The Crystal Structure of Hexabromobenzene: Constrained Refinement of Neutron Powder Diffraction Data

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Abstract

The structure of hexabromobenzene, C_6Br_6, has been determined at 300 K by neutron powder diffraction. The crystal is monoclinic, $a = 15 \cdot 357$ (4), $b = 4 \cdot 007$ (1), $c = 8 \cdot 364$ (2) Å, $\beta = 92 \cdot 65$ (2)°, space group $P2_1/n$, $Z = 2$. The problem is well suited for a constrained refinement with the program *EDINP*. Within the accuracy of the analysis the orientation of a planar molecule is found and all intramolecular separations correspond to normal van der Waals interactions. No explanation of the multiple-crystal formation can be proposed and, in fact, packing considerations would support twinning on (101) which has not been observed.

Introduction

Hexabromobenzene is a molecular crystal whose cell dimensions at room temperature have been reported by Herbstein (1963). The molecular geometry of C_6Br_6 was established in a vapour-phase electron diffraction study by Bastiansen & Hassel (1947). The present paper reports the determination, through neutron powder diffraction, of the detailed structure.

A powder diffraction pattern was measured at room temperature on the PANDA instrument at AERE, Harwell. The run was carried out with an incident neutron wavelength of 1·54 Å and diffraction data were recorded at intervals of 0·1° of 2θ, between 8 and 80°, counting for about 55 s at each point. The summed counts from three detectors, spaced $5 \cdot 00 \pm 0 \cdot 03°$ apart in the equatorial (2θ) plane, were used in the structure refinement.

Structure determination

One of the advantages of the powder technique lies in that it can be used to study samples for which large single crystals are not easily obtainable. C_6Br_6 is particularly suited to this technique because formation of composite crystals occurs readily during crystal growth (Boonstra & Herbstein, 1963).

Herbstein (1963) reported the cell dimensions as $a = 15 \cdot 3816$ (10), $b = 4 \cdot 002$ (3), $c = 8 \cdot 3768$ (8) Å, $\beta = 92 \cdot 691$ (4)°, at 293 K from single-crystal X-ray photographs. It was shown that the structure was monoclinic, $P2_1/n$, with $Z = 2$.

In deriving an approximate trial structure we constructed a three-dimensional model with cardboard molecules which were adjusted to give the most favourable packing in the cell. Estimates of the atomic positions within the molecule were used to determine the molecular orientation in terms of the Eulerian angles φ, θ, ψ, defined according to Goldstein (1964). This structure was used as the starting point for the refinement.

Structure refinement

The structure was refined by least squares with the neutron powder profile refinement program *EDINP* (Pawley, Mackenzie & Dietrich, 1977). Strict constraints, as described by Pawley (1972), are easily applied and were used throughout refinement. The constraint applied in this case allowed the positioning of the atoms in the molecule to be governed by two parameters only: the C—C separation in the benzene ring and the C—Br length. The molecule was constrained to have a regular hexagonal shape and arranged so that one C—Br bond lay along the molecular X_m axis. This basic molecule remains planar at all times and lies in the molecular $X_m Z_m$ plane. Planarity of the molecule is assumed since any molecular distortion which might be present would not be detected with the low resolution of this work. The centre of the molecule is positioned on a symmetry cente at the origin and its orientation is determined by the rotation matrix $R(\varphi, \theta, \psi)$, where the Euler angles φ, θ, ψ are variable. The Euler angles and two bond lengths are refinement parameters, giving five structural parameters in the constrained model, compared with the 18 required for an unconstrained refinement.

Refinement of these parameters together with all the usual profile refinement parameters was stable and rapidly converged to $R = 9 \cdot 3\%$. This is defined as

$$R = \frac{\displaystyle\sum_{\text{scan}} |y^{\text{obs}} - y^{\text{calc}}|}{\displaystyle\sum_{\text{scan}} y^{\text{obs}}} \times 100\%,$$

where y^{obs} is the measured intensity at one point in the scan. Unit weights, which give a more stable refinement than statistical weights, are used throughout. The summation is over all the observed points, including the background regions, giving an R which reflects the reliability of the whole scan.

The final parameters for the constrained refinement are given in Table 1. The positions of the atoms in the orthogonal unit cell are given by $R(\varphi,\theta,\psi) \ x^{\text{molecule}}$; these and the final Euler angles are given in Table 2. The orthogonal cell has axes which are parallel to the crystal axes a and b except for the third axis which is parallel to c^*.

The molecular $X_m Z_m$ plane was found to be inclined at an angle of 18° to the ac plane of the crystal, presenting a choice for the description of the sense of tilt, which is governed, in this case, by the Eulerian angle ψ. This choice can be stated as follows: if the sense of tilt is taken to be ψ then the other possibility is obtained by altering ψ by π. This is equivalent to changing the monoclinic angle β to $180° - \beta$, which is a possible ambiguity as β is very near to a right angle. The choice of tilt direction was obvious after separate refinements had been made, the degree of fit being significantly poorer when the molecular orientation was described by the Eulerian angles $\varphi, \theta, \psi + \pi$.

The observed and calculated profiles are shown in Fig. 1. The measured points (dots) are compared with the best calculated fit (continuous line). It can be seen in Fig. 1 (especially in the difference plot of calculated − observed) that the agreement is good over most of the range of measurements. The fit becomes poorer at higher scattering angles where there is considerable overlap of the diffraction peaks. In the region 67 to 72°

Table 1. *The final parameters for the constrained refinement*

The peak shape full width at half height in degrees is $(u \tan^2 \theta + v \tan \theta + w)^{1/2}$. The errors given derive from the inverted least-squares matrix.

