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A Nuclear Quadrupole Resonance and X-ray Study of the Crystal Structure of 1,2,4,5-Tetrachlorobenzene

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The chlorine nuclear quadrupole resonance has been used to determine the C–Cl bond directions in a single crystal of 1,2,4,5-tetrachlorobenzene. With these data, the phases for the (0*kl*) structure amplitudes were determined directly and used in a Fourier projection. The results for the n.q.r. measurements and the two-dimensional X-ray analysis agree within 1–2° in the bond orientations.

The angle between adjacent C–Cl bonds in the molecule is 63±1°. The interpretation in terms of strained models is discussed in relation to the n.q.r. experiments.

Introduction

The Zeeman splitting pattern of the nuclear quadrupole resonance (n.q.r.) spectrum of a single crystal can provide crystal-structural information. In some circumstances, this can be rather precise data relating to the relative orientation of bond directions otherwise accessible only to the more laborious techniques of a complete three-dimensional X-ray crystal-structure analysis. Alternately it can be used to give the X-ray crystallographer enough preliminary structural data to enable him to proceed directly to the solution of the phase problem.

In this paper, the Zeeman splitting of the Cl^{35} n.q.r. spectrum of 1,2,4,5-tetrachlorobenzene is described. The results were interpreted on the basis of the simple model in which the electric field gradient at a chlorine nucleus is considered to arise solely from the π and σ character of the C–Cl bonds. This gave the relative C–Cl bond and benzene ring orientations. The validity of this generally accepted interpretation was supported by the close correlation with the results from a two-dimensional X-ray analysis. Furthermore, although no great difficulty would be anticipated in solving the phase problem for this particular crystal structure by the standard methods of trial and error or Patterson synthesis, the use of the n.q.r. orientation results did in fact permit a direct solution.

Theory of the n.q.r. method

In n.q.r. the principal fields with which the nuclei interact are electrostatic and originate within the sample itself, unlike the case of nuclear magnetic resonance, in which a large applied magnetic field furnishes the principal interaction. The interaction is described by the tensor product of the electric field gradient, which describes the inhomogeneity of the electric field in the vicinity of the nucleus, with the nuclear quadrupole moment, which describes the amount of ellipticity of the nucleus. The result of the interaction is a torque on the nucleus, so that the different allowed quantum states of orientation of the nucleus have different energies. N.q.r. is the study of the spectra associated with transitions between these different states.

A particular case of the quadrupole interaction is illustrated in Fig. 1. The electric lines of force shown there are those due to the two plus charges. They correctly represent the net effect of a deficit of one electron in an otherwise filled p-shell. The field has

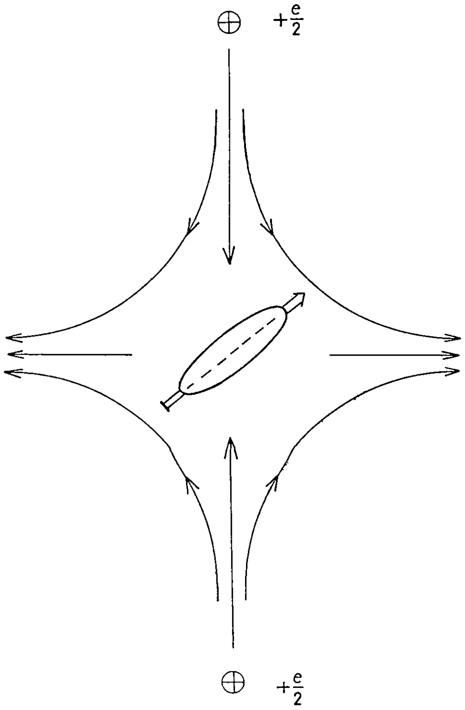


Fig. 1. A particular case of the pure electric quadrupole interaction.

axial symmetry around line joining the two charges. The positive charge of the nucleus is an ellipsoid of revolution about the axis of nuclear spin. The different allowed orientations of the nucleus are described by the value of m, the component of nuclear spin parallel to the axis of symmetry of the field. For Cl^{35}, with a nuclear spin of $\frac{3}{2}$, $m = \pm\frac{3}{2}$ are the degenerate high-energy states, while $m = \pm\frac{1}{2}$ are the degenerate low-energy states. The pure quadrupole absorption spectrum is a single frequency.

If a magnetic field is also applied to a solid which exhibits n.q.r., the nuclei experience additional torques because of their magnetic dipole moments. The energy-level scheme is perturbed, and each individual n.q.r. absorption line is split into components. The details of the splitting depend on the strength and the orientation of the magnetic field with respect to the axes of the electric field gradient. In a single crystal this splitting must be the same for all atoms at the same unit-cell site throughout the crystal, i.e., for all which are related by translations of the unit cell. However, in general it will be different for each different site within the unit cell, even though the sites are related by a symmetry operation, unless the magnetic field has been given a special orientation which is either unchanged or simply reversed by that symmetry operation. Of course this 'exception' is the general rule for an inversion center; this is a corollary of the fact that reversing the magnetic field has no effect on the n.q.r. spectrum.

