

The Crystal and Molecular Structure of Octachlorodibenzo-*p*-dioxin

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The crystal and molecular structure of octachlorodibenzo-*p*-dioxin has been determined by three-dimensional single-crystal X-ray diffraction methods. The monoclinic unit cell (space group $P2_1/c$) has lattice parameters $a = 12.009 \pm 0.003$, $b = 3.828 \pm 0.001$, $c = 16.297 \pm 0.003$ Å, and $\beta = 101.14 \pm 0.01^\circ$, giving a calculated density of 2.077 g.cm^{-3} for M.W. 459.76 and $Z = 2$. The intensities of 1640 independent reflections were measured by using the θ - 2θ scan mode on a Picker four-circle diffractometer and Mo $K\alpha$ radiation. The structure was solved from the Patterson function, and the coordinates and anisotropic temperature factors of all atoms were refined by full-matrix least-squares methods. The final R index was 5.8% for 1459 reflections above background. The molecules are situated about the inversion centers at (0,0,0) and $(0, \frac{1}{2}, \frac{1}{2})$ and are stacked along [010]. Small deviations from planarity occur, whereby the 1, 4 and 2, 3 chlorine pairs occur on opposite sides of the molecular plane. The four unique C-Cl distances range from 1.714 to 1.718 Å, the two C-O distances are 1.373 and 1.374 Å, and the six C-C bonds range between 1.382 and 1.396 Å. The C-O-C angle is 115.8° .

Introduction

The chlorinated derivatives of dibenzo-*p*-dioxin are of current interest because they are potential impurities in chlorinated phenols and phenol esters and because 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and hexachlorodibenzo-*p*-dioxin have been shown to produce severe untoward effects (Jones & Krizek, 1962; Schultz, 1968; Higginbotham, Huang, Firestone, Verrett, Ress & Campbell, 1968; Hegyi, St'ota & Luptakova, 1969; Sparschu, Dunn & Rowe, 1971; Rowe, Norris, Schwetz, Sparschu, Gehring, Emmerson & Gerbig, 1971). Available evidence suggests that octachlorodibenzo-*p*-dioxin possesses a low order of toxicity (Rowe *et al.*, 1971). As part of an overall program to characterize these compounds, X-ray diffraction analysis provides both unambiguous identification of isomers and fundamental data for correlating molecular structure with biological activity. The present report describes the crystal and molecular structure of octachlorodibenzo-*p*-dioxin.

Experimental

A sample of octachlorodibenzo-*p*-dioxin, containing well-formed colorless crystals, was supplied by Dr O. Aniline. A crystal of dimensions $0.051 \times 0.094 \times 1.53$ mm, in directions normal to the {001}, {100}, and {010} planes respectively, was selected and secured to an inside wall of a Lindemann glass capillary, which was then sealed. Since the health hazards incurred with octachlorodibenzo-*p*-dioxin were not known when this study was conducted, special precautions were taken to minimize the risk of exposure of laboratory staff.

The crystal mounting operations were carried out with surgical gloves, which were subsequently destroyed together with the mounting implements.

The crystal was then mounted on a goniometer head and aligned along **b**. An oscillation photograph and Weissenberg photographs of the $h0l$ and $h1l$ levels indicated that the reciprocal lattice symmetry was C_{2h} and that $h0l$ reflections were systematically absent for l odd. At this point the goniometer head was transferred to a Picker four-circle goniostat, where lattice constants were determined by least-squares refinement of the setting angles of 16 reflections, with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The absence of $0k0$ reflections for k odd, as observed on the goniostat, together with our earlier observations on film, gave the probable space group as $P2_1/c$ (C_{2h}^5). With $Z = 2$, the molecules are thus required to possess crystallographic inversion centers.

