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A nuclear quadrupole resonance investigation of the structure of hexachlorobenzene. By

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The Zeeman effect in the nuclear quadrupole resonance of chlorine has been observed in a single crystal of hexachlorobenzene at −78 °C and −195 °C. The measured structure is the same at the two temperatures. The Zeeman constant-splitting loci have Laue symmetry $2/m$; hence the crystal system is monoclinic. The carbon–chlorine bond vectors of each centrosymmetric molecule are found to deviate negligibly from planarity.

Table 1. *Carbon–chlorine bond directions*

	Direction cosines		
Bond	X	Y	Z
1	0·350	±0·355	0·867
2	0·646	∓0·319	−0·694
3	0·988	±0·075	0·133

(Estimated uncertainty in directions, ±1°).

Since the nuclear quadrupole resonance (NQR) method cannot locate the non-symmetry axes a and c of the monoclinic cell, a coordinate system based on the b axis as Y, and the axis of intersection of the molecular plane and the ac plane as X, is chosen. Table 1 lists the direction cosines of the carbon–chlorine σ bonds in this coordinate system. The bonds are numbered according to the resonance frequency of the chlorine nucleus involved. The frequencies measured by Dean (1952) at −15 °C are $\nu_1 = 38{\cdot}017$ Mc; $\nu_2 = 38{\cdot}041$ Mc; $\nu_3 = 38{\cdot}051$ Mc. The measured temperature dependence of each is $d\nu/dT = -3$ kc °C^{-1}. No additional frequency measurements were made here.

Thus the angles between the bonds are: $(\sigma_1, \sigma_2) = 60\frac{3}{4}°$; $(\sigma_2, \sigma_3) = 58\frac{1}{2}°$; $(\sigma_3, \sigma_1) = 60\frac{3}{4}°$. The equations of the planes fitted by least squares through the carbon–chlorine vectors of each molecule are:

$$0{\cdot}000X \pm 0{\cdot}917Y - 0{\cdot}399Z = 0;$$

hence the molecular normals make angles of $23\frac{1}{2}°$ with the monoclinic b axis. The deviations of the sigma bonds from these planes are: $\pm 1\frac{1}{4}°$, ±1°, ±1° for bonds 1, 2, 3 respectively.

The single crystal used in this investigation was grown from the melt by the Bridgman technique (Lipsett, 1957). The normal to the liquid–solid interface during crystallization was found by the subsequent NQR measurements to have direction cosines 0·043, 0·829, −0·558. That is, the b axis was inclined 34° to the growth axis.

Measurements were made at −78 °C of the asymmetry in the electric field gradient tensors, defined by

$$\eta = (\partial^2 V/\partial x^2 - \partial^2 V/\partial y^2)/\partial^2 V/\partial z^2,$$

where V is the electric potential at the nucleus and x,y,z are the principal axes of the tensor, with z along the sigma bond. The result is $\eta = 0{\cdot}151 \pm 0{\cdot}016$ at each chlorine nucleus. The most important source of asymmetry is believed to be double bonding (Bersohn, 1954). This would mean that each x axis lies along a π bond, and here the x axes are found to make angles of 1°, $2\frac{1}{2}°$ and 7° (estimated uncertainty, ±10°) with the molecular normal, results which support the double bond hypothesis.

The hexachlorobenzene NQR has an unusual temperature dependence in that, as the sample warms from −78 °C, the signals remain strong until 0 °C is approached, when they begin to diminish in intensity, finally to disappear. There is no evidence of a crystalline phase change. It is likely that near 0 °C the libration of each molecule about its hexad axis has increased to such an amplitude that discontinuous reorientations of $\pi/3$ occur, at a rate which is comparable to the nuclear precession frequency, thus broadening the NQR signals beyond detection. If, as the temperature increases further, the reorientation rate were to become much greater than the precession frequency, the resonance should reappear, decreased in frequency (Dodgen & Ragle, 1956). Attempts to demonstrate this 'free rotation' by detection of the resonance at 200 °C were unsuccessful.

The only X-ray diffraction analyses on hexachlorobenzene reported to date (Lonsdale, 1931: Tulinsky & White, 1958) were based on observed reflexions from one zone, at room temperature. The crystal system is monoclinic, two molecules in a unit cell, space group $P2_1/c$. The structure described above is probably unchanged at room temperature (that is, in spite of the increased motion of the molecules, the mean orientations of the carbon–chlorine bonds are unchanged, as is the case from −195 °C to −78 °C) but the limited X-ray data preclude meaningful stereochemical comparison. A three-dimensional X-ray analysis based on data taken at several temperatures is needed. The results presented here could aid the analysis.

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References

Bersohn, R. (1954). *J. Chem. Phys.* **22**, 2078.
Dean, C. (1952). Thesis, Harvard University.
Dodgen, H. W. & Ragle, J. L. (1956). *J. Chem. Phys.* **25**, 376.
Lipsett, F. R. (1957). *Canad. J. Phys.* **35**, 284.
Lonsdale, K. (1931). *Proc. Roy. Soc. A.* **133**, 536.
Tulinsky, A. & White, J. G. (1958). *Acta Cryst.* **11**, 7.

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