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Comparison of the two anomers of methyl 2-(*N*-benzylamino)-2,3-dideoxy-4,6-*O*-phenylmethylene-3-*C*-phenylsulfonyl-D-glucopyranoside

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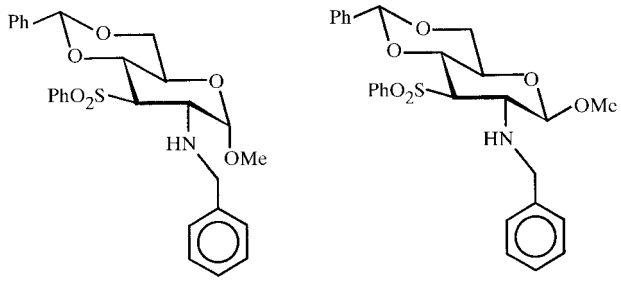
The title compounds, the α and β anomers of methyl 2-(*N*-benzylamino)-2,3-dideoxy-4,6-*O*-phenylmethylene-3-*C*-phenylsulfonyl-D-glucopyranoside, $C_{27}H_{29}NO_6S$, belong to the class of deoxyamino-sugars prepared by the addition of amines at C2. The endocyclic bond lengths of the pyranose ring in the α anomer are shorter than the corresponding bonds in the β anomer. The pyranose ring is in the chair form in the former, while it is in the boat form in the latter. These observed differences could be attributed to the C2 substitution of a bulky group. The phenylsulfonyl and benzylamino groups are in equatorial positions in the α anomer, while the benzylamino group is axial in the β anomer.

Comment

Amino-sugars, in general, are one of the most important classes of carbohydrates. The C—N equatorial bonds at the C2 position of carbohydrates play a significant role because naturally occurring amino-sugars, such as D-glucosamine, D-galactosamine, D-lividosamine *etc.*, have their C—N bonds at C2 in an equatorial configuration. Not many synthetic routes are available for the introduction of *N*-monoalkylated and *N*-dialkylated amines to the C2 atom of pyranoses in equatorial configurations. As part of an ongoing programme on the development of novel synthetic routes for the preparation of new classes of deoxyamino-sugars, we have been studying the stereoselective addition of various amines to phenylsulfonyl-modified carbohydrates. In this context, we have determined the structures of the α, (Iα), and β, (Iβ), anomers of a phenylsulfonyl-modified monosaccharide with amino substitution at C2.

When the geometry of the pyranose rings in the two molecules is compared, the average endocyclic C—C bond length is 1.528 in (Iα) and 1.537 Å in (Iβ). The value of the former is closer to the average values reported for glucopyranose rings (Jeffrey, 1990), whereas that of the latter is higher. The average of the endocyclic bond angles around the C atoms is 111.1 and 111.6°, respectively. These values are higher than the reported average (Jeffrey, 1990). The bond angle around O5 in (Iβ) is wider than that in (Iα).



(Iα) (Iβ)

The pyranose–dioxane double-ring system in (Iα) is in the chair conformation. The dioxane ring alone has the chair form in (Iβ), while the pyranose takes the boat form. The conformations of the pyranoses are thus symbolized as $^4C_1$ in (Iα) and $^{1,4}B$ in (Iβ) (Collins & Ferrier, 1995). In (Iα), the bulky phenylsulfonyl and benzylamino groups attached to the pyranose ring, as well as the phenyl group attached to dioxane, are all equatorially positioned with respect to the double-ring carbohydrate system, while the benzoylamino group is axial in (Iβ) (Figs. 1 and 2).

The main conformational difference between the pyranose rings in the two anomers corresponds to C1 puckering. The observed difference, the chair conformation of the pyranose in (Iα) and the boat conformation in (Iβ), could presumably be the result of C2 substitution. In (Iβ), the observed boat conformation of the pyranose ring causes the benzylamino and glycosidic *O*-methyl groups present at adjacent ring C

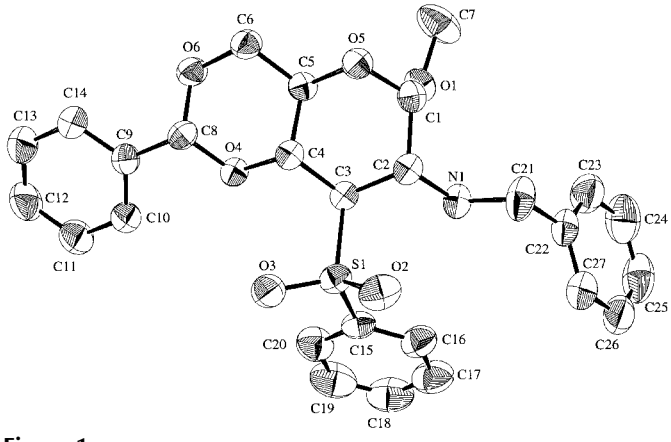


Figure 1
A perspective view of (Iα). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

atoms to orient away from each other. In a chair conformation of the pyranose rings, these groups would have come sterically closer. Another difference between the anomers is in the disposition of the phenyl ring of the phenylsulfonyl. This phenyl ring is positioned away from C2 benzylamino in (Iβ) compared to its position in (Iα). Among the three planar phenyl rings, that of benzylamino is almost orthogonal to the other two in both structures, whereas the phenyl rings of phenylmethylene and phenylsulfonyl make angles of 26.6 (2) and 63.5 (2)° with respect to each other in (Iα) and (Iβ), respectively.

