Data collection

Siemens P4 diffractometer	$\theta_{max} = 27.67°$
$\theta/2\theta$ scans	$h = -11 \rightarrow 11$
Absorption correction: none	$k = 0 \rightarrow 16$
6375 measured reflections	$l = 0 \rightarrow 35$
6055 independent reflections	3 standard reflections
2535 reflections with	every 247 reflections
$F \geq 4\sigma(F)$	intensity decay: none
$R_{int} = 0.06$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.007$
$R = 0.065$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
$wR = 0.059$	$\Delta\rho_{min} = -0.23$ e Å^{-3}
$S = 1.54$	Extinction correction: none
2495 reflections	Scattering factors from
334 parameters	*International Tables for*
H-atom parameters	*X-ray Crystallography*
constrained	(Vol. IV, Table 2.2B)
$w=1/[\sigma(F)]$	

Table 1. *Selected geometric parameters (Å, °)*

O2—C2	1.208 (6)	C3—C4	1.380 (6)
O4—C4	1.299 (6)	C3—C10	1.449 (6)
O9—C9	1.209 (7)	C5—C6	1.610 (7)
O10—C10	1.268 (6)	C6—C7	1.557 (8)
C1—C8	1.562 (6)	C7—C24	1.540 (7)
C1—C9	1.496 (7)	C25—C26	1.302 (9)
C2—C3	1.460 (6)	C26—C27	1.499 (10)
C2—C1—C8	108.6 (4)	C9—C5—C19	111.3 (4)
C2—C1—C9	111.9 (4)	C5—C6—C7	111.5 (4)
C8—C1—C9	105.6 (4)	C6—C7—C8	112.1 (4)
C2—C1—C29	109.3 (4)	C6—C7—C24	117.4 (4)
C1—C2—C3	117.4 (4)	C1—C9—C5	114.2 (4)
C2—C3—C4	118.6 (4)	C3—C10—C11	123.2 (4)
C3—C4—C5	124.6 (4)	C7—C24—C25	112.7 (4)
C4—C5—C9	107.2 (4)	C25—C26—C27	125.5 (6)
C6—C5—C19	113.9 (4)		

The structure was solved by direct methods and analysis of the difference Fourier map. H atoms were placed in calculated positions and considered as riding atoms in the structure-factor calculations. The absolute structure could not be reliably determined [the calculated Flack (1983) parameter was 0 (3)] due to the fact that there is no atom heavier than the O atom.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

References

Delle Monache, F., Delle Monache, G. & Gacs-Baitz, E. (1991). *Phytochemistry*, **30**, 2003–2005.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gustafson, K. R., Blunt, J. W., Munro, M. H. G., Fuller, R. W., McKee, T. C., Cardellina, J. H. II, McMahon, J. B., Cragg, G. M. & Boyd, M. R. (1992). *Tetrahedron*, **48**, 10093–10102.
McCandlish, L. E., Hanson, J. C. & Stout, G. H. (1976). *Acta Cryst.* B**32**, 1793–1801.
Oliveira, C. M. A. de, Porto, A. M., Bittrich, V., Vencato, I. & Marsaioli, A. J. (1996). *Tetrahedron Lett.* **37**, 6427–6430.
Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

β-1-N-Ureido-D-glucopyranose

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Abstract

β-1-N-Ureido-D-glucopyranose, $C_7H_{14}N_2O_6$, adopts a $^4C_1(D)$ conformation. The nearly planar urea moiety is in a Z-anti conformation.

