

Acta Cryst. (1974). B30, 2931***N*-Acetyl- α -D-galactosamine. An Amino Sugar**

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Abstract. C₈H₁₅NO₆, monoclinic, $P2_1$, $a=9.154$ (2), $b=6.321$ (2), $c=9.217$ (2) Å, $\beta=107.91$ (2)°, $Z=2$, $D_x=1.38$ g cm⁻³. Hydrogen bonding, including an intramolecular hydrogen bond not found in any other galactose derivative, dominates the molecular packing.

Introduction. *N*-Acetyl-D-galactosamine is a saccharide residue which occurs often in the polysaccharide chains of natural glycoproteins and proteoglycans. Data were collected from a small crystal (0.10 × 0.10 × 0.04 mm) selected from a commercial sample (Sigma Chemical Company). 893 independent reflections were measured on an automatic computer-controlled diffractometer using Cu $K\alpha$ radiation ($\lambda=1.54178$ Å, Ni-filtered). The θ - 2θ scan mode of data collection was used and 3 standard reflections were monitored after every 50 reflection measurements. No deterioration was noted in the

standards, and data were measured to $\sin \theta/\lambda_{\max}=0.58$.

The structure was solved by application of the symbolic addition procedure for noncentrosymmetric crystals (Karle & Karle, 1966) and refined using full-matrix least-squares methods (Busing *et al.*, 1971) on the full set of 893 reflections. The origin was fixed by holding constant the y coordinate of the geometrical centroid of the non-hydrogen atoms; this constraint was added to the least-squares refinement program. The hydrogen atoms were located in a difference map and their positions were refined. The thermal factors for the hydrogen atoms were constrained in the least-squares refinement to be equal to those of the atom to which they were bonded. The scattering factors of Stewart, Davidson & Simpson (1965) were used for the hydrogen atoms, and those of Hanson, Herman, Lea & Skillman (1964) were used for all other atoms. The function minimized

Table 1. *Fractional coordinates and thermal parameters with standard deviations*

The thermal parameters are of the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. Standard deviations are based solely on the least-squares calculations.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.36042 (54)	0.24112 (0)	0.89681 (53)	2.22 (20)	3.29 (26)	2.45 (22)	0.54 (20)	0.61 (17)	0.12 (21)
C(2)	0.25237 (52)	0.30185 (77)	0.98792 (50)	2.57 (20)	1.55 (21)	2.14 (19)	-0.05 (19)	0.46 (16)	0.33 (19)
C(3)	0.08613 (50)	0.29807 (82)	0.88512 (53)	2.21 (19)	2.64 (26)	3.02 (22)	-0.09 (20)	0.96 (17)	-0.33 (21)
C(4)	0.06893 (57)	0.44225 (85)	0.74912 (61)	2.37 (21)	2.90 (25)	3.20 (24)	0.11 (19)	0.82 (18)	0.47 (21)
C(5)	0.18219 (51)	0.37615 (99)	0.66641 (51)	2.47 (19)	3.31 (28)	2.75 (22)	0.37 (23)	0.67 (17)	-0.03 (24)
C(6)	0.17779 (63)	0.51466 (99)	0.53044 (61)	3.32 (26)	4.40 (34)	2.52 (25)	0.19 (26)	0.84 (18)	0.41 (27)
C(7)	0.38102 (51)	0.18218 (87)	1.24764 (51)	2.29 (19)	3.75 (28)	2.33 (21)	0.17 (21)	0.78 (17)	0.20 (22)
C(8)	0.38224 (71)	0.02154 (99)	1.36861 (66)	3.00 (25)	5.44 (37)	3.42 (30)	0.68 (32)	0.78 (21)	1.52 (31)
O(1)	0.33077 (41)	0.03144 (69)	0.84985 (42)	3.61 (18)	3.22 (18)	4.13 (17)	0.83 (16)	1.74 (14)	-0.32 (16)
N(2)	0.27265 (43)	0.16144 (69)	1.11555 (47)	2.37 (18)	2.58 (23)	2.60 (17)	-0.46 (16)	0.38 (15)	0.26 (17)
O(3)	-0.01713 (43)	0.36684 (66)	0.96170 (36)	3.43 (14)	3.30 (20)	3.71 (19)	0.82 (16)	2.11 (14)	1.12 (16)
O(4)	0.08749 (48)	0.65551 (64)	0.80307 (46)	5.43 (21)	2.46 (19)	4.49 (22)	0.49 (17)	2.86 (16)	0.68 (17)
O(5)	0.33698 (31)	0.38142 (60)	0.76802 (32)	2.46 (14)	3.55 (18)	2.60 (14)	0.18 (15)	0.81 (11)	0.79 (15)
O(6)	0.21007 (43)	0.73113 (66)	0.56907 (43)	3.33 (17)	4.39 (20)	3.54 (17)	0.01 (18)	0.58 (14)	0.97 (16)
O(7)	0.47816 (35)	0.32609 (58)	1.27526 (34)	3.05 (14)	3.80 (20)	2.85 (14)	-1.15 (15)	0.46 (12)	0.32 (14)