An analysis of the magnetic splitting for a sequence of different crystal orientations in the magnetic field can yield the orientation, symmetry, and the relative strength of the electric field gradients at each of the different sites which are occupied by the species of nucleus under investigation. In the work described here the magnetic interaction was kept small compared to the electric quadrupole interaction (Zeeman splitting). In this case all the information can be obtained by searching with a given crystal for what we shall call the zero-splitting loci, i.e., the loci of those particular directions in space along which the applied magnetic field leaves an unsplit component of the spectrum at the pure quadrupole resonance frequency. This is a convenient experimental choice since the occurrence of an unsplit component is unique and is relatively easy to identify. For a field gradient with axial symmetry and a nuclear spin of $\frac{3}{2}$ the loci are two circular cones about its axis, such that the magnetic field is constrained to make an angle of $54^\circ\,44'$ with the axis.

For molecular structures in which the atomic interactions are mainly covalent between bonded atoms and van der Waals elsewhere, the electric field gradient at a nucleus is largely determined by the electron distribution on that one atom. Since the field gradient arises only from the non-spherical part of the distribution of charge density around the nucleus, it is usually satisfactory to explain it in terms of the occupancy of the p-orbitals in the valence electron shell. In compounds which are known to contain chlorine atoms in essentially single bonds, the electric field gradient at the chlorine nuclei can be ascribed to the deficit of approximately one electronic charge in the bonding chlorine p orbital. The two positive charges in Fig. 1 represent the net effect of such a deficit. Thus, to the approximation of this model, the axes of the experimentally observed zero-splitting loci must be parallel to the chlorine bonds in the single crystal sample.

The chlorine bond structure may contain a certain percentage of a double bond. In this case the bonding orbital also contributes to the electric field gradient and destroys its axial symmetry. To the same approximation as above, the zero-splitting loci for nuclei with spin $\frac{3}{2}$ are elliptical cones given by $\sin^2\theta = 2/(3-\eta\cos 2\varphi)$, where θ is the angle between the magnetic field and the direction of the σ bond, φ is an azimuthal angle, which is zero for field directions in the plane containing the axes of both the π bonding and σ bonding p orbitals, and η is a parameter which describes the amount of asymmetry of the electric field gradient and is related to the fractional importance of the π bond.

Further refinements suggest certain modifications of this theoretical model. The formula for $\sin^2\theta$ is rigorously true, but the electric field gradient tensor that is observed may be the resultant of several different terms, so that the principal axes implied by the formula may not coincide precisely with any individual directions of crystallographic significance, i.e., the bond directions. The admixture of fractions of other bond structures with different orientations can have such an effect, (Townes & Dailey, 1952; Kojima *et al.*, 1954; Tsukada, 1956), and in the present material a distortion of one chlorine electron cloud by its very close neighboring chlorine atom might also do this. The electric field gradient that is measured by n.q.r. is actually an average over thermal vibrations, (Dehmelt & Kruger, 1951; Bayer, 1951), so that anisotropic thermal motions can affect the accuracy of our interpretation. The errors in the σ bond orientation due to these neglected terms probably do not exceed the order of 1° or so in most cases, but this is the same order as the apparent distortions of the molecules that were found in the present work. Nevertheless, we feel that results based primarily on the simple model are useful, and we believe that as more molecules are studied in this way we will achieve at least an empirical understanding of the way to take the other factors into account.

The simple model of the relation between quadrupole coupling and bond structure was derived by Townes & Dailey (1949); more recent reviews include Gordy, Smith & Trambarulo (1953), Dehmelt (1954) and Orville-Thomas (1957). The theory of the Zeeman splitting in n.q.r. was given by Bersohn (1952), Dean (1954), and Cohen (1954).

The n.q.r. equipment and experimental technique for single crystals

A super-regenerative r.f. spectrometer was used to record the spectra. In this type of spectrometer the only radio-frequency tuned circuit is the tank circuit of a pulsed oscillator; the sample is inserted into the coil of this circuit, and a resonance is detected by its effect on the oscillation cycle. All of the electronic parts except the coil were mounted conventionally in a small aluminum chassis, which was bolted to a circular brass plate 12 in. in diameter. Along the outer rim of this plate was engraved a circle graduated to the nearest degree. The assembly was mounted with the brass plate horizontal and free to turn about a vertical axis. Readings on this circle were taken as the azimuthal angle Θ in the laboratory coordinate system.

The oscillator coil was suspended about 7 in. below the circular plate. Its axis was horizontal and coincided with the axis of the glass tube and with the axis of rotation of a second graduated circle, to which the sample tube was fastened. Readings on this second circle were taken as the polar angle Φ in the laboratory coordinate system. This part of the system was attached to the large brass circle, and turned with it. The Zeeman magnetic field was furnished by a stationary pair of Helmholtz coils of about 6 in. mean radius, whose common axis was horizontal and was taken to be the pole of the laboratory coordinate system, $\Theta = 0$. The alignment of the magnetic field was determined by using internal checks in the n.q.r. spectra.

The Zeeman magnetic field was modulated at about 1 c.sec.$^{-1}$ with a triangular wave shape whose minimum and maximum values were about 100 and 300 gauss, respectively. The spectra were recorded on a chart by a recording milliameter. The integrating time constant in the circuit which drove the meter was made long enough to suppress the transient signals from the field-dependant components of the spectrum, and to plot with full intensity only an unsplit component when it occurred. This procedure brought out the points on the zero-splitting loci quite clearly, but made it necessary to search quite a dense network of orientations. The spectra were recorded for orientations at 1° intervals along a half of a great circle of constant Φ. This operation took about one day, and was accomplished automatically by means of a system of relays and motors. New great circles were set manually, and the process was repeated, until it was felt that the data were sufficient to specify the location and shape of the required loci of zero-splitting.

