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Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-*α*-D-glucopyranoside

Anja Burkhardt, Axel Buchholz, Helmar Görls and Winfried Plass*

Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Carl-Zeiss-Promenade, 10 07745 Jena, Germany

Correspondence e-mail: sekr.plass@uni-jena.de

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The title compound, $C_{20}H_{23}NO_5$, crystallizes exclusively as the α-anomer. All substituents are in equatorial positions except the benzyl substituent which occupies an axial position. Owing to its two vicinal donor atoms and its enantiomeric purity, the title compound is a suitable *N*,*O*-bidentate ligand for complexation of transition metals.

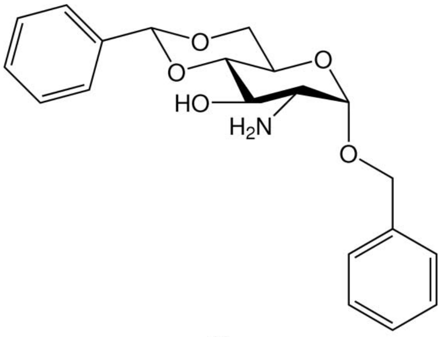
Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.005 Å
R factor = 0.045
wR factor = 0.104
Data-to-parameter ratio = 9.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Owing to their number of chiral centers and their polyfunctionality, carbohydrates are interesting starting materials for enantioselective catalysts. By modification of 2-aminosugars the related nitrosugars (Vega-Perez *et al.*, 1997), triple *N*-methylated ammonium salts (Noorzad & Gross, 1973) and amido-bonded disaccharides (Yoshimura *et al.*, 1976) are available. *N*-Tosylated derivatives of $C_{20}H_{23}NO_5$, (I), are used as chiral ligands for the addition of diethylzinc to aromatic aldehydes (Bauer *et al.*, 2002). The nickel complexes of β-acylaminophosphinites obtained from $C_{20}H_{23}NO_5$ are efficient enantioselective catalysts for hydrovinylation of asymmetric olefins (Park & RajanBabu, 2002). Analogous 2-allosamine-based oxazolidines are chiral auxiliaries for the stereoselective synthesis of oxiranes (Vega-Perez *et al.*, 2001). The Schiff base derivatives of the title compound yield suitable catalysts for asymmetric sulfide oxidation (Cucciolito *et al.*, 2005) and chiral polynuclear copper(II) complexes with interesting magnetic behavior (Burkhardt *et al.*, 2006).



(I)

The anomeric hydroxyl group at C1 is protected *via* a benzyl ether. The hydroxyl groups at C4 and C6 are blocked with a cyclic benzylidene acetal which adopts a chair conformation. The mean plane of the phenyl ring of the 4,6-protective group (defined by C15–C20) and the mean sugar plane (defined by C1, C3, C4, O1) subtend an angle of 21.62 (17)°, accompanied by the equatorial position of the benzylidene acetal.

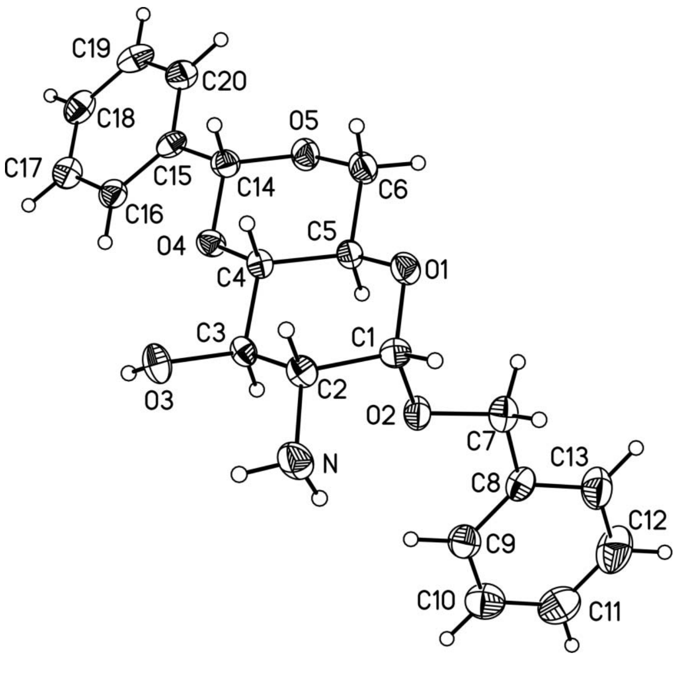


Figure 1
Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

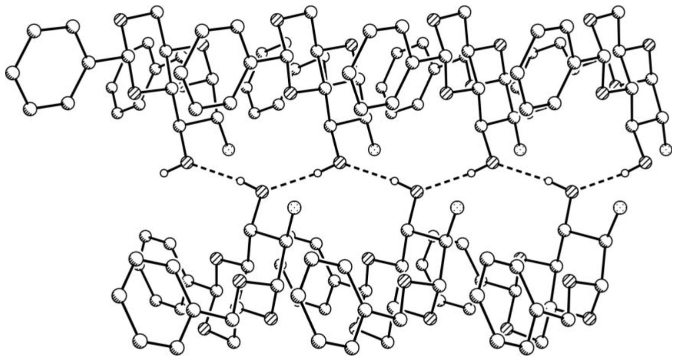


Figure 2
Supramolecular double-chain of $C_{20}H_{23}NO_5$. View perpendicular to the twofold screw axis. Hydrogen bonds are shown as dashed lines and H atoms not involved in these interactions have been omitted.

