2,8-Dichlorodibenzo-*p*-dioxin*

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Abstract. Orthorhombic, *Pnam*, $a = 5.983(6)$, $b = 7.114(10)$, $c = 24.64(3)$ Å, 25°C, $C_{12}H_6O_2Cl_2$, $M = 252.94$, $Z = 4$, $D_x = 1.602$. The molecules are slightly nonplanar with an unusual packing arrangement.

Introduction. Interest in the chlorodioxins is keen principally because of the severe untoward biological effects exhibited by 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Rowe, Norris, Sparschu, Schwetz & Gehring, 1971). As part of a larger program to isolate and characterize the properties of key compounds in this series, an effort (Aniline, 1972) was made to synthesize 2,8-dichlorodibenzo-*p*-dioxin by pyrolysis of the potassium salt of 5-chloro-2-(2,4-dichlorophenoxy)phenol. The product mixture from the original reaction [in bis-(2-ethoxyethyl) ether solution for 15 hr at 200°] was shown, surprisingly, to contain predominantly 2,7-dichlorodibenzo-*p*-dioxin which forms crystals of lath-like habit. However, a few plate-like crystals also occurred, and these were physically isolated and identified in the present study as 2,8-dichlorodibenzo-*p*-dioxin.

Experimental. A crystal of approximate dimensions $0.30 \times 0.27 \times 0.01$ mm was sealed within a 0.3 mm diam-

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* This and the following two articles are the first of the Short Structural Papers, an announcement concerning which is printed on page 2888 of this issue.

eter Lindemann glass capillary. Weissenberg photographs showed reciprocal-lattice symmetry *mmm* (D_{2h}) and the systematic absences characteristic of space groups *Pnam* or *Pna2₁*. Lattice parameters were determined by least-squares refinement of the setting angles of 10 reflections. The θ–2θ scan mode of a Picker diffractometer was used to collect intensity data with Mo $K\bar{\alpha}$ radiation monochromatized by the 002 reflection of a highly oriented graphite crystal. A total of 1206 unique reflections (within the sphere $\sin\theta \leq 0.461$) were measured. The number and quality of the reflection data were somewhat disappointing owing to (1) the weakness of scattering, (2) decomposition of the crystal under irradiation, and (3) the mosaic character of the crystal. A group of 294 reflections satisfying the relatively stringent criteria $\sigma(I)/I < 0.2$ and $I > 0$ were selected for subsequent refinement. The intensities were corrected for absorption ($\mu = 5.12$ cm⁻¹); transmission factors ranged from 0.919 to 0.994.

The crystal structure was solved by Patterson and crystal packing analysis and refined by full-matrix least-squares. The space group was assigned after comparing refinements in *Pna2₁*, where poorly conditioned normal equations were encountered, and in *Pnam*, where the atomic parameters were well-behaved. The final refinement model included anisotropic temperature factors for the Cl, O, and C atoms. Hydrogen atoms were placed at calculated positions 1.01 Å from

Table 1. *Final structure parameters* (*with standard deviations in parentheses*)

(a) Heavy atoms (anisotropic thermal parameters)*

	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^4\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Cl	0.3003 (6)	0.0705 (7)	0.4541 (1)	29 (1)	37 (1)	15 (1)	−4 (1)	−1 (1)	0 (1)
O(1)	0.2586 (20)	0.0973 (21)	0.25	17 (6)	32 (5)	10 (2)	−10 (4)		
O(2)	−0.1758 (22)	−0.0780 (22)	0.25	15 (5)	28 (5)	18 (3)	−7 (6)		
C(1)	0.1492 (25)	0.0443 (18)	0.2969 (6)	20 (6)	10 (3)	13 (4)	−3 (3)	−1 (1)	0 (1)
C(2)	−0.0638 (22)	−0.0372 (18)	0.2971 (5)	9 (6)	17 (4)	17 (4)	−4 (4)	2 (2)	−1 (1)
C(3)	0.2607 (25)	0.0804 (21)	0.3449 (6)	26 (6)	13 (3)	14 (3)	0 (4)	1 (1)	1 (1)
C(4)	−0.1596 (20)	−0.0843 (18)	0.3460 (6)	10 (5)	9 (3)	20 (3)	−3 (4)	1 (1)	0 (1)
C(5)	0.1541 (31)	0.0298 (19)	0.3937 (5)	30 (7)	16 (4)	10 (2)	10 (5)	−1 (1)	−1 (1)
C(6)	−0.0581 (27)	−0.0489 (23)	0.3944 (6)	8 (5)	26 (4)	15 (3)	4 (5)	1 (1)	−1 (1)