In the case of hexapyranoses, the presence of a hydroxyl group at C4 is expected to forbid the orientation of the primary alcohol group C6—OH in a *tg* conformation (Jeffrey, 1990). However, in both the molecules reported here, this group is in a *tg* conformation as a result of dioxan ring formation.

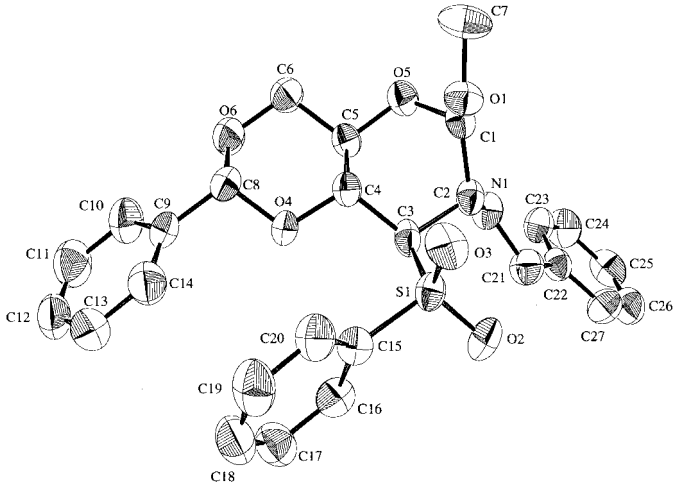


Figure 2
A perspective view of (Iβ). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

The C—O bond shortening at C1 of the pyranose and the preferred *gauche* conformations about the glycosidic bond (*exo*-anomeric effect) are known in carbohydrates (Perez & Marchessault, 1978). The structure of (Iα) reported here belongs to the *gauche–gauche* class which is the allowed class for α anomers. The *trans–gauche* form is favourable in β anomers (Norrestam *et al.*, 1981). Nevertheless, according to glycosodic torsion angles (Table 1), the β anomer has *gauche–gauche* conformation. Presumably, this not so common form of β anomers is found in this structure due to the boat form instead of the more common chair form of the pyranose ring.

The crystal structures are stabilized by the stacking and hydrophobic interactions of the phenyl rings. In (Iβ), there is an intermolecular hydrogen bond between the amino nitrogen and the sulfone oxygen (O3) of the translated molecule along **c**. In (Iα), this nitrogen is involved in a weak intramolecular hydrogen bond with the oxygen (O1) of the glycosidic *O*-methyl group.

Experimental

Methyl 2,3-dideoxy-4,6-*O*-phenylmethylene-3*C*-phenylsulfonyl-α-D-*erythro*-hex-2-enopyranoside and the corresponding -β-D-*erythro*-hex-2-enopyranoside were reacted separately with benzylamine at elevated temperatures (Ravindran *et al.*, 2000). The desired amino-sugars were recrystallized from methanol.

Compound (Iα)

Crystal data

$C_{27}H_{29}NO_6S$
M_r = 495.57
Monoclinic, $P2_1$
a = 10.418 (2) Å
b = 8.880 (6) Å
c = 13.560 (2) Å
β = 91.36 (1)°
V = 1254.1 (9) Å^3
Z = 2
D_x = 1.312 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–30°
μ = 1.501 mm^{-1}
T = 293 (2) K
Needle, colourless
0.80 × 0.31 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.668, T_{max} = 0.687
2810 measured reflections
2667 independent reflections
2563 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 75.62°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 10$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.090
S = 1.054
2667 reflections
318 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0620P)^2 + 0.1489P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0119 (8)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (2)

Table 1
Selected geometric parameters (Å, °) for (Iα).

