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Carbohydrate Research 337 (2002) 79–82

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Note

Crystal structure of 4,6-*O*-ethylidene-*N*-(2-hydroxybenzylidene)-β-D-glucopyranosylamine

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Received 9 October 2001; accepted 19 October 2001

Abstract

4,6-*O*-Ethylidene-*N*-(2-hydroxybenzylidene)-β-D-glucopyranosylamine was synthesized and characterized using analytical, spectral and single-crystal X-ray diffraction methods. The anomeric nature of the saccharide moiety was proposed based on ^{1}H NMR studies and was confirmed by the crystal structure. The lattice structure of this compound was compared with that of its analogues. © 2002 Published by Elsevier Science Ltd.

Keywords: Saccharide moiety; ^{1}H NMR studies; Lattice structure

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We have recently reported the synthesis, characterization and structures of some of the glucose based –C-1–N=CH-containing molecules.[1] Such molecules have been proven to be good complexing ones towards VO_2^+, MoO_2^{2+}, UO_2^{2+}, and Ni^{2+} and Zn^{2+} species.[2–4] These results give rise to an interest in establishing the structure of 4,6-*O*-ethylidene-*N*-(2-hydroxybenzylidene)-β-D-glucopyranosylamine (H_3L^1). In continuation with our work in this direction, this note deals with the synthesis, characterization and structure of H_3L^1, and also comparison of its lattice with those of *N*-(5-bromo-2-hydroxybenzylidene)-4,6-*O*-ethylidene-β-D-glucopyranosylamine (H_3L^2) and 4,6-*O*-ethylidene-*N*-(2-hydroxy-3-methoxybenzylidene)-β-D-glucopyranosylamine (H_3L^3).

4,6-*O*-Ethylidene-*N*-(2-hydroxybenzylidene)-β-D-glucopyranosylamine (H_3L^1) was synthesized, and its formation and purity were confirmed by elemental analysis and by FTIR, ^{1}H NMR, and mass spectroscopy as reported in the Experimental Section. Slow evaporation of the concentrated methanolic solution of H_3L^1 resulted in the formation of single crystals in a monoclinic lattice. An ORTEP view of H_3L^1 is shown in Fig. 1. Selected bond lengths, bond angles and dihedral angles are given in Table 1. The molecule exhibits an intramolecular O–H···N interaction. While the β-anomeric form of H_3L^1 was proposed based on the $J_{\text{C1-H}}$ in the ^{1}H NMR spectrum, the same is confirmed by single-crystal X-ray diffraction study. The saccharide moiety was found in the $^4C_1$ conformation with the 4- and 6-positions protected through the ethylidene moiety and the C-1 modified via glycosyl amine formation. A stereoview of the molecule (Fig. 2) revealed a chair conformation for both the pyranose rings resulting from the saccharide and its protection at the 4- and

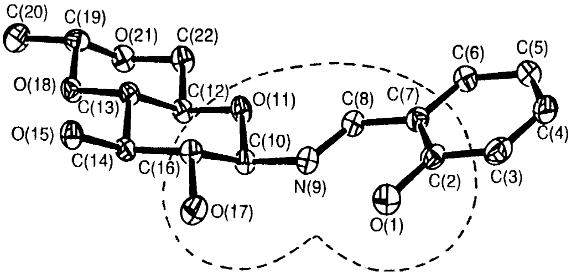

Fig. 1. Molecular structure of H_3L^1 showing 50% probability thermal ellipsoids using ORTEP; the dashed enclosure represents the presence of an ONO core.

