versus electron concentration are shown in Fig. 1. The fault probability is seen to decrease with electron concentration as in the results of Stratton & Kitchingman (1965). This suggests that the faulting probability depends upon the relative free energies of the hexagonal and face-centered cubic phases and electron concentration is only important in so far as it affects these energies. The fault probability is therefore not a function of electron concentration but depends upon the relative free energies of hexagonal and face-centered cubic phases.

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Structural Investigation of Hydrogen Bonds in Deuterated Pentaerythritol by Nuclear Magnetic Resonance

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A single crystal of pentaerythritol with deuterium substituted on the hydroxylic hydrogen positions was investigated by means of nuclear magnetic resonance. The quadrupole splittings of the deuterium magnetic resonance lines were measured as a function of the orientation of the external field with respect to the crystal axes. The electric field gradient tensors at the positions of the deuterium nuclei were evaluated and compared with the results obtained by Chiba in other hydrogen-bonded systems. The results provide evidence for a configuration obtained by taking the oxygen and carbon parameters from Shiono, Cruickshank & Cox (*Acta Cryst.* (1958), **11**, 389) and the hydrogen parameters from Hvoslef (*Acta Cryst.* (1958), **11**, 383).

1. Introduction

Pentaerythritol, $C(CH_2OH)_4$, is probably the only organic compound with exclusively alcoholic hydroxyl groups which can be rather easily obtained in large single crystals. The symmetry of pentaerythritol has been a point of discussion for a long time, but was established as being tetragonal with space group $I\bar{4}$ by Llewellyn, Cox & Goodwin (1937). The external symmetry of the crystals suggests the existence of a fourfold rotation axis, which is, however, not compatible with the internal structure.

The atomic positions were derived by, among others, Llewellyn, Cox & Goodwin (1937) and Shiono, Cruickshank & Cox (1958) from X-ray measurements, while Hvoslef (1958) has performed a neutron-diffraction study. The central carbon atoms are situated at the corners and in the centre of the tetragonal unit cell (Fig. 1). Four molecules whose central carbon atoms form a square in the (001) plane are linked by hydrogen bridges between the oxygen atoms. Four oxygen atoms are situated near the (001) plane at the corners of a distorted square. Between two oxygen atoms, but not exactly on the line connecting these oxygen atoms, a hydrogen atom is found (Hvoslef, 1958). It follows from the space group symmetry that the four hydrogen bridges are crystallographically equivalent. Quantitatively the results of Shiono, Cruickshank & Cox differ considerably from those of Hvoslef, more particularly in so far as the values of the z coordinates are concerned (Table 1). These discrepancies are reflected particularly in the orientations of the hydrogen bonds quoted by the two authors. According to Hvoslef the line connecting the two oxygen atoms of a hydrogen

bond is situated almost in the (001) plane whereas Shiono *et al.* find an angle of $\pm 7°$ with the (001) plane. The distance between the two neighbouring oxygen atoms is 2·74 Å according to Hvoslef and 2·70 Å according to Shiono *et al.* Hvoslef, using the method of isomorphous replacement of H by D, found an O–H distance of $0·94 \pm 0·03$ Å.

At a temperature of about 185 °C a first-order phase transition sets in, corresponding to a loosening of the hydrogen bonds. The molecules in the lattice show a disorder of orientation, the symmetry changes from tetragonal to cubic and the crystal becomes 'plastic'. (Nitta & Watanabé, 1938; Hoshino & Nakasaki, 1950; Nitta, Seki & Momotani, 1950; Nitta, Seki, Momotani, Suzuki & Nakagawa, 1950; Nitta, Watanabé, Seki & Momotani, 1950). The behaviour of pentaerythritol at higher temperatures is very similar to that of other globular molecules (Perdok, 1942).

