Acta Cryst. (1976). B**32**, 964

Crystal Structures of Analogues of D-Galactose. II. 2,3,4,6-Tetra-*O*-acetyl-1-cyano-β-D-galactopyranose (CTAG)

By C. Foces-Foces, F. H. Cano and S. García-Blanco
Instituto de Química-Física, 'Rocasolano', CSIC, Madrid-6, Spain

(*Received* 30 *October* 1975; *accepted* 23 *November* 1975)

Abstract. $C_{15}H_{19}NO_9$, monoclinic, $P2_1$, $Z=2$, M.W. 357·3, $a=11{\cdot}565$ (2), $b=8{\cdot}698$ (1), $c=9{\cdot}125$ (1) Å, $\beta=103{\cdot}55$ (1)°, $V=892{\cdot}3$ Å^3, $D_x=1{\cdot}33$, $D_m=1{\cdot}37$ g cm^{-3} (by flotation). The conformation around the C(5)–C(6) bond is *trans–gauche*. The final unweighted and weighted R values for the observed reflexions are 0·052 and 0·060 respectively.

Introduction. The compound, hereinafter CTAG, was obtained by condensation reactions of glycosyl halides and metallic cyanides in order to synthesize galactoside disaccharides exhibiting the 1–4 glycosidic bond. The resultant products of these types of reactions have been studied (Chacon-Fuertes, 1975), but there remained some doubts on the hydrogen conformation in the CH_2 group of the acetoxymethyl chain and the presence of the C≡N group was not clear as far as the interpretation of the infrared and n.m.r. spectra was concerned.

A crystal of approximate dimensions 0·56 × 0·40 × 0·12 mm was used to record 1721 reflexions up to $\theta < 25°$ on a Philips PW 1100 four-circle diffractometer, operating in the $\omega/2\theta$ scan mode. Mo $K\bar{\alpha}$ radiation through a graphite monochromator was used. A reflexion was considered as unobserved if its intensity was less than $2\sigma(I)$ where $\sigma(I)$ was determined from counting statistics. 397 reflexions were considered as unobserved according to this criterion. The cell dimensions were determined by least-squares refinement of 33 θ values. Systematic absences were consistent with space group $P2_1$ since CTAG was obtained from a D-compound, its optical rotation being determined with a Perkin–Elmer 141 polarimeter. The data were corrected for Lorentz and polarization but not for absorption effects. The phase problem was solved using the *MULTAN* program (Germain, Main & Woolfson, 1971). Tangent formula refinement and a Fourier calculation revealed all the non-hydrogen atoms. The coordinates from this synthesis were used as the starting point for the isotropic full-matrix least-squares refinement. Due to the number of parameters (226), the anisotropic refinement of all positional and thermal parameters was done by block-matrix approximation. The structural parameters were divided into two blocks: (*a*) all oxygen and nitrogen atoms and (*b*) all carbon atoms. The final R value was 0·077. All hydrogen atoms were located in a difference Fourier syn-

Table 1. *Final positional* (× 10^4) *and thermal parameters and their standard deviations for the heavy atoms*

