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Note

X-Ray structure of 3,4,5-tri-*O*-acetyl-2,6-anhydro-D-mannononitrile (2,3,4-tri-*O*-acetyl-α-D-arabinopyranosyl cyanide)

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In connection with work on a new method for the synthesis of glycopyranosyl cyanides[1], the crystal structures of four such 2,6-anhydroaldononitriles have been described[2]. The structure of 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptononitrile (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl cyanide) was published earlier[3]. We now describe, as another example, the conformation which is adopted by the title cyanide **1**[4] in the crystalline state.

Compound **1** is homomorphous to the L enantiomer of the above *galacto* compound. From ^{1}H-n.m.r. measurements[1], it was deduced that, in solution in chloroform, **1** populates the alternative $^5C_2$(D) and $^2C_5$(D) conformers in the ratio 48:52. In benzene as solvent[1], the calculated amount of the $^2C_5$(D) conformer increased to 67%. Thus, the solid state conformation of **1** was not predictable readily from these results and, therefore, the X-ray structure was determined.

3,4,5-Tri-*O*-acetyl-2,6-anhydro-D-mannononitrile (**1**) crystallises in the orthorhombic space-group $P2_12_12_1$. Further crystallographic information is given in Table I. The structure was solved by direct methods using the computer program

TABLE I

CRYSTALLOGRAPHIC DATA FOR **1**

Formula	$C_{12}H_{15}NO_7$	Density (calc.) (g.cm^{-3})	1.30
Mol. wt.	285.25	λ (MoK_α) (pm)	71.069
M.p. (degrees)	136–138[4]	μ (cm^{-1})	0.70
Space group	$P2_12_12_1$	2θ range (degrees)	3–52
Cell constants (pm)		Reflections measured (one octant only)	1500
a	645.6(1)	Reflections with $F_0 > 4\sigma(F_0)$	1093
b	1121.9(1)	Number of refined parameters	217
c	2011.6(1)	Final residual factors	
Volume (pm^3)	1457.03(1) × 10^6	R	0.051
Z	4	R_w	0.054
F(000)	600	Diffractometer	Siemens AED2

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TABLE II

FRACTIONAL POSITIONAL PARAMETERS (× 10^4) AND TEMPERATURE FACTORS U_{eq} (× 10^3) OF CARBON, NITROGEN, AND OXYGEN ATOMS IN **1**

Atom	x	y	z	U_{eq}
O-2	2394(5)	1923(2)	6658(2)	54(2)
O-3	1410(6)	504(3)	5528(2)	67(2)
O-4	2590(6)	−1664(3)	6069(2)	67(2)
O-5	5603(6)	−697(3)	6948(2)	77(2)
O-21	−609(6)	1462(4)	7136(2)	97(3)
O-31	3097(11)	1242(5)	4661(2)	124(4)
O-41	3121(8)	−2927(3)	5226(2)	88(3)
N-11	4278(10)	919(5)	8245(3)	97(4)
C-1	4906(8)	493(5)	6997(3)	62(3)
C-2	2910(8)	680(4)	6608(2)	50(3)
C-3	3337(9)	391(4)	5880(2)	55(3)
C-4	4180(10)	−864(5)	5823(3)	68(3)
C-5	6056(11)	−998(6)	6259(4)	88(5)
C-11	4568(9)	718(5)	7698(3)	72(4)
C-21	555(9)	2200(5)	6941(2)	59(3)
C-22	198(10)	3512(5)	6965(3)	86(4)
C-31	1500(13)	942(4)	4911(3)	76(4)
C-32	−568(14)	989(6)	4601(3)	99(5)
C-41	2248(9)	−2673(4)	5725(3)	60(3)
C-42	656(9)	−3405(4)	6067(2)	69(3)

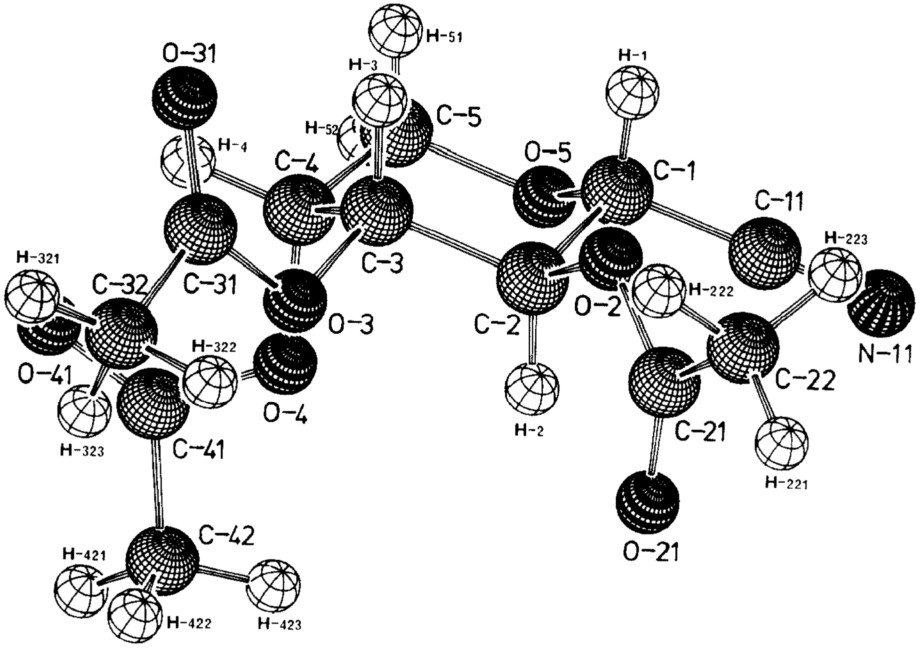

Fig. 1. A SCHAKAL[7] drawing of a molecule of **1** showing atom numbering.

SHELXS-86[5] for the phase problem, and the program SHELX-76[6] (full matrix) for refinement. The final positional parameters (temperature factors U_{eq} included) of the carbon, nitrogen, and oxygen atoms are listed in Table II*.

A SCHAKAL representation[7] of one molecule of **1** is shown in Fig. 1; the numbering follows the glycosyl cyanide nomenclature.

Compound **1** adopts the $^2C_5$(D) conformation ($^1C_4$ when viewed as a glycosyl cyanide). The analogous enantiomeric conformation is found in the related acetylated β-D-galactopyranosyl cyanide[3] due to the bulky exocyclic acetoxymethyl group. The "puckering" parameters[8] of the pyranose ring in **1** are $Q = 58.5$ pm, $\phi = 268.6°$, and $\theta = 177.6°$, which are indicative of an only slightly distorted chair. The respective values for the β-D-galactosyl compound[3] (L enantiomer) are $Q = 56.9$ pm, $\phi = 185.5°$, and $\theta = 172.5°$. The orientation of the acetoxy groups in **1** is also very similar to that found in the homomorphous *galacto* cyanide[3]. Both compounds thus follow trends which are generally observed in carbohydrate acetates (*cf.* the discussion in ref. 1).

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*Lists of observed and calculated structure amplitudes, atomic co-ordinates of the hydrogen atoms (calculated in a late stage of refinement), anisotropic thermal factors U_{ij} for C, N, and O, and Tables of bond lengths and bond angles are deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/401/*Carbohydr. Res.*, 184 (1988) 247–249.