

Fig. 6. Dihedral angles ($^{\circ}$) and bond lengths (\AA) from a packed-molecule calculation.

for the molecules in the crystals. Hence, it requires much care to analyse and interpret experimental and theoretical results. The asymmetry at the tip cannot be reproduced in the calculation; α , however, is increased to 52° to avoid the close contact between C(7) and C(43). The energy difference between the structures of the isolated and packed molecule has been estimated to be 5 kJ mol^{-1} , negligible in comparison with the calculated sublimation enthalpy of 187 kJ mol^{-1} . The inversion barrier between the two boat forms has been calculated to be 64 kJ mol^{-1} (PIMM) in agreement with the observed $\Delta G^* = 65.7 \text{ kJ mol}^{-1}$ (Kessler, 1980). The enthalpy difference between the heptatriene and the isomeric norcaradiene structure is estimated to be about 50 kJ mol^{-1} .

Acta Cryst. (1980). B36, 2367–2371

The Structures of α - and β -Parachloral [2,4,6-Tris(trichloromethyl)-1,3,5-trioxane]

BY D. G. HAY AND M. F. MACKAY

Department of Physical Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083

(Received 15 March 1980; accepted 13 May 1980)

Abstract

Orthorhombic crystals of the α isomer, $\text{C}_6\text{H}_3\text{Cl}_9\text{O}_3$, $(\text{CCl}_3\text{CHO})_3$, belong to the space group $Pnma$ with $a = 10.666$ (2), $b = 15.439$ (1), $c = 9.400$ (1) \AA , $Z = 4$; monoclinic crystals of the β isomer belong to the space group $P2_1/c$ with $a = 13.115$ (4), $b = 5.887$ (1), $c = 20.064$ (7) \AA , $\beta = 100.88$ (2) $^{\circ}$, $Z = 4$. The structures

The calculations were carried out at the Rechenzentrum der Technischen Hochschule Darmstadt. We thank Professor H. Kessler for supplying the crystals and Professor A. Warshel for a copy of the MCA program. The work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
 DAVIS, R. E. & TULINSKY, A. (1966). *J. Am. Chem. Soc.* **88**, 4583–4588.
 HULER, E. & WARSHEL, A. (1974). *Acta Cryst.* B30, 1822–1826.
 KESSLER, H. (1980). To be published.
 KESSLER, H. & BICKER, R. (1976). Private communication.
 LINDNER, H. J. (1974). *Tetrahedron*, **30**, 1127–1132; *Tetrahedron Lett.* pp. 2479–2482.
 MOTHERWELL, W. D. S. (1975). *PLUTO*. A program for plotting molecular and crystal structures. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1977). *SHELX 77*. A program for crystal structure determination. Univ. of Cambridge, England.
 STEGEMANN, J. (1979). PhD Dissertation, Technische Hochschule Darmstadt.
 STEGEMANN, J. & LINDNER, H. J. (1979). *Acta Cryst.* B35, 2161–2165.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 TOCHTERMANN, W. (1970). *Fortschr. Chem. Forsch.* **15**, 378–444.

were refined to $R = 0.070$ (α isomer) and 0.072 (β isomer). The molecular conformations of α - and β -parachloral are boat and chair forms respectively, with all three trichloromethyl substituents in the equatorial positions. In the trioxane ring of each isomer the bond lengths and angles are similar, the mean values being $\text{C—O} = 1.407 \text{ \AA}$, and $\text{C—O—C} = 110.7^{\circ}$, $\text{O—C—O} = 110.4^{\circ}$.