Anisotropic temperature factors are expressed as: $(-2\pi^2\sum U_{ij}a_i^*a_j^*h_ih_j)$ and are multiplied by 10^3.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	−1656 (5)	4876 (8)	−705 (5)	89 (3)	119 (4)	56 (2)	26 (3)	2 (2)	17 (3)
O(2)	4113 (3)	2085 (5)	5747 (4)	42 (2)	41 (2)	49 (2)	3 (2)	4 (1)	4 (2)
O(3)	2531 (3)	4192 (4)	6501 (3)	47 (2)	45 (2)	38 (2)	−6 (2)	14 (1)	−2 (2)
O(4)	1578 (3)	5577 (4)	3784 (4)	43 (2)	39 (2)	50 (2)	1 (2)	23 (1)	7 (2)
O(5)	2237 (3)	3122 (5)	2083 (3)	48 (2)	55 (2)	37 (2)	4 (2)	18 (1)	3 (2)
O(6)	−857 (3)	4037 (6)	1585 (4)	44 (2)	77 (3)	51 (2)	5 (2)	7 (2)	15 (2)
O(7)	5576 (4)	3814 (7)	6041 (7)	51 (2)	75 (3)	143 (5)	−13 (2)	−12 (3)	2 (3)
O(8)	1245 (4)	2997 (6)	7597 (5)	90 (3)	78 (3)	59 (2)	−30 (3)	35 (2)	−6 (2)
O(9)	481 (4)	6378 (5)	5368 (5)	66 (2)	51 (2)	69 (3)	12 (2)	38 (2)	2 (2)
N	4946 (5)	2153 (10)	1994 (8)	70 (3)	109 (5)	102 (4)	12 (4)	50 (3)	−3 (4)
C(1)	3079 (4)	2233 (0)	3111 (5)	47 (3)	49 (3)	40 (2)	3 (2)	15 (2)	2 (2)
C(2)	3339 (4)	3015 (6)	4653 (5)	39 (2)	33 (2)	46 (2)	0 (2)	9 (2)	4 (2)
C(3)	2218 (4)	3238 (6)	5184 (5)	44 (2)	36 (2)	35 (2)	−5 (2)	12 (2)	1 (2)
C(4)	1240 (4)	3996 (6)	3992 (5)	35 (2)	40 (3)	40 (2)	−1 (2)	14 (2)	1 (2)
C(5)	1117 (4)	3172 (7)	2515 (5)	36 (2)	49 (3)	40 (2)	−4 (2)	9 (2)	1 (2)
C(6)	270 (4)	3923 (8)	1187 (5)	47 (3)	65 (4)	40 (2)	3 (3)	9 (2)	5 (3)
C(7)	−1758 (5)	4579 (7)	522 (6)	53 (3)	56 (4)	54 (3)	1 (3)	−2 (2)	4 (3)
C(8)	−2870 (6)	4745 (11)	1071 (9)	51 (4)	93 (5)	89 (5)	7 (4)	10 (3)	19 (4)
C(9)	4152 (5)	2169 (8)	2487 (7)	55 (3)	51 (3)	63 (3)	8 (3)	22 (3)	−1 (3)
C(10)	5193 (5)	2647 (7)	6424 (7)	44 (3)	52 (3)	69 (4)	11 (3)	11 (3)	2 (3)
C(11)	5811 (6)	1641 (11)	7696 (8)	64 (4)	101 (6)	68 (4)	26 (4)	3 (3)	−3 (4)
C(12)	1979 (5)	3970 (7)	7627 (5)	52 (3)	59 (3)	31 (2)	−1 (3)	10 (2)	4 (3)
C(13)	2394 (7)	5106 (9)	8829 (7)	101 (5)	83 (5)	50 (3)	−20 (4)	34 (3)	−16 (3)
C(14)	1137 (4)	6675 (6)	4571 (6)	42 (3)	44 (3)	45 (3)	11 (2)	13 (2)	5 (2)
C(15)	1599 (6)	8205 (8)	4315 (9)	75 (4)	43 (3)	110 (5)	0 (3)	51 (4)	−1 (4)

thesis. A weighting scheme was calculated as $w = K/f(\sin\theta/\lambda)$, where $K = 0{\cdot}1$ and $f(\sin\theta/\lambda) = 36{\cdot}13 - 126{\cdot}69(\sin\theta/\lambda)$ for $(\sin\theta/\lambda) < 0{\cdot}28$ and $f(\sin\theta/\lambda) = 0{\cdot}49 + 0{\cdot}39(\sin\theta/\lambda)$ for $(\sin\theta/\lambda) \geq 0{\cdot}28$. The final least-squares refinement was performed with this weighting scheme and with all the hydrogen atoms included in a third block. The final unweighted and weighted agreement indices for the observed reflexions were $R = 0{\cdot}052$ and $R_w = 0{\cdot}060$, where $R_w = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2}$. A final difference synthesis showed a residual electron density between $\pm 0{\cdot}23$ e Å^{-3}.

