Table 2. *Selected geometric parameters* (Å, °)

C(14)—O(2)	1.250 (3)	C(14A)—O(2A)	1.251 (3)
C(14)—O(1)	1.263 (3)	C(14A)—O(1A)	1.258 (3)
C(7)—N(1)—C(1)	122.4 (2)	C(7A)—N(1A)—C(1A)	124.3 (2)
C(2)—C(13)—C(14)	111.7 (2)	C(2A)—C(13A)—C(14A)	111.1 (2)
O(2)—C(14)—C(13)	118.4 (2)	O(2A)—C(14A)—C(13A)	118.1 (2)
N(2)—C(19)—C(20)	114.8 (2)	C(20A)—C(19A)—N(2A)	113.3 (3)
O(3)—C(20)—C(19)	113.7 (2)	O(3A)—C(20A)—C(19A)	111.8 (3)

C(1)—N(1)—C(7)—C(12)	64.6 (3)
N(2)—C(19)—C(20)—O(3)	−73.4 (3)
C(1A)—N(1A)—C(7A)—C(12A)	59.6 (3)
N(2A)—C(19A)—C(20A)—O(3A)	64.0 (3)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N(2)—H(11)···O(1)	0.94 (3)	1.78 (3)	2.696 (3)	164 (3)
N(2A)—H(11A)···O(2A)	0.93 (3)	1.84 (3)	2.751 (3)	167 (3)
O(3)—H(24)···O(2)	0.87 (3)	1.78 (3)	2.645 (3)	174 (3)
O(3A)—H(24A)···O(1A)	0.87 (3)	1.85 (3)	2.674 (3)	158 (3)
N(1)—H(1)···Cl(1)	0.87 (3)	2.61 (3)	3.031 (3)	111 (2)
N(1A)—H(1A)···Cl(1A)	0.88 (3)	2.68 (3)	2.989 (3)	102 (2)
N(1)—H(1)···O(1)	0.87 (3)	2.22 (3)	2.929 (3)	139 (3)
N(1A)—H(1A)···O(1A)	0.88 (3)	2.05 (3)	2.890 (3)	159 (3)
C(3)—H(2)···Cl(2^i)		2.74	3.618 (4)	157
C(10)—H(7)···O(2^{ii})		2.49	3.376 (4)	160
C(15)—H(12)···O(2A^{iii})		2.48	3.390 (4)	156
C(18A)—H(19A)···O(1^{iii})		2.44	3.347 (5)	154
C(19A)—H(20A)···O(3^{iii})		2.56	3.506 (5)	165

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, 1+y, z$; (iii) $-x, -y, 1-z$.

The H atoms bonded to N and O atoms [H(1), H(1A), H(11), H(11A), H24, H(24A)] were located experimentally and refined with distance restraints. The remaining H atoms were placed in calculated positions and refined riding on the parent atoms (aromatic C—H = 0.93, C_{sp^3}—H = 0.97 Å) with U_{iso} fixed at 1.2 × U_{eq} of attached atom. Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *SCHAKAL*92 (Keller, 1992). Software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1994).

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1-*O*-(2-Iodophenyl)-β-D-galactopyranose

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Abstract

The sugar ring in 1-*O*-(2-iodophenyl)-β-D-galacto-pyranose ($C_{12}H_{15}IO_6$) has the expected $^4C_1$ chair conformation. The molecules form hydrogen-bonded layers which stack together so that the crystal structure contains alternate polar and non-polar slices along the *c* axis.

Comment

The title compound, (1), which was synthesized in this laboratory, was used to prepare a heavy-atom derivative of peanut lectin (Banerjee *et al.*, 1994). As it was also used to locate the sugar binding site in the lectin, its structure was determined.