Introduction

The cyclic trimer of chloral, 2,4,6-tris(trichloromethyl)-1,3,5-trioxane, $(\text{CCl}_3\text{CHO})_3$, known as parachloral, forms two stereoisomers (Chattaway & Kellett, 1928), a low-melting α form (m.p. 387–388 K) and a high-melting β form (m.p. 424–425 K). Following proton magnetic resonance and infrared studies of the two isomers and the dipole-moment measurement of the α isomer (Novak & Whalley, 1958), the α - and β -parachloral molecules were assigned chair conformations, with the α isomer in the one-*trans* form (one CCl_3 group axial) and the β isomer in the all-*cis* form (all CCl_3 groups equatorial). These assignments are in accord with those for 2,4,6-trialkyl-substituted 1,3,5-trioxanes based on NMR and dipole-moment studies (Baron & Hollis, 1964). They also agree with the conformations proposed for the analogous α and β forms of 2,4,6-trisubstituted derivatives of 1,3,5-trithiane (Campaigne, Chamberlain & Edwards, 1962), the all-*cis* form for the β isomer of the trimethyl derivative being confirmed by X-ray analysis (Valle, Busetti, Mammi & Carazzolo, 1969). The present analyses were undertaken to ascertain if in the solid state α - and β -parachloral maintain the conformations established by Novak & Whalley (1958).

Experimental

Weissenberg photographs showed that the crystals of the α and β isomers were orthorhombic and monoclinic respectively and established the space groups. Cell parameters were determined by least squares from 2θ values of 15 strong centred reflections for each crystal on a diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

Crystal data

	α -Parachloral	β -Parachloral
Molecular formula	$\text{C}_6\text{H}_3\text{Cl}_3\text{O}_3$	$\text{C}_6\text{H}_3\text{Cl}_3\text{O}_3$
M_r	442.2	442.2
Space group	$Pnma$	$P2_1/c$
a (Å)	10.666 (2)	13.115 (4)
b (Å)	15.439 (1)	5.887 (1)
c (Å)	9.400 (1)	20.064 (7)
β (°)		100.88 (2)
V_c (Å ³)	1548 (1)	1521 (1)
Z	4	4
$F(000)$	432	432
μ (Cu $K\alpha$) (mm ⁻¹)	14.5	14.8

Intensities for both isomers were measured on a Rigaku-AFC four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The intensities were recorded by an ω - 2θ scan with a scan rate of 2° min^{-1} and 10 s stationary background counts. In each

case, three reference reflections measured after each 50 reflections showed a linear time-dependent decrease in intensity. This could be attributed to radiation-induced polymerization within the crystals, known to occur in these compounds (Hayashi, Nishii & Okamura, 1963). Consequently, three crystals of the α isomer, each with dimensions ca $0.10 \times 0.13 \times 0.11 \text{ mm}$, and two crystals of the β isomer, both with dimensions ca $0.11 \times 0.25 \times 0.10 \text{ mm}$, were used for intensity measurements; all the crystals were aligned with b approximately parallel to the diffractometer φ -axis. For the α isomer, 1264 non-equivalent terms to a 2θ limit of 130° were measured, and 737 with $|F_o| > 2\sigma|F_o|$ were considered observed. For the β isomer, of the 2112 non-equivalent terms measured to a 2θ limit of 125° , 1361 with $|F_o| > 3\sigma|F_o|$ were considered observed. The intensities were corrected for Lorentz and polarization factors but not for absorption. Scattering factors were those of Cromer & Mann (1968) for C, O and Cl and of Stewart, Davidson & Simpson (1965) for H. Anomalous-dispersion corrections were made for the non-hydrogen atoms (Cromer & Liberman, 1970).

Structure analyses

Both structures were solved by direct methods. Phases for 239 (α -parachloral) and 122 (β -parachloral) $|E|$ terms with values >1.2 were derived by a multi-resolution process (Germain, Main & Woolfson, 1971). For each structure, the non-hydrogen atoms were located on the subsequent E maps. Difference maps, calculated after refinement of the C, Cl and O atoms with anisotropic temperature factors, revealed all the H atoms. Final full-matrix least-squares refinements, in which the positional and isotropic thermal parameters of the H atoms were varied, yielded $R = 0.070$ and 0.072 for the α and β isomers respectively, and $R_w = (\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2)^{1/2} = 0.078$ and 0.075 for the 737 (α isomer) and 1361 (β isomer) observed terms.