For a given magnetic field, the angular resolution is limited by the width of the quadrupole resonance; in the present work it was about $\frac{1}{2}$°. Since the Zeeman splitting amplitudes for the quadrupole resonance are proportional to the magnitude of the magnetic field, so also is our ability to resolve barely split lines. Consequently the angular resolution could easily be improved by a factor of ten over the present work. However, with the present technique this would require initial searches at intervals of about 0·1° along the great circles, and this did not seem feasible.

The relative directions of the z axes of the electric field gradients that were finally obtained from the zero-splitting loci are believed to be accurate to ±1°. The internal consistancy of the final data provides a verification of this, since there are numerous arc lengths which were measured at different sections of the goniometer but which are necessarily related by crystal symmetry, and since the dimensions of the elliptical loci must agree with the theoretical formula.

Crystal data

1,2,4,5-tetrachlorobenzene is monoclinic with

$$a = 3{\cdot}850 \pm 0{\cdot}005,\ b = 10{\cdot}602 \pm 0{\cdot}005,$$
$$c = 9{\cdot}725 \pm 0{\cdot}005\ \text{Å},\ \beta = 103{\cdot}28^\circ \pm 5',$$
$$U = 386{\cdot}8\ \text{Å}^3,\ D_m = 1{\cdot}858\ \text{g.cm.}^{-3},\ Z = 2,$$
$$D_X = 1{\cdot}854\ \text{g.cm.}^{-3},\ \text{space group } P2_1/c,$$
$$\text{molecular symmetry, } \bar{1},$$

The crystals for the X-ray study were obtained from CCl_4 solution as needles elongated about the a axis. All crystals examined were twinned about the a-axis, with an angle of 97° between the b-axis directions. The lattice-parameter measurements were made on the G.E. XRD-5 diffractometer with the single-crystal orienter.

For the n.q.r. measurements, a crystal was grown from the melt by slowly lowering out of a furnace a sample of Eastman practical grade in a glass tube approximately 1 cm. in diameter and 10 cm. in length, at one end of which a 10 cm. length of capillary tubing had been attached. Three crystal twins were subsequently identified in the specimen. No preliminary purification was attempted, but the last section to solidify during the growing process was strongly discolored, indicating that a considerable purification of the bulk of the sample had occurred.

The n.q.r. analysis

At room temperature the unperturbed n.q.r. spectrum (zero magnetic field) of the Cl^{35} nuclei in 1,2,4,5-tetrachlorobenzene consists of two lines at about 36·3 mc.sec.$^{-1}$ with a doublet separation of about 65 kc.sec^{-1} (Bray, 1955; Monfils, 1955). Multiple resonances in such cases as this, where all the chlorines are chemically identical, are generally ascribed to the occurrence of non-equivalent chlorine sites in the unit cell. Little is known about the actual mechanism that causes the splitting. The chlorine atomic orbitals at the two sites may be affected by the intermolecular forces in different ways, either directly or by small changes transmitted down the molecule to the chlorine, or the averaging effect of thermal vibrations may be

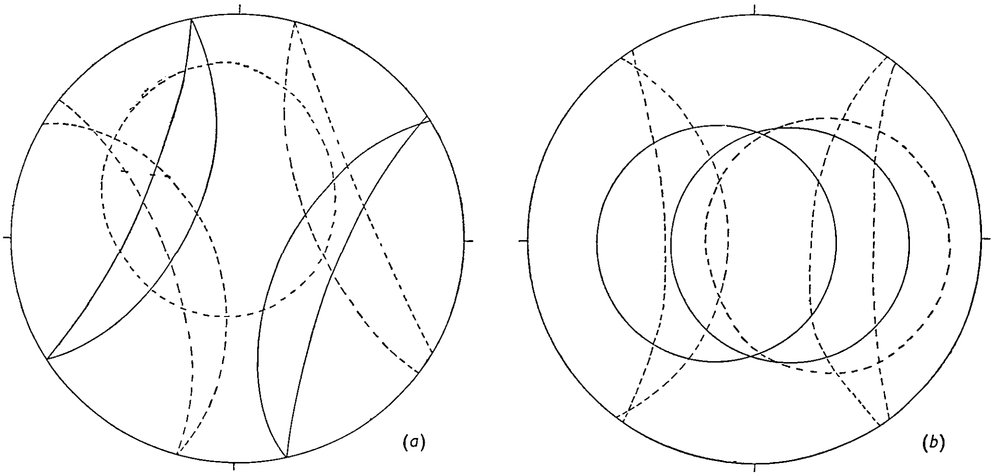


Fig. 2. Stereograms of the observed zero-splitting loci in one hemisphere. The pole of the laboratory coordinate system, $\Theta = 0$, is at the top of the picture. The left half of the rim is $\Phi = 30°$, and Φ increases to the right. (a) High-frequency resonance; (b) low-frequency resonance.

different at the two sites. The amount of splitting here is relatively small, values of up to ten times this amount having been observed in other chlorine compounds.