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

Table 1 (*cont.*)

(b) Hydrogen atoms (isotropic thermal parameters)

	x	y	z	B
H(3)	0.414	0.141	0.345	4.0
H(4)	−0.311	−0.148	0.346	4.0
H(6)	−0.136	−0.080	0.430	4.0

the appropriate carbons, but their coordinates were not refined. Atomic scattering factors, including $\Delta f'$ and $\Delta f''$ for Cl, were obtained from *International Tables for X-ray Crystallography* (1962), except for hydrogen, for which the scattering factor of Stewart, Davidson & Simpson (1965) was used.

Table 2. Structure factors in $e \times 10$

Fig. 1. Bond distances and angles for 2,8-dichlorodibenzo-p-dioxin. Standard errors were computed from the least-squares variance-covariance matrix.

Fig. 2. The crystal structure of 2,8-dichlorodibenzo-p-dioxin as viewed down the b axis. The a axis is horizontal and c is vertical.

Table 3. Intermolecular contacts*

Atom 1	Atom 2	Transform (atom 2)			Distance
O(1)	O(2)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$	3·439 Å
O(1)	O(2)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$	3·500
O(1)	O(2)	$1+x$	y	z	3·604
O(1)	C(1)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$	3·644
O(1)	O(1)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$	3·694
O(2)	C(1)	$x-\frac{1}{2}$	$-\frac{1}{2}-y$	$\frac{1}{2}-z$	3·664
C(1)	C(4)	$\frac{1}{2}+x$	$-\frac{1}{2}-y$	z	3·669
C(2)	C(3)	$x-\frac{1}{2}$	$\frac{1}{2}-y$	z	3·610
C(3)	C(4)	$\frac{1}{2}+x$	$-\frac{1}{2}-y$	z	3·559
C(3)	C(4)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z	3·614
C(4)	C(5)	$1+x$	y	z	3·658
C(4)	C(5)	$x-\frac{1}{2}$	$-\frac{1}{2}-y$	z	3·558
Cl	Cl	$1-x$	$-y$	$1-z$	3·437

* Unique non-hydrogen contacts less than 3·7 Å.

Results and discussion. The molecular structure is slightly nonplanar. A least-squares plane through the six unique carbon atoms and the two oxygen atoms is defined by the equation $0.4237x - 0.9048y - 0.0405z = -0.29$, where the coefficients are components of a unit vector, x, y, and z are atomic coordinates in Å, and the value -0.29 is the normal distance in Å of the plane from the origin. No C or O atom deviates from this plane by more than 0·015 Å, but the Cl atom is 0·07 Å out of plane. The dihedral angle between the two halves of the molecule related by the transverse mirror plane is 175·2°, a value quite close to that found (175·7°) in 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin (Cantrell, Webb & Mabis, 1969), the only other chlorodioxin known to be nonplanar in the solid state.

The bond lengths and angles (Fig. 1) are all normal, and in fact are within experimental error of the corresponding values in a crystal structure study of 2,7-dichlorodibenzo-p-dioxin (Boer & North, 1972) where the atomic parameters have been determined with better precision.