Comment

β-1-N-Ureido-D-glucopyranose, (1), is conceptually amongst the simplest N-linked aldohexoses with a rigid group at the N atom. Analysis of a cocrystal of glucose and urea revealed strong hydrogen bonding between the two substrates (Snyder & Rosenstein, 1971). In this structure, rows of glucose molecules form layers in the channels formed by the urea. We envisioned that (1) could form a channel structure through an array of strong intermolecular hydrogen bonds. In the structure determined, the β-1-N-ureido-D-glucopyranose packs tightly, excluding water from the crystal lattice. Strong intermolecular hydrogen bonding is observed, but there is no evidence of channel formation.
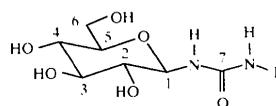
(1)

The title compound was synthesized by the condensation of urea and glucose under acidic conditions (Schoori, 1903). The molecules crystallize in the ortho-

rhombic space group $P2_12_12_1$. This space group is also observed for the crystal structure of β-1-N-acetamido-D-glucopyranose, (2) (Sriram *et al.*, 1997), and the cocrystals of glucose and urea. Compound (1) adopts the $^4C_1$ conformation (IUPAC–IUB Joint Commission on Biochemical Nomenclature, 1980). The C1—N1—C7—N2 torsion angle of the urea moiety is 169.8 (2)°, with the urea carbonyl O7 atom twisting slightly towards O1, as reflected in an O1—C1—N1—C7 torsion angle of −86.0 (2)°. This angle eclipses the H1—C1—N1 plane to a lesser extent (by 7.7°) than observed in (2). These observations suggest that the magnitude of the *exo*-anomeric effect (Lemieux *et al.*, 1979) is greater with a urea moiety than with an acetamido group. The conformation of the primary alcohol is *gauche* to the carbohydrate ring, as in (2).

The C1 and C5 bond distances to the pyran O atom in (1) are non-equivalent, which is commonly observed for β-D-glucopyranoses. This is in contrast to (2), where these bond distances are equivalent. Additionally, the C1—N1 bond in (1) is shorter by 0.01 Å than the analogous bond in (2) (1.42 *versus* 1.43 Å). Given that 1-aminoglucose has a C—N bond distance of 1.39 Å (Jeffrey *et al.*, 1985), our results suggest that the magnitude of the *exo*-anomeric stabilization is greater for glucosylurea than for 1-acetamidoglucose.
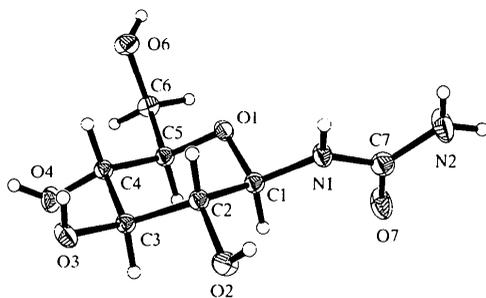
Fig. 1. *SHELXTL* (Siemens, 1994*b*) plot showing 35% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms.

Experimental

The title molecule was prepared by the literature procedure of Schoori (1903). The product was recrystallized from water-ethanol to produce a white solid (m.p. 478–482 K). The crystals were grown by vapour diffusion of absolute ethanol into a 30% (w/v) aqueous solution of the compound. The ^{13}C NMR spectrum was referenced to internal benzene. ^{1}H NMR (399.952 MHz, D$_2$O, p.p.m.): 3.18 (t, 1H, $J_{2,1}$ = 9.12 Hz, H2), 3.21 (dd, 1H, $J_{4,5}$ = 9.80, $J_{4,3}$ = 9.06 Hz, H4), 3.326 (ddd, 1H, $J_{5,4}$ = 9.90, $J_{5,6}$ = 5.5, $J_{5,6}$ = 2.2 Hz, H5), 3.362 (t, 1H, J = 9.13 Hz, H3), 3.537 (dd, 1H, $J_{6A,6B}$ = 12.37, $J_{6,5}$ = 5.51 Hz, H6AB), 3.705 (dd, 1H, $J_{6AB,6AB}$ = 12.36, $J_{6AB,5}$ 2.21 Hz, H6AB) and 4.625 (d, 1H, J = 9.12 Hz, H1); ^{13}C NMR: (100.577 MHz, D$_2$O, p.p.m.): 60.485 (C6), 69.211, 71.796, 76.387, 76.968, 80.823 (C1) and 160.558 (C7).