The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962) for N, O and C atoms and from Stewart, Davidson & Simpson (1965) for hydrogen atoms.*

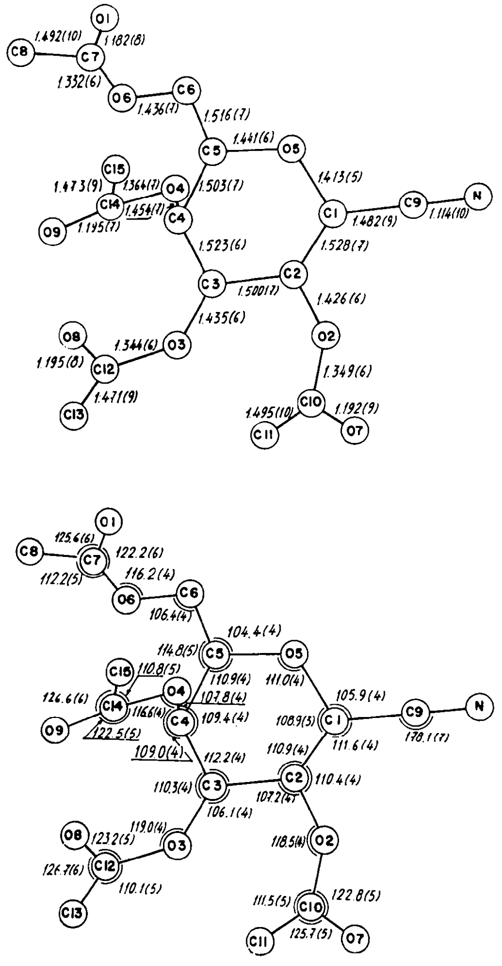

Fig. 1. Bond lengths (Å) and valence angles (°) with their estimated standard deviations referred to the last significant digits.

Tables 1 and 2 summarize atomic and thermal parameters and C–H distances.

Table 2. *Fractional coordinates* ($\times 10^3$), *thermal parameters* ($\times 10^2$) *and bond distances* (Å) *for the hydrogen atoms*

	x	y	z	U	C–H
H(1)	283 (4)	116 (7)	317 (6)	5 (1)	0·98 (6)
H(2)	373 (4)	395 (6)	463 (5)	4 (1)	0·94 (5)
H(3)	193 (4)	222 (6)	538 (5)	2 (1)	0·98 (5)
H(4)	46 (4)	393 (6)	422 (5)	3 (1)	0·98 (5)
H(5)	83 (4)	217 (7)	260 (6)	3 (1)	0·95 (6)
H(6*a*)	27 (4)	335 (7)	27 (6)	4 (1)	0·97 (6)
H(6*b*)	55 (5)	496 (7)	113 (6)	4 (1)	0·96 (6)
H(8*a*)	−299 (4)	378 (7)	169 (6)	9 (2)	1·04 (5)
H(8*b*)	−357 (4)	500 (6)	40 (6)	8 (2)	0·92 (4)
H(8*c*)	−257 (5)	490 (6)	209 (5)	9 (2)	0·92 (4)
H(11*a*)	532 (5)	197 (7)	841 (5)	11 (2)	1·00 (5)
H(11*b*)	660 (5)	208 (6)	852 (6)	13 (2)	1·11 (4)
H(11*c*)	614 (4)	84 (7)	742 (6)	13 (2)	0·86 (6)
H(13*a*)	238 (5)	487 (6)	989 (5)	8 (2)	1·00 (5)
H(13*b*)	204 (4)	603 (7)	896 (5)	10 (2)	0·92 (5)
H(13*c*)	293 (4)	588 (7)	860 (6)	10 (2)	0·98 (5)
H(15*a*)	200 (5)	833 (6)	344 (5)	10 (2)	1·02 (5)
H(15*b*)	110 (5)	913 (7)	386 (6)	18 (2)	1·02 (6)
H(15*c*)	183 (4)	895 (6)	519 (6)	13 (2)	1·01 (5)

