

Structure of 1,2-*O*-(2,2,2-Trichloroethylidene)- $\alpha$ -D-glucofuranose ( $\alpha$ -D-Chloralose)

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**Abstract.**  $C_8H_{11}Cl_3O_6$ ,  $M_r = 309.47$ , hexagonal,  $P3_2$ ,  $a = 13.383$  (3),  $c = 5.692$  (2) Å,  $V = 883.0$  Å<sup>3</sup>,  $Z = 3$ ,  $D_x = 1.746$ ,  $D_m = 1.755$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu(\text{Mo } K\alpha) = 0.792$  mm<sup>-1</sup>. The structure was solved by direct methods and refined to  $R(F) = 0.050$  for 992 independent reflexions. The glucofuranose and dioxolane rings have <sup>3</sup>T<sub>4</sub> and <sup>0</sup>(2)*E* conformations, respectively, and these two rings are rigidly fused. The molecules are packed in a left-handed helix arrangement along the *c* axis. The furanose-ring O atoms form intermolecular hydrogen bonds with the O(3) hydroxyl groups. The intermolecular hydrogen bonds between the O(5) and O(6) hydroxyl groups form right-handed double-helix chains around a threefold screw axis. Cl...Cl intermolecular contacts (3.45 Å) were observed about another threefold screw axis.

**Introduction.**  $\alpha$ -D-Chloralose crystallized from an ethanol–water solution at room temperature. A crystal with dimensions 0.17 × 0.20 × 0.33 mm was used to collect 1967 intensities of the *hkl* and *h $\bar{k}l$*  reflexions by  $\omega$ – $2\theta$  scans to  $\theta = 50^\circ$  on a Rigaku AFC-5 diffractometer. The structure was solved with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1977), using 150 reflexions for phase generation. The first *E* map revealed all of the non-H atoms. The chemically known absolute structure was correctly given for space group  $P3_2$  (two possible space groups,  $P3_1$  and  $P3_2$ , were indicated from the systematic absences  $00l$  with  $l \neq 3n$ ). The structure was refined by full-matrix least squares, minimizing  $\sum w|F_o - kF_c|^2$  with  $w^{-1} = \sigma^2(F_o) + (0.023F_o)^2$  and where  $\sigma(F_o)$  is the standard deviation of  $F_o$  from counting statistics. All H atoms were located from difference Fourier maps and refined isotropically. The final values of  $R = \sum |F_o - k|F_c| / \sum |F_o|$  and  $R_w = (\sum w|F_o - k|F_c|^2 / \sum |F_o|^2)^{1/2}$  were 0.050 and 0.062, respectively, for 992 independent reflexions [ $F_o > 3\sigma(F_o)$ ]. The atomic scattering factors for all atoms were obtained from *International Tables for X-ray Crystallography* (1974). All computations were performed on a FACOM M200 computer at the Data Processing Center, Kyoto University, using the *KPAX* program

system. The atomic parameters are given in Tables 1 and 2.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36731 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates for non-hydrogen atoms in  $\alpha$ -D-chloralose

Estimated standard deviations are given in parentheses.  $B_{\text{eq}}$  is the isotropic equivalent of the anisotropic thermal parameters (Hamilton, 1959).

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$ (Å <sup>2</sup> )
Cl(1)	0.2424 (2)	0.9377 (2)	0.1615 (1)	4.04
Cl(2)	0.2654 (3)	1.1556 (3)	0.2975 (6)	5.13
Cl(3)	0.1399 (2)	1.0423 (3)	−0.1215 (7)	5.68
C(1)	0.5420 (7)	1.1436 (7)	−0.1217 (15)	3.03
C(2)	0.4778 (7)	1.1079 (7)	−0.3527 (16)	3.22
C(3)	0.4862 (7)	1.0048 (7)	−0.4331 (15)	3.02
C(4)	0.4923 (6)	0.9528 (7)	−0.2003 (15)	2.80
C(5)	0.5456 (7)	0.8763 (6)	−0.2112 (15)	2.84
C(6)	0.5673 (7)	0.8395 (7)	0.0254 (14)	2.68
C(7)	0.3681 (8)	1.1343 (8)	−0.0911 (15)	3.11
C(8)	0.2585 (8)	1.0703 (8)	0.0598 (16)	3.88
O(1)	0.4680 (5)	1.1569 (5)	0.0372 (11)	3.08
O(2)	0.3612 (5)	1.0692 (5)	−0.2825 (11)	3.43
O(3)	0.5908 (5)	1.0428 (5)	−0.5602 (11)	3.31
O(4)	0.5607 (5)	1.0525 (4)	−0.0514 (11)	2.88
O(5)	0.4664 (5)	0.7749 (5)	−0.3387 (11)	3.70
O(6)	0.4651 (5)	0.7775 (5)	0.1598 (13)	4.21