$C_7H_{14}N_2O_6$	Mo $K\alpha$ radiation
M_r = 222.20	λ = 0.71073 Å
Orthorhombic	Cell parameters from 4510
$P2_12_12_1$	reflections
a = 7.8978 (1) Å	θ = 4–28°
b = 9.1364 (2) Å	μ = 0.130 mm^{-1}
c = 13.7581 (1) Å	T = 198 (2) K
V = 992.75 (3) Å^3	Platelet
Z = 4	0.44 × 0.40 × 0.12 mm
D_x = 1.487 Mg m^{-3}	Colourless
D_m not measured	

Data collection

Siemens Platform/CCD	R_{int} = 0.031
diffractometer	θ_{max} = 28.25°
ω scans	h = −10 → 10
Absorption correction:	k = −9 → 11
ψ scan (Siemens, 1994*b*)	l = −12 → 17
T_{min} = 0.951, T_{max} = 0.986	241 standard reflections
6480 measured reflections	frequency: 6 min
2348 independent reflections	intensity decay: none
2212 reflections with	
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	Extinction correction:
$R[F^2 > 2\sigma(F^2)]$ = 0.038	*SHELXL*93 (Sheldrick,
$wR(F^2)$ = 0.089	1993)
S = 1.086	Extinction coefficient:
2348 reflections	0.013 (2)
163 parameters	Scattering factors from
All H atoms refined	*International Tables for*
$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2$	*Crystallography* (Vol. C)
$+ 0.4965P]$	Absolute structure:
where $P = (F_o^2 + 2F_c^2)/3$	Flack (1983)
$(\Delta/\sigma)_{max}$ = 0.001	Flack parameter = −0.1 (11)
$\Delta\rho_{max}$ = 0.373 e Å^{-3}	
$\Delta\rho_{min}$ = −0.316 e Å^{-3}	

Table 1. *Selected geometric parameters (Å, °)*

O1—C5	1.431 (2)	O2—C2	1.424 (2)
O1—C1	1.446 (2)	O6—C6	1.428 (2)
O3—C3	1.423 (2)	N1—C7	1.369 (2)
O4—C4	1.426 (2)	C5—C6	1.516 (2)
C1—N1	1.421 (2)	O7—C7	1.235 (2)
C1—C2	1.530 (2)	N2—C7	1.350 (3)
N1—C1—O1	108.48 (14)	C3—C2—C1	110.61 (14)
O1—C1—C2	108.70 (13)	O7—C7—N2	123.5 (2)
C3—C4—C5	109.99 (14)	O7—C7—N1	121.4 (2)
O1—C5—C6	107.20 (14)	N2—C7—N1	115.1 (2)
O1—C5—C4	109.91 (13)	O6—C6—C5	109.20 (14)
C2—C3—C4—O4	167.86 (13)	O1—C1—C2—O2	174.70 (13)
O3—C3—C4—C5	173.97 (13)	C1—N1—C7—O7	−11.3 (3)
O1—C1—N1—C7	−86.0 (2)	C1—N1—C7—N2	169.8 (2)
N1—C1—C2—O2	−65.9 (2)		

Systematic absences suggested the space group unambiguously. The structure was solved by direct methods, with H atoms treated isotropically. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement. The highest peaks in the final difference Fourier map were in the vicinity of atom C7; the final map had no other significant features. A final analysis of variance

between observed and calculated structure factors showed no dependence on amplitude and resolution.

Data collection: *SMART* (Siemens, 1994a). Cell refinement: *SAINT* (Siemens, 1994a). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Siemens, 1994b). Software used to prepare material for publication: *SHELXTL*.