In the refinements, the function minimized was $\sum w(|F_o| - |F_c|)^2$ with the terms weighted according to $w = m/(\sigma^2|F_o| + n|F_o|^2)$. Values of m and n were 1.06 and 4.18×10^{-2} (α isomer) and 1.68 and 2.42×10^{-2} (β isomer). The direct methods and least-squares calculations were carried out with *SHELX 76* (Sheldrick, 1976). Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2. No corrections for thermal effects have been applied to the latter. Perspective views of the molecules are given in Fig. 1, which includes the atom numbering, and have been prepared with *ORTEP* (Johnson, 1965).*

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35415 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^4$, H $\times 10^3$) with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters (\AA^2)

	x	y	z	B_{eq}^*
(a) α -Parachloral				
Cl(11)	7789 (4)	1020 (2)	6469 (3)	6.5 (2)
Cl(12)	6287 (3)	27 (2)	8422 (4)	6.1 (2)
Cl(13)	8435 (3)	984 (2)	9441 (4)	6.0 (2)
Cl(21)	5856 (3)	1570 (2)	12966 (3)	5.2 (1)
Cl(22)	3830 (3)	2500	11665 (4)	5.4 (2)
O(1)	7034 (8)	2500	8205 (9)	3.6 (5)
O(2)	5838 (6)	1759 (5)	9836 (7)	4.1 (3)
C(1)	6327 (9)	1742 (7)	8444 (10)	4.2 (5)
C(2)	6193 (14)	2500	10589 (14)	3.6 (7)
C(11)	7191 (10)	986 (7)	8225 (10)	3.9 (5)
C(21)	5431 (12)	2500	11984 (15)	4.3 (7)
H(1)†	549 (8)	173 (6)	753 (11)	5.7‡
H(2)†	691 (11)	250	1093 (12)	1.8‡
(b) β -Parachloral				
Cl(11)	9998 (2)	7858 (6)	8035 (1)	4.1 (1)
Cl(12)	10008 (2)	7731 (6)	9475 (1)	3.9 (1)
Cl(13)	10138 (2)	3559 (6)	8735 (1)	4.2 (1)
Cl(21)	5385 (2)	2796 (7)	9348 (1)	5.4 (2)
Cl(22)	7098 (2)	4782 (6)	10271 (1)	4.0 (1)
Cl(23)	7394 (3)	613 (6)	9586 (1)	4.8 (2)
Cl(31)	5392 (2)	3025 (8)	6950 (1)	6.0 (2)
Cl(32)	7126 (2)	4993 (6)	6476 (1)	4.2 (2)
Cl(33)	7369 (3)	746 (6)	7192 (1)	5.1 (2)
O(1)	8101 (5)	5089 (13)	7921 (3)	3.1 (3)
O(2)	8094 (5)	5029 (13)	9077 (3)	3.0 (3)
O(3)	6722 (5)	3475 (13)	8319 (3)	3.1 (3)
C(1)	8408 (7)	6194 (22)	8546 (4)	2.6 (4)
C(2)	7011 (8)	4707 (24)	8932 (4)	3.2 (5)
C(3)	7026 (8)	4740 (24)	7788 (4)	3.3 (5)
C(11)	9606 (8)	6366 (19)	8699 (4)	2.6 (5)
C(21)	6735 (8)	3255 (20)	9512 (5)	3.0 (5)
C(31)	6749 (8)	3399 (20)	7145 (4)	2.8 (5)
H(1)†	828 (7)	794 (18)	856 (5)	3.6‡
H(2)†	653 (7)	600 (18)	891 (4)	3.6‡
H(3)†	655 (7)	611 (17)	772 (4)	3.6‡

* Calculated from the refined anisotropic thermal parameters (deposited).

† Given the same numbering as the C atom to which it is bonded.

‡ Isotropic temperature factors. For β -parachloral an overall B was refined.