Scale factor		0·0667 (8)
Zero error in 2θ (°)		−0·075 (6)
Background count		256 (2)
Peak-shape parameters (deg²)	u	0·78 (13)
	v	−0·48 (10)
	w	0·18 (2)
Cell parameters	a (Å)	15·357 (4)*
	b (Å)	4·007 (1)*
	c (Å)	8·364 (2)*
	β (°)	92·65 (2)
Cell volume (Å³)		514·2
Overall isotropic temperature factor (B) (Å²)		0·43 (9)
C—C length (Å)		1·446 (9)
C—Br length (Å)		1·752 (16)
R (%)		9·3

* The errors for the cell edges are relative to each other, but are all systematically affected by the wavelength calibration error. The wavelength used was 1·5405 (4) Å.

Table 2. *Final coordinates of the atoms* (Å) *with respect to the orthogonal cell*

x and y are parallel to the monoclinic axes, z is along c^*. The orientation of the molecule is determined by the Euler angles (φ,θ,ψ) |2·707 (9), 2·697 (3), −0·320 (9)| (in radians).

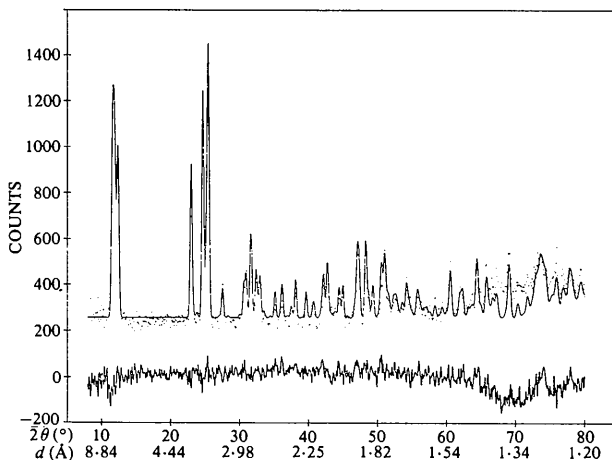|	x	y	z
C	−0·878	0·566	−0·999
C	−1·418	0·109	0·262
C	−0·539	−0·457	1·261
Br	−1·943	1·252	−2·210
Br	−3·136	0·242	0·580
Br	−1·193	−1·011	2·790

Fig. 1. Comparison of the observed (dots) and calculated (continuous line) neutron powder diffraction profile of $C_6 Br_6$ as a function of 2θ. The difference (heavy line) between the calculated and observed profiles ($y^{\text{calc}} - y^{\text{obs}}$) and the reflection interplanar spacing d are given.
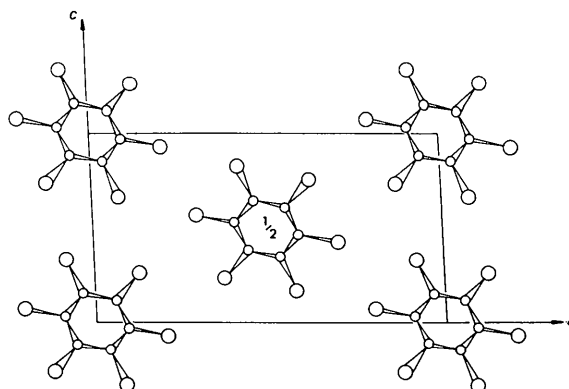

Fig. 2. Projection on the (010) plane of the structure of $C_6 Br_6$.

of 2θ there appears to be an excessive background, but it is apparent that the calculated profile peaks follow those of the observed faithfully in this region.

Fig. 2 shows the projection on the (010) plane of the structure of C_6Br_6. All the intermolecular Br-Br separations <4 Å were calculated; all these contacts correspond to normal van der Waals interactions. No intermolecular contacts have been given as none was unusually short.

Multiple crystals

Boonstra & Herbstein (1963) show that the unavoidable multiple crystals of C_6Br_6 are not formed by a proper twinning process. With a clear picture of the molecular orientation we should now be in a position to search for a plausible microscopic explanation of this phenomenon. However, for any such argument to gain credence it should first be established that proper twinning is not favoured by such an argument. This we are unable to do; indeed it appears most surprising that the twinning does not in fact occur.

The molecular tilt of $18°$ out of the (010) plane takes place very nearly about the line in the (101) plane. This line is indicated in Fig. 3, and it follows that rotation of a molecule through $180°$ about this line brings it close to self-coincidence, differing only by a small rotation about the molecular sixfold axis. (If this rotation were applied to all the molecules in the crystal it would produce the structure defined by φ, θ, $\psi + \pi$.)

Fig. 3 shows four molecules (top left) in one crystal, with heights up b given in units of $0\cdot1$ Å. Molecule B is produced from molecule A by rotation of $180°$ about the line indicated in the (101) plane, and the remaining molecules depicted (bottom right) are related to B by crystal symmetry. The stippled regions mark the boundary between 'crystal A' and 'crystal B'. This is true twinning on (101) as the composition plane, in which the positive b points in opposite directions in the two component crystals. It is therefore clear that from simple packing considerations, twinning would be favoured. This makes it most surprising that twinning is not observed, but supports the conclusion of Boonstra & Herbstein (1963) that a macrogeometric rather than

Fig. 3. A possible packing arrangement in the (010) plane for twinning on (101). The heights marked for each atom are in units of $0\cdot1$ Å, so that 20 corresponds to half the b separation. The (101) line is approximately the tilt axis of a molecule. Rotation of $180°$ about the line indicated puts molecule A on molecule B. 'Crystal A' and 'crystal B' clearly pack very favourably.

a microgeometric description is required for the mechanism of crystal growth before the oriented overgrowth or agglutination can be understood.

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