along $C^{(1)}-C^{(2)}$.

in α-parachloral for the atoms $Cl^{(1,1)}$ and $Cl^{(1,2)}$:
$\measuredangle$ (plane $(Cl^{(4)}-C^{(4)}-O^{(3)})$, $\Phi_{yy}(Cl^{(4)})) = 27.9°$;
$\measuredangle$ (plane $(Cl^{(6)}-C^{(4)}-O^{(2)})$, $\Phi_{yy}(Cl^{(6)})) = 5.6°$.

The second group CCl_3 of the Chloralide molecule has a different intramolecular configuration. It is shown in Figure 10. No pseudo mirror plane exists for the group $C^{(1)}-Cl^{(1,2,3)}$. It is found that $\Phi_{yy}(Cl^{(2)})$ is oriented along a mean plane through $Cl^{(2)}$, $C^{(2)}$, $C^{(3)}$, and $O^{(1)}$, forming an angle of $\sim 3°$ with this plane.

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