The magnetic zero-splitting loci that were observed for each of the two different pure quadrupole resonances are shown in stereographic projection in Fig. 2. Only one hemisphere is plotted for each resonance. The hidden hemisphere is obtained from that shown by an inversion through the origin, a symmetry which is always present in n.q.r. regardless of the crystal symmetry. The solid curves were drawn through sequences of points for which the unsplit resonance was relatively intense and for which the identification of the individual loci was quite obvious. There were over twenty-five points for each of these curves. Except for a few points which were unreliable because of the proximity of more than one resonance, the points all fell within 1° of the smoothed curves. The dashed curves were drawn along series of points corresponding to resonances which were somewhat less intense, but which were for the most part clearly recorded. All of the loci were slightly elliptical.

Although it is felt that the same interpretations of the zero-splitting loci could probably have been made independently, the X-ray diffraction work to be described below was started before the n.q.r. data were completed, and at each step of the analysis the current results from both investigations were taken into account. In practice this was very helpful, since on the whole the two techniques deal with different aspects of the structural problem and give complementary information. Particularly useful was the preliminary X-ray data showing that the molecular symmetry was centric and that there were two molecules in a unit cell related by a twofold axis. This, with the further warning that twinned crystals might be expected, clearly suggested that the four loci of more intense resonances might correspond to the four chlorine directions in the most abundant of several twins. Supporting this was the fact that, aside from abundance, the intensity of a resonance depends only on the angle between the Cl σ orbital and the axis of the r.f. coil in the spectrometer, and in the present data this could not account for the observed intensity differences.

The axes of the cones described by the intense loci were determined. It was assumed that each molecule of the unit cell had to be represented by two of the Cl–C bond directions thus indicated, one from each of the two pure quadrupole resonance frequencies. On the further assumption that the angle between these two directions should be the order of 60°, a clear and reasonable picture emerged showing the orientations of the two molecules in the unit cell together with the

Table 1*a*. *Orientations of the chlorine bond orbitals for the two molecules* (*A*, *B*) *in the principal twin, referred to the laboratory coordinate system**

		Θ (°)	Φ (°)	M (°)	m (°)
A	σ(I)	88½	136¼	—	—
	σ(II)	111	196	—	—
	π(I)	157	50	112½	106
	π(II)	156	47	112¾	105½
	π	155¼	49½	—	—
B	σ(I)	87¾	106½	—	—
	σ(II)	68	44	—	—
	π(I)	20	201	113¼	106¼
	π(II)	25	198	113	107
	π	23½	201¾	—	—

Symmetry Axis { 88·1 121·4 (From (I) for A and B)
87·9 120·8 (From (II) for A and B)

Angle between σ(I) and σ(II): 62½° (Molecule A)
63¾° (Molecule B)

* The nomenclature is the same as in Fig. 3. M and m are the diameters, in arc of great circles, of the elliptical zero-splitting loci.

orientation of the twofold axis. These orientations are listed in Table 1*a* and are plotted as the points σ in Fig. 3, relative to the same laboratory coordinate system as in Fig. 2. The twofold axis must of course be the screw axis identified by the diffraction data, and since it appears almost at center of the stereogram the glide plane that the diffraction data also demand must very nearly coincide with the plane of the paper.

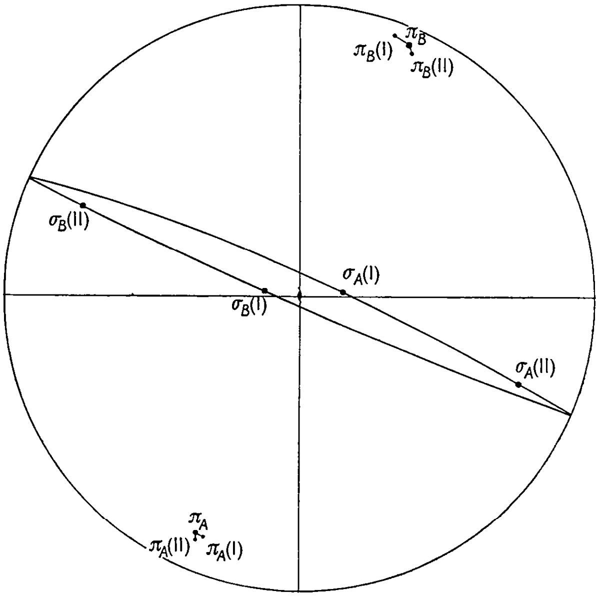


Fig. 3. Stereogram of the σ and π bond orbital directions for the principal twin, as deduced from the loci shown in Fig. 2. $\pi(\mathrm{I})$ and $\pi(\mathrm{II})$ are the orientations of the π-bond orbitals as found from the ellipticity of the individual zero-splitting loci. π is the normal to the proper pair of σ-bond directions. I and II designate the atom giving the lower and the higher frequencies, respectively, in the unperturbed n.q.r. doublet.

This information of the orientations of molecules relative to the symmetry elements was subsequently used in combination with the diffraction data for the Fourier synthesis described later.

The remaining loci of weaker resonance could be grouped to represent two twins of this crystal, provided that one assumed that the resonances corresponding to two further loci had been overlooked in the original data. This seemed reasonable for both missing loci, on the argument that they were obscured by their proximity to the stronger loci. The bond directions are listed in Table 1*b*. The axis of twinning that was implied by this analysis corresponded approximately to the axis of the capillary tube, which would explain how all of the twins could survive the crystal-growing process. The angle of rotation from one twin to the next was about 97°, in substantial agreement with the later X-ray results. Although the details for these weaker loci were in substantial agreement with those for the intense ones, their accuracy was lower, and they were not used in the final analysis.