Discussion. Interatomic distances and angles for the heavy atoms are illustrated in Fig. 1. The average values of C–C and C–O distances in the six-membered ring are 1·514 and 1·427 Å respectively. These are in good agreement with the mean values given in the references (Kim & Jeffrey, 1967). The C≡N distance is slightly shorter than would be expected for this bond, but it could be explained in terms of thermal motion. The pyranose ring has a normal chair conformation as can be seen from the torsional angles (Klyne & Prelog, 1960) and from the mean least-squares plane calculations shown in Table 3. We observed the existence of a large puckering about the C(5)–O(5) and O(5)–C(1) bonds and a smaller one about the C(2)–C(3) and C(3)–C(4) bonds while the C(1)–C(2) and C(4)–C(5) bonds have values ranging between 55·8° and 61·7°. This range has been given by Kim & Jeffrey (1967) as the ideal for these rings. The conformation about the C(5)–C(6) bond turns out to be *trans-gauche*, the torsional angles O(5)–C(5)–C(6)–O(6) and C(4)–C(5)–C(6)–O(6) having values of −178·4 and −56·8° respectively (Fries, Rao & Sundaralingam, 1971). Taking into account the atoms bonded to the six-membered ring, four substituents appear as equatorial [chains at C(1), C(2), C(3) and C(5)] and one as axial [chain at C(4)]. We observed that the torsional angles involving both equatorial substituents [C(9)–C(1)–C(2)–O(2) = −68·1 and O(2)–C(2)–C(3)–O(3) = 68·7°] are greater than those involving an equatorial and an axial substituent [O(3)–C(3)–C(4)–O(4) = 49·7 and O(4)–C(4)–C(5)–C(6) = −54·9°]. The packing in the crystal is entirely due to van der Waals forces.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31529 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Least-squares planes*

(*a*) Deviations (Å) of the atoms from some least-squares planes in the molecule, with their dihedral angles. (* denotes the atoms not used in the plane calculations.)

Plane 1		Plane 2		Plane 3	
C(1)	−0·688*	C(2)	0·187*	C(3)	−0·048*
C(2)	−0·036	O(2)	0·001	O(3)	−0·002
C(3)	0·035	O(7)	0·002	O(8)	−0·003
C(4)	0·641*	C(10)	−0·005	C(12)	0·008
C(5)	−0·037	C(11)	0·001	C(13)	−0·002
O(5)	0·038				

Plane 4		Plane 5	
C(4)	0·063*	O(1)	−0·006
O(4)	0·002	C(5)	−0·127*
O(9)	0·002	C(6)	0·024
C(14)	−0·006	O(6)	−0·031
C(15)	0·002	C(7)	−0·005
		C(8)	0·018

∠(Plane 1) (Plane 2)	62·8°	∠(Plane 1) (Plane 4)	95·7°
∠(Plane 1) (Plane 3)	126·0	∠(Plane 1) (Plane 5)	18·7

(*b*) Main torsional angles around the bond defined by the central atoms

Pyranose ring		Conformation
C(1)–C(2)–C(3)–C(4)	−50·3°	−*sc*
C(2)–C(3)–C(4)–C(5)	49·3	*sc*
C(3)–C(4)–C(5)–O(5)	−55·3	−*sc*
C(4)–C(5)–O(5)–C(1)	65·0	*sc*
C(5)–O(5)–C(1)–C(2)	−64·1	−*sc*
O(5)–C(1)–C(2)–C(3)	56·8	*sc*

Table 3 (*cont.*)

