Hexachlorobenzene, C_6Cl_6: The Crystal and Molecular Structure
from Least-Squares Refinement with New X-ray Data*

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$P2_1/n$, $a = 8.0476$ (8), $b = 3.8363$ (5), $c = 14.8208$ (29) Å, $\beta = 92.134$ (14)°, $Z = 2$ [23.5 ± 1.0 °C, λ(Mo $K\alpha$) = 0.71069 Å]; 1457 Mo $K\alpha$ intensities corrected for absorption. Starting parameters were from Strel'tsova & Struchkov [*Zh. Strukt. Khim.* (1961). **2**, 312–326]; $R(F) = 0.046$ for 1174 F_o^2's > $\sigma(F_o^2)$. The C–C bond lengths average 1.393 Å; r.m.s. deviation = 0.002, e.s.d. for individual C–C = 0.003 Å. The C–Cl lengths average 1.715 Å; r.m.s. deviation = 0.002, individual e.s.d. = 0.002 Å. The average corrected bond lengths are 1.401 and 1.722 Å. Angles C–C–C have individual e.s.d.'s ~0.17° and r.m.s. deviation of 0.12° from the average 120.00°. Angles C–C–Cl have e.s.d.'s ~0.15° and r.m.s. deviation of 0.30° from the average 120.00°. The maximum deviation of a carbon atom from the best plane through the C_6 ring is 0.0008 Å; the three independent Cl atoms deviate 0.014, 0.020 and 0.015 Å, adjacent atoms being displaced in opposite directions. The perpendicular spacing between adjacent molecules along **b** is 3.52 Å. The molecular plane makes an angle 23.3° with the *ac* plane. Shortest intermolecular C···C, C···Cl, and Cl···Cl distances are 3.56, 3.59, and 3.52 Å. Intramolecular near-neighbor Cl···Cl distances are all 3.11 Å.

Introduction

The three-dimensional structure of crystalline hexachlorobenzene has been known only approximately from the X-ray analysis of Strel'tsova & Struchkov (1961), which was based on $h0l$ and $h1l$ reflections only.‡ The structure parameters have been used in calculating the equilibrium intermolecular atomic separations, the lattice energy, and the frequencies of lattice vibrations (Strel'tsova & Struchkov, 1961; Reynolds, Kjems & White, 1972; Bonadeo & D'Alessio, 1973). We undertook refinement of the structure to provide a firmer experimental basis for similar calculations in this laboratory by Bates & Busing (1974).

Data and refinement

Prismatic crystals displaying the same faces as recorded by Lonsdale (1931) and by Groth (1917) were grown by slow evaporation of a benzene solution by J. B. Bates. A specimen about $0.15 \times 0.3 \times 0.4$ mm in dimensions was cut from a prism. The previously reported space group, $P2_1/c$, was verified, and the cell parameters were redetermined by the least-squares method from observations at 23.5 ± 1.0 °C of the 2θ angles of 12 unresolved Mo $K\alpha$ reflections in the range 36 to 44°. The new cell parameters for the setting $P2_1/c$ are: $a = 8.0476$ (8), $b = 3.8363$ (5), $c = 16.5992$ (20) Å, $\beta = 116.844$ (14)° [λ(Mo $K\alpha$) = 0.71069 Å]. These are in good agreement with the parameters reported previously but are more precisely determined. In our

description of the structure we use the setting $P2_1/n$, for which c changes to 14.8208(29) Å and β to 92.134 (14)°; we prefer the β near 90°. The prefactor matrix $M = (\bar{1}00/0\bar{1}0/101)$, which is its own reciprocal, transforms the crystal base vectors and the face and reflection indices from one setting to the other. The transposed matrix $\tilde{M} = (\bar{1}01/0\bar{1}0/001)$ transforms the fractional coordinates.

Mo $K\alpha$ radiation was used with the Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968) to record the 1457 symmetrically nonequivalent reflections in the 2θ range 0 to 62°. Because the mosaic spread was large (1.4 to 2.3° about various axes through the specimen), it was necessary to use an ω-scan technique to achieve proper integration of the reflection intensities. The technique used (Levy, 1966, unpublished), involving for each reflection one step-scan through the peak plus an upper and a lower background scan through the streak, has been described briefly (Brown, 1969) for recording low-angle data in the determination of the structure of 6-mercaptopurine monohydrate. A niobium filter was used in the 2θ range 25 to 55°; no filter was used either below or above that range. The critical consideration in the ω-scan technique with a crystal of wide mosaic spread is whether the height of the receiving aperture (dimension along the θ–2θ axis) can be set large enough to integrate properly at the higher Bragg angles. Fortunately, the hexachlorobenzene crystal was mounted in such a way that the maximum height (1.6°) was sufficient. It was shown by actual testing that the reflection intensities were independent of the height within experimental error in the range near the maximum height, at which the aperture was always set.