Pentaerythritol offers two interesting possibilities for an investigation by means of nuclear magnetic resonance (n.m.r.):

(1) The phase transition will give rise to a narrowing of the n.m.r. line when the transition temperature is passed. This effect has been observed by us in pentaerythritol powder. At 160 °C already a narrowing sets in. The mean square of the line width, which is about 20 Oe² at temperatures below 160 °C falls to less then 0·1 Oe² above the transition temperature. However, these measurements did not reproduce very well, probably because of the bad heat conductivity in the sample giving rise to large temperature inhomogeneities. We will not deal with the results here, because we believe that the inaccuracy of the measurements does not allow a quantitative analysis. The measurements will be continued with single crystals and better precautions for the establishment of temperature homogeneity.

(2) Nuclear resonance of deuterium substituted at the hydroxylic hydrogen positions will give information about the nature of the hydrogen bond. The deuterium nucleus has a quadrupole moment, the spin quantum number being $i = 1$. Electric field gradients at the position of the deuteron give rise to a splitting of the n.m.r. lines. The splitting is dependent on the direction of the external magnetic field with respect to the crystal axes. It is possible to determine the field gradient tensor from a systematic investigation of the quadrupole splittings as a function of the direction of the external field. Investigations of this type have been carried out in some other crystals (Chiba, 1963, 1964; Weissmann, 1966; Jackson & Rabideau, 1964; Waldstein, Rabideau

& Jackson, 1964), but, as far as the authors know, not in compounds with alcoholic hydrogen bonds. Our work on quadrupole splittings will be discussed below.

2. Experimental

Single crystals of deuteropentaerythritol were obtained by slowly cooling a saturated solution of partially deuterated pentaerythritol in heavy water. The addition of a small amount of hydrochloric acid proved to be useful to prevent the formation of brownish condensation products. According to the experience of Kuznetsova & Gavrilova (1962) the temperature range of cooling was chosen in the vicinity of 80 °C. At room temperature a cloudy white deposit was formed.

Crystal growing was carried out inside a double walled glass vessel. The temperature was maintained by a steady stream of warm water between the glass walls. The water was supplied and kept at constant temperature by a Bühler pumping thermostat. All the equipment was in turn placed in a room which was kept at a temperature which was constant to within 0·1 °C. The liquid had to be allowed to cool very slowly. As a typical example a crystal of about 0·95 cm³ was obtained by cooling a 20 cm³ solution from 83 °C to 79 °C in 8 days.

It was assumed that by growing from a solution in heavy water only the hydroxylic hydrogen atoms are
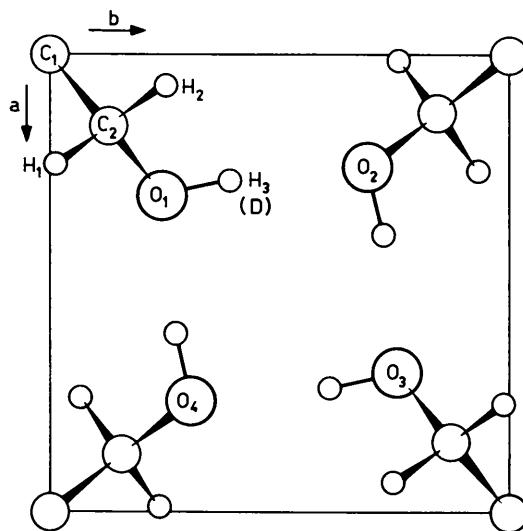

Fig. 1. Projection of the unit cell of pentaerythritol on to the (001) plane, according to Hvoslef (1958). The molecule at the body centre of the unit cell has been omitted.

Table 1. *Parameters of* C *and* O *positions*

	C			O		
	Hvoslef	Shiono *et al.*	s.d.	Hvoslef	Shiono *et al.*	s.d.
x	0·157	0·1621	0·0016	0·310	0·3172	0·0013
y	0·126	0·1242	0·0016	0·243	0·2476	0·0013
z	0·099	0·1059	0·0018	0·004	0·0188	0·0015

substituted by deuterium. Proton magnetic resonance measurements, undertaken incidentally, supported this assumption. The degree of deuteration of the hydroxylic hydrogen positions was estimated to be 90–95%, from the known solubility of pentaerythritol in water.