Table 1. Crystal data

Molecular formula	$C_{12}O_2Cl_8$
Molecular weight	459.76
Crystal habit	Needle
Space group	$P2_1/c$
Cell constants	
(25°C)	a 12.009 ± 0.003 Å
	b 3.828 ± 0.001
	c 16.297 ± 0.003
	β 101.14 ± 0.01
Volume	V 735.0 Å ³
Density	ρ_c 2.077 g cm ⁻³ ($Z = 2$)
Absorption coefficient (Mo $K\alpha$)	15.05 cm ⁻¹
Number of independent reflections	1640.

The θ - 2θ scan mode of the Picker diffractometer and Mo $K\alpha$ radiation, monochromatized with the 002 reflection of a highly oriented graphite crystal, were used to obtain the intensity data. The X-ray tube was at a 3.0° takeoff angle, and the scintillation detector was

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Table 2. Final structure parameters with standard deviations in parentheses

The anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

E.s.d.'s are referred to the least significant figure of the parameter values.

	x	y	z	10 ⁴ β ₁₁	10 ³ β ₂₂	10 ⁴ β ₃₃	10 ⁴ β ₁₂	10 ⁴ β ₁₃	10 ⁴ β ₂₃
Cl(1)	0.36887 (8)	0.1125 (3)	0.23425 (6)	49 (1)	82 (1)	25 (1)	-16 (2)	-4 (1)	-12 (2)
Cl(2)	0.44176 (8)	0.2322 (3)	0.07846 (7)	40 (1)	82 (1)	33 (1)	34 (2)	6 (1)	13 (2)
Cl(3)	0.11407 (8)	0.3190 (3)	0.22562 (6)	58 (1)	56 (1)	22 (1)	-7 (2)	7 (1)	-22 (1)
Cl(4)	0.25867 (8)	-0.3520 (3)	-0.08448 (6)	59 (1)	67 (1)	25 (1)	38 (2)	11 (1)	-18 (2)
O	-0.0329 (2)	0.1580 (10)	0.0705 (2)	40 (2)	103 (4)	27 (1)	47 (7)	-2 (1)	-74 (5)
C(1)	0.0773 (3)	0.0630 (12)	0.0704 (2)	43 (3)	50 (3)	23 (1)	7 (8)	4 (1)	-11 (6)
C(2)	0.1098 (3)	-0.0887 (12)	0.0017 (2)	45 (2)	44 (3)	23 (1)	12 (8)	2 (1)	-7 (6)
C(3)	0.1574 (3)	0.1261 (11)	0.1419 (2)	50 (3)	36 (3)	19 (1)	-1 (8)	8 (2)	7 (5)
C(4)	0.2222 (3)	-0.1749 (11)	0.0033 (2)	46 (3)	37 (3)	23 (1)	19 (8)	8 (2)	1 (6)
C(5)	0.2699 (2)	0.0359 (11)	0.1449 (2)	42 (3)	43 (3)	17 (1)	-5 (8)	-1 (1)	14 (5)
C(6)	0.3031 (3)	-0.1153 (11)	0.0758 (2)	36 (2)	43 (3)	28 (2)	2 (8)	9 (2)	21 (6)

Table 3. Observed and calculated structure factors (×10)