Table 1*b*. *Approximate details for the weaker twins, distinguished by the subscripts* 2 *and* 3

		Θ_2 (°)	Φ_2 (°)	Θ_3 (°)	Φ_3 (°)
A	$\sigma(\mathrm{I})$	88	39½	—	—
	$\sigma(\mathrm{II})$	—	—	111	5
B	$\sigma(\mathrm{I})$	92	12	91½	272
	$\sigma(\mathrm{II})$	72	307½	70	211
Symmetry axis		90	26	92	287

Each of the loci that was identified in the data was clearly elliptical. The major and minor diameters of the intense loci, measured in arc of great circles, are tabulated in Table 1*a* as *M* and *m*, respectively. The asymmetry parameter evaluated from this data is $\eta = 0{\cdot}125 \pm 0{\cdot}025$, over 50% larger than the values

Table 2. *Correlation between n.q.r. and X-ray data*

The direction cosines and angles between the chlorine bond directions C–Cl, Cl–Cl′, the molecular axes, *L*, *M*, *N*, and the crystallographic axes *a*, *b*, *c* sin β. The X-ray values are in normal type and the n.q.r. italicized

	a	*b*	*c* sin β
$\mathrm{C_1{-}Cl_1}$	*−0·0065, 90° 23′*	*0·9665, 14° 52′*	*0·2566, 75° 8′*
$\mathrm{C_1{-}Cl_1'}$	+0·120, 83°	0·949, 19°	0·292, 73°
$\mathrm{Cl_1{-}Cl_1}$	+0·120, 83°	0·956, 17°	0·277, 74°
$\mathrm{C_2{-}Cl_2}$	*−0·3669, 111° 28′*	*0·2252, 76° 59′*	*0·9026, 25° 30′*
$\mathrm{C_2{-}Cl_2}$	−0·357, 110°	0·241, 76°	0·901, 25°
$\mathrm{Cl_2{-}Cl_2'}$	−0·371, 111°	0·232, 77°	0·899, 26°
L	*0·3442, 69° 50′*	*0·7078, 44° 56′*	*−0·6169, 128° 55′*
	0·435, 64°	0·680, 47°	−0·589, 126°
M	*−0·2192, 102° 20′*	*0·6994, 45° 37′*	*0·6803, 47° 8′*
	−0·161, 98°	0·707, 45°	0·685, 47°
N	*0·913, 24° 4′*	*−0·0989, 95° 19′*	*0·3958, 66° 37′*
	0·993, 6°	−0·051, 92°	0·106, 84°

Orientation in the *a*-axis projection with respect to the *b*-axis

$\mathrm{C_1{-}Cl_1}$	*14·9°*	$\mathrm{C_2{-}Cl_2}$	*76·2°*
$\mathrm{C_1{-}Cl_1}$	17°	$\mathrm{Cl_2{-}Cl_2}$	75°
$\mathrm{C_1{-}Cl_1'}$	16°	$\mathrm{Cl_2{-}Cl_2'}$	75°

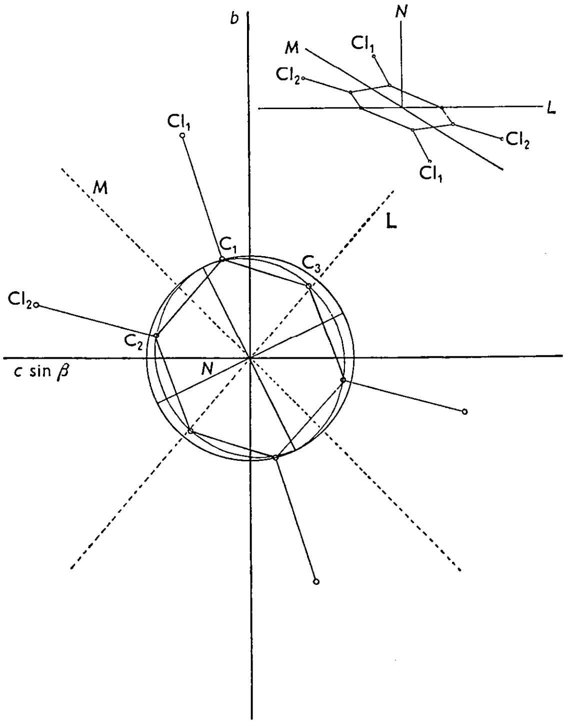


Fig. 4. Diagram of relative orientations of crystal axes, molecular axes and chlorine vectors.