Table 1 (cont.)

	x	y	z
H(1)	0.477 (5)	0.251 (8)	0.964 (4)
H(2)	0.280 (5)	0.442 (8)	1.017 (5)
H(3)	0.055 (5)	0.143 (8)	0.845 (5)
H(4)	-0.034 (5)	0.434 (8)	0.680 (5)
H(5)	0.156 (5)	0.235 (10)	0.625 (5)
H(6A)	0.072 (5)	0.504 (9)	0.449 (4)
H(6B)	0.239 (5)	0.449 (9)	0.481 (5)
H(8A)	0.475 (5)	0.008 (10)	1.445 (5)
H(8B)	0.378 (6)	-0.097 (11)	1.323 (6)
H(8C)	0.299 (5)	-0.016 (10)	1.387 (5)
H(O1)	0.408 (5)	0.003 (9)	0.820 (5)
H(N2)	0.219 (5)	0.068 (9)	1.112 (5)
H(O3)	-0.019 (7)	0.286 (9)	1.009 (7)
H(O4)	0.127 (7)	0.703 (9)	0.753 (6)
H(O6)	0.309 (5)	0.749 (9)	0.610 (5)

was $\sum w(|F_o| - |F_c|)^2$ where the weights (w) were calculated according to a procedure outlined by Gilardi (1973). The final R index is 0.066 ($R_w=0.037$). At the end of the refinement procedure the standard deviation of an observation of unit weight $\{[\sum w(|F_o| - |F_c|)^2 / (M - N)]^{1/2}$ where $M=893$ and $N=180\}$ was 1.25. Table 1 lists the final coordinates and thermal factors. Bond distances and angles are listed in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30630 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths (Å) and angles (°) with standard deviations

C(1)–O(1)	1.395 (4)	O(1)–C(1)–O(5)	111.3 (4)
C(1)–O(5)	1.444 (5)	O(1)–C(1)–C(2)	108.2 (4)
C(1)–C(2)	1.530 (6)	O(5)–C(1)–C(2)	109.8 (3)
C(2)–N(2)	1.439 (6)	N(2)–C(2)–C(3)	110.6 (4)
C(2)–C(3)	1.526 (6)	N(2)–C(2)–C(1)	110.6 (4)
C(3)–O(3)	1.411 (6)	C(3)–C(2)–C(1)	110.2 (4)
C(3)–C(4)	1.518 (7)	O(3)–C(3)–C(4)	108.2 (4)
C(4)–C(5)	1.522 (6)	O(3)–C(3)–C(2)	112.2 (4)
C(4)–O(4)	1.429 (7)	C(4)–C(3)–C(2)	109.5 (4)
C(5)–O(5)	1.439 (5)	O(4)–C(4)–C(3)	107.9 (4)
C(5)–C(6)	1.519 (8)	O(4)–C(4)–C(5)	114.0 (5)
C(6)–O(6)	1.422 (8)	C(3)–C(4)–C(5)	109.6 (4)
C(7)–O(7)	1.243 (6)	O(5)–C(5)–C(6)	107.1 (4)
C(7)–N(2)	1.319 (6)	O(5)–C(5)–C(4)	110.7 (4)
C(7)–C(8)	1.506 (8)	C(6)–C(5)–C(4)	113.9 (5)
		O(6)–C(6)–C(5)	113.4 (5)
		O(7)–C(7)–N(2)	123.3 (5)
		N(2)–C(7)–C(8)	116.7 (5)
		C(7)–N(2)–C(2)	124.4 (4)
		C(5)–O(5)–C(1)	112.9 (4)