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PII: S0008-6215(01)00284-1

Table 1
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for H_3L^1

Bond lengths			
O(1)–C(2)	1.355(2)	C(12)–C(13)	1.525(2)
C(2)–C(7)	1.410(2)	C(13)–C(14)	1.509(2)
C(7)–C(8)	1.461(2)	C(14)–O(15)	1.428(2)
C(8)–N(9)	1.276(2)	C(14)–C(16)	1.526(2)
N(9)–C(10)	1.444(2)	C(16)–O(17)	1.420(2)
C(10)–O(11)	1.436(2)	C(16)–C(10)	1.536(2)
O(11)–C(12)	1.428(2)		
Bond angles			
O(1)–C(2)–C(7)	121.7(1)	C(2)–C(7)–C(8)	121.8(1)
C(7)–C(8)–N(9)	121.0(1)	C(8)–N(9)–C(10)	120.9(1)
N(9)–C(10)–O(11)	110.9(1)	C(10)–O(11)–C(12)	111.6(1)
O(11)–C(12)–C(13)	109.1(1)	C(12)–C(13)–C(14)	108.6(1)
C(13)–C(14)–C(16)	107.9(1)	C(16)–C(10)–N(9)	108.3(1)
C(14)–C(16)–C(10)	110.1(1)	C(16)–C(10)–O(11)	110.6(1)
Torsion angles			
N(9)–C(10)–O(11)–C(12)	−179.4(1)	N(9)–C(10)–C(16)–C(14)	177.0(1)
O(11)–C(10)–C(16)–O(17)	176.0(1)	C(13)–C(14)–C(16)–O(17)	−174.7(1)
O(15)–C(14)–C(16)–C(10)	−175.6(1)	C(12)–C(13)–C(14)–O(15)	−178.7(1)
O(18)–C(13)–C(14)–C(16)	179.8(1)	O(11)–C(12)–C(13)–O(18)	175.7(1)
C(22)–C(12)–C(13)–C(14)	176.4(1)	C(22)–C(12)–O(11)–C(10)	177.4(1)
C(7)–C(8)–N(9)–C(10)	177.5(1)	C(2)–C(7)–C(8)–N(9)	0.2(2)

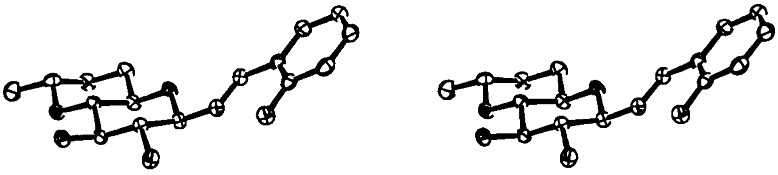

Fig. 2. Stereoview of H_3L^1.

6-positions. This view also supported the presence of an ONO tridentate chelating core (Fig. 1). Torsion angles (Table 1) supported the β-anomeric form of the saccharide moiety and a trans orientation of the aromatic and saccharide ring with respect to imine C=N bond. Cremer–Pople parameters,[5] as well as asymmetric parameters[6] obtained using the program PLATON99, are as follows: Q, 0.605 Å; θ, 4.6°; ϕ, 257.25°; ΔC_s (C-1, C-4), 0°; ΔC_s (C-2, C-5), 0° and ΔC_s (C-3, O-5), 0°. In the crystal lattice, each molecule is surrounded by four other molecules interacting through two O–H···O and one C–H···O hydrogen bonds as shown in Fig. 3. The metric data for the hydrogen bonds are given in Table 2. In the lattice, the molecules are arranged in layers where the molecules in each layer are connected through O–H···O interactions. The adjacent layers are further connected via C–H···O type of interactions, resulting in a three-dimensional network that resembles a channel-type structure as shown in Fig. 4.