Periodic observations of a strong reference reflection, 008, showed only the expected statistical fluctuations in intensity. Absorption corrections (Busing &

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‡ For earlier, two-dimensional analyses see Lonsdale (1931) and Tulinsky & White (1958).

Levy, 1957) were applied ($\mu = 17.9$ cm^{-1}); the minimum and maximum absorption corrections were 1·28 and 1·68, respectively. For the subsequent least-squares refinement the weight of each observation F_o^2 was taken to be $1/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2)$ includes an empirical correction $(0.03\ F_o^2)^2$ added to the purely statistical variance (Peterson & Levy, 1957).

Least-squares refinement was started with the atomic parameters reported by Strel'tsova & Struchkov (transformed for our $P2_1/n$ setting) and it proceeded smoothly. The largest coordinate shift was 0·066 Å along axis b for atom Cl(3). The final goodness-of-fit indicators,* based on all 1457 observations, are as follows: $R(F) = 0.064$; $R(F^2) = 0.047$; $R_w(F^2) = 0.080$; $\sigma_1 = 1.312$. For the 1174 reflections with $F_o^2 > \sigma(F_o^2)$, $R(F) = 0.046$. There was no evidence of extinction. The atomic scattering factors of Hanson, Herman, Lea & Skillman (1964) were used, with dispersion corrections for chlorine ($\Delta f' = 0.132$, $\Delta f'' = 0.159$) from Cromer &

Liberman (1970). In the final cycle of refinement no coordinate or anisotropic thermal parameter β_{ij} changed in magnitude by as much as 10^{-5}; the scale factor changed by 1 part in 10^5, about 0·005 times the corresponding standard error. A final difference map showed no significant detail. The largest excursions of density were $+0.59$ and -0.59 e Å^{-3}; for comparison, the peak heights in a final electron density map were about 12 and 35 e Å^{-3} for the carbon and chlorine atoms, respectively. The final atomic parameters are given in Table 1; a table of observed and calculated $|F|$'s and standard errors is available.† There are nine values of $\Delta F^2/\sigma(F_o^2)$ greater than 4, of which the largest is 5·1.

Discussion

A rigid-body analysis (Cruickshank, 1956; Schomaker & Trueblood, 1968) made with Johnson's (1970a) segmented-body program *ORSBA*, gave a good fit of

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* The indicators $R(F)$ and $R(F^2)$ are the usual discrepancy indices calculated on the basis of F and F^2 values, respectively; $R_w(F^2)$ is the weighted index for F^2 values; σ_1 is the standard deviation of fit. For explicit definitions, see Brown (1969), among others.

† This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30268 (10 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic parameters* ($\times 10^5$) *for the hexachlorobenzene crystal structure* ($P2_1/n$ *setting*)

The parameters β_{ij} are for the temperature factor exp $(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−15272 (23)	−11190 (57)	3027 (13)	741 (25)	4356 (147)	318 (8)	108 (52)	14 (11)	176 (29)
C(2)	−3330 (23)	2262 (57)	9141 (12)	966 (28)	4835 (160)	248 (7)	404 (57)	15 (11)	61 (29)
C(3)	11972 (24)	13409 (56)	6102 (13)	867 (27)	4252 (148)	297 (8)	83 (52)	−103 (12)	34 (28)
Cl(1)	−34074 (06)	−25323 (20)	6742 (04)	888 (07)	9092 (060)	456 (3)	−526 (19)	77 (03)	417 (11)
Cl(2)	−7620 (08)	5380 (22)	20344 (03)	1526 (10)	11013 (070)	251 (2)	206 (22)	85 (03)	−74 (10)
Cl(3)	26662 (07)	29525 (18)	13671 (04)	1241 (09)	7620 (054)	398 (3)	−462 (19)	−227 (04)	−232 (10)

Table 2. *Librational and translational motion of the hexachlorobenzene molecule from the segmented-body analysis*

L_{ext}, L_{int}, and T are tensors for overall external libration, internal libration, and translational vibration respectively. Unit vector i of the reference Cartesian coordinate system is directed from C(1) to C(1)* (see Fig. 1): unit vector k has the direction of i∧m, where m is a vector from C(2) to C(2)*; j completes the right-handed system.