Average distances and angles involving hydrogen atoms. Standard deviations quoted are simple unweighted averages of the individual standard deviations for distances or angles

Distance	Range (σ)	Angle	Range (σ)
C–H	0.96 (5) 2	H–C–C	109.6 (2.9) 4
O–H	0.78 (5) 2	H–C–H	101.7 (4.6) 4
N–H	0.76 (5)	H–C–O	109.3 (2.9) 3
		H–O–C	104.2 (4.4) 2
		H–N–C	117.8 (3.6) 1
		H–C–N	113.1 (2.9)

Discussion. The configuration of the molecule is illustrated in Fig. 1. The pyranose ring has a normal 4C_1 conformation. Within the ring, those torsion angles (Table 3) which include the ring oxygen as a central atom are slightly larger than the others. This difference can also be seen in the reported conformational parameters of α -glucuronamide (Flippin & Gilardi, 1974). The average C–OH bond length [excluding the anomeric C(1)–O(1) bond] is 1.421 (7) Å and the mean C–C bond length [excluding C(7)–C(8)] is 1.523 (7) Å. These values are in good agreement with distances of 1.425 Å for C–OH bonds and 1.524 Å for C–C bonds quoted by Strahs (1970) in his review of carbohydrate structures. He also gives a value of 1.401 Å as the mean distance for an axial anomeric hydroxyl bond. The anomeric C–OH bond length in this molecule is 1.395 (4) Å. The C(7)–C(8) distance of 1.506 (8) Å is reasonable for a carbon–carbon single bond next to a C=O bond. The carbonyl bond, C(7)–O(7), at 1.243 (6) Å is

somewhat long, but may be accounted for by the participation of O(7) as an acceptor in two strong hydrogen bonds. Similar distances were noted in the α -glucuronamide where the C–C distance was 1.508 Å and the C=O distance was 1.258 Å.

Table 3. Torsion angles (°)

N(2)–C(2)–C(1)–O(1)	57.5 (4)
N(2)–C(2)–C(3)–O(3)	61.5 (4)
O(3)–C(3)–C(4)–O(4)	53.7 (5)
O(4)–C(4)–C(5)–C(6)	–57.3 (5)
C(4)–C(5)–C(6)–O(6)	59.2 (6)
O(5)–C(5)–C(6)–O(6)	–63.6 (6)
Pyranose ring	
O(5)–C(1)–C(2)–C(3)	56.6 (4)
C(1)–C(2)–C(3)–C(4)	–55.8 (5)
C(2)–C(3)–C(4)–C(5)	55.8 (5)
C(3)–C(4)–C(5)–O(5)	–57.5 (6)
C(4)–C(5)–O(5)–C(1)	60.2 (5)
C(5)–O(5)–C(1)–C(2)	–59.3 (4)
N-Acetyl group	
C(1)–C(2)–N(2)–C(7)	82.8 (5)
C(3)–C(2)–N(2)–C(7)	–154.9 (5)
C(2)–N(2)–C(7)–O(7)	–0.4 (8)
C(2)–N(2)–C(7)–C(8)	179.0 (5)

N-Acetylgalactosamine contains five hydrogen atoms connected to nitrogen or oxygen atoms and they all participate in hydrogen bonding (see Table 4). However, not all of the hydroxyl oxygens serve as acceptors. The carbonyl oxygen, O(7), accepts two hy-

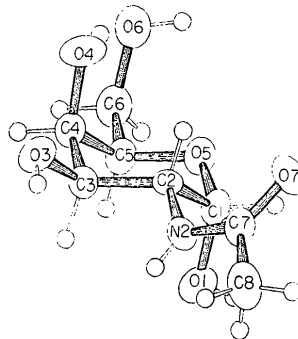


Fig. 1. A computer-drawn perspective illustration based on the final refined coordinates of all atoms. The ellipsoids drawn for the non-hydrogen atoms represent surfaces enclosing 50% of the Gaussian thermal distributions obtained in the refinement of the model (Johnson, 1965).