(1)
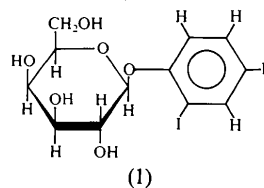
The sugar ring in the title structure has an almost ideal $^4C_1$ chair conformation (Stoddart, 1971) with θ = 0.02 (2)° (Pickett & Strauss, 1970). C(1) and C(4) are displaced by −0.668 (3) and 0.683 (3) Å, respectively, from the mean plane through the remaining ring atoms. The phenyl ring is inclined at 45.1 (3)° to this plane. The I atom is displaced from the plane of the phenyl ring by 0.091 (1) Å. The torsion angle between the two rings, H(1)—C(1)—O(1)—C(11), is 34 (1)°. The torsion angle C(4)—C(5)—C(6)—O(6), which defines the position of the CH₂OH group with respect to the sugar ring, can assume three sterically favourable values corresponding to three staggered conformations. The angle in the title compound is −58.9 (4)° compared to 176.3° in β-D-galactose (Sheldrick, 1976a).

The molecules in the crystal form hydrogen-bonded layers parallel to the *ab* plane (Fig. 2). The hydrogen bonds spiral around 2_1 screw axes and the

layers stack along the *c* axis to form the crystal. As inter-layer interactions involve primarily the non-polar phenyl rings, the crystal structure contains alternate polar and non-polar slices along the *c* axis.
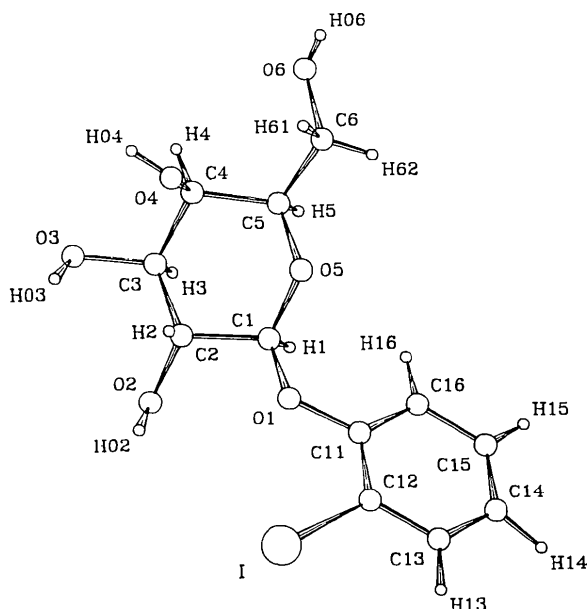

Fig. 1. The molecular structure of 1-*O*-(2-iodophenyl)-β-D-galac-topyranose.
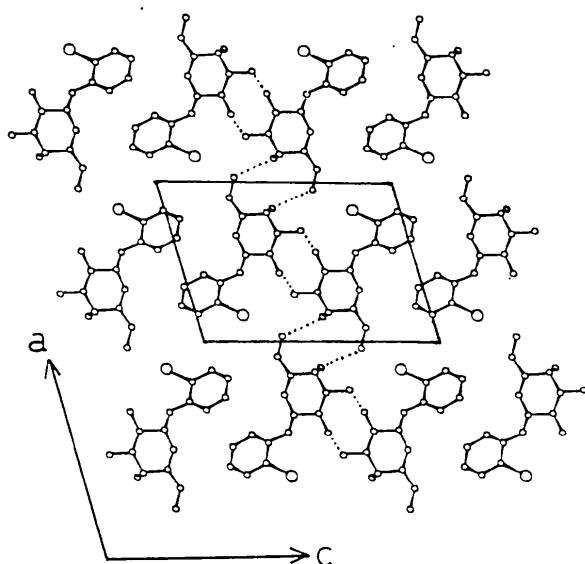

Fig. 2. The crystal structure of 1-*O*-(2-iodophenyl)-β-D-galacto-pyranose. The broken lines indicate hydrogen bonds.