h	k	l	F _o	F _c	ΔF	h	k	l	F _o	F _c	ΔF	h	k	l	F _o	F _c	ΔF
0	0	0	1000	1000	0	1	0	0	100	100	0	2	0	0	100	100	0
0	0	1	100	100	0	0	1	0	100	100	0	0	1	1	100	100	0
0	1	0	100	100	0	0	0	1	100	100	0	0	0	2	100	100	0
0	1	1	100	100	0	0	0	1	100	100	0	0	0	1	100	100	0
1	0	0	100	100	0	1	0	0	100	100	0	1	0	0	100	100	0
1	0	1	100	100	0	1	0	1	100	100	0	1	0	1	100	100	0
1	1	0	100	100	0	1	1	0	100	100	0	1	1	0	100	100	0
1	1	1	100	100	0	1	1	1	100	100	0	1	1	1	100	100	0
2	0	0	100	100	0	2	0	0	100	100	0	2	0	0	100	100	0
2	0	1	100	100	0	2	0	1	100	100	0	2	0	1	100	100	0
2	1	0	100	100	0	2	1	0	100	100	0	2	1	0	100	100	0
2	1	1	100	100	0	2	1	1	100	100	0	2	1	1	100	100	0
3	0	0	100	100	0	3	0	0	100	100	0	3	0	0	100	100	0
3	0	1	100	100	0	3	0	1	100	100	0	3	0	1	100	100	0
3	1	0	100	100	0	3	1	0	100	100	0	3	1	0	100	100	0
3	1	1	100	100	0	3	1	1	100	100	0	3	1	1	100	100	0
4	0	0	100	100	0	4	0	0	100	100	0	4	0	0	100	100	0
4	0	1	100	100	0	4	0	1	100	100	0	4	0	1	100	100	0
4	1	0	100	100	0	4	1	0	100	100	0	4	1	0	100	100	0
4	1	1	100	100	0	4	1	1	100	100	0	4	1	1	100	100	0
5	0	0	100	100	0	5	0	0	100	100	0	5	0	0	100	100	0
5	0	1	100	100	0	5	0	1	100	100	0	5	0	1	100	100	0
5	1	0	100	100	0	5	1	0	100	100	0	5	1	0	100	100	0
5	1	1	100	100	0	5	1	1	100	100	0	5	1	1	100	100	0
6	0	0	100	100	0	6	0	0	100	100	0	6	0	0	100	100	0
6	0	1	100	100	0	6	0	1	100	100	0	6	0	1	100	100	0
6	1	0	100	100	0	6	1	0	100	100	0	6	1	0	100	100	0
6	1	1	100	100	0	6	1	1	100	100	0	6	1	1	100	100	0
7	0	0	100	100	0	7	0	0	100	100	0	7	0	0	100	100	0
7	0	1	100	100	0	7	0	1	100	100	0	7	0	1	100	100	0
7	1	0	100	100	0	7	1	0	100	100	0	7	1	0	100	100	0
7	1	1	100	100	0	7	1	1	100	100	0	7	1	1	100	100	0
8	0	0	100	100	0	8	0	0	100	100	0	8	0	0	100	100	0
8	0	1	100	100	0	8	0	1	100	100	0	8	0	1	100	100	0
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13	1	0	100	100	0	13	1	0	100	100	0	13	1	0	100	100	0
13	1	1	100	100	0	13	1	1	100	100	0	13	1	1	100	100	0
14	0	0	100	100	0	14	0	0	100	100	0	14	0	0	100	100	0
14	0	1	100	100	0	14	0	1	100	100	0	14	0	1	100	100	0
14	1	0	100	100	0	14	1	0	100	100	0	14	1	0	100	100	0
14	1	1	100	100	0	14	1	1	100	100	0	14	1	1	100	100	0
15	0	0	100	100	0	15	0	0	100	100	0	15	0	0	100	100	0
15	0	1	100	100	0	15	0	1	100	100	0	15	0	1	100	100	0
15	1	0	100	100	0	15	1	0	100	100	0	15	1	0	100	100	0
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17	0	0	100	100	0	17	0	0	100	100	0	17	0	0	100	100	0
17	0	1	100	100	0	17	0	1	100	100	0	17	0	1	100	100	0
17	1	0	100	100	0	17	1										

31.6 cm from the crystal and screened with a 4 mm square aperture. Incident- and exit-beam collimators, 1.5 mm in diameter, were used to restrict stray radiation. Attenuators were employed to prevent the count rate from exceeding 12,000 per sec. The scan speed was 2° per min over 2θ angles of $2.0^\circ + \Delta$, where Δ is the separation of the $K\alpha$ doublet; this range was sufficient to allow for the observed mosaic spread of the crystal. Stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. A hemisphere bounded by $\sin \theta \leq 0.46$, equivalent to the Cu $K\alpha$ limit, was examined. The $\bar{3}12$ reflection was monitored after every 50 measurements and showed fair stability, as indicated by a root mean square deviation of 1.7% in intensity and a maximum deviation of 4.9%. An error $\sigma(I) = [(0.02I)^2 + N_o + k^2N_b]^{1/2}$ was assigned to the net intensity $I = N_o - kN_b$ of each reflection in order to establish the weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement, where the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. Here N_o is the gross count, N_b is the background count, k is the ratio of scan time to background time, and the F^2 s are the intensities corrected for Lorentz and polarization effects using the expression $Lp^{-1} = \sin 2\theta(1 + \cos^2 2\theta_m)/(1 + \cos^2 2\theta \cos^2 2\theta_m)$, where $2\theta_m$ is the monochromator setting angle. The 181 reflections for which $I < 0$ or $I/\sigma(I) < 2.0$ were denoted absent and were not used in the refinement. The intensity data were corrected for absorption; transmission factors ranged from a minimum of 0.860 to a maximum of 0.929.