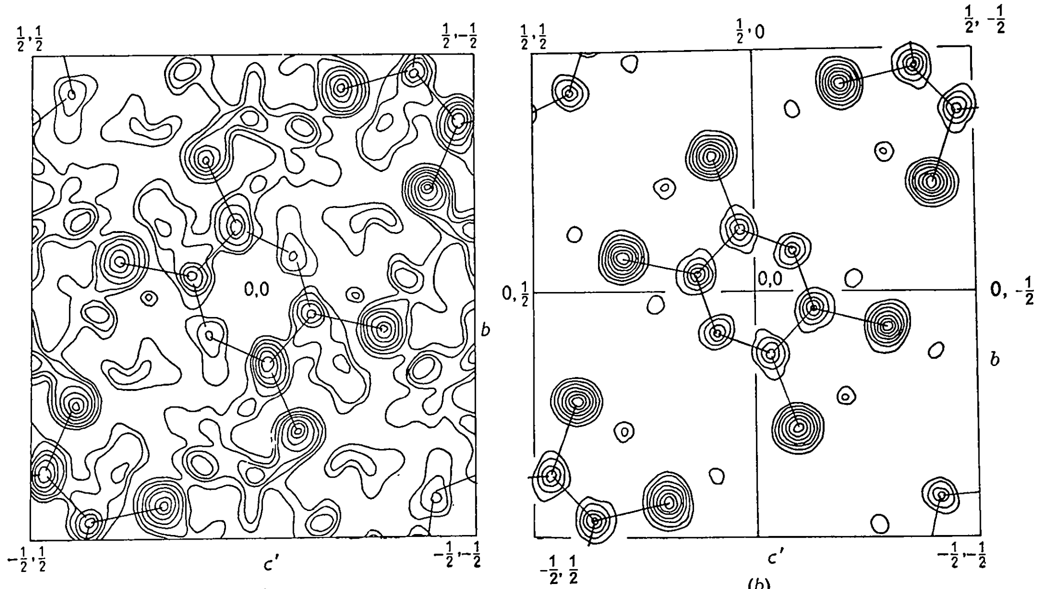
found by Dean (1952*a*, *b*) and by Meal (1956) for single chlorines bonded to a benzene ring. If this asymmetry were due only to the existence of partial π bonds to the chlorines, the major axes of the ellipses should indicate the orientation of the chlorine *p* orbitals that form them and thereby specify the normal to the appropriate benzene ring. These directions are designated by π(I) and π(II) in Table 1*a* and Fig. 3. The normal to the ring is also presumably given as the intersection of great circles drawn around each of the two C–Cl bond directions found for that molecule. This direction is shown as π in Table 1*a* and Fig. 3. The good agreement obtained here suggests that this simple interpretation is reasonably correct, and incidentally provides one of the internal checks on the alignment of the equipment.

The final structural information derived from this analysis of the n.q.r. data is summarized in Table 2. The orientations are specified here with respect to the crystal axes as they were identified in the n.q.r. results. The twinning axis was taken as *a*, the twofold axis as *b*. The third axis *c'*, was chosen to form a right-handed rectangular coordinate system. The molecular axes *L*, *M*, and *N* are defined in Fig. 4, which also shows the relative orientations of the relevant axes and chlorine vectors.

The X-ray analysis

The short *a* axis clearly indicated the direction for a resolved projection. Accordingly, the (0*kl*) intensity data were recorded on multi-film Weissenberg photographs with Cu *K* radiation. To prevent evaporation during the exposure of intensity photographs the crystal was enclosed in a thin-walled glass capillary. The intensities were estimated by eye and reduced to structure amplitudes by the usual angle factors. No corrections were made for crystal absorption, but the errors were reduced by dissolving the edges of the crystal until it was approximately cylindrical. Of the 132 0*kl* reflections available, 121 were recorded.

The n.q.r. data gave the relative orientation of two pairs of C–Cl bond directions, one pair for each centro-



(*a*) (*b*)

Fig. 5. Fourier projections on (100): (*a*) first projection; (*b*) second projection.

symmetrical molecule, as shown on the stereographic projection in Fig. 3. The poles $\sigma_A(\mathrm{I})$, $\sigma_A(\mathrm{II})$, $\sigma_B(\mathrm{I})$, $\sigma_B(\mathrm{II})$, associated with each molecule A, B, lie on great circles 11° apart. They define the direction of the screw axis with relation to the bonds, which in this orientation is nearly the N–S axis; similarly, the mirror plane is close to the equatorial plane of the diagram. The angles between the C–Cl_1, and C–Cl_2 directions and the screw axis are respectively 15° and 77°. Since the molecules lie about parallel to (100) by reason of the short a axis, these angles are approximately equal to those in the a-axis projection and were used to define the orientation of the molecule in that projection. The chlorine coordinates were then obtained by assuming a distance of 3·15 Å from the center of the molecule to the atoms. These positions were roughly checked by noting that they were such as gave large structure-factor contributions to the strong higher-order reflections and some small readjustment of the positions were made. The coordinates obtained were Cl_1 (0·29, 0·10) and Cl_2 (0·07, 0·30).

Using the chlorine contributions only, the signs of 60 structure factors were determined for use in the first Fourier projection, which is shown in Fig. 5(a). Although this showed some false detail, the position of the molecule was clearly confirmed. The second synthesis, with signs obtained from structure factors calculated with all the atomic parameters derived from the first synthesis, is shown in Fig. 5(b).

The scale and a uniform isotropic temperature factor were deduced from a Wilson plot, and the parameters were further refined by difference synthesis. With isotropic temperature factors of $B_{\mathrm{Cl}} = 0{\cdot}5$ Å^2, $B_{\mathrm{C}} = 2{\cdot}0$ Å^2, and the atomic coordinates given in Table 3, the reliability factor was 0·20.