Experimental

Crystal data

$C_{12}H_{15}IO_6$
$M_r = 382.15$

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å

Monoclinic
$P2_1$
$a = 10.049\ (2)$ Å
$b = 4.679\ (1)$ Å
$c = 14.429\ (1)$ Å
$\beta = 107.28\ (3)°$
$V = 647.82\ (22)$ Å^3
$Z = 2$
$D_x = 1.958$ Mg m^{-3}
$D_m = 1.96\ (2)$ Mg m^{-3}
D_m measured by flotation in CHBr$_3$–CCl$_4$

Cell parameters from 25 reflections
$\theta = 5.28$–$16.76°$
$\mu = 2.527$ mm^{-1}
$T = 296$ K
Needle
$0.28 \times 0.22 \times 0.12$ mm
Colourless
Crystal source: recrystallized from aqueous methanol

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical (Walker & Stuart, 1983)
$T_{min} = 0.811$, $T_{max} = 1.107$
3308 measured reflections
2816 independent reflections

2777 observed reflections
$[I > 0]$
$R_{int} = 0.0124$
$\theta_{max} = 27°$
$h = -12 \rightarrow 12$
$k = -5 \rightarrow 5$
$l = -18 \rightarrow 18$
3 standard reflections frequency: 60 min intensity variation: 4%

Refinement

Refinement on F
$R = 0.031$
$wR = 0.035$
$S = 0.7150$
2777 reflections
231 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0034F^2]$

$(\Delta/\sigma)_{max} = 0.627$
$\Delta\rho_{max} = 1.974$ e Å^{-3}
$\Delta\rho_{min} = -1.581$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
I	0.16805 (2)	0.0000	0.19788 (1)	0.034 (1)
C(1)	0.5467 (3)	0.5452 (7)	0.2869 (2)	0.025 (2)
O(1)	0.4375 (3)	0.3591 (6)	0.2409 (2)	0.032 (2)
C(2)	0.5555 (3)	0.5371 (7)	0.3955 (2)	0.023 (2)
O(2)	0.4345 (3)	0.6629 (6)	0.4096 (2)	0.029 (2)
C(3)	0.6853 (4)	0.6942 (7)	0.4526 (2)	0.024 (2)
O(3)	0.7024 (3)	0.6866 (6)	0.5557 (2)	0.030 (2)
C(4)	0.8151 (3)	0.5786 (7)	0.4328 (3)	0.022 (2)
O(4)	0.8417 (3)	0.2905 (7)	0.4636 (2)	0.033 (2)
C(5)	0.7925 (4)	0.5874 (7)	0.3233 (3)	0.026 (2)
O(5)	0.6700 (3)	0.4306 (6)	0.2721 (2)	0.030 (2)
C(6)	0.9088 (4)	0.4487 (9)	0.2932 (3)	0.035 (3)
O(6)	1.0383 (3)	0.5872 (7)	0.3399 (2)	0.039 (2)
C(11)	0.3722 (4)	0.3928 (8)	0.1425 (2)	0.027 (2)
C(12)	0.2477 (4)	0.2437 (8)	0.1056 (2)	0.028 (2)
C(13)	0.1746 (5)	0.2636 (9)	0.0074 (3)	0.039 (3)
C(14)	0.2253 (5)	0.4346 (10)	-0.0528 (3)	0.047 (3)
C(15)	0.3459 (5)	0.5857 (10)	-0.0164 (3)	0.044 (3)
C(16)	0.4227 (4)	0.5655 (18)	0.0821 (3)	0.036 (2)

Table 2. *Selected geometric parameters* (Å, °)

C(12)—I	2.085 (4)	O(3)—C(3)	1.447 (4)
O(1)—C(1)	1.403 (4)	C(4)—C(3)	1.516 (5)
C(2)—C(1)	1.545 (4)	O(4)—C(4)	1.420 (4)
O(5)—C(1)	1.423 (4)	C(5)—C(4)	1.528 (5)