The external crystal shape was a tetragonal pyramid or bipyramid. From the symmetry of the point group ($\bar{4}$) it follows that the general form is a tetragonal bisphenoid, but the morphological development suggests the existence of a fourfold rotation axis. Only a set of four crystal faces belonging to a pseudo-form was well developed because the crystals tended to grow at the surface of the solution.

The (001) plane is characterized by a set of four sharp edges forming a rectangle and by perfect cleavage. These features were a great help in the orientation of the crystal. X-ray rotation photographs showed that each of the edges was parallel to either the a or the b axis of the tetragonal unit cell.

The deuteron magnetic resonance experiments were performed with the help of a 12" Varian magnet and a Varian VF 16 detecting system with 'fieldial' field control system. The system was adjusted for the dispersion mode and phase sensitive detection of the a.f. signals was applied. In order to obtain a reasonable signal to noise ratio a Computer of Average Transients (CAT) was used. Typical values for the different settings were: Frequency 10 MHz and 6·5 MHz respectively for two series of measurements, scanning amplitude 1 kOe, scanning time 1 minute, modulation 6 Oe at 20 Hz. The measurements were repeated during $\frac{1}{2}$–1 hour with use of a sawtooth scanning. The signals were then read out on a X–Y recorder. A typical example of the signal accumulated in the CAT is shown in Fig. 2. The scanning field was calibrated by making overlapping recordings of deuterium resonance in D_2O at different frequencies with the same detection system as was used for the measurement on pentaerythritol.

The quadrupole splittings of the deuterium resonance are strongly dependent on the orientation of the crystal with respect to the external field. The full benefit from the high accuracy, that in principle can be obtained, can only be realized if the crystal is accurately oriented with respect to the magnetic field. This has been done in the following way. Because of the (pseudo-)fourfold rotation axis (in fact the $\bar{4}$ axis) it was necessary to mark one of the crystal faces. A set of coordinate axes

X, Y, Z with respect to the crystal was then defined by choosing the Z axis parallel to the tetragonal c axis and the X and Y axes parallel to the edges mentioned in the (001) plane. There remains an ambiguity in the relation between these axes and the crystallographic axes, because the external symmetry does not allow us to distinguish between the positive and the negative c direction, i.e. the projection of the atoms on to the XY plane, observed if one 'looks' along the positive Z axis may be either similar to that in Fig. 1 or to its mirror image.

A lucite crystal holder (Fig. 3) was constructed, that could be mounted to the Varian probe head, if the head was provided with the thick aluminum bottom plate normally used in connexion with the variable temperature accessory. In the crystal holder the crystal can be mounted with adhesive wax to the top surface of a lucite cylinder. This surface is exactly perpendicular to the axis of the cylindrical hole of the Varian probe head. The cylinder can be rotated about this axis and the angle of rotation can be read on a cylindrical scale S. The top C of the cylinder can be removed from the crystal holder and screwed to a two circle goniometer for careful adjustment of the crystal. Finally the Varian probe head had to be mounted exactly parallel to the pole faces of the magnet. The final accuracy obtained in this way is estimated to be within $\pm 1°$.

Measurements were performed while the external magnetic field was rotated in the XY plane and in the YZ plane. Because from these measurements the electric field gradients at the position of the deuterons cannot be derived without ambiguity, also measurements were performed with the external field in a plane through the Z axis which makes an arbitrarily chosen angle of 18° with the YZ plane.
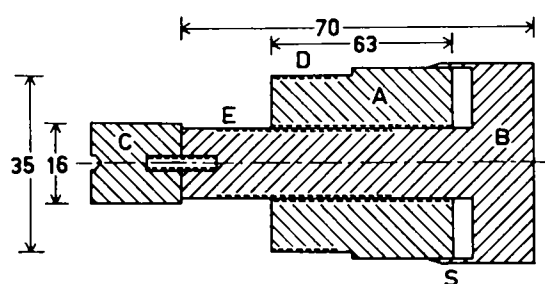