S1—C3	1.832 (2)	O1—C7	1.436 (3)
O5—C1	1.417 (3)	C2—N1	1.455 (3)
O5—C5	1.418 (3)	C2—C3	1.537 (3)
C1—O1	1.394 (4)	C3—C4	1.522 (3)
C1—C2	1.537 (3)	C4—C5	1.518 (3)
C1—O5—C5	111.1 (2)	C4—C3—S1	110.17 (15)
O1—C1—O5	111.4 (2)	C2—C3—S1	109.5 (2)
O1—C1—C2	108.2 (2)	O4—C4—C5	106.8 (2)
O5—C1—C2	112.8 (2)	O4—C4—C3	110.5 (2)
C1—O1—C7	112.8 (3)	C5—C4—C3	109.4 (2)
N1—C2—C3	109.5 (2)	O5—C5—C4	109.6 (2)
N1—C2—C1	112.6 (2)	O5—C5—C6	109.0 (2)
C3—C2—C1	113.4 (2)	C4—C5—C6	109.5 (2)
C4—C3—C2	110.5 (2)	C2—N1—C21	114.9 (2)
C5—O5—C1—O1	64.4 (2)	C1—O5—C5—C4	67.0 (2)
C5—O5—C1—C2	−57.4 (3)	C1—O5—C5—C6	−173.2 (2)
O5—C1—O1—C7	70.5 (3)	O4—C4—C5—O5	176.8 (2)
O1—C1—C2—N1	47.0 (3)	C3—C4—C5—O5	−63.7 (2)
O5—C1—C2—C3	45.7 (3)	O4—C4—C5—C6	57.2 (3)
C1—C2—C3—C4	−42.9 (3)	O6—C6—C5—O5	−173.4 (2)
C2—C3—C4—C5	51.1 (3)	O6—C6—C5—C4	−53.5 (3)

Compound (Iβ)

Crystal data

$C_{27}H_{29}NO_6S$
M_r = 495.57
Triclinic, $P\overline{1}$
a = 8.3190 (10) Å
b = 13.197 (2) Å
c = 5.750 (2) Å
α = 100.84 (2)°
β = 98.61 (2)°
γ = 89.430 (10)°
V = 612.9 (2) Å^3
Z = 1
D_x = 1.343 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 18 reflections
θ = 29.5–46.0°
μ = 1.536 mm^{-1}
T = 293 (2) K
Irregular flakes, colourless
0.40 × 0.14 × 0.06 mm

Data collection

AFC-7*S* diffractometer
ω–2θ scans
Absorption correction: sphere (Weber, 1969)
T_{min} = 0.709, T_{max} = 0.722
2739 measured reflections
2261 independent reflections (plus 146 Friedel-related reflections)
2407 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 70.09°
$h = 0 \rightarrow 10$
$k = -16 \rightarrow 16$
$l = -6 \rightarrow 6$
3 standard reflections
every 150 reflections
intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.203
S = 1.106
2425 reflections
318 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1392P)^2 + 0.4772P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.005$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.100 (10)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (4)

H atoms were located using geometrical considerations and a difference Fourier map. They were treated as riding on the heavier atoms to which they were attached.

For compound (Iα), data collection and cell refinement: *CAD*-4-*PC Software* (Enraf–Nonius, 1993); for compound (Iβ), data collection, cell refinement and data reduction: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); for compound (Iα), data reduction: *NRCVAX DATRD*2 (Gabe *et al.*, 1989). For both compounds, program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

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Table 2
Selected geometric parameters (Å, °) for (Iβ).

S1—C3	1.763 (7)	C2—N1	1.453 (7)
O5—C1	1.414 (7)	C2—C3	1.574 (8)
O5—C5	1.433 (7)	C3—C4	1.522 (8)
C1—O1	1.382 (7)	C4—C5	1.516 (8)
C1—C2	1.537 (9)	N1—C21	1.442 (9)
O1—C7	1.438 (8)		
C1—O5—C5	115.6 (4)	C4—C3—S1	116.0 (4)
O1—C1—O5	112.4 (5)	C2—C3—S1	109.8 (4)
O1—C1—C2	110.1 (5)	O4—C4—C5	105.8 (4)
O5—C1—C2	113.0 (5)	O4—C4—C3	109.0 (5)
C1—O1—C7	111.0 (5)	C5—C4—C3	110.4 (5)
N1—C2—C1	108.5 (5)	O5—C5—C6	107.0 (5)
N1—C2—C3	115.6 (5)	O5—C5—C4	113.1 (5)
C1—C2—C3	111.5 (5)	C6—C5—C4	109.6 (5)
C4—C3—C2	110.1 (5)	C21—N1—C2	115.6 (5)
C5—O5—C1—O1	−87.1 (6)	C1—O5—C5—C6	141.3 (5)
C5—O5—C1—C2	38.3 (7)	C1—O5—C5—C4	20.5 (7)
O5—C1—O1—C7	−62.2 (7)	O6—C6—C5—O5	178.6 (5)
O1—C1—C2—N1	−161.5 (5)	O6—C6—C5—C4	−58.4 (7)
O5—C1—C2—C3	−56.7 (6)	O4—C4—C5—O5	179.4 (5)
C1—C2—C3—C4	14.0 (6)	C3—C4—C5—O5	−62.8 (6)
C2—C3—C4—C5	40.9 (6)	O4—C4—C5—C6	60.1 (6)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1104). Services for accessing these data are described at the back of the journal.

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