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The Combination of X-ray Diffraction and Nuclear Quadrupole Resonance Studies of Crystals

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Abstract

The application of single-crystal Zeeman nuclear quadrupole resonance (NQR) in combination with diffraction studies is discussed. Bond directions and bond angles are found by the Zeeman spectroscopy of NQR, as are symmetry elements of the structures. Centrosymmetry may be differentiated from polar structures. Weak deformations of the valence electron shell by mutual polarization can be recognized and the double-bond character of a bond may be estimated. The method is quite valuable in the study of hydrogen bonds and of dynamics of molecules such as D_2O and the groups $-CD_3$ and ND_3. Most useful is the method of the combination of *X*- and *N*-diffraction because of its sensitivity to the charge distribution around atoms and its location of time scale in dynamical effects.

Introduction

In the periodic system the majority of elements contain one or more stable isotopes with a nuclear spin $I \geq 1$ and the nuclei possess a nuclear electric moment eQ [$e =$ unit charge, $Q =$ nuclear moment (10^{-24} cm^2)] connected to the angular momentum (Kopfermann, 1956; Brix, 1986). eQ interacts with the electric-field gradient tensor, EFGT, at the site of the nucleus considered and a nonvanishing EFGT with the principal tensor axes Φ_{zz}, Φ_{yy}, Φ_{xx} is always present in a solid if the site symmetry of the atom with the nucleus considered is noncubic. Since the nuclear angular momentum is quantized, which is determined by the EFGT, we can determine the energy levels by introducing transitions between them. The interaction energy, $eQ\Phi_{zz}h^{-1}$, with $h =$ Planck's constant, is measured most conveniently in the solid state by nuclear quadrupole resonance (NQR) in the radio frequency region (Dehmelt & Krüger, 1950, 1951; Pound, 1950) or on gaseous species by microwave spectroscopy (Townes & Schawlow, 1955). The vast majority of NQR experiments have been performed on polycrystalline material, from which some useful information on the symmetry properties of the solid considered may be gained (Jeffrey & Sakurai, 1964). A complete collection of experimental data exists (Chihara & Nakamura, 1988–1989, 1993). Here we deal with nuclear quadrupole interaction (NQI) in connection with crystal structures and shall focus on NQR, or more generally, on NQI in single crystal work. A report on single-crystal Zeeman NQR spectroscopy has been given by Weiss (1989).

Theoretical background

The EFGT is a second-rank tensor, described by its principal axes Φ_{xx}, Φ_{yy} and Φ_{zz}, which are the second derivatives of the electrical potential with respect to the principal axes system at the site of the nucleus considered. By convention one defines $|\Phi_{zz}| \geq |\Phi_{yy}| \geq |\Phi_{xx}|$ and, since the tensor is three-axial, the asymmetry parameter $\eta = |\Phi_{xx} - \Phi_{yy}|/|\Phi_{zz}|$.

The EFGT is oriented and the orientations in a single crystal are 'rigid' with respect to the nucleus considered and, therefore, to the respective atomic coordinates and the crystal coordinate system. The nuclear angular momentum is quantized and under the influence of an external magnetic field **B**, the degeneracy of the energy levels (tensors are quadratic functions) is lifted. For the case of nuclear spin $I = 3/2$, the situation is shown in Fig. 1.

A main point of interest in performing NQR single-crystal studies is the comparison of the magnitude of the EFGT axes and their orientation in the unit cell of the

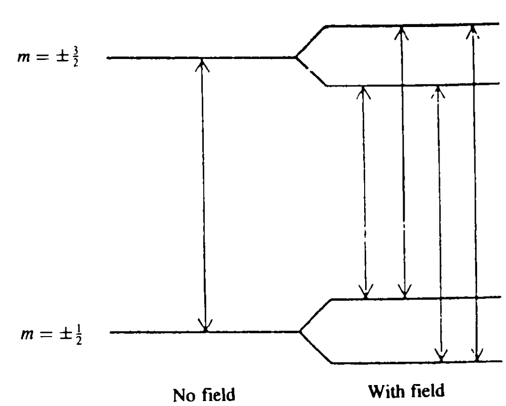


Fig. 1. Energy levels and transitions for the pure quadrupole spectrum of a nucleus with $I = 3/2$ with and without an externally applied magnetic field.

crystal with information from diffraction studies, point positions, symmetry elements, bond directions and charge distributions in the molecules (solids) due to the relation

$$\Phi_{zz}, \eta = f\{\rho(x, y, z)\mathrm{d}\tau \cdot r^{-3}\}. \qquad (1)$$

The theoretical background is thoroughly presented by Das & Hahn (1958) and Lucken (1969).

Experimental

Focusing interest on the determination of $eQ\Phi_{zz}h^{-1}$ and η only, for all nuclei with $I \geq 1$, $I \neq 3/2$, information on these properties is available from resonance experiments on polycrystalline solids after certain simple calculations. For $I = 3/2$, there is a method devised (Morino & Toyama, 1961) which allows the evaluation of the two values from a powder Zeeman experiment. The shape of Zeeman NQR lines in crystal powder is considered by Brooker & Creel (1974). However, literature shows that only in a few cases are the correct data found. A well known example is the estimate of $\eta(^{35}\mathrm{Cl})$ in $HgCl_2$. The values $0.09 \leq \eta[\mathrm{Cl}(1)] \leq 0.70$, $0.10 \leq \eta[\mathrm{Cl}(2)] \leq 0.39$ have been offered; $\eta = 0.037$ and 0.012, respectively, are the correct values (Sengupta, Giezendanner & Lucken, 1980), showing that the Hg—Cl bond is not deviating much from rotation symmetry, and besides, the Cl—Hg—Cl angle is deviating from 180°. Furthermore, vital information on structure and chemical bonds in the solid, and the direction cosines α, β and γ of the EFGT axes are not available.

The study of nuclear quadrupole interaction in solids needs a rather large single crystal to have good signal-to-noise ratio (*S/N*), a radio frequency spectrometer and a magnetic field to lift the degeneracy of the energy levels. The main drawback of this type of spectroscopy is the enormous volume in $eQ\Phi_{zz}h^{-1}$ (in MHz) nature produces. The nuclear quadrupole moment Q covers the range $6 \times 10^{-4} \leq Q/(\times 10^{-24}\ \mathrm{cm}^2) \leq 8$ and Φ_{zz} covers a range of at least six powers. As an example, $eQ\Phi_{zz}h^{-1}$ (^{127}I) is 2160 MHz (300 K) in crystalline iodine and 7.9 MHz (300 K) in iodine in the β-phase of AgI. In contrast to NMR, the method must be adjusted to the wide scale of NQI and to the problem of crystal chemistry in question.

There are two experimental approaches to the problem. For small Q or weak Φ_{zz} the studies are limited to rather strong external magnetic fields ≥ 1 T, or the NQI must dominate the energy term and the field **B** is the perturbation. This was the original method for studying quadrupole interactions, introduced by Pound (1950), and an excellent introduction to the method and the results gained is due to Cohen & Reif (1957). For minerals and salts containing the atoms Li, Na, K, Rb, Cs, Be, B, Al, Mg *etc.*, the high field method (the nuclear magnetic interaction is large compared with the NQI) is the most useful way of studying NQI in connection with the crystal structure. Also, the EFGT's at the deuteron, ^{14}N and ^{17}O sites are favorably investigated by the high field method. There is a good chance that the combination of diffraction and NQI studies will attract more attention in future, because in many laboratories there are now high-field magnets with $|\mathbf{B}| = 6$–10 T available. Thus, solids containing the abovementioned atoms can be studied with the introduction of a one- or two-circle goniometer into the magnet bore and some additional electronic components. For a discussion on the problem of how to explore crystal symmetry for the determination of the EFGT's from NMR–NQR rotation patterns, see Kind (1986).

In solids with molecules or molecular ions, incorporation atoms such as Cl, Br, I, N, As, Sb, Bi, Ga, In *etc.* in partially covalent bonds, Zeeman split NQR is the appropriate method (Dean, 1952, 1954). For monographs on the subject, see Das & Hahn (1958) and Lucken (1969). Here the magnetic field is the perturbation, lifting the degeneracy of the energy levels. The most simple method uses, besides the necessary electronics, a 4π-Zeeman goniometer, which allows a fixed crystal position in its center and rotation of the magnetic vector in any direction of space. Variation of temperature at the crystal site and high accuracy in the determination of the direction cosines of the EFGT with respect to the crystal axes and the symmetry elements of the unit cell are not problems (Nagarajan, Weiden, Wendel & Weiss, 1982). In Fig. 2, the simple physics background on how to construct such a system is shown.

Most work in the literature is performed using one pair of Zeeman coils and a one-circle mechanical goniometer, see *e.g.* Bucci, Cecchi & Colligiani (1964), Bucci, Cecchi & Scrocco (1964), and Bucci & Cecchi (1964) for precise instrumentation and an application to Zeeman split ^{81}Br in 1,3,5-tribromobenzene [Bucci, Cecchi,

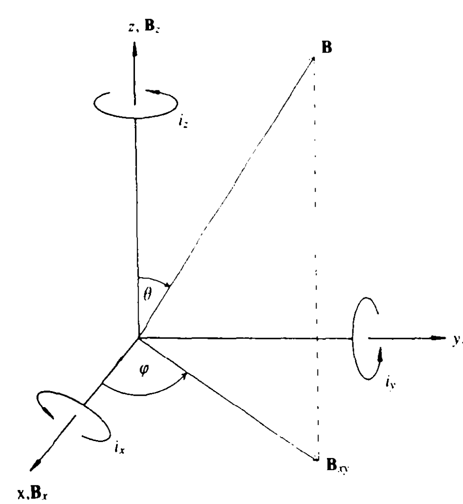


Fig. 2. Laboratory coordinate system x,y,z, currents i_x, i_y, i_z and magnetic field $\mathbf{B}(\mathbf{B}_x, \mathbf{B}_y, \mathbf{B}_z)$ for a 4π-Zeeman NQR spectrometer.

