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The Structure of Pentachlorobenzene

BY PHILIP MARSH AND DONALD E. WILLIAMS

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, USA

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Abstract. C_6HCl_5 , orthorhombic, $Pca2_1$, $Z = 4$, $a = 16.802$ (5), $b = 3.856$ (1), $c = 13.279$ (2) Å, $D_c = 1.893$ Mg m⁻³. The structure was solved from an $h0l$ projection and refined to $R = 0.023$ for 665 independent reflections. Intramolecular Cl...Cl repulsions produce shortenings in the C(1)–C(6) and C(5)–C(6) bonds.

Introduction. The crystal structure of the title compound was determined to provide a large data base in connection with a study of Cl...Cl nonbonded interactions in crystals (Hsu & Williams, 1980). In the cited work, no evidence for nonbonded anisotropy above a threshold level was found in a study of five perchlorohydrocarbons: hexachlorobenzene, octachloronaphthalene, octachlorofulvalene, decachlorophenanthrene, and decachloropyrene. However, Wheeler & Colson (1976) and Munowitz, Wheeler & Colson (1977) claim that significantly anisotropic Cl...Cl interactions are present in one or more of the three crystal forms of *p*-dichlorobenzene.

Translucent crystals with good face development were grown with material obtained from the Aldrich Chemical Company; an approximately cubic-shaped crystal with an edge length of 0.2 mm was selected. X-ray diffraction data showed the crystals to be orthorhombic, with systematic absences $h0l:h = 2n$ and $0kl:l = 2n$, space group $Pca2_1$. 863 independent reflections were collected with an Enraf–Nonius CAD-4 diffractometer (Mo $K\alpha$ radiation), using the $\theta, 2\theta$ scan

method. 464 of the lowest-angle reflections were collected as Friedel pairs. Three reference reflections remained essentially constant throughout the data collection. Lorentz and polarization corrections were made in the usual manner.

The structure was solved from an $h0l$ projection with *SHELX* 76 (Sheldrick, 1976). A rigid-body projection was refined for the x direction to $R = 24\%$. A difference Fourier map was sufficient to determine the rotational orientation. The geometric constraints were removed and the structural parameters were refined to $R = 5\%$.

The structure was then refined for the entire data set with a constrained benzene ring to $R = 27\%$. The thermal parameters of the Cl atoms were converted to anisotropic ones and the refinement continued to $R = 4\%$. The H atom was found on a difference Fourier map and refined with an isotropic temperature factor. The H scattering factors were those of Stewart, Davidson & Simpson (1965). The C and Cl scattering factors were those of Cromer & Mann (1968). The benzene ring was unconstrained and the thermal parameters were anisotropic. This final refinement adjusted 102 structural parameters, plus a scale factor, to minimize the R factor $\{R = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}\}$. The weights were defined as the squares of the reciprocals of the estimated standard deviations of the structure factors. The final R was 0.023 for reflections significantly above background [665 reflections with $F > 3\sigma(F)$]. The final electron density

difference Fourier map shows no distinguishing features.*

Discussion. The final coordinates are given in Table 1. A thermal-ellipsoid plot (Johnson, 1965) of the molecule is shown in Fig. 1, with the atomic-numbering system. The bond distances are also shown in the figure; the estimated standard deviations are 0.005, 0.007 and 0.07 Å for C–Cl, C–C and C–H, respectively. The average C–Cl bond distance is 1.722 Å. The average C–C distance is 1.382 Å. All bond angles are within two e.s.d.'s of 120°. The largest deviation from the molecular plane is 0.04 Å. Fig. 2 illustrates the molecular packing. The molecules stack along the short-lattice-constant direction. The molecules show a herring-bone type of packing when viewed

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35709 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters ($\times 10^4$) and equivalent values for the temperature factors ($\text{Å}^2 \times 10^2$) (Willis & Pryor, 1975)

	x	y	z	U
C(1)	-53 (3)	1639 (13)	1353 (4)	4.0 (2)
C(2)	93 (3)	3005 (12)	2302 (4)	4.0 (2)
C(3)	854 (3)	4097 (12)	2553 (4)	4.1 (2)
C(4)	1467 (3)	3843 (13)	1852 (5)	4.4 (2)
C(5)	1295 (3)	2504 (13)	898 (4)	4.6 (2)
C(6)	545 (3)	1414 (14)	664 (4)	4.4 (2)
Cl(1)	-990 (1)	167 (4)	1039 (2)	5.31 (5)
Cl(2)	-670 (1)	3393 (4)	3167 (2)	5.87 (5)
Cl(3)	1043 (1)	5768 (4)	3728 (2)	6.09 (5)
Cl(4)	2408 (1)	5170 (4)	2159 (2)	6.80 (6)
Cl(5)	2036 (1)	2224 (4)	0	7.58 (7)
H	411 (34)	667 (141)	84 (53)	

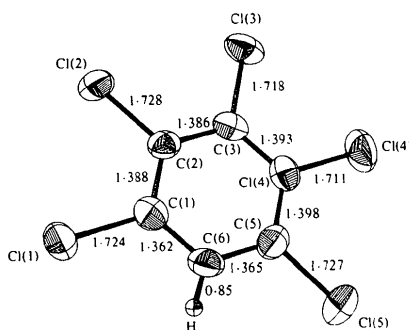


Fig. 1. The molecular structure showing the atomic-numbering system and the bond lengths (Å). The thermal ellipsoids enclose 50% probability (Johnson, 1965).

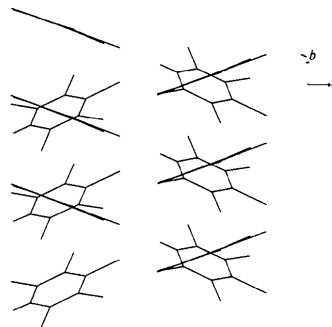


Fig. 2. The packing of the molecules shown about the screw axis. The view is perpendicular to *c* at an angle of 76° to the *bc* plane.

perpendicular to the screw axis at an angle of 76° to the *bc* plane. The intermolecular distances are in the normally expected range for nonbonded contacts; the shortest intermolecular distance is a Cl...Cl, at 3.447 Å.

Intramolecular Cl...Cl repulsions produce significant shortenings of the C(1)–C(6) and C(5)–C(6) bonds. Although the C atoms are planar to within 0.006 Å, the Cl atoms deviate from the best molecular plane by -0.036, 0.039, 0.005, -0.025 and 0.031 Å for Cl(1) through Cl(5), respectively.

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