Table 4. Hydrogen bonds

Donor A–B	Acceptor C	Distance B–C	Distance A–C	Angle A–B–C
O(1)–H(O1)	O(7) ($1-x, y-\frac{1}{2}, 2-z$)	1.91 (5) Å	2.704 (4) Å	153 (5)°
N(2)–H(N2)	O(3) ($\bar{x}, y-\frac{1}{2}, 2-z$)	2.17 (5)	2.902 (6)	160 (5)
O(3)–H(O3)	O(4) ($\bar{x}, y-\frac{1}{2}, 2-z$)	2.18 (6)	2.786 (5)	150 (7)
O(4)–H(O4)*	O(6) (x, y, z)	2.07 (5)	2.762 (5)	158 (6)
O(6)–H(O6)	O(7) ($1-x, y+\frac{1}{2}, 2-z$)	1.97 (5)	2.836 (5)	170 (5)

* Intramolecular.

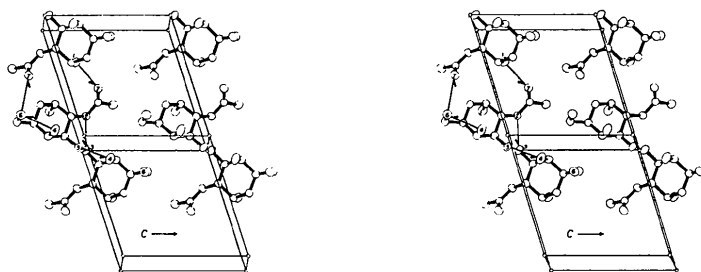


Fig. 2. A stereo view illustrating some features of the packing. Each of the five hydrogen bonds of the structure is shown once, as an arrow pointing from donor to acceptor. The b axis is directed out of the paper towards the viewer. Some of the oxygen and nitrogen atoms are numbered, to indicate the orientation of the individual molecules.

drogen bonds while the hydroxyl oxygen, O(1), accepts none. There is an intramolecular hydrogen bond in this structure which has not been reported in other galactopyranose structures. The C(6)–O(6) bond is rotated about the C(5)–C(6) bond to a position in which there are two unfavorable *gauche* interactions with adjacent ring bonds; however, this location allows the formation of a hydrogen bond between O(6) and the neighboring axial hydroxyl oxygen, O(4). The intermolecular hydrogen bonds connect the molecules in layers which extend parallel to the ab plane; no hydrogen bonds link these layers. A portion of this network is shown in Fig. 2.

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Lanthanum Tetraboride

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Abstract. LaB_4 , tetragonal, $P4/m\bar{b}m$, $a=7.324(1)$, $c=4.181(1)$ Å, $Z=4$, $D_x=5.396$ g cm $^{-3}$. The crystals were prepared from a molten lanthanum metal flux. The structure, homotypic with that of CeB_4 , ThB_4 and UB_4 , was refined by the least-squares method based on 520 X-ray diffraction intensities. The B–B distances range from 1.75 to 1.85 Å, the La–B distances from 2.818 to 3.155 Å.

Introduction. The crystals were prepared according to the method described by Deacon & Hiscocks (1971). The unit-cell dimensions were obtained by the least-squares method based on the 2θ angles measured on a four-circle diffractometer (Rigaku) using monochromated Mo $K\alpha$ radiation ($\lambda=0.70926$ Å); they agree with the values reported by Fisk, Cooper,

Schmidt & Castellano (1972). The intensities were collected on the same diffractometer. In the range $2\theta \leq 90^\circ$, 2147 reflexions were measured of which 1863 were greater than zero. The specimen used was prismatic, $0.13 \times 0.10 \times 0.24$ mm in size and bounded predominantly by $\{110\}$. The observed intensities were corrected for absorption ($\mu=190$ cm $^{-1}$ for Mo $K\alpha$ radiation) and then reduced to a set of 520 independent reflexions by averaging the equivalent ones.

Evidently LaB_4 is isostructural with CeB_4 , ThB_4 and UB_4 ; the systematic absences $h0l$ with $h \neq 2n$ agree with those expected for the space group $P4/m\bar{b}m$ in which these borides crystallize. The coordinates of the lanthanum atom were therefore taken from their structural data and refined by the full-matrix least-squares method with the computer program *ORFLS*