Tensor elements $ij \times 10^5$ (standard errors $\times 10^5$)

Tensor	11	22	33	12	13	23
L_{ext} (rad^2)	494 (5)	463 (5)	322 (2)	−96 (2)	−62 (3)	112 (3)
L_{int} (rad^2)			253 (20)			
T (Å^2)	2653 (16)	2585 (16)	2039 (43)	119 (13)	197 (17)	−254 (17)

Principal r.m.s. amplitudes and orientations of principal axes

		Principal axis K		
		1	2	3
L_{ext} r.m.s. amplitude (°)		4·53	3·60	2·92
Direction cosines of axes K	i	0·6583	0·7515	0·0428
with respect to Cartesian	j	−0·6519	0·5976	−0·4668
base vectors	k	−0·3764	0·2794	0·8833
L_{int} r.m.s. amplitude (°)				2·88
T r.m.s. amplitude (Å)		0·166	0·163	0·137
Direction cosines of axes K	i	0·8119	0·5124	0·2797
	j	0·5836	−0·7260	−0·3639
	k	0·0166	0·4587	−0·8886

rigid-body motional parameters to the 36 observed U_{ij} parameters;[*] the r.m.s. deviation between observed and calculated U_{ij}'s was 0·0008 Å². However, analysis of the residual ellipsoids suggested that there is excess motion of the carbon atoms which can be ascribed chiefly to libration of the ring about the normal to the ring plane through the center of the ring. A segmented-

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[*] The U_{ij}'s are vibrational tensor components referred to a molecular Cartesian coordinate system; they are simply related to the β_{ij}'s of Table 1. The same weight was used for all 18 U_{ij}'s of the chlorine atoms; this weight was 6·5 times the constant weight used for the 18 U_{ij}'s of the carbon atoms, in accordance with the inverse ratio of the averages of the squares of the standard errors of the β_{ij}'s for the two kinds of atoms.
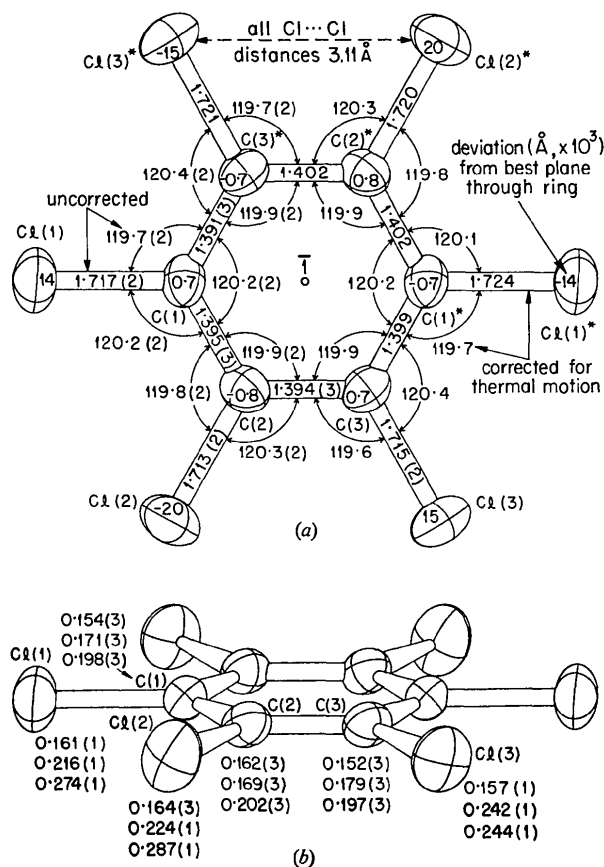

Fig. 1. (a) The centrosymmetric molecule in crystalline hexachlorobenzene, nonperspective view perpendicular to the molecular plane. Atoms are represented by their ellipsoids of 50% probability. Atoms C(1) and C(1)*, and so forth, are related by inversion through the molecular symmetry center at the cell origin. Uncorrected bond lengths (Å) and angles (°) calculated using the full least-squares covariance matrix, with standard errors in parentheses, are given in one half of the molecule; bond lengths and angles corrected for thermal motion are given in the other half. Deviations of atoms from the best least-squares plane through the six carbon atoms are shown inside the atom ellipsoids, in units of 10^{-3} Å. (b) View of the molecule in a direction 70° from that of (a). Principal axial r.m.s. vibrational amplitudes and standard errors (Å) are attached to the six atoms of the asymmetric unit.

body fit to the U_{ij}'s was made assuming that a rigid C_6 ring oscillates in this manner with reference to a rigid Cl_6 ring. The r.m.s. ΔU_{ij} was reduced to 0·0004 Å². The internal r.m.s. librational amplitude was calculated to be 2·9°; the calculated molecular r.m.s. principal librational amplitudes, 2·9, 3·6, and 4·5°, were almost exactly as calculated first on the assumption of a rigid molecule. The principal axial directions for molecular libration and translation (Table 2) were also almost the same as in the first calculation. It seems odd to describe the six chlorine atoms as a rigid group while at the same time including the internal motion; however, the excellent fit suggests that the chlorine atoms do behave much as a rigid group. As far as in-plane motion is concerned, this may be rationalized on the basis that the chlorine atoms are heavy and their relative motion is restricted by the close intramolecular near-neighbor Cl···Cl contacts at 3·11 Å.