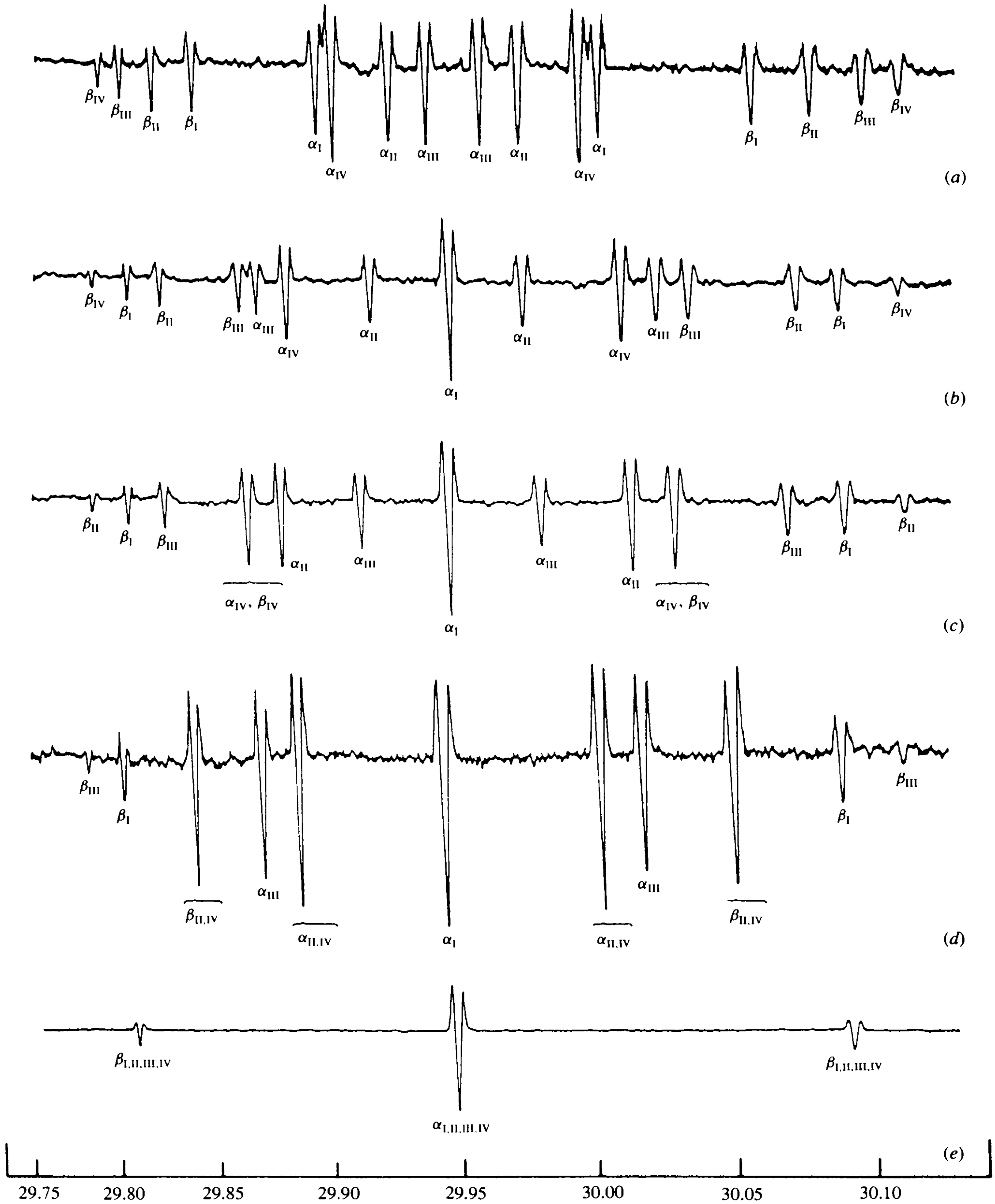


Fig. 3. ^{35}Cl NQR-Zeeman spectrum of $NaClO_3$; $|\mathbf{B}| = 200 \times 10^{-4}$ T. $\alpha_{I\ldots IV}$, $\beta_{I\ldots IV}$ are the satellites I···IV corresponding to the number of tensors (see text); T = room temperature.

Spectrum no.	$\mathbf{B}_x$ (10^{-4} T)	$\mathbf{B}_y$ (10^{-4} T)	$\mathbf{B}_z$ (10^{-4} T)	φ (°)	ϑ (°)
(a)	−33.71	−183.55	−72.13	259.59	111.13
(b)	165.75	60.14	94.39	19.94	61.84
(c)	−61.84	−100.13	161.71	238.30	36.05
(d)	133.33	−133.33	−66.41	315.00	109.47
(e)	200.00	0	0	0	90.00

$\nu_\alpha = \nu_Q \pm (1/2)[3 - (1 + 4\tan^2\delta)^{1/2}]\gamma B \cos\delta$, $\nu_\beta = \nu_Q \pm (1/2)[3 + (1 + 4\tan^2\delta)^{1/2}]\gamma B \cos\delta$.

Colligiani & Landucci (1965); crystal structure: Milledge & Pant (1960)], to ^{81}Br in *para*-bromophenol and ^{35}Cl in *para*-chlorophenol [Bucci, Cecchi & Colligiani (1969); crystal structure of 4-ClC_6H_4OH: Wu (1968), 4-ClC_6H_4OH is not isomorphous to the bromine compound].

In the early days of single-crystal NQR, Ting, Manring & Williams (1954) studied the ^{35}Cl NQR Zeeman spectrum of cubic $NaClO_3$. The structure is well known, space group $P2_13$, $Z = 4$ and the ClO_3^- ions are located on three axes (Zachariasen, 1929). In Fig. 3, the Zeeman split ^{35}Cl NQR spectrum taken with the 4π-goniometer is shown for different orientations of the field vector **B** with respect to the axis [100]. From the general orientation, which shows 16 resonance lines, one can discover more symmetric situations and the simplest is $\mathbf{B}\|[100]$.

Automatization of such a 4π-Zeeman NQR spectrometer is possible, working without any mechanical motion (Markworth, Weiden & Weiss, 1987).

Zeeman split NQR and crystal structure

The bond C—Cl *in aromatic systems*

Combinations of X-ray diffraction and NQR studies began by Jeffrey and coworkers in the late fifties in connection with the problem of the double-bond character of C—Cl [described by the asymmetry factor $\eta(^{35}\mathrm{Cl})$] and the overcrowded substitution in benzene derivatives. Combined crystal structure and ^{35}Cl NQR work on the overcrowded system 1,2,4,5-tetrachlorobenzene is reported (Dean, Pollak, Craven & Jeffrey, 1958; Rehn, 1963). There have been some problems due to the use of twinned crystals in both experiments. Agreement to within 1–2° between bond directions derived from diffraction and NQR data was found. The observed $\eta(^{35}\mathrm{Cl})$ is rather high, 0.125 (25). The crystal structure of 1,4-dihydroxy-2,3,5,6-tetrachlorobenzene in combination with ^{35}Cl single-crystal NQR was studied (Sakurai, 1962*a*; Rehn, 1963). Pentachlorophenol was also investigated in this way (Sakurai, 1962*b*; Rehn, 1963). Note that $\eta(^{35}\mathrm{Cl})$ is quite high for the five Cl atoms in pentachlorophenol and there is a rough correlation between the bond length C—Cl and $\eta(^{35}\mathrm{Cl})$ (hydrogen-bonded chlorine excluded). The structure and ^{35}Cl NQR of 2,5-dichloroaniline have also been reported (Sakurai, Sundaralingam & Jeffrey, 1963). The bond distances C—Cl of 174 pm correspond to the low $\eta(^{35}\mathrm{Cl})$ of 0.07. Bond directions and bond angles determined by diffraction and NQR, respectively, coincide within the limits of error. An extensive study of crystal structures and ^{35}Cl, ^{14}N NQR (on polycrystalline material) of dichloroanilines was recently reported (Dou, Weiden & Weiss, 1993). The hydrogen-bond scheme is common to all dichloroanilines. Tetrachloro-*p*-benzoquinone as a quinoidic system was studied by Zeeman split ^{35}Cl NQR and X-ray diffraction (Chu, Jeffrey & Sakurai, 1962). The high $\eta(^{35}\mathrm{Cl})$ value of 0.21 found corresponds to $d(\mathrm{C—Cl}) = 171$ pm.

In molecular solids, the combination of crystal structure determination and single-crystal NQR is an interesting method for the study of intermolecular interactions. Most promising is the situation of several solid states for one molecule (Weiss, 1993). Such an experiment was performed on 2,6-dichloroacetanilide, Phase I and phase II (Nagarajan, Paulus, Weiden & Weiss, 1986). From an ethanolic solution large single crystals of phase II ($P2_1/c$, $Z = 4$) grow by slow evaporation of the solvent at room temperature. From the melt, by Bridgeman's technique, crystals of phase I are grown ($P2_12_12_1$, $Z = 4$) and this phase is metastable at room temperature, probably stabilized over weeks by a small amount of impurity. The C_6 ring is planar (±1 pm) in both phases; Cl and N atoms are slightly out of the plane (± ≤ 10 pm). Comparing the bond distances C—Cl(1) for both phases shows no difference within the limits of error: $d[\mathrm{C—Cl(2,6)}]_{\mathrm{I,II}} = 173.1$ (4) pm. $\eta(^{35}\mathrm{Cl})$ is between 0.1031 (15) and 0.1307 (15) for the four situations. We believe that η is a soft bond parameter, whereas $eQ\Phi_{zz}h^{-1}$, $34.543 \leq eQ\Phi_{zz}h^{-1}$ (MHz) ≤ 35.304, is rather hard. The differences in $eQ\Phi_{zz}h^{-1}$ show lower values for phase I compared with phase II. This and the spread of $\eta(^{35}\mathrm{Cl})$ are due to intermolecular interactions. The packing in the lattice of phase II is reasonably higher than in phase I (volume contraction *ca* 4%).

Interesting information gained from the diffraction–NQR experiment is the mutual deformation of the outer electron shell of the atoms. Neutron diffraction measures the positions and motions of the nuclei, X-ray diffraction, the electron distribution and from *X–N* we should ideally

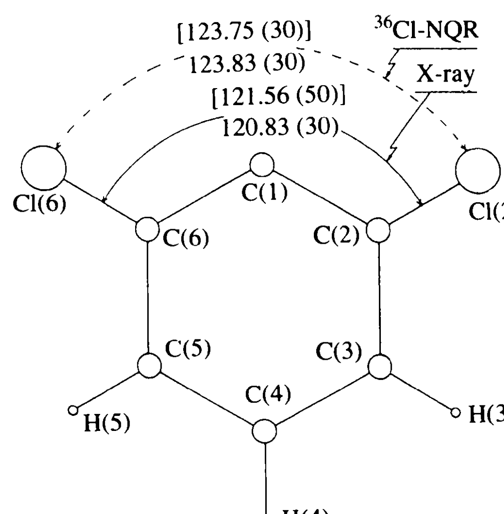


Fig. 4. Comparison of the angles C(6)—Cl(6), C(2)—Cl(2) (°) and $\Phi_{zz}(6)$, $\Phi_{zz}(2)$ for 2,6-$Cl_2C_6H_3NHCOCH_3$, phases I and II. Numbers in square brackets correspond to the low-temperature phase II.

obtain a precise electron distribution in the unit cell. The additivity in the scattering of the X-rays does not distinguish between the closed spherical shells and the nonspherical valence electrons. In NQR closed shells do not, in good approximation, contribute to the EFGT at the nuclear site [besides some inner shell polarization *via* the Sternheimer effect (Sternheimer, 1986)]. Therefore, the main principal axis Φ_{zz} of the EFGT is not necessarily parallel to the bond direction, even when $\eta \approx 0$, but may deviate more or less depending on the strength of the bond in which the atom considered is involved. In Fig. 4 the repulsion of the outer electrons of the Cl atoms in $2,6\text{-}Cl_2C_6H_3NHCOCH_3$ is shown. This repulsion is mainly due to the acetamide group between the Cl atoms. The angles $\{\Phi_{zz}$ [Cl(2)], Φ_{zz} [Cl(6)]$\}$ are wider than the corresponding bond angles. Figs. 5 and 6

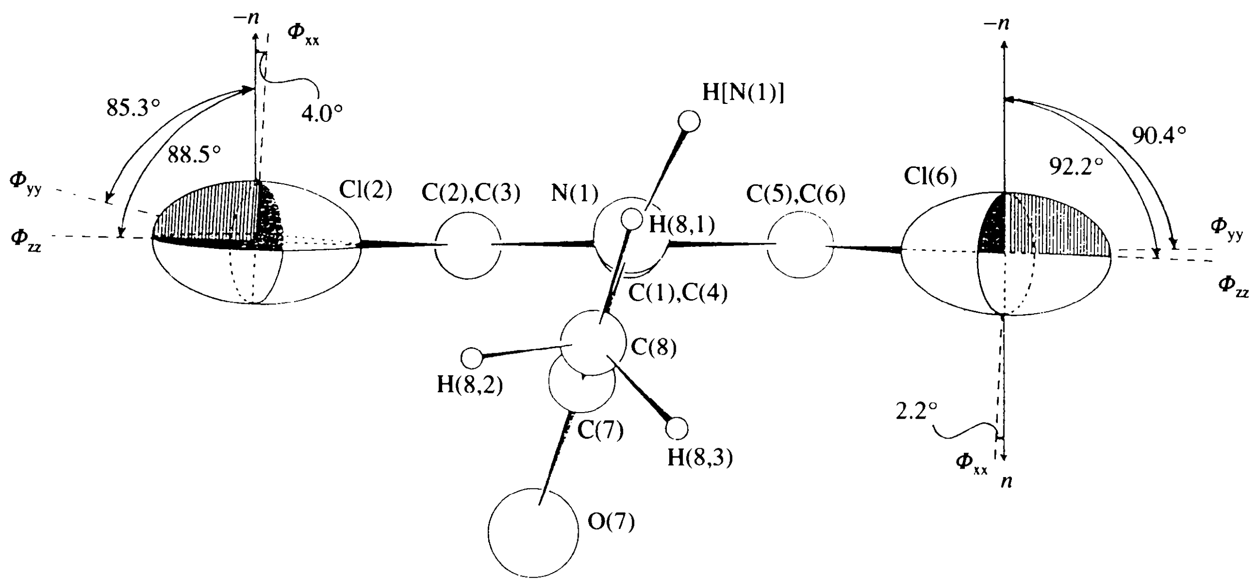


Fig. 5. Projection of the molecular structure and $\Phi_{ii}(j)$ (^{35}Cl) tensors along C(1)···C(4), low-temperature phase II of $2,6\text{-}Cl_2C_6H_3NHCOCH_3$. ^{35}Cl(2): $\nu = 35.304$ (2) MHz, $\eta = 0.1214$ (15), $eQ\Phi_{zz}h^{-1} = 70.435$ (4) MHz, $T = 295$ K. ^{35}Cl(6): $\nu = 35.184$ (2) MHz, $\eta = 0.1031$ (15), $eQ\Phi_{zz}h^{-1} = 70.244$ (4) MHz, $T = 295$ K.