Table 3. *Atomic coordinates from X-ray Fourier projection*

	y	z
Cl_1	0·2805	0·0915
Cl_2	0·0690	0·2985
C_1	0·125	0·038
C_2	0·029	0·132
C_3	−0·092	0·083

For comparison with the more accurate n.q.r. data, which became available later in the work, the orientation of the molecule was determined within the limits of the information given by the single a-axis projection. Two ellipses were drawn, one passing through the carbon positions, the other with the same orientation of major and minor passing through the two chlorine atoms (see Fig. 4). The molecular-orientation data given in Table 2 were then obtained by projecting the carbon ellipse on to a circle the diameter of which was the major axis of the ellipse. The C–Cl bond orientation were obtained similarly from the ellipse passing through the chlorine positions. These values are independent of assumptions about bond lengths but will correspond to the true orientation of the molecule only in so far as the benzene ring is regular and planar. The mean bond lengths taken from the major axis of the ellipse were C–C = 1·39, C–Cl = 1·74 Å, in good agreement with the accepted values.

Correlation of the structural results

The n.q.r. and X-ray results are shown in Table 2 in terms of direction cosines and angles with respect to the orthogonal crystal axes a, b, and $c' \equiv c \sin \beta$.

The most accurate structure information from the n.q.r. is that for the C–Cl bond directions. This can be compared with the X-ray data either for the C–Cl bonds or for the Cl–Cl′ vectors through the center of symmetry. The correlation is good with the exception of the angle between the a axis and C_1–Cl_1, which was particularly unfavorable orientation for determination from the X-ray electron-density projection. The most direct comparison is between the n.q.r. and the X-ray C–Cl bond directions; on the other hand, the Cl–Cl′ vectors are likely to be the more accurate X-ray values since they are independent of the carbon atom positions. In fact the agreement is somewhat better for the latter, being within about 2° overall and better than 1° for the mean deviation (excluding C_1–Cl_1 versus the a axis), as against within about 4° and less than 2° for the mean of the direct comparison of the bond directions. Clearly any information relating to out-of-plane bending of the C–Cl bonds which could be obtained from a comparison of these measurements is within the experimental errors of the X-ray analysis.

The angle between the C_1–Cl_1 and C_2–Cl_2 is 63° 30′ from the n.q.r., as compared with 64·5° between the Cl–Cl′ vectors from the X-ray analysis. A similar variation of about 1–2° is obtained by comparing the orientations in projection (see Table 2). For the axes in the plane of the molecule, L and M (see Fig. 4), the mean difference between the n.q.r. and X-ray orientation data is less than 2½°. Much larger discrepancies appear for the orientation of the normal to the plane of the molecule. This is not surprising since in the X-ray analysis the orientation of the molecule is such as to make it impossible to obtain more than a rough estimate of the tilt of the benzene ring from the a-axis projection alone.

The n.q.r. data are estimated to have a standard deviation of 1° on the angles as given in Table 2. The accuracy of the X-ray values is difficult to estimate since it will vary with the orientation of the bond direction or molecular axis relative to the plane of the electron-density projection. There are no values in the correlation for which the X-ray results significantly contradict the more precise n.q.r. orientations.

The agreement on the orientation of the Cl bonds shows that effect of the various perturbing factors on the principal axis of the electric field gradient is at most only the order of the combined uncertainties of the X-ray and n.q.r. measurements. For a planar molecule the orientations of these two bonds would prescribe the normal to the benzene ring, so that the further agreement on this direction is to be expected. However, it is gratifying to find that the orientation of the π-bonding chlorine orbitals also appears to be given with reasonable accuracy by the asymmetry of the n.q.r. zero-splitting loci for the individual chlorines (directions indicated by π(I), π(II), in Table 1*a*). Since the asymmetry is small for halogens, it is a more delicate feature to detect and it is also more subject to the influence of such perturbations as thermal vibrations, strains, and unanticipated secondary bonding structures.

Discussion of the steric strain in the molecule

In this molecule there is a possibility of strain arising from the non-bonding interaction of the chlorine atoms, which will increase the angle between adjacent C–Cl bonds over the value of 60°. From electron-diffraction work with similar molecules Bastiansen & Hassel (1947) have concluded that the principal distortion consists of a bending of the bonds out of the plane of the benzene ring. Their model of this molecule would accordingly have each pair of chlorines split with one atom above and one below the plane of the ring, each bond being strained by 12–18°.

Although there is some uncertainty due to our approximate model of the n.q.r. interaction (the precision that is desired for the strain problem exceeds that of the correlation with the X-ray results), we can make a preliminary application of the results. The value of $63\pm1°$ between the σ-bond directions for the adjacent chlorines confirms the presence of strain. However, with this molecule it is impossible to determine by n.q.r. whether the deviation from 60° represents bending within the benzene plane or whether out-of-plane bending is also involved. If it were pure out-of-plane bending, each chlorine bond would have to lie about $10\pm2°$ out of the benzene plane, a result of the same order as that suggested by Bastiansen & Hassel (1947).

With out-of-plane bending, there can be three steric isomers of this molecule. If u and d indicate whether a chlorine is up or down with respect to the benzene ring (horizontal), taken in the order 1, 2–4, 5, the u, d–d, u molecule has a center of symmetry, and only two bond directions will be distinguished by n.q.r. (n.q.r. discerns only the orientation of the axis, not the sense of direction). The u, d–u, d and the d, u–d, u molecules are right- and left-handed versions of a molecule for which n.q.r. would locate four different bond directions. For a crystal containing only one isomer the n.q.r. results would agree with the space group determined by X-ray diffraction in requiring that if the real molecule is one of the out-of-plane isomers it must be the one with the center of symmetry.