Fig. 3. Probe holder. The screw-thread D fits to the bottom plate of the probe holder. S is the cylindrical scale; the top C of the cylinder can be screwed to a goniometer.
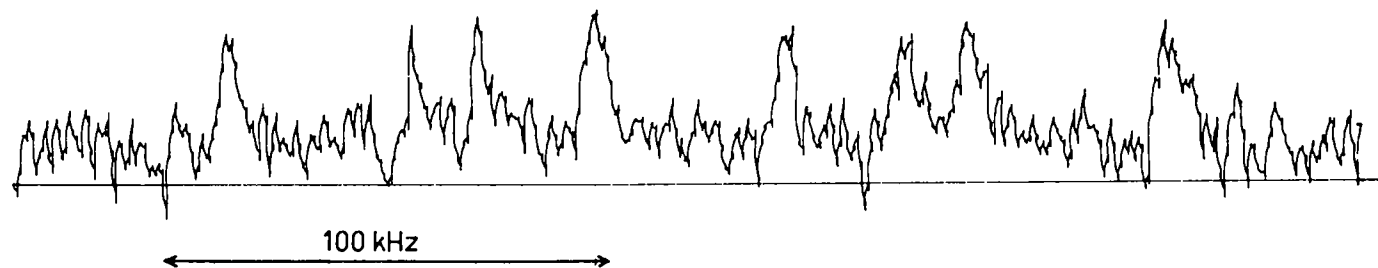

100 kHz

Fig. 2. Example of recorded splitting of the resonance line, accumulated in the 'CAT'. The recording corresponds to a value of $\alpha = 33°30'$ with H_0 in the YZ plane. The absorption signals are in arbitrary units, and the deuteron magnetic resonance splittings are given in kHz.

3. Experimental results and analysis

Fig. 4 illustrates the quadrupole splittings of the n.m.r. lines as a function of the direction of the external field H_0. H_0 was rotated in the YZ plane; α denotes the angle between H_0 and the Y axis. Although the field was varied during the measurements, the splittings are expressed in frequency units (kHz of the deuterium resonance frequency).

Fig. 5 shows the same splitting for H_0 in the XY plane. Here α is the angle between H_0 and the X axis.

The analysis of the data was carried out following the method described by Volkoff, Petch & Smellie (1952). The experimental data should then fit their equation (9), which we write as:

$$2\Delta v = A + B\cos 2\alpha + C\sin 2\alpha$$
$$= A + (B^2 + C^2)^{1/2}\cos 2(\alpha + \delta). \quad (1)$$

Δv is the displacement of the line in frequency units. If the constants A, B and C are properly chosen an accuracy of about 1·5 kHz can be achieved in fitting the experimental data to equation (1). The constants A, B and C are then related to the components of the field gradient tensor by equation (10) of Volkoff et al., which reads for rotation about the X axis of the crystal:

$$\begin{aligned} A_X &= \tfrac{1}{2}K(\Phi_{YY} + \Phi_{ZZ}) = -\tfrac{1}{2}K\Phi_{XX} \\ B_X &= \tfrac{1}{2}K(\Phi_{YY} - \Phi_{ZZ}) \\ C_X &= -K\Phi_{YZ} \end{aligned} \right\} \quad (2)$$

where

$$K = \frac{3e\Phi(2m - 1)}{2i(2i - 1)h} \quad (3)$$

if a transition $m \to m - 1$ is observed. Here $e\Phi$ is the quadrupole moment of the nucleus, i its spin quantum number, m the magnetic spin quantum number and h Planck's constant. Φ_{XX}, Φ_{XY}, etc. are components of the field gradient tensor. For rotation about the Y and Z axes analogous formulae can be derived by applying cyclic permutation to equation (2).

It follows from the point symmetry of the crystal that polar vectors like the electric field occur in sets of four; if one vector is given by (X_0, Y_0, Z_0) the remaining vectors are $(-X_0, -Y_0, Z_0)$, $(Y_0, -X_0, -Z_0)$ and $(-Y_0, X_0, -Z_0)$. These four vectors correspond to the four deuterons in the distorted square near the (001) plane of the unit cell. The nuclear spin of the deuteron being $i = 1$ generally eight resonance lines can be expected. This is in agreement with the pattern of Fig. 4. By applying the point group symmetry relations to the equations for A_Z, B_Z and C_Z (rotation about the Z axis) one can derive that in this case the lines coincide in pairs, the number of lines being reduced to four. This is in agreement with the pattern of Fig. 5 and is also reflected in the symmetry of the pattern of Fig. 4 with respect to the line $\alpha = 0°$, where the curves cross in pairs. For $\alpha = 90°$ all deuteron resonance lines have the same quadrupole splitting.