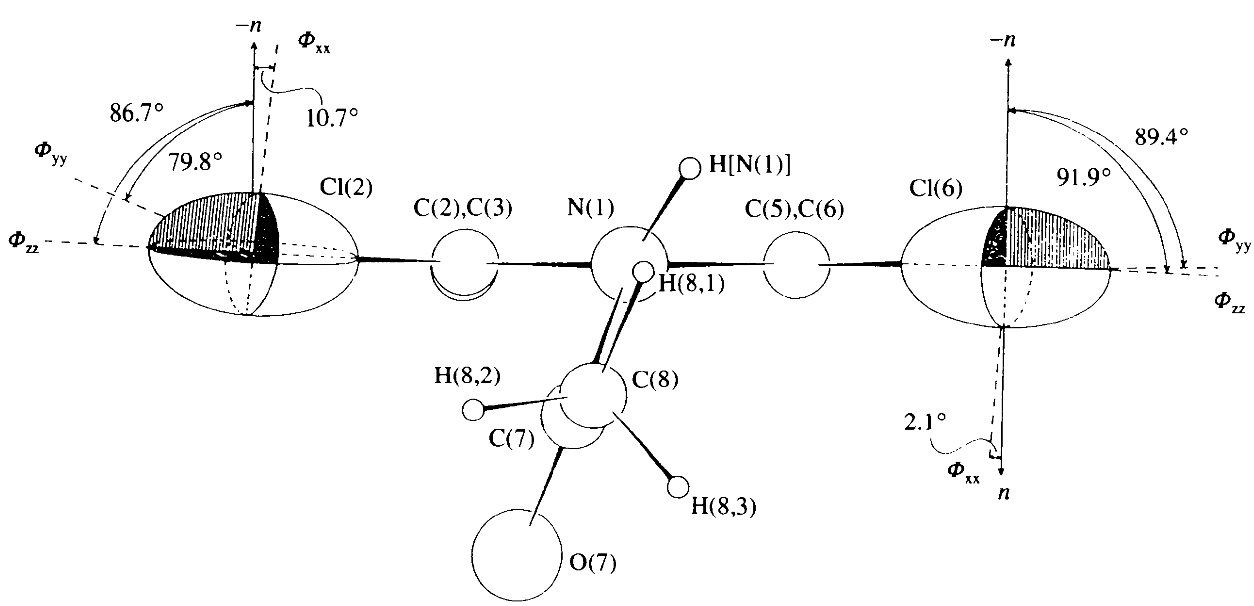


Fig. 6. Projection of the molecular structure and the $\Phi_{ii}(j)$ (^{35}Cl) tensors along C(1)···C(4), high-temperature phase I of $2,6\text{-}Cl_2C_6H_3NHCOCH_3$. ^{35}Cl(2): $\nu = 34.943$ (2) MHz, $\eta = 0.1293$ (15), $eQ\Phi_{zz}h^{-1} = 69.674$ (4) MHz, $T = 295$ K. ^{35}Cl(6): $\nu = 34.543$ (2) MHz, $\eta = 0.1307$ (15), $eQ\Phi_{zz}h^{-1} = 68.890$ (4) MHz, $T = 295$ K.

show the positions of the EFGT axes at the Cl sites with respect to the molecule of 2,6-dichloroacetanilide in phase II and phase I, respectively.

There is an intrinsic difficulty in the assignment of EFGT's to the crystallographic positions in benzene derivatives (or other 'planar' molecules) if an atom *A* is located in an 'opposite' position but the molecule has no center of symmetry. This problem also appears for almost octahedral ions. The EFGT is a quadratic function and one cannot distinguish between the 'positive' or 'negative' sign of the EFG. As an example, we shall discuss the molecular compound 2,3,6-trichlorophenyl acetate (Weiden, Paulus & Weiss, 1983). The EFGT's of Cl(3) and Cl(6) practically coincide. Therefore, assignment is made using the tendency to widen the angles between Φ_{zz} axes in comparison to the bond angles. Fig. 7 shows the two possible choices. It is worthwhile to mention that the axes Φ_{xx} of the three Cl–EFGT's are almost perpendicular to the C_6-plane and this observation is common to all benzene derivatives studied. Single-crystal ^{35}Cl NQR and crystal structure studies of 1,2-dichloro-3-nitrobenzene are reported by Sharma, Paulus, Weiden & Weiss (1986).

Extended single-crystal ^{35}Cl and ^{2}H NQR studies were performed on 1,2,3-trichlorobenzene. The crystal structure of the protonated and deuterated compound was studied by neutron diffraction (Hazell, Lehmann & Pawley, 1972; Groke, Heger, Schweiss & Weiss, 1994). ^{35}Cl, ^{1}H NMR and dielectric measurements prove an order–disorder mechanism (Tatsuzaki, 1958). Single-crystal ^{35}NQR at 140–250 K shows no significant changes in the ^{35}Cl EFGT's of the six crystallographically independent Cl atoms. Comparison of ^{35}Cl Zeeman split NQR and the structure gives a clear example of the repulsion of neighboring atoms' valence-electron distribution, as seen in Fig. 8. However, near 250 K the resonances fade out at slightly different temperatures for the two inequivalent molecules. From relaxation time measurements, activation energies for the fade out process of 30.6 and 35.6 kJ mol^{-1} are found (Sharma, Weiden & Weiss, 1986). Using crystals of 1,2,3-trichlorobenzene-d_3, the ^{2}H NMR spectra were studied at 193 and 295 K. Within 0.5°, Φ_{zz} is parallel to the bond direction C—Cl for the six inequivalent Cl atoms, $\eta(^{35}\mathrm{Cl})$ is between 0.06 and 0.07, $176 \leq eQ\Phi_{zz}h^{-1} \leq 178$ MHz. That the ^{2}H NMR fades out as the ^{35}Cl NQR does, a model of order–disorder in 1,2,3-$Cl_3C_6H_3$ was developed (Wigand, Weiden & Weiss, 1990). Refinement of the crystal structure by neutron diffraction on 1,2,3-$Cl_3C_6D_3$ at two temperatures gives, however, no indication for order–disorder.

Aliphatic C—Cl *bond*

Work on single-crystal NQR and X-ray diffraction on aliphatic and hydroaromatic compounds found much less interest in research. It is, however, for the theory of the C—Cl (C—Br) bond, also of importance because $\eta(^{35}\mathrm{Cl})$ will be much smaller than in aromatic systems

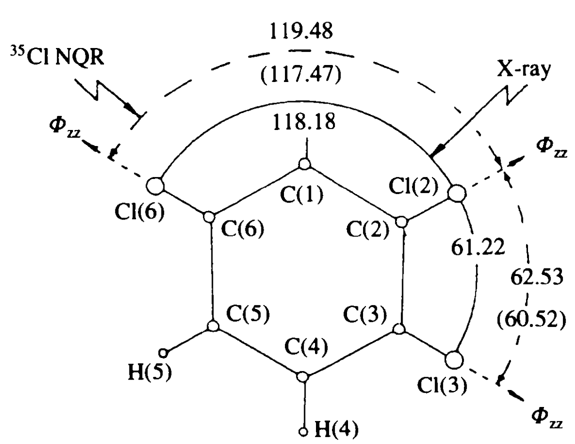


Fig. 7. 2,3,6-Trichlorophenyl acetate. Angles (°) between the C—Cl directions and the two possibilities for the angles between the Φ_{zz}'s. The angles in parentheses correspond to the second assignment, the less probable one.

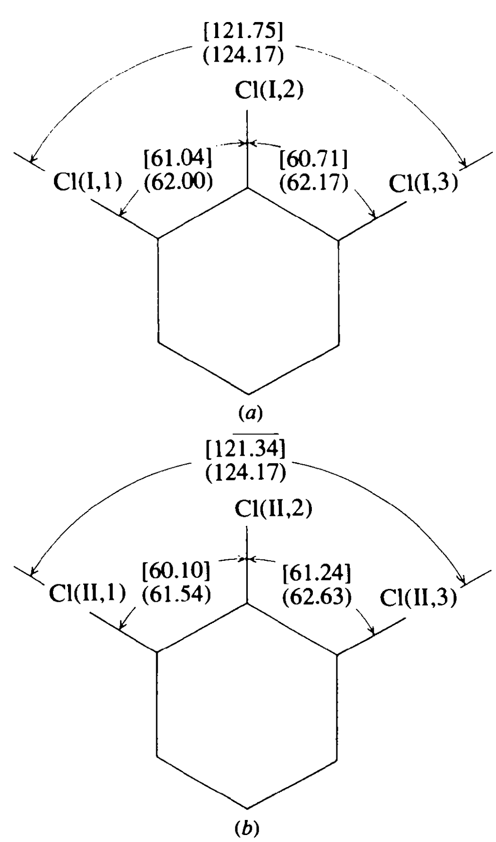
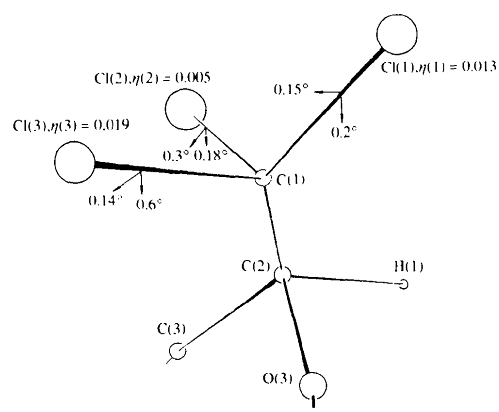


Fig. 8. Angles [Cl(*N*,1)—C(*N*,1), C(*N*,2)—Cl(*N*,2)], [Cl(*N*,2)—C(*N*,2), C(*N*,3)—Cl(*N*,3)], and [Cl(*N*,1)—C(*N*,1), C(*N*,3)—Cl(*N*,3)] (°), *N* = (I,II), determined by neutron diffraction [ ] and by single-crystal Zeeman split ^{35}Cl NQR ( ). (*a*) Molecule (I) of the unit cell, (*b*) molecule (II) of the unit cell.

and more sensitive to intermolecular interactions. Hashimoto, Paulus & Weiss (1980) have studied the structure and phase transition of trichloroethylidene trichlorolactic ester (chloralide) and its single-crystal ^{35}Cl NQR spectrum (Hashimoto, Nagarajan, Weiden & Weiss, 1983). Also α-2,4,6-tris(trichloromethyl)-1,3,5-trioxane (α-parachloral) was studied (Hashimoto, Weiden & Weiss, 1985), the structure of which was known (Hay & Mackay, 1980). In both compounds there are two crystallographically independent trichloromethyl groups. As one expects, the asymmetry parameter is very low, showing a rotational symmetric distribution in the electron density around the Cl atom; $0.005 \le \eta(^{35}\mathrm{Cl}) \le 0.053$ for chloralide, $0.002 \le \eta(^{35}\mathrm{Cl}) \le 0.046$ for α-parachloral. In Fig. 9 the orientation of the EFGT's for one of the CCl_3 groups in chloralide is shown.