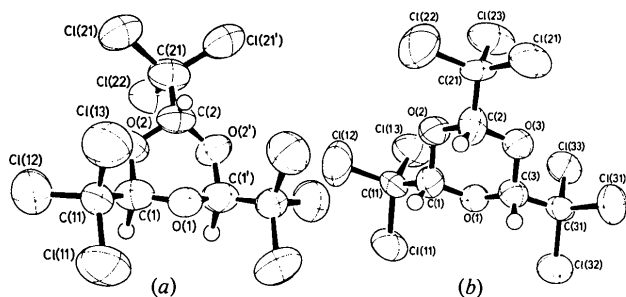


Fig. 1. Perspective views of the molecules with thermal ellipsoids scaled to 75% probability. (a) α -Parachloral, (b) β -parachloral.

Discussion

β -Parachloral adopts the chair conformation with all the CCl_3 groups in equatorial positions, *i.e.* the all-*cis* form (Fig. 1b). This agrees with the structural assignment of Novak & Whalley (1958) and of Baron & Hollis (1964). However, contrary to their assignment of the one-*trans* chair form to α -parachloral, the X-ray results have established the boat conformation with all the CCl_3 substituents equatorial (Fig. 1a). The molecules are in the special position m , so that α -parachloral has exact σ_v symmetry.

α -Parachloral deviates significantly from a regular boat form. This is reflected in the torsion angles around the trioxane ring (Fig. 2a). The angles between the plane of C(1), O(2), C(1'), O(2') and the planes formed by O(2), C(2), O(2') and C(1), O(1), C(1') are 130.2° and 148.9° respectively, and the intramolecular distance $\text{H}(2)\cdots\text{O}(1)$ is 2.6 \AA . Other non-bonded dimensions in the trioxane ring are given in Table 3(a). β -Parachloral does not deviate significantly from $3m$ symmetry (Fig. 2b and Table 3b). All the $\text{C}\cdots\text{O}$ distances across the ring are 2.70 \AA , and the three $\text{O}\cdots\text{O}\cdots\text{O}$ angles vary only from 59.9° to 60.3° . The planes of the three C and the three O atoms in the trioxane ring are nearly parallel (interplanar angle 2.0°) and at a distance of 0.45 \AA . A similar distance (0.462 \AA) was noted in the low-temperature structure of 1,3,5-trioxane (Buseti, Del Pra & Mammi, 1969), while a slightly longer distance (0.513 \AA) was reported for the room-temperature structure (Buseti, Mammi & Carazzolo, 1963).

As the bond lengths and angles derived for each isomer are in good agreement, the discussion of numerical values will refer to the mean values for the two structures. The dimensions of the trioxane rings are similar to those in 1,3,5-trioxane. The C—O length is 1.407 \AA (mean deviation 0.007 \AA) and the C—O—C and O—C—O angles are 110.7° and 110.4° respectively with mean deviations of 1.4 and 0.8° . Viewed down the exocyclic C—C bonds the configurations are staggered. The C—Cl and C—C bonds have lengths of 1.762 and 1.526 \AA respectively with mean deviations of 0.012 and 0.016 \AA . These lengths compare favourably with those noted in other trichloro-substituted compounds (Hovmöller, Smith & Kennard, 1978). As expected, the Cl—C—Cl and Cl—C—C angles are close to the regular tetrahedral value.

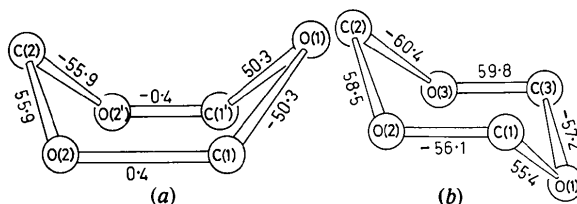


Fig. 2. Torsion angles ($^\circ$) around the trioxane rings. E.s.d.'s range from 0.9 to 1.1° . (a) α -Parachloral, (b) β -parachloral.