Lateral angles		Conformation
C(2)–O(2)–C(10)–O(7)	63·7°	*sc*
C(3)–O(3)–C(12)–O(8)	−1·0	−*sp*
C(4)–O(4)–C(14)–O(9)	−1·9	−*sp*
C(5)–C(6)–O(6)—C(7)	−175·7	−*ap*
C(6)–O(6)–C(7)—O(1)	3·7	*sp*
H(5)–C(5)–C(6)—H(6*a*)	−61·9	−*sc*
H(5)–C(5)–C(6)—H(6*b*)	177·5	*ap*

We wish to record our thanks to Dr Martin-Lomas and Dr Chacon-Fuertes, CSIC (Madrid), for the crystals. We also thank the Centro de Proceso de Datos del Ministerio de Educación y Ciencia (Madrid) for allowing us to use the 1108 UNIVAC computer. All calculations were performed with the X-RAY System of Crystallographic Programs.

References

Chacon-Fuertes, M. E. (1975). Thesis, Madrid.

Fries, D. C., Rao, J. T. & Sundaralingam, M. (1971). *Acta Cryst.* B**27**, 994–1005.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* B**27**, 368–376.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Kim, H. S. & Jeffrey, G. A. (1967). *Acta Cryst.* B**22**, 537–545.

Klyne, W. & Prelog, V. (1960). *Experientia*, pp. 521–523.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1976). B**32**, 966

The Structure of $[CH_3S(CH_2)_2SCH_3Mo(CO)_3(SnCl_3)Cl](CH_2Cl_2)$

By R. A. Anderson and F. W. B. Einstein

Department of Chemistry, Simon Fraser University, Burnaby, B.C., Canada, V5A 1S6

(*Received* 27 *August* 1975; *accepted* 11 *September* 1975)

Abstract. Triclinic, $P\bar{1}$, $a=9{\cdot}835$ (3), $b=11{\cdot}068$ (3), $c=9{\cdot}006$ (2) Å, $\alpha=92{\cdot}04$ (2), $\beta=119{\cdot}28$ (2), $\gamma=96{\cdot}36$ (2)°, $V=845{\cdot}4$ Å^3, $Z=2$, $D_c=2{\cdot}21$ g cm^{-3}, $D_m=2{\cdot}17$ g cm^{-3} (by flotation in an iodomethane–chloroform mixture). Mo $K\alpha_1$ radiation, $\lambda=0{\cdot}70926$ Å, μ(Mo $K\alpha$) = 30·1 cm^{-1}, $T=21$ (1) °C, final $R=0{\cdot}086$ for 2192 observed reflexions. An irregular capped octahedral geometry exists about Mo; Sn (which occupies the capped position) has an irregular trigonal bipyramidal arrangement. One Cl atom is bonded to both Mo and Sn with bond lengths 2·535 (5) and 2·781 (4) Å respectively. The Sn–Mo distance is 2·688 (2) Å.

Introduction. Small red air-stable crystals of the title compound were obtained by crystallization from CH_2Cl_2. Weissenberg and precession photographs of one of these crystals (mounted about **a** and **a*** respectively) indicated triclinic Laue symmetry. Cell dimensions were obtained from 12 strong reflexions ($2\theta>24°$) centred on the Mo $K\alpha_1$ peak ($\lambda=0{\cdot}70926$ Å) without the use of a monochromator. Intensities were collected in two shells $0°<2\theta<30°$ and $30°<2\theta<50°$ with a θ, 2θ scan and monochromatized $K\alpha_1$ radiation. Otherwise the data were collected as reported by Einstein & Jones (1972). The variation of standard reflexions was approximately ±5%.

The data set consisted of 3000 unique reflexions of which 2192 were classed as observed $\{I>2{\cdot}35\sigma(I)$, $\sigma(I)=[(T)+(\mathrm{ts/tb})^2(B_1+B_2)+(KI)^2]^{1/2}$ where T = total count, ts = scan time, tb = total background count time, B_1 and B_2 are the background counts, K is a constant equal to 0·03, and I is the net count$\}$. The intensities