The crystal structure, illustrated in Fig. 2, contains two distinct layers of molecules centered on the mirror planes at $c/4$ and $3c/4$. Within each layer herring-

bone packing occurs: the molecule forms an angle of 25·2° with the *a* axis and the molecules related by the *a* glide in the **b** direction form angles of 50·4° with each other. Intermolecular contact distances within the *x, y* layers are normal (Table 3). Molecules in adjacent layers are aligned head-to-tail and make contact through pairs of Cl···H(6) interactions of 3·02 Å about the center of symmetry at $(0,0,\frac{1}{2})$. In addition, there is a rather short Cl···Cl interaction of 3·44 Å across the center of symmetry at $(\frac{1}{2},0,\frac{1}{2})$. This structure differs fundamentally from those of the centrosymmetric chlorodioxins, 2,7-dichlorodibenzo-*p*-dioxin (Boer & North, 1972), 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Boer, van Remoortere, North & Neuman, 1972), and octachlorodibenzo-*p*-dioxin (Neuman, North & Boer, 1972), where the molecules are stacked along very short lattice periods of about 3·8 Å.

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Sodium Rubidium Dichromate and Sodium Caesium Dichromate

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Abstract. Sodium rubidium dichromate is monoclinic, space group $P2_1/c$, $a = 12·947$ (15), $b = 11·133$ (11), $c = 10·037$ (18) Å, $\beta = 93·42$ (8)°, formula $NaRbCr_2O_7$, $Z = 8$, $D_x = 2·98$. Prepared from a melt of a 1:1 mixture of $Na_2Cr_2O_7$ and $Rb_2Cr_2O_7$. The structure contains blocks of composition $(RbCr_2O_7)_4$ which are similar to those found in $Rb_2Cr_2O_7$ structures. The Na atoms all lie between the blocks. Sodium caesium dichromate, $NaCsCr_2O_7$, is isotypic with $a = 12·98$ (2), $b = 11·58$ (2), $c = 10·10$ (2) Å, $\beta = 93·8$ (2)°.

Introduction. The crystals are hygroscopic and were sealed in quartz capillaries under dry nitrogen.

The crystal size was approximately 0·2 mm across, $\mu(\text{Mo } K\alpha) = 10·2 \text{ mm}^{-1}$. Cell constants were determined from the angular settings of 14 low angle reflexions measured with Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å) on a Syntex diffractometer. Systematic absences were observed for *h0l* reflexions with *l* odd and *0k0* reflexions with *k* odd. Intensities measured on the Syntex diffractometer with Mo $K\alpha$ radiation included all in the range $5 < 2\theta < 55°$ and some in the range $55 < 2\theta < 65°$ for the quadrant of reciprocal space with *k* and $l \geq 0$. In all, 3200 reflexions of a possible 5200 were measured and 1406 of these were within three standard deviations (counting statistics) of zero after correction for absorption (the crystal shape was defined by 12 faces). Lorentz and polarization corrections were then applied. The structure was solved by

Patterson methods and refined by least squares to give an unweighted residual $(R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|)$ of 0·046 and a weighted residual $\{R_2 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}\}$ of 0·058 where $w = (17·710 - 0·3817|F_o| +$
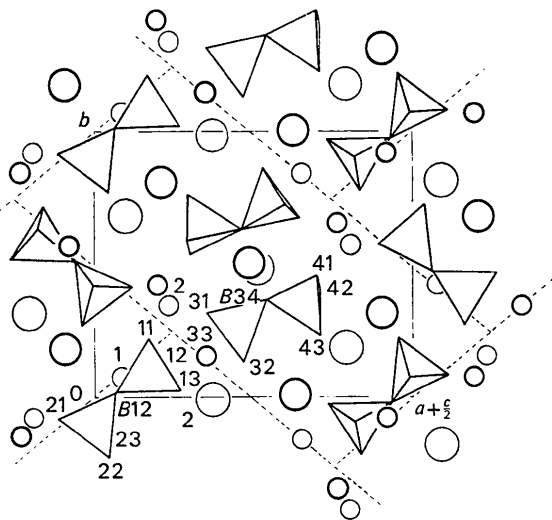

Fig. 1. Projection of $NaRbCr_2O_7$ perpendicular to (20Ī). The dichromate groups are shown by linked tetrahedra, the sodium atoms by small circles, the rubidium atoms by large circles. The $(RbCr_2O_7)_4$ units are outlined. The cations all lie above and below the plane of the dichromate ions.