Because the X-ray diffraction process can take a spatial average over many unit cells, a single-crystal compound of a random mixture of out-of-plane isomers could give diffraction pattern very similar to that for the planar 'average' molecule, although with abnormally large apparent 'temperature factors'. However, this seems to be ruled out by the clearly defined n.q.r. data, since an observed n.q.r. spectrum is always the total of the spectra contributed by each individual nucleus. Apart from the multiplicity of bond directions that n.q.r. should show for such a random mixture, the local small variations in environment of the individual molecules would cause differences in the pure quadrupole frequency from one molecule to the next, thus creating what would be observed as an anomalous line width (Dean, 1955).

An alternate possibility was also pointed by Bastiansen & Hassel (1947). Even if the staggered out-of-plane configuration represents a potential minimum for a pair of chlorines, the potential barrier between it and the reversed configuration (u, d to d, u) could be low enough to permit frequent conversion between the two forms. The X-ray result would be about the same as the random mixture mentioned above. However, in n.q.r. the effective electric field gradient at a nucleus is the time average, so that if the conversions were frequent enough the n.q.r. data might also represent the average molecule.

Since it is not known what effects a rapid conversion between isomers may produce in n.q.r., this process cannot be ruled out unequivocally. However, the spectra in the present sample appear to be quite normal as to line width, relaxation times, and temperature dependance, and we may provisionally assume that this normality rules out the rather violent fluctuations in field gradient which would accompany the conversion process. Thus, if there is out-of-plane bending, we are led to choose the fixed centric isomer as being correct, with the magnitude of the strain essentially that proposed by Bastiansen & Hassel (1947).

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The Structure of Annotinine Bromohydrin*

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Crystals of annotinine bromohydrin are orthorhombic, space group $P2_12_12_1$ with $a = 11{\cdot}89$, $b = 13{\cdot}40$, $c = 9{\cdot}68$ Å and $Z = 4$. Its crystal and molecular structure has been determined from a three-dimensional Patterson synthesis interpreted by vector convergence method. Ambiguities arising from the presence of the bromine atom close to a special position ($x = 0{\cdot}779$, $y = 0{\cdot}263$, $z = 0{\cdot}012$) were discriminated by simultaneous study of the agreement between observed and calculated data and of ϱ_o and $\varrho_o-\varrho_c$ maps for the three projections. Final atomic coordinates have been obtained from a three-dimensional observed differential synthesis which was not corrected for finite summation errors. Six-membered rings of the molecule are in 'chair' form and the bromine atom is *trans* with respect to the hydroxyl group. The carbon atom of the methyl group is directed towards the lactone ring.

Introduction

The alkaloid annotinine has been isolated by Manske & Marion (1943) from species of the *Lycopodium* family. A great deal of work has been done on the chemistry of this compound, and several different structures have been proposed on the basis of chemical degradation studies (Anet & Marion, 1954; Wiesner, Valenta & Bankiewicz, 1956; Martin-Smith, Greenhalgh & Marion, 1957).

In the present investigation no chemical assumptions have been made in deriving the skeleton structure of annotinine bromohydrin and chemical evidence has been used only in distinguishing the oxygen and nitrogen atoms from carbon atoms. The structure had already been determined from this X-ray analysis and was at the refinement stage (Przybylska & Marion, 1957) when Wiesner, Ayer, Fowler & Valenta (1957) proposed a complete structure for annotinine. Their structure has been fully confirmed by our results.

X-ray crystallographic data for several *Lycopodium* alkaloids have been published by Knop & MacLean (1952), but annotinine bromohydrin was not included in their work. It has been chosen for the present study since the bromine atom is directly bonded to a large-membered ring (MacLean & Prime, 1953).

Experimental

Crystal data

Pure, chemically analysed, large colourless crystals of annotinine bromohydrin, $C_{16}H_{22}O_3NBr$, were prepared by Dr M. Martin-Smith, who obtained this compound by heating annotinine with 20% HBr. This reaction was first described by Manske & Marion (1947). The crystals were recrystallized from ethyl alcohol. They were found to belong to the orthorhombic disphenoidal class. They were elongated along the c axis and showed prism faces (110), sphenoids (111) and small brachypinacoids (010). The systematic extinctions determined uniquely the space group as $P2_12_12_1$, (D_2^4). The unit-cell dimensions, measured from precession photographs (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å) are:

$$a = 11{\cdot}89\pm0{\cdot}03,\quad b = 13{\cdot}40\pm0{\cdot}03,\quad c = 9{\cdot}68\pm0{\cdot}02 \text{ Å}.$$

There are four molecules per unit cell. The density measured at 23·2 °C. by flotation method using carbon tetrachloride and 1,1,1-trichloroethane mixture was found to be 1·528 g.cm.$^{-3}$. The calculated value is 1·533 g.cm.$^{-3}$. The number of electrons per unit cell, $F(000)$, is 736. The absorption coefficient for Cu $K\alpha$ radiation is 39·5 cm.$^{-1}$.

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