Table 2. Bond lengths (\AA) and angles ($^\circ$) involving the non-hydrogen atoms, with e.s.d.'s in parentheses

	α -Parachloral	β -Parachloral		α -Parachloral	β -Parachloral
Cl(11)—C(11)	1.77 (1)	1.75 (1)	C(1)—C(11)	1.50 (1)	1.55 (1)
Cl(12)—C(11)	1.78 (1)	1.74 (1)	C(2)—C(21)	1.54 (2)	1.54 (2)
Cl(13)—C(11)	1.75 (1)	1.79 (1)	C(3)—C(31)		1.50 (2)
Cl(21)—C(21)	1.77 (1)	1.76 (1)	C(1)—O(1)	1.41 (1)	1.40 (1)
Cl(22)—C(21)	1.73 (1)	1.75 (1)	C(1)—O(2)	1.41 (1)	1.39 (1)
Cl(23)—C(21)		1.77 (1)	C(2)—O(2)	1.40 (1)	1.41 (1)
Cl(31)—C(31)		1.76 (1)	C(2)—O(3)		1.42 (1)
Cl(32)—C(31)		1.78 (1)	C(3)—O(1)		1.40 (1)
Cl(33)—C(31)		1.75 (1)	C(3)—O(3)		1.42 (1)
Cl(11)—C(11)—C(1)	109.0 (7)	108.3 (7)	Cl(31)—C(31)—Cl(32)		108.1 (5)
Cl(12)—C(11)—C(1)	107.5 (8)	109.4 (6)	Cl(31)—C(31)—Cl(33)		109.8 (7)
Cl(13)—C(11)—C(1)	112.2 (8)	108.7 (9)	Cl(32)—C(31)—Cl(33)		108.6 (6)
Cl(11)—C(11)—Cl(12)	108.5 (6)	111.4 (7)	C(11)—C(1)—O(1)	107.1 (9)	108.5 (8)
Cl(11)—C(11)—Cl(13)	109.6 (7)	109.0 (5)	C(11)—C(1)—O(2)	111.6 (9)	108.4 (8)
Cl(12)—C(11)—Cl(13)	110.0 (6)	109.9 (6)	C(21)—C(2)—O(2)	106.8 (8)	106.9 (9)
Cl(21)—C(21)—C(2)	108.0 (7)	108.4 (8)	C(21)—C(2)—O(3)		108.0 (10)
Cl(22)—C(21)—C(2)	111.8 (11)	107.9 (9)	C(31)—C(3)—O(1)		108.3 (9)
Cl(23)—C(21)—C(2)		111.7 (8)	C(31)—C(3)—O(3)		108.3 (9)
Cl(21)—C(21)—Cl(22)	110.1 (6)	109.8 (5)	O(1)—C(1)—O(2)	109.3 (9)	112.3 (10)
Cl(21)—C(21)—Cl(21'),(23)	108.8 (6)	109.8 (7)	O(1)—C(3)—O(3)		110.5 (8)
Cl(22)—C(21)—Cl(23)		109.2 (6)	O(2)—C(2)—O(2'),(3)	109.9 (9)	110.0 (8)
Cl(31)—C(31)—C(3)		109.1 (7)	C(1)—O(1)—C(1'),(3)	112.2 (7)	110.3 (7)
Cl(32)—C(31)—C(3)		108.3 (8)	C(1)—O(2)—C(2)	112.7 (9)	109.9 (8)
Cl(33)—C(31)—C(3)		112.8 (8)	C(2)—O(3)—C(3)		108.5 (9)

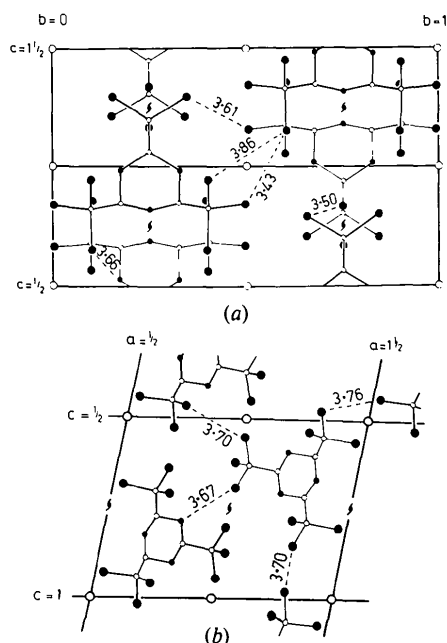
Table 3. Non-bonded intramolecular dimensions (\AA and deg) in the trioxane rings(a) α -Parachloral