Solution and refinement of the structure

The structure was solved from a three-dimensional Patterson function. A structure factor calculation based on the initial atomic coordinates gave $R_1 = \sum ||F_o| - |F_c||/|F_o| = 0.44$ and $R_2 = \{\sum w[F_o - F_c]^2 / \sum wF_o^2\}^{1/2} = 0.58$ for the 1459 reflections above background. Full-matrix least-squares refinement of atomic positions, and (after the first cycle) of atomic isotropic

temperature factors, converged at $R_1 = 0.122$ and $R_2 = 0.119$. Refinement was completed assuming anisotropic thermal parameters for all atoms, yielding final values of 0.058 and 0.053 for R_1 and R_2 respectively. In the final cycle no parameter shift exceeded 0.05σ . The atomic scattering factors for Cl, C, and O, which included a correction for anomalous scattering by Cl, were obtained from *International Tables for X-ray Crystallography* (1962). The final difference Fourier synthesis contained as the largest peak, $0.4 \text{ e.}\text{\AA}^{-3}$, and as the lowest negative value, $-0.3 \text{ e.}\text{\AA}^{-3}$. A correction for secondary extinction was not made, although six strong reflections appeared to be moderately affected, showing negative variations from 4.5 to 10.5%.

Final atomic parameters and their standard deviations as calculated in the last cycle of least-squares refinement are given in Table 2. Table 3 lists observed and calculated structure factors. Intramolecular distances and angles with standard deviations obtained from the least-squares variance-covariance matrix are presented in Fig. 1. The amplitudes of anisotropic thermal motion with their standard errors are given in Table 4, and the corresponding thermal ellipsoids, drawn at 50% probability, can be seen in Fig. 2.

Table 4. Root-mean-square amplitudes of thermal motion along the principal axes*

	Axis 1	Axis 2	Axis 3
Cl(3)	0.158 (2) Å	0.204 (1) Å	0.209 (2) Å
Cl(4)	0.164 (2)	0.199 (2)	0.237 (2)
Cl(1)	0.154 (2)	0.217 (2)	0.247 (2)
Cl(2)	0.164 (2)	0.204 (2)	0.252 (2)
O	0.160 (3)	0.161 (3)	0.303 (5)
C(1)	0.168 (6)	0.172 (6)	0.198 (6)
C(2)	0.167 (6)	0.172 (7)	0.196 (6)
C(3)	0.151 (7)	0.168 (9)	0.189 (6)
C(4)	0.157 (8)	0.171 (8)	0.188 (6)
C(5)	0.137 (7)	0.174 (8)	0.193 (7)
C(6)	0.157 (6)	0.165 (7)	0.204 (6)

* Ordered on increasing magnitude.