By applying equations (1) and (2) to the curves of Fig. 4 it is possible to determine:

(1) $\Phi_{XX}, \Phi_{YY}, \Phi_{ZZ}$ and Φ_{YZ} for each of the deuterons.
(2) Φ_{XZ}, by making use of the appropriate symmetry relations.

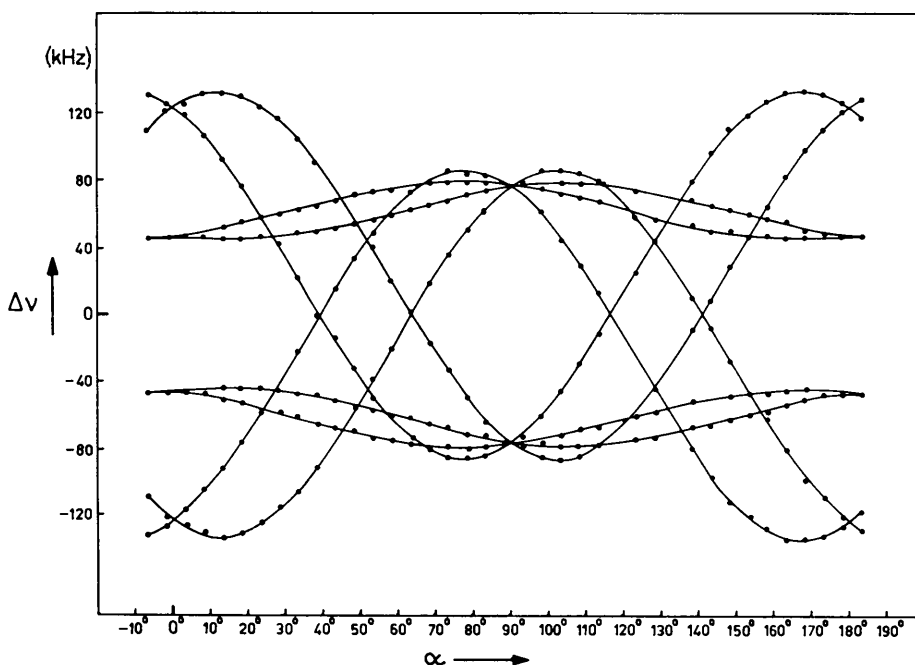However, the curves are not 'labelled', i.e. we do not know which deuteron is responsible for each of the

Fig. 4. Splitting of the resonance lines for H_0 in the YZ plane; α is the angle between H_0 and the Y axis.

curves. For this reason there remains an ambiguity in the sign of the different values of Φ_{XZ}, as shown in Table 2, A.

The measurements with H_0 in the XY plane yield Φ_{XX}, Φ_{YY} and Φ_{ZZ} values that are in good agreement with those from the measurements in the YZ plane (see Table 2, A,B). The remaining ambiguity in the sign of Φ_{XZ} is removed by measurements in an oblique plane (see § 2). By performing the appropriate tensor transformation, it can be shown that the combinations of tensor components given in Table 2, C, are the only ones that are compatible with all the measurements. There still remains another ambiguity which cannot be removed by our measurements: it is allowed to multiply all the components of each tensor by -1 without making them conflict with the experiments.

