C13	0.81515 (10)	−0.1281 (3)	0.77101 (6)	0.0463 (5)
C14	0.87689 (10)	−0.0704 (3)	0.78221 (6)	0.0458 (4)
C15	0.92491 (10)	−0.0651 (3)	0.74900 (7)	0.0500 (5)
C16	0.91160 (11)	−0.1171 (3)	0.70461 (7)	0.0517 (5)
C17	1.00865 (12)	0.2936 (3)	0.53767 (9)	0.0576 (6)
C18	0.94625 (14)	0.1770 (4)	0.38825 (9)	0.0663 (7)
C19	0.75146 (15)	−0.0931 (4)	0.40725 (9)	0.0682 (7)
C20	0.8398 (2)	−0.4960 (3)	0.54555 (10)	0.0679 (7)
C21	0.8513 (3)	−0.5626 (4)	0.64410 (11)	0.0915 (11)
C22	0.70538 (12)	−0.1482 (5)	0.79541 (10)	0.0672 (7)
C23	0.9065 (2)	−0.1339 (5)	0.85823 (9)	0.0846 (9)
C24	1.03674 (13)	−0.0203 (5)	0.73362 (12)	0.0824 (9)

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

O1—C2	1.367 (2)	C3—C4	1.394 (3)
O1—C17	1.421 (3)	C4—C5	1.390 (3)
O2—C3	1.377 (2)	C5—C6	1.391 (3)
O2—C18	1.420 (3)	C6—C7	1.503 (2)
O3—C4	1.365 (2)	C7—C8	1.549 (3)
O3—C19	1.431 (3)	C8—C20	1.506 (3)
O4—C7	1.426 (2)	C8—C9	1.557 (3)
O4—C10	1.431 (2)	C9—C21	1.515 (3)
O5—C13	1.360 (2)	C9—C10	1.534 (3)
O5—C22	1.410 (3)	C10—C11	1.511 (2)
O6—C14	1.380 (2)	C11—C12	1.385 (3)
O6—C23	1.408 (3)	C11—C16	1.391 (3)
O7—C15	1.371 (2)	C12—C13	1.391 (3)
O7—C24	1.416 (3)	C13—C14	1.390 (3)
C1—C6	1.390 (3)	C14—C15	1.388 (3)
C1—C2	1.391 (3)	C15—C16	1.385 (3)
C2—C3	1.395 (3)		
C2—O1—C17	118.2 (2)	C20—C8—C7	111.2 (2)
C3—O2—C18	113.7 (2)	C20—C8—C9	117.1 (2)
C4—O3—C19	117.3 (2)	C7—C8—C9	102.65 (15)
C7—O4—C10	103.06 (14)	C21—C9—C10	112.5 (2)
C13—O5—C22	118.6 (2)	C21—C9—C8	117.0 (2)
C14—O6—C23	115.3 (2)	C10—C9—C8	102.70 (15)
C15—O7—C24	117.2 (2)	O4—C10—C11	110.3 (2)
C6—C1—C2	119.9 (2)	O4—C10—C9	104.59 (14)
O1—C2—C1	125.1 (2)	C11—C10—C9	117.1 (2)
O1—C2—C3	114.7 (2)	C12—C11—C16	120.2 (2)
C1—C2—C3	120.2 (2)	C12—C11—C10	119.1 (2)
O2—C3—C4	120.0 (2)	C16—C11—C10	120.7 (2)
O2—C3—C2	120.1 (2)	C11—C12—C13	120.0 (2)
C4—C3—C2	119.8 (2)	O5—C13—C14	115.4 (2)
O3—C4—C5	124.6 (2)	O5—C13—C12	124.9 (2)
O3—C4—C3	115.5 (2)	C14—C13—C12	119.7 (2)
C5—C4—C3	119.8 (2)	O6—C14—C15	120.3 (2)
C4—C5—C6	120.3 (2)	O6—C14—C13	119.5 (2)
C1—C6—C5	120.1 (2)	C15—C14—C13	120.0 (2)
C1—C6—C7	121.7 (2)	O7—C15—C16	125.1 (2)
C5—C6—C7	118.2 (2)	O7—C15—C14	114.6 (2)
O4—C7—C6	111.9 (2)	C16—C15—C14	120.3 (2)
O4—C7—C8	105.54 (14)	C15—C16—C11	119.7 (2)
C6—C7—C8	115.8 (2)		

The structure was solved by direct methods and refined by the full-matrix least-squares method. All H atoms were located from difference Fourier maps and were refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93. Geometrical calculations: *PARST* (Nardelli, 1983*b*).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1215). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 3-*O*-Benzoyl-4,6-*O*-benzylidene-2-*O*-trifluoromethylsulfonyl-α-D-mannopyranoside

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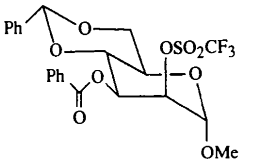
Abstract

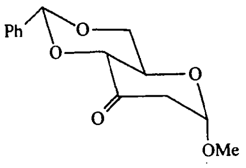
The title compound, $C_{22}H_{21}F_3O_9S$, is of interest as a potential precursor of 2-azido-2-deoxy-D-glucopyranose derivatives. The conformation of the molecule is as expected.