O(1)...C(2)	2.40 (1)	C(1)...C(2)	2.34 (2)
O(2)...C(1')	2.70 (1)	C(1)...C(1')	2.34 (2)
O(1)...O(2)	2.30 (2)	H(1)...H(1')	2.4 (2)
O(2)...O(2')	2.29 (1)	H(2)...O(1)	2.6 (1)
O(1)...O(2)...O(2')	60.1 (10)		
O(2)...O(1)...O(2')	59.7 (8)		
C(1)...C(2)...C(1')	60.0 (11)		
C(2)...C(1)...C(1')	60.0 (11)		

(b) β -Parachloral

O(1)...C(2)	2.70 (1)	C(1)...C(2)	2.29 (4)
O(2)...C(3)	2.70 (1)	C(1)...C(3)	2.30 (3)
O(3)...C(1)	2.70 (1)	C(2)...C(3)	2.30 (2)
O(1)...O(2)	2.32 (2)	H(1)...H(2)	2.8 (3)
O(1)...O(3)	2.31 (2)	H(1)...H(3)	2.8 (3)
O(2)...O(3)	2.31 (2)	H(2)...H(3)	2.4 (2)
O(1)...O(2)...O(3)	59.9 (12)		
O(1)...O(3)...O(2)	60.3 (12)		
O(2)...O(1)...O(3)	59.9 (12)		
C(1)...C(2)...C(3)	60.1 (17)		
C(1)...C(3)...C(2)	59.7 (18)		
C(2)...C(1)...C(3)	60.1 (15)		

The molecular packing in α -parachloral is illustrated in Fig. 3(a). The molecules are orientated with the plane of the four ring atoms, C(1), O(2), C(1'), O(2'), inclined at 21.7° to the (100) plane. Viewed down *a*, there is no overlap of the trioxane rings within the unit cell, and there are no close approaches between molecules related by the *a* translation. The β -para-

Fig. 3. The projections of the structures of (a) α -parachloral down *a* and of (b) β -parachloral down *b*.

chloral molecules are stacked directly one above the other to form rows parallel to *b* (Fig. 3b). This contrasts with the packing of the 1,3,5-trioxane molecules (Busetti, Del Pra & Mammi, 1969). The latter stack in rows with the ring O atoms nearly superimposed on the ring C atoms of adjacent

Table 4. *Intermolecular approaches* $<3.9 \text{ \AA}$ E.s.d.'s range from 0.01 to 0.02 \AA .(a) α -Parachloral

Cl(11)···O(2) ^I	3.66	Cl(13)···Cl(11) ^{IV}	3.86
Cl(22)···C(2) ^{II}	3.82	Cl(21)···Cl(12) ^V	3.61
Cl(22)···C(4) ^{II}	3.84	Cl(21)···Cl(13) ^{VI}	3.67
Cl(22)···Cl(11) ^{III}	3.89	Cl(22)···Cl(21) ^{VI}	3.50
Cl(12)···Cl(11) ^{IV}	3.43		

(I)*	$\frac{1}{2} + x, \quad y, \quad 1\frac{1}{2} - z$	(IV)	$1\frac{1}{2} - x, \quad -y, \quad \frac{1}{2} + z$
(II)	$-\frac{1}{2} + x, \quad \frac{1}{2} - y, \quad 2\frac{1}{2} - z$	(V)	$1 - x, \quad -y, \quad 2 - z$
(III)	$-\frac{1}{2} + x, \quad \frac{1}{2} - y, \quad 1\frac{1}{2} - z$	(VI)	$-\frac{1}{2} + x, \quad y, \quad 2\frac{1}{2} - z$