The four tensors were diagonalized with the help of an electronic computer (Telefunken TR4 of the University Computing Centre). For each tensor we find a set of eigenvalues together with the corresponding principal axes. They are given for one of the field gradient tensors in Table 3. The eigenvalues and principal axes of the remaining field gradient tensors are related to those of the given tensor by the appropriate symmetry operations.
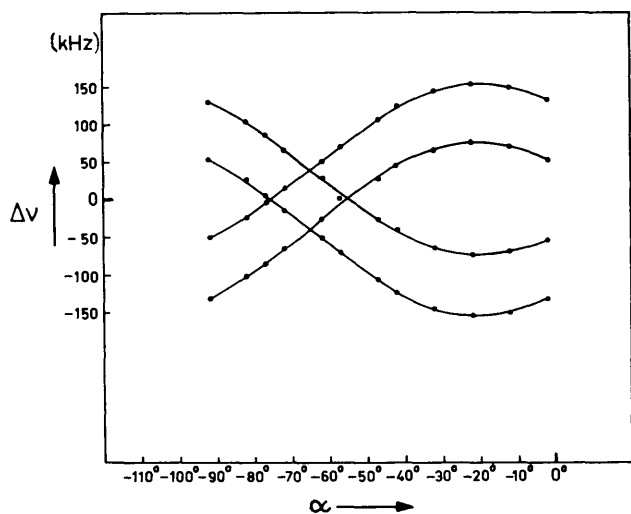

Fig. 5. Splitting of the resonance lines for H_0 in the XY plane; α is the angle between H_0 and the X axis.

The eigenvalues of the tensor given in Table 3 are denoted by $\Phi_{X'X'}$, $\Phi_{Y'Y'}$ and $\Phi_{Z'Z'}$ ($|\Phi_{X'X'}| < |\Phi_{Y'Y'}| < |\Phi_{Z'Z'}|$); the corresponding principal axes are characterized by unit vectors $P_{X'}$, $P_{Y'}$ and $P_{Z'}$.

Table 3. *Eigenvalues (multiplied by K) and directions of principal axes of one of the field gradient tensors*

Eigenvalues of $K\Phi$		Components of the unit vector parallel to each principal axis		
		X	Y	Z
$K\Phi_{Z'Z'}$ 318kHz	$P_{Z'}$	0·925	0·332	0·186
$K\Phi_{Y'Y'}$ −178kHz	$P_{Y'}$	−0·307	0·364	0·879
$K\Phi_{X'X'}$ −140kHz	$P_{X'}$	−0·224	0·870	−0·439

The quadrupole coupling constant turns out to be 212 kHz; the asymmetry factor $\eta = 0.12$.

4. Discussion

It is not possible to derive from the measurements and the known crystal structure a one to one correspondence between each of the four field gradient tensors and the four deuterons in the distorted square. But comparison with earlier work (Chiba, 1964) makes a reliable assignment possible.

First of all, the orientation of our XYZ coordinate system relative to the crystal axes should be determined. Apart from the sign we know that the Z axis is by definition parallel to the c axis of the crystal. An X-ray (Weissenberg) investigation showed that the crystallographic a and b axes are each parallel to either the X or the Y axis.

We will use the empirical rule, that the principal axis $P_{Z'}$ of the field gradient tensor should be almost parallel to the direction of the hydrogen bond (Chiba, 1964). Generally the deviation is not more than a few degrees although there are exceptions to this rule. Experiments have also shown that in hydrogen bonds there might be a rather considerable difference between the O–H and O$\cdots$O directions. By a tentative inspection we will find out which of the O–H or O$\cdots$O directions allowed by the external symmetry of the crystal corresponds most probably to the tensor given in Table 3 (arbitrarily chosen out of the set of four).

Consider first the projections of the hydrogen bond and of $P_{Z'}$ onto the XY plane. The projection of $P_{Z'}$ makes an angle of $+19°30'$ with the X axis. Following

Table 2. *Tensor components of $K\Phi$ in kHz*

	A H_0 in YZ plane				B H_0 in XY plane		C Final values of the field gradient components			
$K\Phi_{XX}$	94·1	96·3	−247·5	−246·4	94·2	−250·8	$K\Phi_{XX}$	94·5	94·5	−248·0	−248·0
$K\Phi_{YY}$	−247·2	−248·3	93·7	94·1	−250·8	94·2	$K\Phi_{YY}$	−248·0	−248·0	94·5	94·5
$K\Phi_{ZZ}$	153·1	151·9	153·9	152·3	156·6	156·6	$K\Phi_{ZZ}$	153·6	153·6	153·6	153·6
$K\Phi_{XY}$					144·6	−144·6	$K\Phi_{XY}$	144·6	144·6	−144·6	−144·6
$K\Phi_{YZ}$	89·2	−89·2	−15·0	16·8			$K\Phi_{YZ}$	89·2	−89·2	−15·9	15·9
$K\Phi_{XZ}$	±15·9*	∓15·9*	±89·2*	∓89·2*			$K\Phi_{XZ}$	−15·9	15·9	−89·2	89·2

* Use has been made of symmetry relations.