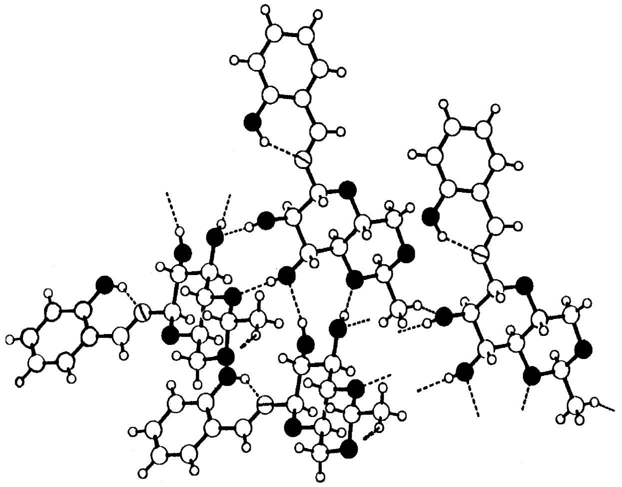

Fig. 3. Interaction of the central molecule with three other molecules (for clarity) through hydrogen bonding interactions present in H_3L^1. Key: ●, oxygen; ⊖, nitrogen; ○, carbon; o, hydrogen; ---, hydrogen bonds.

Table 2
Hydrogen bond data for H_3L^1

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)	Symmetry
O(1)–H(1)···N(9)	0.906	1.804	2.611	147.1	
O(15)–H(15)···O(18)	0.916	1.892	2.790	166.3	$1-x, -1/2+y, -z$
O(17)–H(17)···O(15)	0.842	2.076	2.894	163.5	$1-x, -1/2+y, -z$
C(20)–H(20c)···O(17)	0.913	2.563	3.332	142.2	$-1+x, 1+y, z$

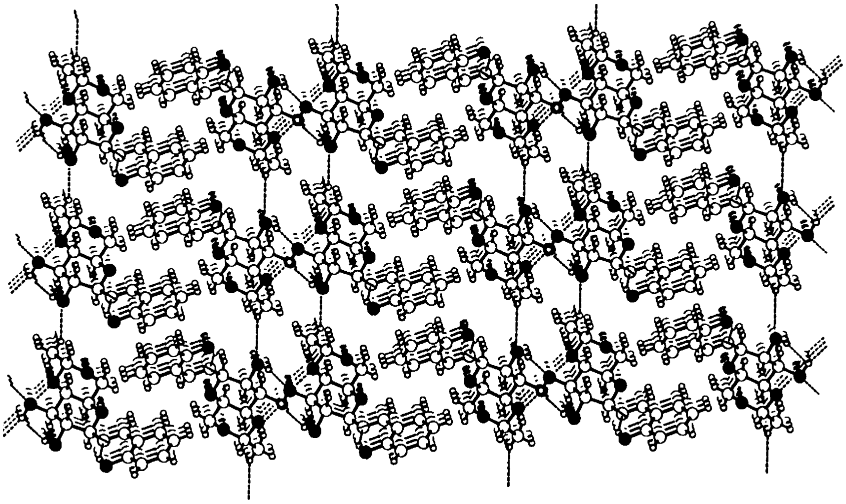

Fig. 4. Packing diagram of H_3L^1 in three-dimensions exhibiting layer-type structure. Key: ●, oxygen; ⊖, nitrogen; ○, carbon; o, hydrogen; ---, hydrogen bonds.

Thus the lattice structure of H_3L^1 substantially differs from that of its analogues, H_3L^2 and H_3L^3. While H_3L^2 exhibits an antiparallel β-sheet type lattice, the H_3L^3 exhibits a channel-type lattice filled with a chloroform molecules.[1] In the case of H_3L^3, the saccharide molecules are connected only along two directions through hydrogen bonds, but in the present case the molecules are connected along all three directions through such interactions. H_3L^1 was used in the synthesis of the VO_2^+, MoO_2^{2+}, UO_2^{2+}, and Ni^{2+} and Zn^{2+} species. The ligand exhibited tridentate dianion behavior towards VO_2^+, MoO_2^{2+}, tridentate dianion plus two bridging interactions towards Ni^{2+}, tetradentate dianion behavior plus one bridging interaction towards UO_2^{2+} and bidentate monoanion behavior towards Zn^{2+}. Thus is demonstrated the complexing ability of the H_3L^1.