The crystal structure of the title compound (Fig.1) shows that the sugar ring adopts the more stable $^4C_1$ chair conformation. The benzyl group at C1 is in the axial position, corresponding to the exclusive presence of the α-anomer of the saccharide groups. This is confirmed by the ^{1}H NMR data. H1 leads to a doublet with $^3J_{1,2}$ = 3.7 Hz associated with the *cis*-configuration of atoms H1 and H2. The mean plane of the phenyl ring of the benzyl ether (C8–C13) and the mean sugar plane (C1/C3/C4/O1) subtend an angle of 59.27 (11)°. This angle indicates a considerably larger tilt for the phenyl ring of the anomeric substituent as compared with that of the 4,6-protective group with respect to the sugar backbone.

The molecules are connected *via* intermolecular hydrogen bonds forming one-dimensional double chains with a twofold screw symmetry (Table 1, Fig. 2).

Owing to the vicinal positioned donor groups at C2 and C3 stable five-membered chelate rings can be formed with transition metal ions.

Experimental

All chemicals were purchased from commercial suppliers and used without further purification. Benzyl 2-acetylamino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside was obtained by a two-step synthesis from *N*-acetylglucosamine (Györgydeák, 1991).

Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside was synthesized following the reported procedure (Gross & Jeanloz, 1967). A solution of benzyl 2-acetylamino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (11.91 g, 0.030 mol) and KOH (60.01 g, 1.070 mol) in 200 ml of ethanol (96%) was refluxed overnight. After cooling to 313 K the orange–brown solution was poured into 1.5 l of 333 K hot water, resulting in the precipitation of pale-yellow microcrystalline needles. The reaction mixture was kept at 281 K overnight for complete crystallization. The product was collected by filtration, washed with water and dried *in vacuo* at 55 mbar. Single crystals suitable for X-ray determination were obtained by three weeks of slow evaporation of a solution of the title compound (80 mg, 0.22 mmol) in 10 ml of a mixture of $CHCl_3$, ethanol (96%) and water (3:6:1). Yield: 10.29 g (96.6%). M.p. 451–452 K ($CHCl_3$, ethanol, water).

Crystal data

$C_{20}H_{23}NO_5$	V = 892.1 (4) Å^3
M_r = 357.39	Z = 2
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
a = 13.089 (3) Å	μ = 0.10 mm^{-1}
b = 4.9156 (10) Å	T = 183 (2) K
c = 15.196 (3) Å	0.5 × 0.5 × 0.5 mm
β = 114.15 (3)°	

Data collection

Nonius KappaCCD diffractometer	2278 independent reflections
Absorption correction: none	1607 reflections with $I > 2\sigma(I)$
6072 measured reflections	$R_{\rm int}$ = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.104	$\Delta\rho_{\max}$ = 0.18 e Å^{-3}
S = 1.05	$\Delta\rho_{\min}$ = −0.24 e Å^{-3}
2278 reflections	
244 parameters	
1 restraint	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O3$^{\rm i}$	0.84	1.90	2.735 (5)	170

Symmetry code: (i) $-x, y-\frac{1}{2}, -z+1$.

H atoms were positioned geometrically [C—H = 0.95 (Csp^2), 0.99 (methylene) and 1.00 Å (methine), and O—H = 0.84 Å] and treated as riding atoms with fixed displacement parameters, $U_{\rm iso}$(H) = $xU_{\rm eq}$(C,O), where x = 1.5 for the OH group and 1.2 for all others. The H atoms at the N atom were found in a difference map and refined with an isotropic displacement parameter. The refined distances are 0.89 (4) and 0.92 (4) Å. In the absence of significant anomalous scatterers 1439 Friedel pairs were merged prior to the final refine-

o2528 Burkhardt et al. • $C_{20}H_{23}NO_5$ Acta Cryst. (2007). E63, o2527–o2529

ment. The absolute configuration was assigned by reference to the chiral starting material and the evidence provided by NMR spectroscopy.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *XP*.

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Acta Cryst. (2007). E**63**, o2527–o2529 Burkhardt *et al.* • $C_{20}H_{23}NO_5$ **o2529**