For the connection between bond length and Φ_{zz} equation (1) is valid. This relation is shown in Fig. 10 for the chloralide. It is unfortunate that the measurements in the literature have not been critically evaluated in this respect and, even more so, many single-crystal NQR measurements have no counterpart in X-ray diffraction; in most cases, no problem would arise in crystal structure determination because crystal growth is solved for the NQR studies as there is a convenient temperature for the diffraction experiment.



1) Plane [C(2)—C(1)—Cl(1)]:
($\Phi_{zz}^{(1)}$, plane): δ = 0.2° in plane; 0.15° $\perp$ plane.
($\Phi_{xx}^{(1)}$, plane): δ = 3° ($\Phi_{xx}^{(1)}$ in plane).
($\Phi_{yy}^{(1)}$, plane): δ = 87° ($\Phi_{yy}^{(1)}$ $\perp$ plane).

2) Plane [C(2)—C(1)—Cl(2)]:
($\Phi_{zz}^{(2)}$, plane): δ = 0.18° in plane; 0.3° $\perp$ plane.
($\Phi_{xx}^{(2)}$, plane): δ = 56°; no correlation.
($\Phi_{yy}^{(2)}$, plane): δ = 34°; no correlation.

3) Plane [C(2)—C(1)—Cl(3)]:
($\Phi_{zz}^{(3)}$, plane): δ = 0.6° in plane; 0.14° $\perp$ plane.
($\Phi_{xx}^{(3)}$, plane): δ = 15° towards O$^{(3)}$.
($\Phi_{yy}^{(3)}$, plane): δ = 75°.
Remark: H$^{(1)}$ almost in plane (C$^{(2)}$—C$^{(2)}$—Cl$^{(3)}$).

Fig. 9. Chloralide, $Cl_3CCHOCOCHOCCl_3$, 294 K, phase II. EFGT orientations for one CCl_3 group C(1)Cl(1,2,3).

Table 1. *Comparison of bond angles (°), derived from the X-ray crystal structure determinations and angles formed by the main principal axes of the electric-field gradient tensors*

$KH(Cl_3CCOO)_2$

∡[Cl(1)—C(1)—Cl(2)]	108.9 (2)	∡[Φ_{zz}(1), Φ_{zz}(2)]	109.4 (2)
∡[Cl(2)—C(1)—Cl(3)]	108.7 (2)	∡[Φ_{zz}(2), Φ_{zz}(3)]	108.7 (2)
∡[Cl(1)—C(1)—Cl(3)]	109.7 (2)	∡[Φ_{zz}(1), Φ_{zz}(3)]	110.4 (2)

k Cl(k)	∡[C(2)—C(1)—Cl(k)]	∡[C(2)—C(1), Φ_{zz}(k)]	∡[C(1)—Cl(k), Φ_{zz}(k)]
1 Cl(1)	111.3 (3)	111.4 (4)	0.9 (4)
2 Cl(2)	111.3 (3)	111.2 (4)	0.4 (4)
3 Cl(3)	106.8 (3)	105.7 (4)	1.5 (4)

$RbH(Cl_3CCOO)_2$

∡[Cl(1)—C(1)—Cl(2)]	108.6 (2)	∡[Φ_{zz}(1), Φ_{zz}(2)]	108.2 (2)
∡[Cl(2)—C(1)—Cl(3)]	109.0 (2)	∡[Φ_{zz}(2), Φ_{zz}(3)]	108.8 (2)
∡[Cl(1)—C(1)—Cl(3)]	108.8 (2)	∡[Φ_{zz}(1), Φ_{zz}(3)]	119.5 (2)

k Cl(k)	∡[C(2)—C(1)—Cl(k)]	∡[C(2)—C(1), Φ_{zz}(k)]	∡[C(1)—Cl(k), Φ_{zz}(k)]
1 Cl(1)	109.3 (2)	109.3 (3)	1.0 (3)
2 Cl(2)	113.2 (2)	113.4 (3)	1.4 (3)
3 Cl(3)	107.4 (2)	106.6 (3)	2.0 (3)

A combination of crystal structure determination and single-crystal NQR concerning the CCl_3 group is also reported for the trichloroacetates $M\mathrm{H(Cl_3CCOO)_2}$, M = K, Rb (Markworth, Paulus, Weiden & Weiss, 1991). Again the EFGT's are almost rotationally symmetric: $0.017 \le \eta(^{35}\mathrm{Cl}) \le 0.020$ kHz for the Cl atoms in the potassium compound and $0.003 \le \eta\text{-}(^{35}\mathrm{Cl}) \le 0.050$ kHz for Cl in the rubidium salt. The two compounds are not isomorphous. In Table 1 the Cl—C—Cl angles of the CCl_3 group are compared with the corresponding angles Φ_{zz} includes.

The ^{35}Cl NQR of two small molecules CH_2Cl_2 (CD_2Cl_2) and $CDCl_3$ have been studied by Zeeman spectroscopy (Litzistorf, Sengupta & Lucken, 1981). The structures are known (CH_2Cl_2: Kawaguchi, Tanaka, Takeuchi & Watanabé, 1973; $CDCl_3$: Fourme & Renaud, 1966). Also microwave data are available for CH_2Cl_2 (Flygare & Gwinn, 1962) and $CDCl_3$ (Wolfe, 1956). The structure of CH_2Cl_2 contains two molecules in the asymmetric unit and four η-values have been found, $0.055 \le \eta(^{35}\mathrm{Cl}) \le 0.082$, in the range expected for an

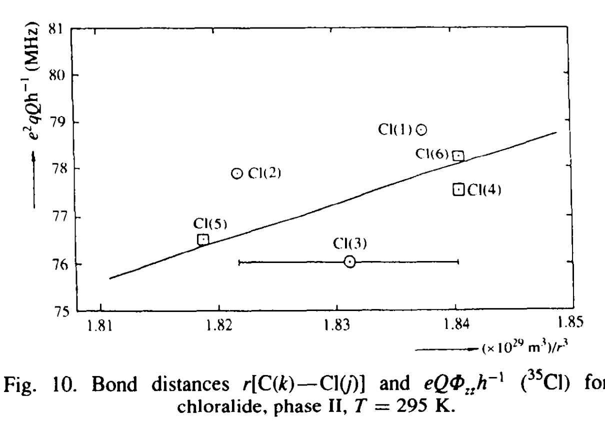


Fig. 10. Bond distances r[C(k)—Cl(j)] and $eQ\Phi_{zz}h^{-1}$ (^{35}Cl) for chloralide, phase II, T = 295 K.

aliphatic C—Cl bond. The Cl—C—Cl angles, 110.2 and 110.4° for CH_2Cl_2 are in good agreement with the diffraction [112.0 (10)] and microwave (111.78°) results. For CD_2Cl_2 the authors report EFGT angles of 111.8 and 113.3°, a difference which deserves some attention. Also the Cl—C—Cl angle in $CDCl_3$ found by NQR (111.0°) agrees well with the microwave measurements (110.92°).

We shall shortly discuss a few single-crystal ^{35}Cl NQR investigations of X^{IV}—Cl bonds for which there are no complete crystal structure determinations available (some qualitative data can be found). Sengupta, Litzistorf & Lucken (1981) studied the Ge—Cl bond in $GeCl_4$ by ^{35}Cl single-crystal NQR. Four resonances are found, the ^{35}Cl η-values lying between 0.030 and 0.086; the Cl—Ge—Cl angles are found between 106.5 and 111.3°. Orthorhombic symmetry for the space group is concluded from NQR, *mmm* or D_{2h}. Mano and co-workers (Mano, 1977, 1978; Mano, Giezendanner, Sengupta & Lucken, 1980; Mano, Sengupta, Giezendanner & Lucken, 1983) studied several cyclic chlorocarbons with unknown molecular and crystal structure. For perchloro-1,2-dimethylenecyclobutane, Mano (1977) found four ^{35}Cl NQR lines corresponding to four chemically and crystallographically different Cl atoms. From X-ray diffraction it was proposed that the crystal is monoclinic, *Cc* or *C*2/*c*, $Z = 4$. NQR proves *C*2/*c* symmetry with $\eta(^{35}Cl) = 0.01$–0.02 for the Cl atoms at the cyclobutane ring and 0.147–0.150 for the olefinic Cl atoms, which show the lower Φ_{zz} values.

Perchloro-5-methylcyclopentadiene reveals from the Zeeman ^{35}Cl NQR study (Mano, 1978) that the crystal must be orthorhombic, *mm*2 or *mmm*. Five resonances are found for the eight Cl atoms of the molecule. Already, the intensities of the lines of polycrystalline material (Wulfsberg, West & Rao, 1975; Wulfsberg, 1975) show that the molecule has a mirror plane. Again, low η-values are found for the Cl atoms of the CCl_3 group at C(2) of the ring and the Cl atom at C(2): $0.009 \leq \eta(^{35}Cl) \leq 0.024$. The Cl atoms of the diene group have asymmetry parameters of the EFGT's between 0.115 and 0.145.

The ^{35}Cl NQR spectrum at 294 K of perchloro-3-cyclopentenone (Mano, Giezendanner, Sengupta & Lucken, 1980) is a triplet. The authors find C_2 symmetry for the molecule in the crystal, asymmetry parameters between 0.027 and 0.035 for the methylene chlorines, and 0.144 for the diene chlorines. From the direction cosines it is shown that the five-membered ring is almost planar.

An interesting compound is tetrachlorocyclopentene-1,3-dione (Mano, Sengupta, Giezendanner & Lucken, 1983). The ^{35}Cl NQR spectrum is a doublet at 77 K and at room temperature. From the habitus of the crystals and from microscopic inspection, high symmetry of the crystal is concluded and confirmed by X-ray powder diffraction: space group *Fd*3 or *Fm*3, $a = 2191.0$ pm, $Z = 48$. The Zeeman spectrum is quite complicated, each line leading to 12 differently oriented EFGT's in the magnetic field. η-values of 0.058 and 0.216 have been found for the Cl atoms bonded to one C atom and at the double bond, respectively.

Single-crystal ^{35}Cl NQR and structure studies were performed on 2,3,4,4-tetrachloro-1-oxo-1,2-dihydronaphthalene, called β-TKN and 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthalene [α-TKN; Brummer, Weiden & Weiss (1990)]. The compounds have found interest over the years because of their photochromic properties. The crystal structure of β-TKN has been reported by Veenvliet & Michelsen (1971). α-TKN is described in the polar space group $P2_1$, $Z = 2$ (Zweegers, Varma & de Graaff, 1979). This is in contrast to the ^{35}Cl NQR which shows a triplet spectrum with the intensity ratio 2:1:1. Therefore, the structure determination was repeated and it is now described in the space group $P2_1/m$, with very minor changes of the atomic coordinates. This is an example of the value of single-crystal NQR in connection with *X*(*N*) structure work. The results gained from the EFGT determination are very satisfactory. Quite small deviations of Φ_{zz} from the bond directions C—Cl are observed for Cl(2,3) in β-TKN and for Cl(3,4) in α-TKN. Also, $\eta(^{35}Cl)$ differentiate well between the methylene group Cl atoms from the diene Cl atoms, in full agreement with the crystal structures. An open question is, however, the observed optical nonlinearity of α-TKN with respect to the crystal structure. An interesting study of bond angles by ^{35}Cl Zeeman NQR studies on δ-hexachlorocyclohexane was reported by Morino, Toyama & Itoh (1963), the structure of which was determined by van Bommel, Strijek & Bijvoet (1950).