Table 2. Fractional coordinates and isotropic thermal parameters (Å<sup>2</sup>) for hydrogen atoms in  $\alpha$ -D-chloralose

E.s.d.'s for *B* values are 1.1–2.1 Å<sup>2</sup>.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(C1)	0.622 (5)	1.214 (5)	−0.110 (11)	2.0
H(C2)	0.501 (6)	1.172 (6)	−0.484 (13)	3.2
H(C3)	0.418 (6)	0.941 (6)	−0.540 (11)	2.5
H(C4)	0.414 (5)	0.912 (5)	−0.128 (10)	1.6
H(C5)	0.626 (6)	0.932 (6)	−0.292 (11)	2.6
H(C6A)	0.611 (6)	0.793 (6)	0.005 (12)	3.2
H(C6B)	0.623 (7)	0.911 (7)	0.131 (13)	3.6
H(C7)	0.374 (5)	1.211 (5)	−0.149 (11)	2.1
H(O3)	0.571 (8)	1.041 (8)	−0.723 (16)	5.8
H(O5)	0.494 (7)	0.797 (8)	−0.496 (13)	4.7
H(O6)	0.410 (6)	0.713 (7)	0.074 (13)	3.8

**Discussion.** The atomic numbering and thermal ellipsoids are shown in Fig. 1. The bond lengths and valence angles for non-H atoms are given in Fig. 2. The estimated standard deviations for the bond lengths are less than 0.015 Å and those for the valence angles are less than 0.9°. The average C–H and O–H bond lengths are 1.04 and 0.96 Å, respectively. The glucofuranose ring has the  $^3T_4$  conformation with the pseudorotation phase angle  $P = 35.5^\circ$  (Altona & Sundaralingam, 1972). The dioxolane ring has the  $^0E$  conformation. The torsion angles O(1)–C(1)–C(2)–C(3) and O(2)–C(2)–C(1)–O(4) are  $-131.3(6)$  and  $100.9(6)^\circ$ , respectively. The fused-ring conformation is in good agreement with that of 1,2-*O*-isopropylidene-glucosyl furanose (Takagi & Jeffrey, 1979), and the  $^3T_4$  conformation of the furanose ring agrees with that of 1,2-*O*-isopropylidene-lyxofuranose (Depmeier, Jarchow, Stadler, Sinnwell & Paulsen, 1974). It differs from those of any other pento- and ketohexofuranoses observed hitherto (Altona & Sundaralingam, 1972; Swaminathan, Anderson & Sundaralingam, 1979). The torsion angles O(4)–C(4)–C(5)–O(5) and O(5)–C(5)–C(6)–O(6) are  $173.7(6)$  and  $-59.7(9)^\circ$ , respectively. The conformation about the C(4)–C(5)–C(6) bonds is similar to those observed in other glucofuranoses: 1,2-isopropylidene-glucosyl furanose (Takagi & Jeffrey, 1979) and ethyl 1-thio-glucosyl furanoside (Parthasarathy & Davis, 1967). The trichloroethyl group has a staggered conformation. The torsion angles about the C(7)–C(8) bond with respect to O(1) are  $-58.9(8)$ ,  $62.6(10)$ , and  $-177.8(6)^\circ$  for Cl(1), Cl(2), and Cl(3), respectively.

A stereoview showing the molecular packing is given in Fig. 3. The molecules are packed in the form of a left-handed helix along the *c* axis. The Cl(3) atoms are close to each other about the  $3_2$  axis through the origin. The Cl...Cl intermolecular distance of 3.450(5) Å is slightly shorter than the sum of the van der Waals radii [1.75 Å for a Cl atom (Bondi, 1964)]. The O(3) hydroxyl group forms an intermolecular hydrogen bond with the ring atom O(4) of the neighbouring molecule. The hydrogen-bond distances are 2.837(9) and 1.89(9) Å for O(3)...O(4) and H(O3)...O(4),

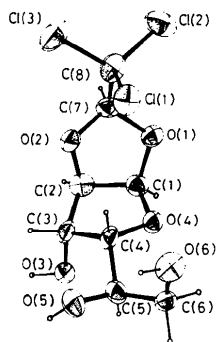


Fig. 1.  $\alpha$ -D-Chloralose: atomic numbering and thermal ellipsoids at 50% probability.