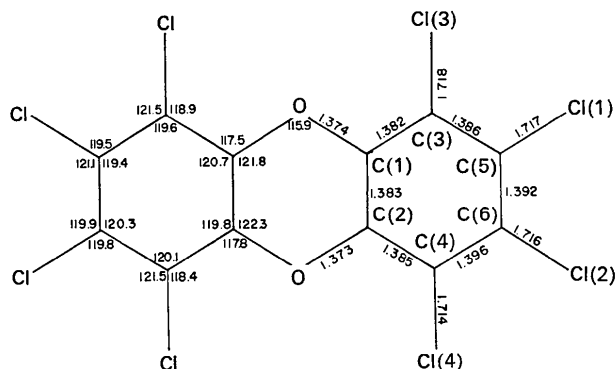


Fig. 1. Bond distances and angles in octachlorodibenzo-*p*-dioxin. Standard errors, as computed from the variance-covariance matrix obtained in the final least-squares cycle are C-Cl, ± 0.004 ; C-O, ± 0.004 ; C-C, ± 0.005 Å; C-O-C, ± 0.3 ; C-C-O, ± 0.3 ; C-C-C, ± 0.4 ; C-C-Cl, $\pm 0.3^\circ$.

Discussion

The crystal structure, illustrated in Fig. 3, is based on herringbone packing between stacks of molecules centered on $(0,0,0)$ and $(0, \frac{1}{2}, \frac{1}{2})$. The short (3.828 Å) b axis forms the direction of the stack, and the normals to the molecular planes are tilted by 24.6° with respect to this axis resulting in an interplanar spacing of 3.479 Å. Since in 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Boer, van Remoortere, North & Neuman, 1972) the plane normals made angles of 22.6 and 24.6° with respect to the short (3.783) a axis, and in 2,7-dichlorodibenzo-*p*-dioxin (Boer & North, 1972) an angle of 25.9° is formed with respect to a translation axis of 3.878 Å, this type of molecular stack appears to be a favored mode of packing for the chlorinated dibenzodioxins.

The crystal contains only five unique intermolecular

contacts shorter than 3.6 Å. Three of these occur as a result of the cell translation along **b**: C(3)···Cl(3), 3.481 ± 0.005 ; C(1)···C(2), 3.181 ± 0.006 ; and C(4)···Cl(4), 3.521 ± 0.005 Å. In addition, there are two fairly short Cl···Cl interactions: Cl(3)···Cl(3), 3.555 ± 0.004 and Cl(1)···Cl(2), 3.487 ± 0.004 Å. The former arises from the screw diad at $x=0, z=\frac{1}{4}$ and the latter from the screw at $x=\frac{1}{2}, z=\frac{1}{4}$. These values are both less than the sum of two chlorine van der Waals radii (3.6 Å). Cl···Cl intermolecular contacts in the range 3.4–3.55 Å have also been observed in the

crystal structures of the 2,7-dichloro-, 2,8-dichloro-, and 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxins, but no contacts below 3.57 Å were found in the 2,3,7,8-tetrachloro compound.

Although the molecular structure obeys D_{2h} symmetry fairly closely, a more detailed examination of the atomic positions reveals some deviations from planarity of sufficient magnitude to be considered significant. These deviations are largest at the Cl atoms, for which the e.s.d. of an out-of-plane distance is 0.006 Å. For example, the chlorines deviate from a least-squares