Hvoslef the angle φ between the projection of the O–H direction and the crystallographic a axis is $+14°30'$. Then the angle relative to the X or Y axis can still be $+14°30'$ or $-14°30'$ depending on whether the XY plane as seen along the positive Z direction looks similar to Fig. 1 or to its mirror image. It is reasonable to reject the possibility of the minus sign on account of the general rule mentioned. Comparison with the $O\cdots O$ direction from Shiono *et al.* instead of the O–H direction from Hvoslef leads to the same conclusion.

Secondly the angle ψ with the XY plane should be considered. $P_{Z'}$ makes an angle of $10°30'$ with the (001) plane while the O–H direction from Hvoslef and the $O\cdots O$ direction from Shiono *et al.* make angles of $\pm 0°30'$ and $\pm 7°$ respectively with the (001) plane. It should be noted that now directions corresponding to both signs occur in the crystal. Best agreement is obtained here by choosing the value $+7°$ by Shiono *et al.* The results are summarized in Table 4, where also the calculated angles between the principal axis $P_{Z'}$ and possible $O\cdots O$ or O–H directions are tabulated.

Closer inspection of the data mentioned in Table 4 shows that there is a strong evidence for a structure in which the positions of the atoms are found by taking the oxygen positions from Shiono *et al.* and the hydrogen positions from Hvoslef (row 3 of Table 4). For the following reasons we believe that this is a reasonable proposition for the positions of the deuterons and oxygen atoms.

(1) The corrections made by Shiono *et al.* to the work of Llewellyn, Cox & Goodwin pertain for the greater part to the z parameters of the carbon and oxygen positions. Hvoslef's determination of these parameters is probably less accurate.

(2) The hydrogen x and y parameters from Hvoslef may be rather accurate, just as his x and y parameters for the carbon and oxygen positions agree rather well with those of Shiono *et al.*

(3) Possible inaccuracy in Hvoslef's determination of the oxygen z parameters does not imply that the hydrogen positions are affected in the same degree, because they are situated somewhere between the two oxygen atoms and therefore are confined to a small layer near the (001) plane.

For further comparison with the rules mentioned by Chiba we refer again to Table 4. $P_{Y'}$ should be perpendicular to the COD plane. The deviation from the normal is given in Table 4. Again the best agreement is obtained by taking the hydrogen position from Hvoslef and the oxygen and carbon positions from Shiono *et al.*

In Fig. 6, taken from Chiba's paper, the quadrupole coupling constants of hydrogen bonds in different materials are plotted against the $O\cdots O$ distance. Our value fits quite well to the other data. Also the value of the asymmetry factor η is within the range of values normally found.

Finally we may mention that the O–H distance of 0.935 Å corresponding to the proposed situation of the hydrogen and oxygen atoms is in serious disagreement with the relation between $O\cdots O$ distance and O–H distance given by Nakamoto, Margoshes & Rundle (1955). The same applies to the value of 0.94 Å for the O–H distance given by Hvoslef.

Dr H. J. C. Berendsen and Mr C. Migchelsen (Physical Chemistry Laboratory of the University) kindly put their nuclear resonance equipment at our disposal.
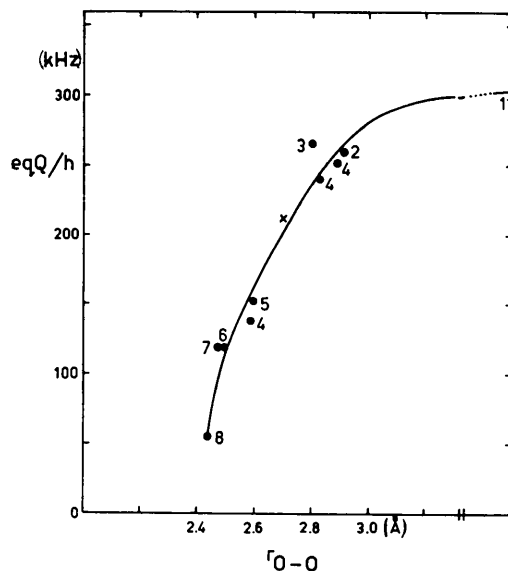