Nitro compounds

Aliphatic and aromatic nitro compounds have found wide interest in X-ray crystallography, as well as in ^{14}N NQR and ^{35}Cl NQR (in chloronitrobenzenes) and combined investigations are available. Such a point of interest is the polymorphism of nitrochlorobenzenes and the polymorphism may originate in two processes. The nitro group rotates easily around the C—N bond and several potential minima for the rotation angle may be possible. Furthermore, strong group dipole moments may promote differing van der Waals packings in the solid state. For one compound several solid states are likely. As examples: two phases of 1-chloro-3-nitrobenzene have been described, one with m.p = 317.6 K and $d_x = 1.582$ g cm^{-3} [phase II (Hasselblatt, 1913; Steinmetz, 1915)] and the other with m.p. = 296.7–297 K (phase I), metastable and transforming easily to phase II (Laubenheimer, 1876; Hasselblatt, 1913). 1-Chloro-2,4-dinitrobenzene still has a more complicated phase diagram. The stable phase, numbered I here (Jungfleisch, 1868), shows no phase transition from 77 K up to the melting point of 323 K, as found from ^{35}Cl NQR

(Sharma, Weiden & Weiss, 1989). A second phase melting at 316 K and crystallizing bisphenoidal is described (Jungfleisch, 1868). A third phase was observed with the melting point 300 K (Müller, 1914), and finally the existence of four more phases with melting points at 295, 301, 308 and 313 K was reported by Brandstätter (1946, 1947).

The crystal structure of 1-Cl-3-$NO_2C_6H_4$ is determined (Gopalakrishna & Ramamurty, 1962; Gopalakrishna, 1965); it was refined by Sharma, Paulus, Weiden & Weiss (1985), including ^{35}Cl NQR. There is no unusual feature about the C_6 ring distances introduced by the substitution $137.3 \le d(\mathrm{C—C}) \le 138.3$ pm, but a small modulation of the ring angles. The NO_2 group is lying in the ring plane. The deviation of the direction of Φ_{zz} from the bond direction C(1)—Cl is 0.45°. The EFGT is strongly related to the C_6 plane, with Φ_{yy} and Φ_{zz} deviating from the plane by 0.6 and 1°, respectively. These small deviations from the plane may be caused by intermolecular interactions. Fig. 11 explains the orientation of the EFGT(^{35}Cl) with respect to the molecule and the next intermolecular neighbors.

Many organic nitro compounds have been studied by ^{14}N NQR. However, the question of the orientation of the EFGT(^{14}N) and the Φ_{zz} axis with respect to the NO_2 plane was for a long time controversial. Hiyama & Brown (1981) solved the problem by performing a ^{14}N–^{1}H single-crystal double resonance experiment on 1-methyl-4-nitrobenzene; the crystal structure of the compound was known (Barve & Pant, 1971). Hiyama and Brown have shown that the EFGT-axis Φ_{zz} is along the C—N bond with a deviation of <1°. Φ_{yy} is perpendicular to the normal of the C—NO_2 plane and the deviation is 6.2 (4)°; finally, Φ_{xx} is in this plane, deviating by not more than 2.6°.

The structures of overcrowded chloro-nitrobenzenes 1,2,4,5-tetrachloro-3,6-dinitrobenzene and 1,3,5-trichloro-2,4-dinitrobenzene are available (Wigand, Walz, Weiden & Weiss, 1987). In a molecule of 1,2,4,5-tetrachloro-3,6-dinitrobenzene (the compound crystallizes in the space group $C2/m$, $Z = 2$), the atoms Cl(1,2) are 4 pm above the C_6-plane, Cl(4,5) are 4 pm below the plane. Both NO_2 groups NO_2(3,6) are rotated, with the NO_2-plane 90° away from the C_6 plane. The

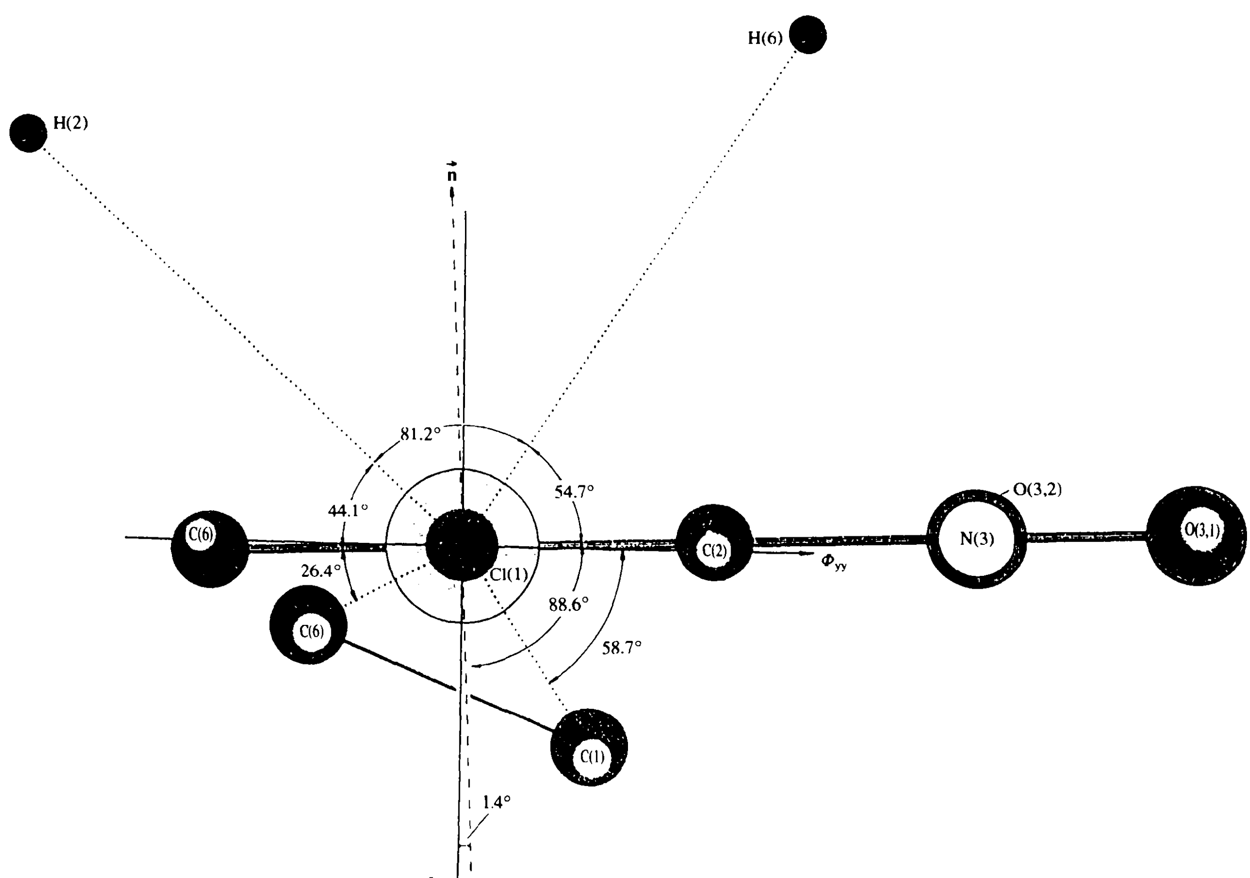
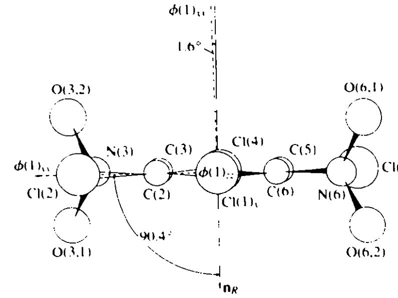


Fig. 11. Projection of the molecular structure of $C_4H_4Cl(1)(NO_2)(3)$ along the bond C(1)—Cl(1) onto the paper plane. The next four van der Waals intermolecular neighbors are drawn together with the intersection (dotted lines) of the four planes containing the bond Cl(1)—C(1) and one of these four atoms, respectively, with the paper plane. The rotation of Φ_{xx} and Φ_{yy} out of the benzene plane is shown.

Table 2. *Angles (°) between the principal axes of the* ^{35}Cl *and* ^{14}N *EFGT's and structure elements of the molecule* 1,2,4,5-Cl_4-3,6-$(NO_2)_2C_6$



Projection of the molecule 1,2,4,5-Cl_4-3,6-$(NO_2)_2C_6$ along the bond Cl(1)—C(1). The principal axes of the ^{35}Cl(1) EFGT are plotted like vectors in order to show a right-handed system corresponding to the direction cosines. $\mathbf{n}_R$ is the normal to the ring plane.

Due to the symmetry of the crystal and the molecules in the solid, respectively, the angles are the same for Φ_{zz}[Cl(i)], C(i)—Cl(i), i = 1,2,4,5, and Φ_{zz}[N(i)], C(i)—N(i), i = 3,6, T = 295 K.

Cl(1)	$\measuredangle[\Phi_{zz}$, C(1)—Cl(1)]	0.5
	$\measuredangle(\Phi_{xx}, \mathbf{n}_R)$	−1.6
	$\measuredangle(\Phi_{yy}, \mathbf{n}_R)$	90.4
	$\measuredangle(\Phi_{zz}, \mathbf{n}_R)$	91.5
	$\measuredangle$[C(1)—Cl(1), $\mathbf{n}_R$]	91.2
N(6)	$\measuredangle[\Phi_{zz}$, C(6)—N(6)]	3.3
	$\measuredangle(\Phi_{xx}, \mathbf{n}_R)$	90.0
	$\measuredangle(\Phi_{yy}, \mathbf{n}_R)$	2.8
	$\measuredangle(\Phi_{zz}, \mathbf{n}_R)$	87.2
	$\measuredangle$[C(6)—N(6), $\mathbf{n}_R$]	90.5

^{35}Cl NQR spectrum is a singlet from 77 up to 490 K, as is the ^{14}N spectrum. In Table 2 the orientation of the EFGT's of ^{35}Cl and of ^{14}N, respectively, are listed (Wigand, Weiden & Weiss, 1989). The deviations of the tensor axes from the 'ideal' orientation are very small.

1,3,5-Trichloro-2,4-dinitrobenzene is less symmetric, having a triplet ^{35}Cl NQR spectrum from 77 K up to the melting point. There is more space in the periphery of the molecule; the Cl atoms deviate by not more than 1 pm from the C_6 plane and the NO_2 groups are rotated by 80 and 87.6° out of the C_6 plane. Zeeman split NQR shows the orientation of the EFGT at the ^{35}Cl and ^{14}N sites and the results are listed in Table 3.

There is an interesting correlation between the ^{14}N EFGT asymmetry parameter $\eta(^{14}N)$ of the nitro group and the twist angle α [the angle between the normal to the benzene ring $\mathbf{n}_R$, and the normal to the NO_2 group $\mathbf{n}$, as pointed out by Marino & Connors (1983)]. The correlation is proved by Zeeman split ^{14}N NQR. In Fig. 12 the results are shown. There also seems to be a correlation between the twist angle α of the NO_2 group and the angle ϵ between Φ_{xx} and the C_6 plane in nitrobenzenes (Weiss & Wigand, 1990). This is shown in Fig. 13. More structural and single-crystal ^{14}N studies are necessary to prove this relation and it is open to interesting theoretical work.

Table 3. *Angles (°) between the principal axes* Φ_{ii} *of the* ^{35}Cl *and* ^{14}N *EFGT's and structure elements of the molecule* 1,3,5-Cl_3-2,4-$(NO_2)_2C_6H$ *in the solid state*

$\mathbf{n}_R$ = normal to the ring plane; $\mathbf{n}$ = normal to the respective NO_2 plane; T = 295 K.