$C_{12}H_{15}IO_6$

C(11)—O(1)	1.385 (4)	O(5)—C(5)	1.435 (4)
O(2)—C(2)	1.419 (4)	C(6)—C(5)	1.509 (5)
C(3)—C(2)	1.510 (4)	O(6)—C(6)	1.430 (5)
C(2)—C(1)—O(1)	105.4 (3)	C(5)—C(4)—C(3)	108.2 (3)
O(5)—C(1)—O(1)	106.8 (3)	C(5)—C(4)—O(4)	107.8 (3)
O(5)—C(1)—C(2)	110.7 (3)	O(5)—C(5)—C(4)	111.1 (3)
C(11)—O(1)—C(1)	118.7 (3)	C(6)—C(5)—C(4)	113.3 (3)
O(2)—C(2)—C(1)	110.0 (3)	C(6)—C(5)—O(5)	104.5 (3)
C(3)—C(2)—C(1)	108.7 (3)	C(5)—O(5)—C(1)	112.4 (2)
C(3)—C(2)—O(2)	111.0 (3)	O(6)—C(6)—C(5)	110.1 (4)
O(3)—C(3)—C(2)	111.6 (3)	C(12)—C(11)—O(1)	115.7 (3)
C(4)—C(3)—C(2)	112.1 (3)	C(16)—C(11)—O(1)	124.0 (3)
C(4)—C(3)—O(3)	109.8 (3)	C(11)—C(12)—I	120.1 (3)
O(4)—C(4)—C(3)	111.8 (3)	C(13)—C(12)—I	120.0 (3)

D—H···A	D···A	D—H···A
O(2)—H(O2)···O(3^i)	2.742 (4)	170 (1)
O(3)—H(O3)···O(2^{ii})	2.925 (4)	173 (1)
O(4)—H(O4)···O(6^{iii})	2.892 (5)	160 (2)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, 1 - z$; (ii) $1 - x, \frac{1}{2} + y, 1 - z$; (iii) $2 - x, y - \frac{1}{2}, 1 - z$.

The structure was solved by direct methods using *MULTAN*11/84 (Main, Germain & Woolfson, 1984) and refined using *SHELX*76 (Sheldrick, 1976b). Friedel pairs were not merged. The reported configuration refined to a lower value of R than its enantiomorph. Complex scattering factors were used for iodine. High peaks in the residual electron density appear only in the vicinity of the heavy I atom. The figures were prepared using *PLUTO* (Motherwell & Clegg, 1978).

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Formation and Identification of Rotameric 9-Pivaloylfluorene Oximes. Structure of ap-(Z)-9-Pivaloylfluorene Oxime

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Abstract

Reaction of hydroxylamine with sterically hindered *ap*-9-pivaloylfluorene (I) produced the rotameric antiperiplanar (*ap*) and synperiplanar (*sp*) oximes (40% yield) as determined by ^{1}H NMR (CDCl$_3$ or DMSO-d_6). Their E/Z configurations (substituent geometry in C=N) could not be ascertained this way. Evaporation of solutions containing both rotamers consistently provided only *one* solid oxime which was shown to be the *ap*-(Z) oxime (II*a*) [*ap*-(Z)-9-pivaloylfluorine oxime, C$_{18}$H$_{19}$NO] by single-crystal X-ray diffraction. When crystalline (II*a*) was redissolved (CDCl$_3$ or DMSO-d_6) *both* rotamers were present in ratios dependent on the concentration. The proximity of the oxime O atom to the fluorene-ring plane in (II*a*), 2.598 Å, results in a repulsion which raises the ground-state energy, thereby lowering the rotational barrier leading to the isomeric *sp*-(Z) oxime (III*a*). This repulsion is reflected in the larger angle, 123.9 (2)° (C9—C10—N1), in *ap* oxime (II*a*), compared with 119.2 (4)° (C9—C10—O1) in the *ap* ketone (I). The rotational barrier (III*a*) → (II*a*) is also low because of the proximity of the *tert*-butyl group in (III*a*) to the fluorene-ring plane. Together these results demonstrate that rotational interconversion of (II*a*) and (III*a*) occurs in solution at ambient temperatures at a rate which is slower than the NMR timescale, and that the crystal packing for (II*a*) is more favorable than for (III*a*).

Comment

We have reported a variety of observations of significant steric effects operating in 9-pivaloylfluorene (Meyers, Lutfi, Varol & Robinson, 1993; Meyers, Tunnell, Robinson, Hua & Saha, 1992; Meyers, Lutfi, Carr, Robinson, Saha & Hua, 1992; Meyers, Wahner, Manohar, Carr, Chan-Yu-King & Robinson, 1991; Meyers, 1990; Mey-