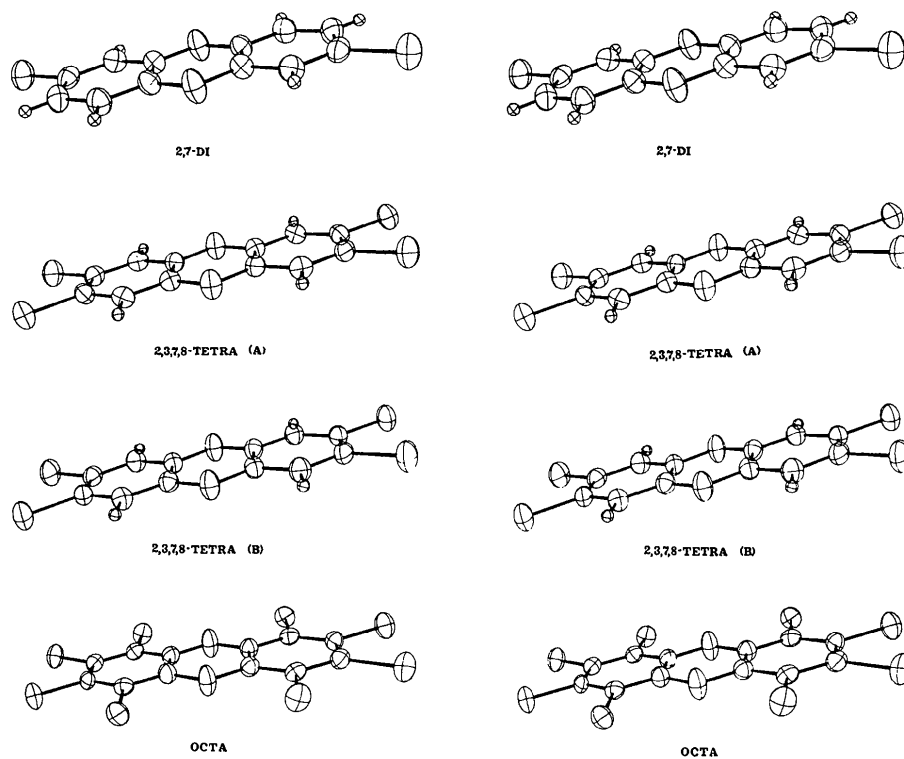


Fig. 2. Thermal ellipsoids, drawn at 50% probability, for three chlorinated dibenzo-*p*-dioxins. The letters (A) and (B) refer to the two independent molecules in the unit cell of the 2,3,7,8-tetra derivative (see Boer, van Remoortere, North & Neuman, 1972).

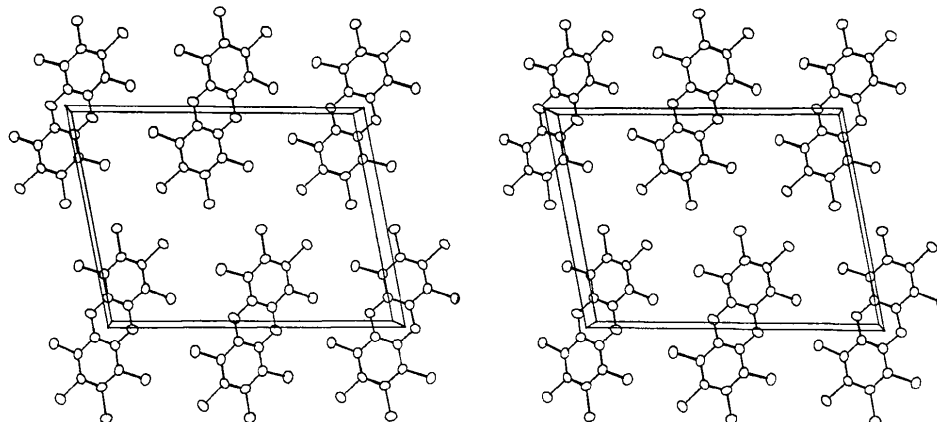


Fig. 3. A stereo view of the crystal packing along the *b* axis. The origin is in the lower left corner with the *c* axis horizontal and the *a* axis nearly vertical.

plane fitted to the carbon-oxygen skeleton by 0.022 at Cl(3), 0.053 at Cl(4), -0.016 at Cl(1), and -0.025 Å at Cl(2), whereas the deviations for the light atoms are 0.000 at C(1), -0.002 at C(2), 0.001 at C(3), 0.012 at C(4), -0.006 at C(5), -0.002 at C(6), and 0.011 Å at O. The equation of this plane is $2.882x + 3.473y - 6.273z = 0$; displacements for the atoms related by the molecular center are of equal magnitude and opposite sign. For a least-squares plane calculated using all 22 atoms of the molecule, the equation of plane is $2.872x + 3.477y - 6.235z = 0$, and the respective atomic displacements are 0.030 at Cl(3), 0.046 at Cl(4), -0.010 at Cl(1), -0.028 at Cl(2), 0.002 at C(1), -0.004 at C(2), 0.006 at C(3), 0.009 at C(4), -0.003 at C(5), -0.003 at C(6), and 0.015 Å at O.