Cl(1)	$\measuredangle[\Phi_{zz}$, C(1)—Cl(1)]	0.5
	$\measuredangle(\Phi_{xx}, \mathbf{n}_R)$	3.2
	$\measuredangle(\Phi_{yy}, \mathbf{n}_R)$	93.2
	$\measuredangle(\Phi_{zz}, \mathbf{n}_R)$	90.1
	$\measuredangle$[C(1)—Cl(1), $\mathbf{n}_R$]	90.0
Cl(3)	$\measuredangle[\Phi_{zz}$, C(3)—Cl(3)]	0.1
	$\measuredangle(\Phi_{xx}, \mathbf{n}_R)$	−4.6
	$\measuredangle(\Phi_{yy}, \mathbf{n}_R)$	85.4
	$\measuredangle(\Phi_{zz}, \mathbf{n}_R)$	89.8
	$\measuredangle$[C(3)—Cl(3), $\mathbf{n}_R$]	89.7
Cl(5)	$\measuredangle[\Phi_{zz}$, C(5)—Cl(5)]	0.4
	$\measuredangle(\Phi_{xx}, \mathbf{n}_R)$	−1.5
	$\measuredangle(\Phi_{yy}, \mathbf{n}_R)$	91.2
	$\measuredangle(\Phi_{zz}, \mathbf{n}_R)$	89.5
	$\measuredangle$[C(5)—Cl(5), $\mathbf{n}_R$]	89.8
N(2)	$\measuredangle[\Phi_{zz}$, C(2)—N(2)]	1.0
	$\measuredangle(\Phi_{xx}, \mathbf{n})$	−28.3
	$\measuredangle(\Phi_{yy}, \mathbf{n})$	−61.7
	$\measuredangle(\Phi_{zz}, \mathbf{n})$	89.8
	$\measuredangle(\Phi_{xx}, \mathbf{n}_R)$	−72.0
	$\measuredangle(\Phi_{yy}, \mathbf{n}_R)$	18.0
	$\measuredangle(\Phi_{zz}, \mathbf{n}_R)$	89.3
	$\measuredangle$[C(2)—N(2), $\mathbf{n}_R$]	90.0
N(4)	$\measuredangle[\Phi_{zz}$, C(4)—N(4)]	1.2
	$\measuredangle(\Phi_{xx}, \mathbf{n})$	2.6
	$\measuredangle(\Phi_{yy}, \mathbf{n})$	88.1
	$\measuredangle(\Phi_{zz}, \mathbf{n})$	88.2
	$\measuredangle(\Phi_{xx}, \mathbf{n}_R)$	89.5
	$\measuredangle(\Phi_{yy}, \mathbf{n}_R)$	1.2
	$\measuredangle(\Phi_{zz}, \mathbf{n}_R)$	88.9
	$\measuredangle$[C(4)—N(4), $\mathbf{n}_R$]	89.8

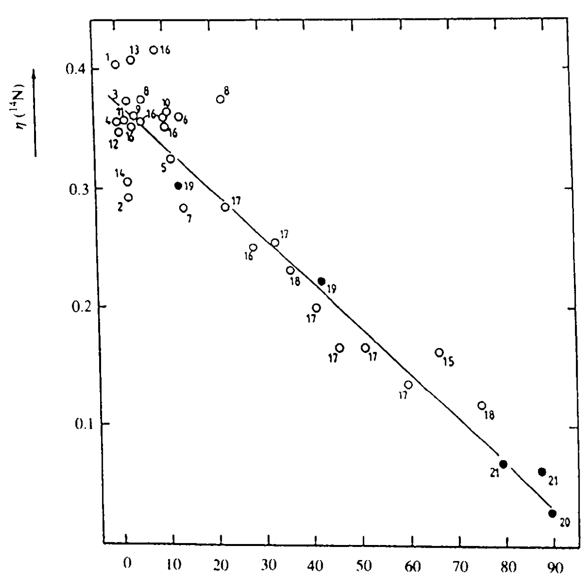


Fig. 12. Dependence of $\eta(^{14}N)$ of nitrogen on NO_2 groups attached to a substituted benzene ring from the twist angle α. α is defined as the angle between the normal to the benzene ring, $\mathbf{n}_R$, and the normal to the plane of the NO_2 group, $\mathbf{n}$, $0 \leq \alpha \leq 90°$.

Single-crystal NQR in complex chemistry

The combination of single-crystal structure and NQR studies on organic compounds suffers from a principal deficiency in the periodic system: There are no isotopes with nonzero Q available for carbon, silicon, phosphorus and the natural concentration of ^{17}O and of ^{33}S is so low that in the single-crystal NQR experiment the study of the EFGT's at these nuclei is quite laborious. Thus, in a wide field of structural chemistry we miss the chance to find total spin systems, *i.e.* the chance to measure at each occupied site in the crystal the EFGT. The situation is somewhat different with inorganic compounds where total spin systems can be studied. As an example we consider $^{23}Na^{27}Al^{35}Cl_4$ (Scheinert & Weiss, 1976). In such complex salts, an interesting aspect is the bond character (bond ionicity) and NQR is a valuable method of estimating this along the MO line model developed by Townes & Dailey (1949) and Townes & Schawlow (1955). In $NaAlCl_4$ d(Al—Cl) distances are in the range $212.1 \le d \le 214.4$ pm and for ^{35}Cl $21.646\ (3) \le eQ\Phi_{zz}h^{-1} \le 23.033\ (30)$ MHz and $0.197\ (10) \le \eta(^{35}Cl) \le 0.315$. It turns out that the directions Φ_{zz} and d(Al—Cl) are parallel to within 1° for three Al—Cl bonds, and within 5° for the fourth. The NQR parameters of ^{27}Al can be correlated with the symmetry of the $AlCl_4$ tetrahedron. A quantitative discussion of structure and electric-field gradients needs an extended cluster calculation due to the mixture of an ionic lattice with a partially covalent molecular ion.

Yamada and coworkers (Yamada & Weiss, 1983; Yamada, Weiden & Weiss, 1983) have studied the isomorphous complexes $A_2InX_5H.H_2O$ (A = K, NH_4, Rb, Cs; X = Cl, Br), for which the crystal structure is known (Klug, Kummer & Alexander, 1948; Wignacourt, Loriaux-Rubbens, Barbier, Mairesse & Wallart, 1982). From single-crystal NQR (^{81}Br, ^2H) on $(ND_4)_2InBr_5.D_2O$, it is found that the main principal axis of the EFGT's of the four inequivalent Br atoms is almost

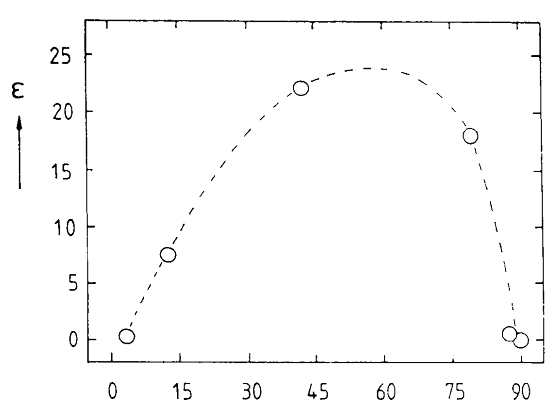


Fig. 13. Dependence of the angle ϵ (angle Φ_{xx}, C_6-plane) on the twist angle α.

parallel to the bond direction In—Br; D_2O is flipping at room temperature and the ND_4 ion is nearly freely rotating.

The salts $MX_2(Hal)_7$ (M = Li, Na, K, Rb, Cs; X = Al, Ga; Hal = Cl, Br) are also complete spin systems. The bromides have been extensively investigated with Br NQR by Yamada (1977). The crystal structures of KAl_2Br_7 and $(NH_4)Al_2Br_7$ are known (Rytter, Rytter, Oye & Krogh-Moe, 1973, 1975). Terminal and bridging bromines are distinguished by Br Zeeman NQR and the dependence of the asymmetry parameter $\eta(^{81}Br)$ of the bridging atom on the angle Al—Br—Al is discussed. From the Hiroshima group, a number of NQR Zeeman spectroscopy studies have been published and for some of the compounds treated the crystal structures are known, *e.g.* $AlBr_3$ (Okuda, Terao, Ege & Negita, 1970); $AlBr_3.C_6H_6$ (Okuda, Furukawa & Negita, 1972); $AlBr_3.SbBr_3$, $AlBr_3.BiBr_3$, $AlI_3.SbI_3$ (Okuda, Yamada, Ishihara & Negita, 1977); various $AlBr_3$ complexes (Okuda, Ishihara, Yamada & Negita, 1978; Okuda, Ohta, Ishihara, Yamada & Negita, 1980; Okuda, Yamada, Ishihara & Ichiba, 1987); $PBr_3.BBr_3$ (Terao, Fukura, Okuda & Negita, 1983); Bi^{III} halides (Furukawa, 1973). For the crystal structure of $BiCl_3$, see Nyburg, Ozin & Szymanski (1971, 1972); for the structure of BiI_3 see Trotter & Zobel (1966). The Zeeman spectroscopy removes an ambiguity about the center of symmetry in the space group of $BiCl_3$. Many other M^{II} and M^{III} halides and halide complexes have been studied by this group *via* Zeeman single-crystal NQR, *e.g.* Zn-, Cd- and Hg-halide molecular complexes (Hiura, 1982).

The single-crystal NQR is also very helpful in the study of Cu^I compounds. $^{63,65}Cu$ are easy-to-handle isotopes, both with $I = 3/2$ and since a pure tetrahedral coordination of copper leads to a vanishing EFGT, deviation from the tetrahedral symmetry can be studied conveniently by Cu NQR. Zeeman spectroscopy of Cu^I halide complexes with triphenylphosphate is reported by Negita, Hiura, Yamada & Okuda (1980) and of bis(triphenylphosphine)copper(I) by Okuda, Hiura & Negita (1981). Several single-crystal studies by diffraction combined with NQR have been carried through by Lucken and coworkers in recent times. Binuclear Cu^I polyhalide anions have been studied by Ramaprabhu & Lucken (1991), as well as bis(1-alkylimidazolidine-2-thione)copper(I) iodides and related compounds (Ramaprabhu, Lucken & Bernardinelli, 1993). Cu NQR is also reported on polycrystalline material, including crystal structure determinations for Cu^I halides with phosphorus containing ligands (Ramaprabhu, Amstutz, Lucken & Bernardinelli, 1993) and for Cu^I complexes of 2,6-dimethylpyrimidin-2-thione (Ramaprabhu, Lucken & Bernardinelli, 1994). For a summary of this work, see Lucken (1994).

A more easily interpretable system is bis(tetramethylammonium)pentachloroethylstannate. In a study of polycrystalline samples of the salts A_2 $[(C_2H_5SnCl_5]$, $A^+ = [(CH_3)_4N]^+$, $[C_5H_5NH]^+$, $[CH_3NH_3]^+$ and $[4\text{-}CH_3C_5H_4NH]^+$, the tetramethylammonium compound was found to have a phase transition at 180 (1) K. The crystal structures of the compounds were determined at room temperature; they are of a distorted K_2PtCl_6-type (Storck & Weiss, 1989). From phase I of the methylammonium compound, large single crystals were grown and ^{35}Cl Zeeman spectroscopy performed (Storck, Weiden & Weiss, 1990). In Fig. 14 the structure of the tetramethylammonium compound is shown in projection and in Fig. 15 the relation between the EFGT axes and the structure of the $SnCl_5$ unit.

From the single-crystal study and from the ^{35}Cl NQR measurements on highly symmetric compounds, *e.g.* of the K_2PtCl_6-type, one can conclude that the asymmetry parameter $\eta(^{35}Cl)$ in Sn—Cl bonds is small. This is seen for $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$ from Table 4 where bond distances, bond angles *etc.* are compared. This is the basis of a simple correlation between ^{35}Cl NQR frequencies and bond distances d(Sn—Cl) (Storck & Weiss, 1990). In Fig. 16 a plot of $\nu(^{35}Cl)$ *versus* $1/d^3$ (Sn—Cl) is shown and the usefulness of such a correlation.