(b) β -Parachloral

Cl(33)···C(1) ^I	3.88	Cl(23)···Cl(12) ^V	3.70
Cl(23)···Cl(12) ^I	3.87	Cl(21)···Cl(31) ^{VI}	3.84
Cl(23)···C(1) ^I	3.73	Cl(21)···Cl(32) ^{VI}	3.78
Cl(11)···O(1) ^{II}	3.67	Cl(31)···C(3) ^{VI}	3.84
Cl(11)···Cl(11) ^{III}	3.65	Cl(31)···O(3) ^{VI}	3.82
Cl(13)···Cl(11) ^{III}	3.55	Cl(21)···Cl(22) ^{VII}	3.76
Cl(33)···Cl(11) ^{III}	3.78	Cl(32)···Cl(22) ^{VIII}	3.70
Cl(12)···Cl(12) ^{IV}	3.40	Cl(32)···Cl(23) ^{VIII}	3.89
Cl(13)···Cl(12) ^V	3.71	Cl(33)···Cl(22) ^{VIII}	3.82
Cl(12)···O(2) ^V	3.81		

(I)*	$x, -1 + y, \quad z$	(V)	$2 - x, \quad 1 - y, \quad 2 - z$
(II)	$2 - x, \quad \frac{1}{2} + y, \quad 1\frac{1}{2} - z$	(VI)	$1 - x, \quad -\frac{1}{2} - y, \quad 1\frac{1}{2} - z$
(III)	$2 - x, \quad -\frac{1}{2} + y, \quad 1\frac{1}{2} - z$	(VII)	$1 - x, \quad 1 - y, \quad 2 - z$
(IV)	$2 - x, \quad 2 - y, \quad 2 - z$	(VIII)	$x, \quad \frac{1}{2} - y, \quad -\frac{1}{2} + z$

* Roman numeral superscripts denote equivalent positions relative to the reference molecule at x, y, z .

molecules at a distance of 3.65 \AA , and, consequently, each axial H atom points towards an O atom. The bulky CCl_3 substituents in molecules of adjacent rows do not allow this mode of packing in β -parachloral in which the trioxane rings are separated by the **b** translation (5.89 \AA).

With a value 1.77 \AA for the van der Waals radius of Cl (Bondi, 1964), the short Cl(12)···Cl(11) distance of 3.43 \AA in α -parachloral and the two distances Cl(12)···Cl(12) and Cl(13)···Cl(11) of 3.40 and 3.55 \AA respectively in β -parachloral provide examples

of the effect of polar flattening (Nyburg, 1979). Intermolecular approach distances $<3.9 \text{ \AA}$ are listed in Table 4.

We thank ICI Australia Ltd, who suggested the problem and supplied the compounds. One of us (DGH) acknowledges the support of an Australian Commonwealth Postgraduate Research Award.

References

- BARON, M. & HOLLIS, D. P. (1964). *Recl Trav. Chim. Pays-Bas*, **83**, 391–399.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- BUSETTI, V., DEL PRA, A. & MAMMI, M. (1969). *Acta Cryst.* **B25**, 1191–1194.
- BUSETTI, V., MAMMI, M. & CARAZZOLO, G. (1963). *Z. Kristallogr.* **119**, 310–318.
- CAMPAIGNE, E., CHAMBERLAIN, N. F. & EDWARDS, B. E. (1962). *J. Org. Chem.* **27**, 135–138.
- CHATTAWAY, F. D. & KELLETT, E. G. (1928). *J. Chem. Soc.* pp. 2709–2714.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HAYASHI, K., NISHII, M. & OKAMURA, S. (1963). *J. Polym. Sci.* **4**, 839–848.
- HOVMÖLLER, S., SMITH, G. & KENNARD, C. H. L. (1978). *Acta Cryst.* **B34**, 3016–3021.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- NOVAK, A. & WHALLEY, E. (1958). *Can. J. Chem.* **36**, 1116–1120.
- NYBURG, S. C. (1979). *Acta Cryst.* **A35**, 641–645.
- SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- VALLE, G., BUSETTI, V., MAMMI, M. & CARAZZOLO, G. (1969). *Acta Cryst.* **B25**, 1631–1636.