Use of the program *ORSBA* provided values of bond lengths and valence angles corrected for the overall external motion of the molecule but not for the internal motion of carbon atoms relative to chlorine atoms described above. The corrections were 0·005 to 0·006 Å for the C–C bonds and 0·007 to 0·008 Å for the C–Cl bonds. An additional correction of 0·002 Å was calculated for the effects of the internal motion on each C–C bond length by use of the equation given by Busing & Levy (1964) under their section heading *Molecular libration*. No such additional correction is required for the C–Cl bond lengths, since to the approximation that the carbon and chlorine atoms of each bond are rigidly linked the apparent positions of the two atoms will be shifted by the same vector as a result of the internal motion.

The molecular structure is described in detail by the numerical data in Fig. 1 on bond lengths and valence angles (including values corrected for thermal motion, as described above) and on deviations from strict planarity. Fig. 1 shows the ellipsoids of 50% probability (Johnson, 1970b) and includes the numerical values of the r.m.s. principal-axial atomic displacements.

The molecule displays almost perfect 6/mmm symmetry, the largest deviations being exhibited by the C–C–Cl angles and by the displacements of 0·014 to 0·020 Å of the chlorine atoms from the least-squares best plane through the nearly exactly coplanar ring of carbon atoms. The equation of this plane for the reference molecule at the origin is:

$$2·9625x - 3·5235y + 1·9429z = 0 ,$$

where x, y, and z are fractional coordinates in the crystal system. A positive deviation in Fig. 1 has a negative y component.

The average uncorrected and corrected bond lengths are: C–C 1·393 and 1·401 Å; C–Cl 1·715 and 1·722 Å. Root-mean-square deviations are about 0·002 Å for each kind of bond. The average corrected lengths are in excellent agreement with the lengths 1·404 (6) and 1·717 (5) Å [both $r_g(1)$ values in the notation of Bartell

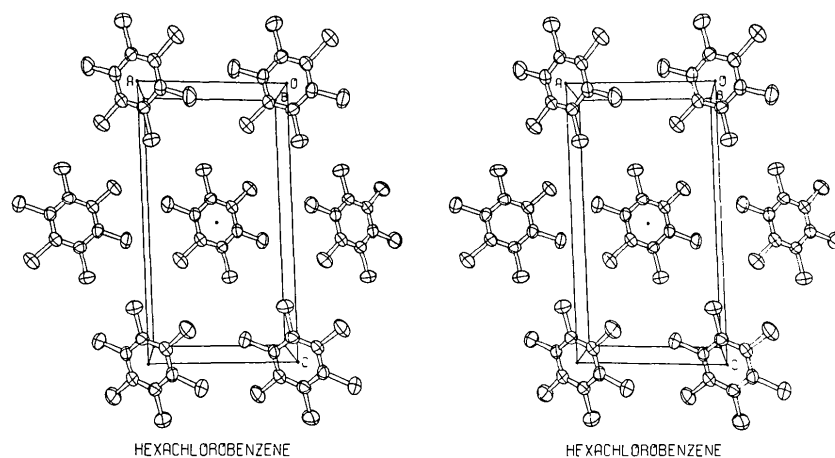HEXACHLOROBENZENE   HEXACHLOROBENZENE

Fig. 2. Stereoscopic view down the *b* axis of the crystal structure of hexachlorobenzene, showing the atomic ellipsoids of 75 % probability.

(1955)] reported from a gas-phase electron-diffraction study (Strand & Cox, 1966). It is interesting that the C–C bond length in this benzene ring bearing six substituent chlorine atoms is not significantly different from the length in benzene itself as reported from various structural studies: gas-phase electron diffraction, 1.397_4 Å (Bastiansen, 1957); Raman spectroscopy, 1.397_3 Å (Langseth & Stoicheff, 1956); X-ray crystal-structure analysis, 1.392 (10) Å* (Cox, Cruickshank & Smith, 1958); neutron crystal-structure analysis, 1.398 (7) Å* (Bacon, Curry & Wilson, 1964).

The average C–Cl bond length is consistent with Rudman's (1971) inference from the available data that C–Cl bond lengths for bonds on aromatic and quinoid rings are significantly shorter (averaging 1.709 Å)† when the bonds are *ortho* to each other than when they are more widely separated or in isolation (averaging 1.737 Å).† It is of interest that the C–Cl bond lengths in decachlororuthenocene and in diethoxy-octachloroferrocene (Brown, Hedberg & Rosenberg, 1972, 1973) are also short, averaging 1.703 and 1.709 Å, respectively (uncorrected).

A stereoscopic view of the crystal structure along the *b* axis is shown in Fig. 2. The molecular plane makes an angle $23.3°$ with the *ac* plane. The shortest intermolecular C–C, C–Cl, and Cl–Cl distances are 3.56, 3.59, and 3.52 Å, respectively.

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