Deuteron Zeeman NQR–NMR and crystal structure

One of the most intensively studied quantities in NQR is the EFGT at the deuteron site in molecules. It is the bond of the deuteron, *e.g.* in hydrogen-bonded systems for which the EFGT may give valuable additional information to the crystal structure determination and it is the information about the dynamics of molecules, such as D_2O in crystals, and of groups, such as CD_3—, ND_3— and ND_2 in molecules. Experimentally, because of the low nuclear electric quadrupole moment of the

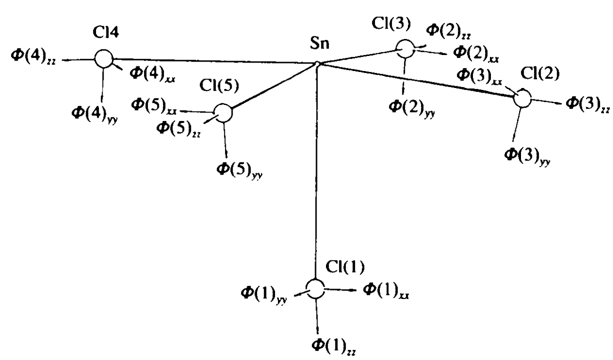


Fig. 15. Sketch of the orientation of the EFGT's (^{35}Cl) in the pentachloroethylstannate(II) ion. Representation of the orientation of the tensor axes $\Phi_{zz}^{(i)}$, $\Phi_{yy}^{(i)}$, $\Phi_{xx}^{(i)}$, $i = 1$–5, with respect to the crystal geometry of the bonds Sn—Cl(k) of the $[(C_2H_5)SnCl_5]^{2-}$ anion that follows from the assignment of the $\nu_i(^{35}Cl)$ to certain Cl(k) atoms given in Table 5. Note that the numbers i of $\nu_i(^{35}Cl)$ and $\Phi_{ij}^{(i)}$ are not identical with the numbers k of Cl(k). Cl(k) are numbered according to the crystal structure [4], while the numbers of $\Phi_{ij}^{(i)}$ follow the sequence of the ^{35}Cl NQR frequencies $\nu(^{35}Cl)$. $\nu_1(^{35}Cl)$ is the highest NQR frequency and $\nu_5(^{35}Cl)$ the lowest.

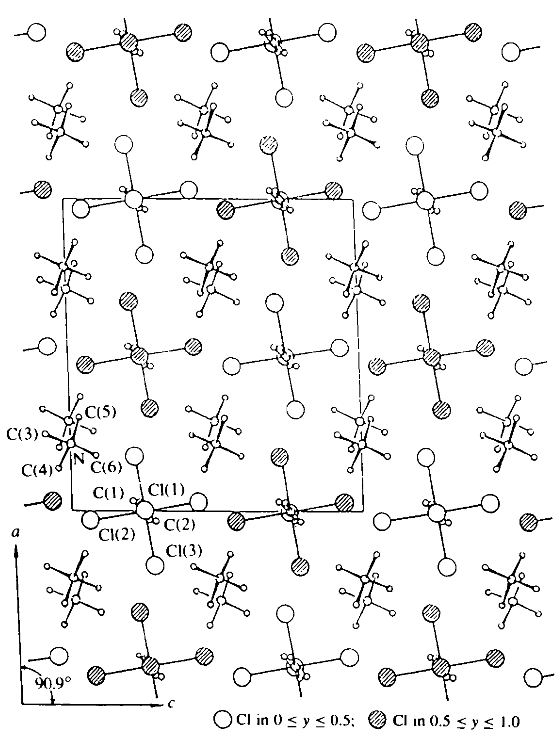


Fig. 14. Projection of the unit cell of $(Me_4N)_2EtSnCl_5$, phase I, onto the ac-plane. Space group: $C2/c$, $Z = 4$. The ethyl group seems to rotate at room temperature.

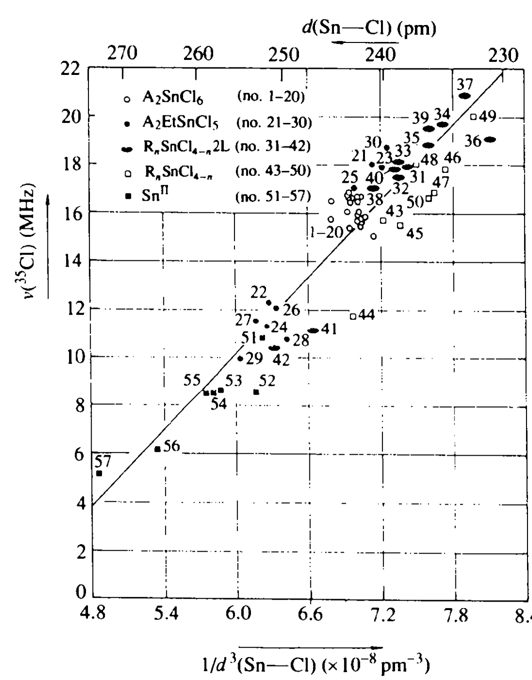


Fig. 16. Correlation between ^{35}Cl NQR frequencies and Sn—Cl bond lengths in inorganic and organometallic tin compounds.

Table 4(*a*). *Final assignment of* ^{35}Cl *NQR frequencies*, ν_i(Cl), *quadrupole coupling constants*, $eQ\Phi_{zz}^{(i)}h^{-1}$, *and asymmetry parameters*, $\eta_i(^{35}\mathrm{Cl})$, i = 1–5, *to certain* Cl(k) *atoms*, k = 1–5, *in* $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$

The Cl atoms are numbered according to the crystal structure [4] while the numbers i of $\nu_i(^{35}\mathrm{Cl})$, $eQ\Phi_{zz}^{(i)}h^{-1}$ and $\eta_i(^{35}\mathrm{Cl})$ increase with decreasing NQR frequency. Errors are given in parentheses.

No. of ^{35}Cl NQR	Cl(k)	$\nu(^{35}\mathrm{Cl})$ (MHz)	$eQ\Phi_{zz}^{(i)}h^{-1}(^{35}\mathrm{Cl})$ (MHz)	$\eta(^{35}\mathrm{Cl})$	d[Sn—Cl(k)] (pm)	$\measuredangle[\Phi_{zz}^{(i)}, d(\mathrm{Sn—Cl}(k))]$ (°)
ν_1	Cl(1)	17.032 (5)	34.046 (10)	0.056 (3)	242.6 (1)	3.1
ν_2	Cl(3)	12.072 (5)	24.089 (10)	0.117 (3)	250.7 (1)	1.9
ν_3	Cl(2)	11.537 (5)	22.992 (10)	0.146 (3)	253.1 (1)	2.8
ν_4	Cl(4)	10.770 (5)	21.455 (10)	0.154 (3)	249.7 (1)	2.9
ν_5	Cl(5)	9.969 (5)	19.842 (10)	0.171 (3)	254.9 (1)	1.7

Table 4(*b*). *Angles* (°) *between the x-components of the* EFG *tensor* $\Phi_{xx}^{(i)}$ *and the bond directions* Sn—Cl(k) *in* $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$

	Sn—Cl(1)	Sn—Cl(2)	Sn—Cl(3)	Sn—Cl(4)	Sn—Cl(5)	$\Phi_{xx}^{(1)}$	$\Phi_{xx}^{(2)}$	$\Phi_{xx}^{(3)}$	$\Phi_{xx}^{(4)}$
Sn—Cl(2)	85.9								
Sn—Cl(3)	85.7	92.1							
Sn—Cl(4)	86.7	171.9	90.7						
Sn—Cl(5)	85.2	88.6	170.8	87.4					
$\Phi_{xx}^{(1)}$	92.9	7.2	94.3	174.9	87.5				
$\Phi_{xx}^{(2)}$	88.1	2.2	91.9	174.0	89.2	5.3			
$\Phi_{xx}^{(3)}$	114.1	92.6	160.0	87.3	28.9	88.2	92.1		
$\Phi_{xx}^{(4)}$	69.0	89.4	16.7	91.2	154.2	93.4	89.8	176.4	
$\Phi_{xx}^{(5)}$	86.9	172.4	89.8	0.9	88.3	175.8	174.5	88.0	90.4

Table 4(*c*). *Angles* (°) *between the y-components of the* EFG *tensor* $\Phi_{yy}^{(i)}$ *and the bond directions* Sn—Cl(k) *in* $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$

	Sn—Cl(1)	Sn—Cl(2)	Sn—Cl(3)	Sn—Cl(4)	Sn—Cl(5)	$\Phi_{yy}^{(1)}$	$\Phi_{yy}^{(2)}$	$\Phi_{yy}^{(3)}$	$\Phi_{yy}^{(4)}$
Sn—Cl(2)	85.9								
Sn—Cl(3)	85.7	92.1							
Sn—Cl(4)	86.7	171.9	90.7						
Sn—Cl(5)	85.2	88.6	170.8	87.4					
$\Phi_{yy}^{(1)}$	89.2	91.6	173.4	84.9	4.8				
$\Phi_{yy}^{(2)}$	4.7	87.8	89.9	84.6	80.9	84.8			
$\Phi_{yy}^{(3)}$	24.1	88.9	109.5	83.0	61.3	65.1	19.7		
$\Phi_{yy}^{(4)}$	22.0	79.3	106.7	92.7	64.4	68.7	18.7	10.0	
$\Phi_{yy}^{(5)}$	5.6	83.0	81.1	89.9	89.9	94.0	10.3	29.3	25.8

deuteron, the high-field method (Pound, 1950) is appropriate. The unfortunate situation in this research genre is that in many cases only X-ray diffraction studies can be compared with the deuterium EFGT studies, which is, as for hydrogen bonds, often not satisfactory.

Work has started by Ketudat (1957) and Ketudat & Pound (1957), who studied the EFGT at the sites of the D atoms in $Li_2SO_4.D_2O$. A redetermination of the EFGT(^{2}H) is due to Berglund & Tegenfeldt (1977). The crystal structure of the compound was determined by X-ray (Larson & Helmholz, 1954) and neutron diffraction (Smith, Peterson & Levy, 1968). It was found that at 164 K the D_2O molecule is static, whereas at 298 K the molecule is flipping around its twofold axis. For the static situation, Φ_{zz} of the EFGT is almost (within 2°) parallel to the bond direction D—O for both D atoms and $\eta \approx 0.10$, whereas in the dynamic case the two atoms become dynamically equivalent, Φ_{zz} being perpendicular to the plane (DOD), becoming large ($\eta \approx 0.8$). Of course, these results are not straightforwardly comparable with the diffraction experiments which work at completely different time-scales as far as dynamic effects are concerned.

Also for $BeSO_4.4D_2O$, there is *X*- and *N*-crystal structure determination available (Dance & Freeman, 1969; Sikka & Chidambaram, 1969), as there is a single-crystal EFGT(^{2}H) determination published (Berglund & Tegenfeldt, 1977). The NQI(^{2}H) of beryllium sulphate tetrahydrate is somewhat weaker compared with the lithium sulphate monohydrate, and the bond lengths O—D are shorter in the latter. Again the static and the flipping situations have been studied. Other examples of a combined study of the EFGT(^{2}H) in the bond O_W—D···O are $Na_2S_2O_6.2D_2O$ (NQR: Ketudat, Berthold & Weiss, 1967*a*,*b*; *X*–*N* diffraction: Berthold & Weiss, 1967; Kirfel, Will & Weiss, 1980; Zwoll, 1974).