Fig. 6. Deuteron quadrupole coupling constant as a function of $O\cdots O$ distance; all data, except for pentaerythritol, taken from Chiba (1964) (1) HDO (free molecule), (2) $Li_2SO_4 . D_2O$, (3) $Ba(ClO_3)_2 . D_2O$, (4) $(COOD)_2 . 2D_2O$, (5) $KDCO_3$, (6) KD_2PO_4, (7) $ND_4D_2PO_4$, (8) K,D maleate, × Pentaerythritol.

Table 4. *Orientation of the principal axes relative to possible carbon, oxygen and deuterium positions*

	$O\cdots O$		O–D		Angle between $P_{Z'}$ and O–D	Angle between $O\cdots O$ and O–D	Normal to COD plane		Angle between $P_{Y'}$ and normal on to COD plane
	φ	ψ	φ	ψ			φ	ψ	
Shiono	9°	7°							
Hvoslef	8°30'	1°30'	14°30'	0°30'	11°30'	6°	−74°30'	−52°30'	16°
Hvoslef + Shiono	9°	7°	17°30'	8°30'	3°	8°30'	−58°0'	−58°30'	5°
$P_{Z'}$			19°30'	10°30'					
$P_{Y'}$							−50°	−61°30'	

Mr J. R. Luyten performed the diagonalization of the field gradient tensors with the help of the Telefunken TR4 Computer of the 'Rekencentrum' of the University. Dr P. Bennema helped in growing the single crystals. Mr S. Postma constructed the crystal holder.

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Optical Rotatory Power of Liquid Crystals

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A theory of the very high rotatory power exhibited by cholesteric liquid crystals is developed by the use of the Jones calculus for optical systems. The calculations are based on the model proposed by de Vries in which the liquid crystal is regarded as built up of a large number of thin birefringent layers arranged helically. When light is incident normal to the layers, *i.e.* along the screw axis, selective reflexion of one of the circularly polarized components takes place and the rotatory dispersion in the neighbourhood of the region of reflexion is anomalous. The reflexion curve and the amplitude attenuation factor, $\exp(-\xi)$, for circularly polarized light at normal incidence are derived as functions of wavelength by setting up difference equations closely similar to those formulated by Darwin in his dynamical theory of X-ray diffraction. Within the range of total reflexion, ξ is real, primary extinction occurs and the medium is highly circularly dichroic. The spectral width of the reflexion and the primary extinction coefficient predicted by theory compare favourably with the experimental values. Outside the region of total reflexion, ξ is imaginary and opposite in sign on opposite sides of the reflected band. This is responsible for the reversal of the sign of the rotation on crossing the band. The anomalous part of the rotation is a direct measure of the phase of the primary wave given by the dynamical theory.

Introduction

Friedel (1922) discovered that a certain class of liquid crystals, which he named 'cholesteric', have optical rotatory powers of the order of several thousands of degrees per millimetre. The very large rotation is associated with some other equally remarkable optical properties. When white light is incident on the surface of the liquid crystal, selective reflexion takes place over a small region of the spectrum, the wavelength of maximum reflexion varying with angle of incidence in ac-

cordance with Bragg's law. At normal incidence, the reflected light is circularly polarized; one circular component is totally reflected over a spectral range of some 200 Å, whilst the other passes through unchanged. Further, contrary to usual experience, the reflected wave has the same sense of circular polarization as that of the incident wave.

In the neighbourhood of the region of reflexion, the rotatory dispersion is anomalous and the sign of the rotation opposite on opposite sides of the reflected band. The behaviour is therefore similar to that of an