The net effect is to displace the two 'outside' chlorine atoms, Cl(1) and Cl(2), in opposite directions to the inside chlorine atoms, Cl(3) and Cl(4), with respect to the central plane. These distortions, along with the increased exocyclic bond angles of $121.5 \pm 0.3^\circ$ at C(3) and C(4), may arise from intramolecular Cl...Cl repulsions. However, intermolecular forces (*vide infra*) appear to be appreciable in this crystal and may also serve as a source of strain affecting the molecular geometry.

Excellent agreement is obtained among chemically similar bonds. The four C-Cl bond lengths are 1.718, 1.714, 1.717 and 1.716 Å, all ± 0.004 Å. These bonds are slightly shorter than the four independent C-Cl bonds (1.726, 1.727, 1.728 and 1.730 ± 0.003 Å) in 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, and considerably shorter than the C-Cl distance of 1.742 ± 0.004 Å in 2,7-dichlorodibenzo-*p*-dioxin. The two independent C-O bond distances, 1.373 and 1.374 ± 0.004 Å, are in good agreement with each other and with the structures of other chlorinated dioxins (Boer *et al.*, 1972; Boer & North, 1972). The six C-C bonds are also quite normal: 1.383, 1.382, 1.385, 1.386, 1.396 and 1.392 Å. The C-O-C angle is $115.9 \pm 0.3^\circ$, very similar to values of 115.6° , 115.8° and 116.3° found in the 2,3,7,8-tetrachloro and 2,7-dichloro derivatives. As a consequence, the C-C-O angles in the heterocycle are slightly larger than the trigonal angle and average 122.1° .

The thermal ellipsoids of octachlorodibenzo-*p*-dioxin (Fig. 2) show a conspicuous feature found in each of the centrosymmetric chlorodioxin structures (see also Fig. 2), namely a large component of thermal motion at the oxygen atom in a direction approximately normal to the molecular plane. In octachlorodibenzo-*p*-dioxin, the largest vibrational component has a magnitude of 0.303 Å and is directed only 4.7° from the plane normal. In 2,7-dichlorodibenzo-*p*-dioxin the largest amplitude was 0.282 Å, directed 8.4° from the plane normal, and in 2,3,7,8-tetrachlorodibenzo-*p*-dioxin the two independent molecules had principal axes of 0.254 Å (*A*) and 0.262 Å (*B*) in directions 5.5° and 8.8° respectively from the plane normals. Not surprisingly then, the thermal motion of the centrosymmetric chlorodioxins is not particularly well approximated by the rigid body

approximation, at least as applied to the molecule as a whole. When the TLS program of Schomaker & Trueblood (1968) was applied to the complete octachlorodibenzo-*p*-dioxin molecule, the root mean square Δu_{ij} was 0.0071 \AA^2 , a fairly poor fit. If one benzene ring, its chlorine substituents and the two directly bonded oxygens are taken as the rigid body, the fit improves greatly to 0.0023 \AA^2 . An even better r.m.s. Δu_{ij} of 0.0018 \AA^2 is obtained if the oxygen atoms are omitted from the previous calculation. Almost parallel results were obtained in a series of TLS calculations for the di- and tetra-chlorodioxins, where the r.m.s. Δu_{ij} 's were 0.0018 \AA^2 (2,7), 0.0013 \AA^2 (2,3,7,8-*A*) and 0.0025 \AA^2 (2,3,7,8-*B*) for the one-ring model omitting oxygen atoms. We interpret these results as suggesting that the centrosymmetric chlorodioxins, while exhibiting a planar structure on time average in the crystalline state, may nevertheless be quite flexible with respect to a folding motion hinged at the O...O axis. This surmise is supported by the slightly bowed structures exhibited in the solid by the nonplanar chlorodioxins 2,8-di- (Boer, Neuman & Aniline, 1972) and 1,2,3,7,8,9-hexa- (Cantrell, Webb & Mabis, 1969), and the severely nonplanar structures of the homologous thianthrenes (Lynton & Cox, 1956; Rowe & Post, 1958).

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