Cupris sulfate pentahydrate, $CuSO_4.5D_2O$, is an example for a quite complicated structure (as far as

NQR is concerned) with five crystallographically independent D_2O molecules with 10 different EFGT(^2H). Crystal-structure determinations (*X*, *N*) have been reported by Beevers & Lipson (1934), Bacon & Curry (1962), Bacon & Titterton (1975). The EFGT's of ^2H have been studied by Clifford & Smith (1967) and by Soda & Chiba (1969) over a wide range of temperature.

The EFGT(^2H) on the α-alum $RbAl(SO_4)_2.12D_2O$ was recently investigated by Ramakrishna, Weiden & Weiss (1990). It is interesting to note that the hydrogen bonds of the D_2O molecules belonging to the $Rb(D_2O)_6$ coordination must be weaker than those in the $Al(D_2O)_6$ coordination because they are flipping at 295 K, whereas D_2O around Al is static at this temperature.

An important topic in the study of hydrates is of course water and water vapor and ice. The gaseous phase was thoroughly explored by microwave spectroscopy and in the solid state the large number of ice phases have been studied by diffraction (*X*, *N*) and ^2H NMR (NQR). In all phases of ice the EFGT's (^2H) show the static behavior of the D_2O molecules. The hydrogen bond network prohibits the flipping of the molecules around their twofold axis. For a discussion of the NQR, IR and structural data of ice phases, see Weiss & Weiden (1980). There are many more investigations (*X*, *N*, NQI) of crystal hydrates reported in the literature, including discussions on hydrogen bonds $O_w—D\cdots$halogen and $O_w—D\cdots O$; this chapter is summarized up to 1980 by Weiss & Weiden (1980).

A recent example of the study of the $O_w—D\cdots$halogen bond by NQR is the investigation of the EFGT's of the halogens Br and I and of the deuterons in deuterated glycyl-L-alanine hydrobromide monohydrate and in the analogous hydroiodide (Kehrer, Weiden & Weiss, 1992; for the crystal structures see Kehrer, Dou & Weiss, 1989, 1992). In the bromide, at room temperature, the ND_3 group is rotating, leading to a single EFGT(^2H) with a coupling constant of 54 kHz, $\eta = 0.103$. The D_2O molecule is flipping and Φ_{zz} deviates by 13° from the normal to the plane (DOD). In the COOD group, Φ_{zz} deviates by 7° from the O—D bond direction. Φ_{zz} (^{81}Br) is almost parallel to the shortest bond, $D\cdots Br$.

Chemical shift and EFGT for the amide and carboxyl H atoms in *N*-acetyl-D,L-valine by single-crystal D NMR have been studied by Gerald II, Bernhard, Haeberlen, Rendell & Opella (1993). The structure is known (Carroll, Stewart & Opella, 1990). The EFGT's of the amide and the carboxyl D atoms have been assigned to the crystallographic positions.

The investigation of carboxylic acids and salts of carboxylic acids has found wide interest and X–N/EFGT(^2H) studies are known. An intensively studied compound within this group is oxalic acid dihydrate. The neutron diffraction structure of the α- and the β-phase is reported by Coppens & Sabine (1969), Coppens, Sabine, Delaplane & Ibers (1969), Sabine, Cox & Craven (1969), Delaplane & Ibers (1969), Feld (1979), and Iwasaki & Saito (1967). The EFGT(^2H) in these compounds was studied by Chiba (1964), Chiba & Soda (1967, 1971), and Saraswati & Vijayaraghavan (1976). A study of both the chemical shift and the EFGT of ^2H is reported by Achlama (1980). The axes of the deuterium chemical shift tensor are not deviating much from the orientation of the EFGT(^2H) axes. By ^2H NMR line-shape analysis and two-dimensional deuterium exchange spectroscopy, Birczyński, Sułek, Müller & Haeberlen (1992) investigated the hydrogen motions in α-oxalic acid dihydrate. Besides the D_2O flipping, they identified the exchange of a D atom of the carboxyl group with the D atoms of the next nearest-neighbor hydrogen-bonded water molecules [this process has already been proposed by Chiba (1979)] and finally an exchange of the carboxyl D atoms with distant, nonhydrogen-bonded water molecules was observed. Hydrogen diffusion has also been recognized.

The structure of $KHCO_3$ was studied by Thomas, Tellgren & Olovsson (1974) by neutron diffraction. Positional disorder of the H atoms in the hydrogen carbonate dimer ions was observed. Benz, Haeberlen & Tegenfeldt (1986) studied the EFGT(^2H) as a function of temperature and determined the principal axes of the EFGT(^2H) and their orientation for the two sites, and for the averaged site of the D atoms on single crystals. The site population ratio changes strongly with temperature; at 25 K the occupation p is restricted to one side, whereas at 300 K $p_1/p_2 = 0.18$.

Chiba (1964) proposed a functional dependence of $eQ\Phi_{zz}h^{-1}$ (^2H) from the distance $r(O_w\cdots O)$ and the relation was experimentally realized by Soda & Chiba (1969) and Berglund, Lindgren & Tegenfeldt (1978).

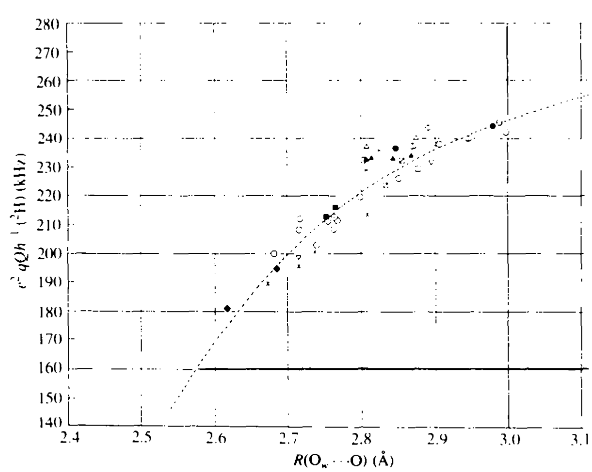


Fig. 17. e^2qQh^{-1} (^2H) as a function of the hydrogen-bond distance $R(O_w\cdots O)$ ($eq \equiv \Phi_{zz}$). The 'static' case is considered. Key: ×: $NaDC_2O_4.D_2O$; ⦶: $Li_2SO_4.D_2O$; ◇: $Ba(ClO_3)_2.D_2O$; ⊙: $(ND_4)_2C_2O_4.D_2O$; ▽: $LiDCOO.D_2O$; ◆: $BeSO_4.4D_2O$; ●: $Na_2S_2O_6.2D_2O$; ■: $D_2O(I_h)$; ×: $Sr(DCOO)_2.2D_2O$; ◇: $K_2C_2O_4.D_2O$; □: α-$D_2C_2O_4.2D_2O$; △: L-serine hydrate; ⊖: $LiClO_4.3D_2O$; ○: $CuSO_4.5D_2O$; ▨: β-$D_2C_2O_4.2D_2O$; ▲: L-asparagine hydrate.

The latter authors formulated (r in Å)

$$eQ\Phi_{zz}h^{-1}(^2\mathrm{H})/(\mathrm{kHz}) = 271 - 8.63 \times 105\exp[-3.48r(\mathrm{O_w}\cdots\mathrm{O})]. \quad (2)$$

Since the data for $r(\mathrm{O_w}\cdots\mathrm{O})$ are quite reliable from both diffraction experiments, X and N, the relation can be used successfully for an estimate of the distance from NQR measurements and *vice versa*. In Fig. 17 the relation is shown for a number of crystal hydrates. From equation (1) we expect a linear dependence of the nuclear quadrupole coupling constant from the reciprocal third power of the hydrogen-bond distance $r(\mathrm{D}\cdots X)$, see Fig. 18.

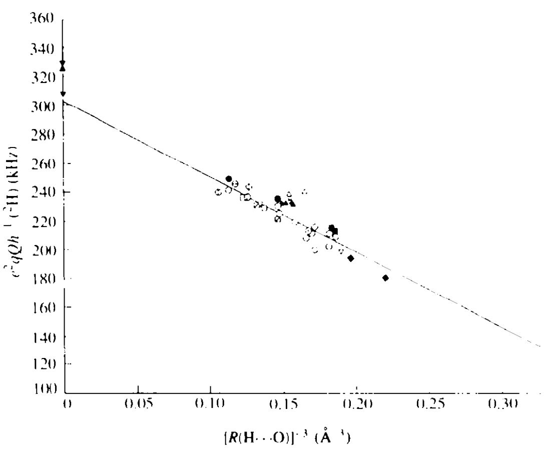


Fig. 18. e^2qQh^{-1} (^{2}H) as a function of $R(\mathrm{O_w}\cdots\mathrm{O})$ ($eq \equiv \Phi_{zz}$). $e^2qQ/h(^2\mathrm{H})$ as a function of the distance $R(\mathrm{H}\cdots\mathrm{O})$; $e^2qQ/h(^2\mathrm{H}) = f[1/R^3(\mathrm{H}\cdots\mathrm{O})]$. Key: ×: $NaDC_2O_4.D_2O$; ⏀: $Li_2SO_4.D_2O$; ⏀: $Ba(ClO_3)_2.D_2O$; ⊙: $(ND_4)_2C_2O_4.D_2O$; ▼: HDO (gas); ▽: $LiDCOO.D_2O$; ◆: $BeSO_4.4D_2O$; ●: $Na_2S_2O_6.2D_2O$; ■: $D_2O(I_h)$; x: LiOD (77 K); ×: $Sr(DCOO)_2.2D_2O$; ◇: $K_2C_2O_4.D_2O$; □: α-$D_2C_2O_4.2D_2O$; △: L-serine hydrate; ⊖: $LiClO_4.3D_2O$; ○: $CuSO_4.5D_2O$; ⊠: β-$D_2C_2O_4.2D_2O$; ▲: L-asparagine hydrate.

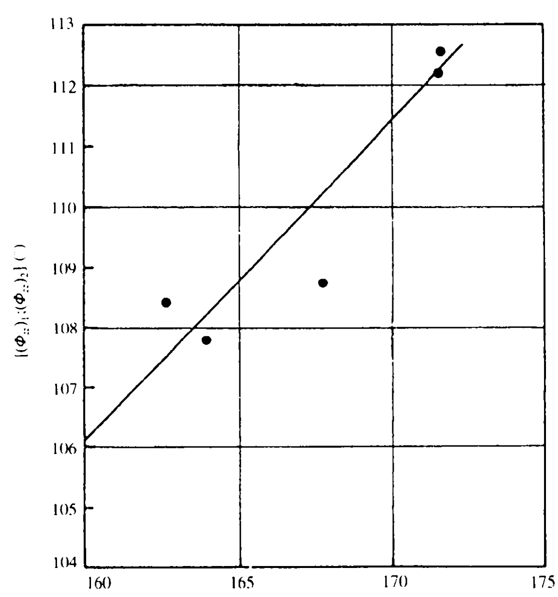


Fig. 19. Angle $\{(\Phi_{zz})_1, (\Phi_{zz})_2\}$ within one D_2O molecule as a function of the crystallographic angle ($\mathrm{O—D}\cdots\mathrm{O}$) in $CuSO_4.5D_2O$.

There are several relations between the deuteron coupling constant and physical properties of solids reported in the literature, see *e.g.* Weiss & Weiden (1980). We show one of them in Fig. 19: the correlation between the hydrogen-bond angle $\mathrm{O—D}\cdots\mathrm{O}$ and the angle the main principal axes of the two D atoms of the D_2O molecules in $CuSO_4.5D_2O$ enclose.

Concluding remarks

The Zeeman single-crystal NQR spectroscopy, in combination with diffraction studies of the structures, offer advantages in the study of the chemical bond. The combination of the methods is a promising way of studying intermolecular forces in molecular crystals, particularly if one investigates the small changes of effects in the electron distribution of molecules arising in phase transitions. The concentration on systems with 'small' molecules, including the evaluation of the molecular structure by microwave spectroscopy of chiral systems, may be a promising step in structural chemistry.

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