References

Flack, H. D. (1983). *Acta Cryst.* A39, 876–881.
IUPAC-IUB Joint Commission on Biochemical Nomenclature (1980). *Eur. J. Biochem.* 111, 295–298.
Jeffrey, G. A., Samudzi, C. T. & Ruble, J. R. (1985). *Carbohydr. Res.* 142, 39–45.
Lemieux, R. U., Koto, S. & Voisin, D. (1979). In *Anomeric Effect: Origin and Consequences*, edited by D. Horton & W. Szarek. ACS Symposium Series, No. 87.
Schoori, M. N. (1903). *Recl Trav. Chim. Pays-Bas*, 22, 31–77.
Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994a). *SMART and SAINT. Area Detector Control and Integration Software*. Version 4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994b). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Snyder, R. L. & Rosenstein, R. D. (1971). *Acta Cryst.* B27, 1969–1975.
Sriram, D., Sreenivasan, H., Srinivasan, S., Priya, K., Vishnu Thirtha, M. & Loganathan, D. (1997). *Acta Cryst.* C53, 1075–1077.

2,5-Diethoxy-1,4-bis(3,4-ethylenedioxy-2-thienyl)benzene and its Tetrahydrofuran 0.33-Solvate

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Abstract

The crystal structures of the title compounds, 2,5-diethoxy-1,4-bis(3,4-ethylenedioxy-2-thienyl)benzene, C$_{22}$H$_{22}$O$_6$S$_2$, (I), and its one-third tetrahydrofuran (THF) solvate, C$_{22}$H$_{22}$O$_6$S$_2$.$\frac{1}{3}$C$_4$H$_8$O, (II), were studied to determine the relative geometry of the benzene and thienyl rings. The dihedral angles between the benzene and thienyl rings are 6.04 (9) and 2.0 (1)° in (I) and (II), respectively, compared with 27.5 (2)° in the unsubstituted analog 1,4-bis(3,4-ethylenedioxy-2-thienyl)benzene. The benzene and thienyl rings are more distorted in the title structures compared with the unsubstitued analog.

Comment

Thiophene-based polymers and oligomers have been the focus of much attention, due to their synthetic flexibility, environmental stability, and broad electrochemical stability range. However, one of the problems associated with direct thiophene electropolymerization is that the oxidation potential of the monomer is sufficiently high to degrade the polymer being formed, a process that has become known as overoxidation. We, and others, have overcome this problem by lowering the oxidation potential using electron-rich heterocyclic systems in combination with multi-ring conjugated monomers. The most interesting of these are 3,4-ethylenedioxythiophene (EDOT) derivatives (Jonas *et al.*, 1991; Kumar & Reynolds, 1996; Sankaran & Reynolds, 1997). We have developed a broad family of monomers such as the bis(2-heterocycle)benzenes (Reynolds *et al.*, 1993; 1994; Child *et al.*, 1995; Sotzing *et al.*, 1996; Irvin & Reynolds, 1998), which lead to polymers with rationally controlled electronic properties.

In order for the polymer to stabilize charge carriers, the conjugated backbone must easily attain a fully planar conformation across a number of the heterocyclic and benzene rings. Previously (Reynolds *et al.*, 1991), we calculated the optimized geometry for two bis(2-thienyl)benzenes at the PRDDO level [partial retention of diatomic differential overlap (*CHEMX*; Chemical Design Ltd, 1988)], and found that the unsubstituted analog had a calculated dihedral angle of 24.3° between the planes of the benzene and thienyl rings. The 2,5-dimethoxy substituted compound had a calculated angle of 40°. In the previously determined crystal structure of 1,4-bis(3,4-ethylenedioxy-2-thienyl)benzene, (III), the EDOT-to-benzene-ring angle was determined to be 27.5 (2)° (Sotzing *et al.*, 1996). In analogy to the calculations carried out on the 2-thienyl derivative, we expected that with 2,5-disubstitution by the more sterically demanding ethoxy group, the dihedral angle would be increased. Thus the crystal structures of both 2,5-diethoxy-1,4-bis(3,4-ethylenedioxy-2-thienyl)benzene, (I), and its tetrahydrofuran solvate, (II), were undertaken to determine the relative geometry of the EDOT ring (S, C1, C2, C5 and C6) with respect to the benzene ring (C7–C9 and their inversion counterparts). In contrast to our expectation, the 2,5-diethoxy substitution leads to an essentially planar compound, where the dihedral angles of (I) and (II) are 6.04 (9) and 2.0 (1)°,