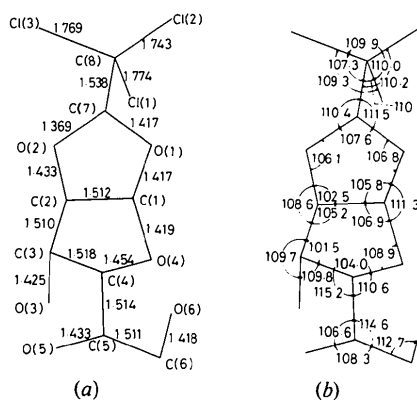


Fig. 2. Molecular dimensions of  $\alpha$ -D-chloralose. (a) Bond lengths (Å) and (b) valence angles ( $^\circ$ ).

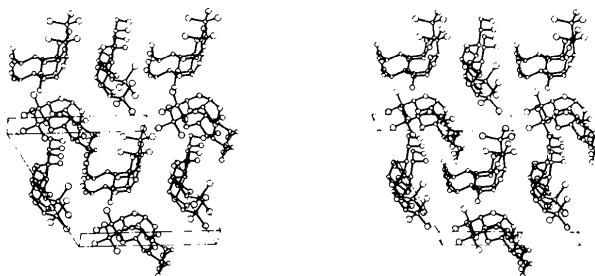


Fig. 3. Molecular packing in  $\alpha$ -D-chloralose.

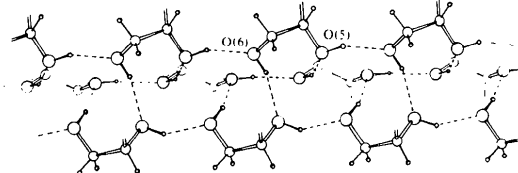


Fig. 4. A perspective view of the O(5)...O(6) hydrogen bonding in the crystal structure of  $\alpha$ -D-chloralose.

respectively. The H(O3)–O(3)...O(4), C(1)–O(4)...H(O3), and C(4)–O(4)...H(O3) angles are  $7(4)$ ,  $114(5)$ , and  $123(4)^\circ$ , respectively, and the O(3) hydrogen bond is directed to a lone pair of the ring O atom O(4). As shown in Fig. 4, the O(5) and O(6) hydroxyl groups also form intermolecular hydrogen bonds around the  $3_2$  axis. The hydrogen-bonding chains form a right-handed threefold double helix. The O(5)...O(6), H(O5)...O(6), O(6)...O(5), and H(O6)...O(5) distances are 2.855(9), 1.99(8), 2.977(8), and 2.13(8) Å, respectively, and the H(O5)–O(5)...O(6), H(O6)–O(6)...O(5), O(6)...O(5)...O(6)', and O(5)...O(6)...O(5)' angles are  $21(4)$ ,  $17(4)$ ,  $107.7(6)$ , and  $107.7(6)^\circ$ , respectively. The donor–acceptor sequences of the two hydrogen-bonding chains in the double helix have the same direction. The hydrogen-bond system is stabilized by the head-and-tail interactions of the electrically polar hydrogen bonds.

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**Tetraaquabis(monochloroacetato)nickel(II) dihydrate: erratum.** By X. SOLANS and C. MIRAVITLLES, *Departamento de Cristalografía y Mineralogía, Universidad de Barcelona, UEI de Rayos-X y Estructuras Cristalinas, Instituto 'Jaime Almera' del Consejo Superior de Investigaciones Científicas, Egipcíacas 13, Barcelona 1, Spain*

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#### Abstract

Errors in Table 1 of the paper by Solans & Miravittles [*Acta Cryst.* (1981), **B37**, 1407–1409] are corrected. The correct  $y$  atomic coordinates for four of the atoms are as follows

( $\times 10^5$ , for H  $\times 10^3$ ): Cl(1) –28969 (9), C(2) –24586 (34), C(3) –15401 (32), H(C22) –277 (4).

All the relevant information is given in the *Abstract*.