1. Experimental

General methods.—4,6-*O*-Ethylidene-D-glucopyranose and 4,6-*O*-ethylidene-β-D-glucopyranosylamine was synthesized as per our earlier report.[1,7] Elemental analyses were carried out on a Carlo–Erba elemental analyzer, FTIR spectra were recorded on a Nicolet Impact 400 instrument using a KBr matrix. Absorption spectra were measured on a Shimadzu UV2101PC spectrophotometer. ^1H NMR spectra were recorded on a Varian XL-300 spectrometer in $(CD_3)_2SO$. Short label-

Table 3
Summary of crystallographic data for H_3L^1

Empirical formula	$C_{15}H_{19}NO_6$
Molecular weight	309.31
T (K)	173(2)
Crystal system	monoclinic
Space group	$P2_1$
Cell constants	
a (Å)	8.013(1)
b (Å)	6.286(1)
c (Å)	15.031(1)
β (°)	96.05(1)
V (Å^3)	752.89(16)
Z	2
D_{calc} (Mg m^{-3})	1.364
Total reflections	4073
Unique reflections	3130[$R_{int} = 0.0271$]
Max/min transmission	0.9843 and 0.9107
Parameters	275
Final R [$I > 2\sigma(I)$]	0.0301
R_w	0.0752

ing, such as, 'Sac', 'Prot' and 'Ar' used in the spectral assignments refer to saccharide, protection and aromatic groups, respectively.

H_3L^1.—Salicylaldehyde (11.0 mL, 0.10 mol) was added to a suspension of 4,6-*O*-ethylidene-β-D-glucopyranosylamine (20.52 g, 0.10 mol) in MeOH (80 mL), and the reaction mixture was allowed to reflux for 5 h. During the course of reflux, a small amount of yellow solid formed. The reaction mixture was then allowed to cool to rt and was left as such overnight. The solid product was collected by filtration, and washed with a small portion of MeOH, followed by petroleum ether, and the product was dried under vacuum. The filtrate was concentrated to dryness, and CH_2Cl_2 was added to dissolve the pasty mass. Petroleum ether was added to this mixture resulting in a second crop of solid. Total yield 27.14 g (88%); mp 170–171 °C; IR (KBr): ν 3450 (Ar-OH), 3379 (Sac-OH) and 1637 cm^{-1} (–C=N–); UV–Vis (Me_2SO): λ_{max} 261 nm ($\varepsilon = 19{,}812$ L mol^{-1} cm^{-1}) and λ_{max} 319 nm ($\varepsilon = 7879$ L mol^{-1} cm^{-1}); ^1H NMR (300 MHz, Me_2SO-d_6, ppm): 12.91 (1 H, s, Ar OH), 8.58 (1 H, s, HC=N), 7.53 (H, d, *J* 7.69 Hz, Ar H), 7.37 (1 H, t, *J* 7.69 Hz, Ar H), 6.91 (2 H, m, Ar H), 5.54 (1 H, dd, *J* 1.66, 5.68 Hz, Sac OH), 5.36 (1 H, d, *J* 5.13 Hz, Sac OH), 4.75 (1 H, q, *J* 5.13 Hz, Prot CH), 4.56 (1 H, d, *J* 8.06 Hz, β anomer, Sac H-1), 4.05 (1 H, m, Sac H-5), 3.0–3.6 (5 H, m, Sac), 1.25 (3 H, d, *J* 4.76 Hz, Prot CH_3); FABMS: *m*/*z* 310 ($[M+H]^+$, 100%); Anal. Calcd for $C_{15}H_{19}NO_6$: C, 58.24; H, 6.19 N, 4.53; Found: C, 58.72; H, 6.33; N, 4.35.

Crystal structure determination.—The procedures used for the data collection, solving and refining the structure, and the figure production were same as those reported in our earlier paper.[1] Other details of data collection and structure refinement are provided in Table 3.

2. Supplementary material

Full crystallographic details, excluding structure factors, have been deposited with Cambridge Crystallographic Data Center (CCDC 162413). These data may be obtained, on request, from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

Acknowledgements

C.P.R. acknowledges the financial support from the Council of Scientific and Industrial Research, and the Department of Science and Technology. We thank RSIC, CDRI Lucknow for Mass Spectral measurements.

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