Comment

In connection with the synthesis of glycosyl-phosphatidylinositols (Cottaz, Brimacombe & Ferguson, 1993), the need for a short and efficient route to 2-azido-2-deoxy-D-glucopyranose derivatives led us to examine the displacement reaction of an azide ion with the title compound, (I), which contains an excellent leaving group at C2 and which is readily available from methyl 3-*O*-benzoyl-α-D-mannopyranoside (Tsuda, Haque & Yoshimoto, 1983). In the event, the reaction of compound (I) with the azide ion in dimethylformamide at 343 K, representing the stage at which the azido group is introduced at C2 with inversion of the configuration, gave only a minor proportion (27%) of the displacement product, in agreement with Vos, van Boom, van Boeckel & Beetz (1984).



(I)



(II)

The structure determination of (I) revealed the expected stereochemistry with no unusual bond lengths or angles and no significant intermolecular interactions. There is no inherent structural reason for the poor yield for the reaction of (I) with azide but this may be due to unfavourable dipolar interactions developed in the transition state (Richardson, 1969) and to a more favourable reaction pathway leading to methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose, (II).

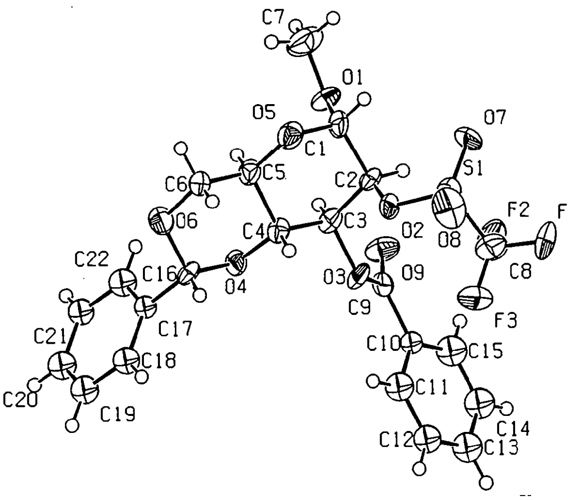


Fig. 1. Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-trifluoromethylsulfonyl-α-D-mannopyranoside. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

(I) was prepared from methyl 3-*O*-benzoyl-α-D-mannopyranoside (Tsuda, Haque & Yoshimoto, 1983) and recrystallized from ethyl acetate–hexane. Analysis: found C 50.7, H 4.1%; calculated C 51.0 H 4.1%. $[\alpha]_D = -25$ (*c*1, $CHCl_3$).

Crystal data

$C_{22}H_{21}F_3O_9S$
$M_r = 518.45$
Monoclinic
*C*2
$a = 36.714\ (43)$ Å
$b = 5.754\ (7)$ Å
$c = 11.220\ (23)$ Å
$\beta = 99.85\ (7)°$
$V = 2335.3\ (62)$ Å^3
$Z = 4$
$D_x = 1.475$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å
Cell parameters from 250 reflections
$\theta = 2$–$25°$
$\mu = 0.213$ mm^{-1}
$T = 150\ (1)$ K
Plate
0.24 × 0.16 × 0.002 mm
Colourless

Data collection

Enraf–Nonius CAD-4 FAST system
Area-detector scans
Absorption correction: none
5155 measured reflections
3082 independent reflections

1038 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.107$
$\theta_{\rm max} = 25.08°$
$h = -42 \rightarrow 42$
$k = -6 \rightarrow 6$
$l = -8 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.168$
$S = 0.610$
3066 reflections
235 parameters
H atoms refined with a riding model
$w = 1/[\sigma^2(F_o^2) + (0.0173P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.073$

$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = −0.17 (22)

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

$U_{\rm iso}$ for C10–C22; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	*y*	*z*	$U_{\rm eq}/U_{\rm iso}$
C1	0.3710 (2)	0.1692 (17)	0.0376 (7)	0.038 (3)
O1	0.3606 (2)	−0.0627 (12)	0.0183 (5)	0.043 (2)
C2	0.3896 (2)	0.1806 (16)	0.1720 (6)	0.035 (3)
O2	0.40430 (14)	0.4140 (11)	0.1986 (4)	0.034 (2)
C3	0.3609 (2)	0.1354 (16)	0.2529 (6)	0.033 (2)
O3	0.3777 (2)	0.1742 (12)	0.3788 (5)	0.040 (2)
C4	0.3293 (2)	0.3071 (16)	0.2210 (6)	0.029 (2)
O4	0.2995 (2)	0.2444 (10)	0.2828 (4)	0.034 (2)
C5	0.3127 (2)	0.2795 (17)	0.0852 (7)	0.036 (3)
O5	0.3412 (2)	0.3238 (11)	0.0131 (5)	0.043 (2)
C6	0.2821 (2)	0.4516 (19)	0.0575 (6)	0.044 (3)
O6	0.25464 (14)	0.4004 (11)	0.1310 (4)	0.044 (2)
C7	0.3487 (3)	−0.1144 (18)	−0.1066 (7)	0.066 (3)
S1	0.44440 (6)	0.4708 (5)	0.1828 (2)	0.0431 (7)
O7	0.4572 (2)	0.3174 (12)	0.1011 (5)	0.056 (2)
O8	0.4472 (2)	0.7143 (12)	0.1745 (5)	0.066 (2)
C8	0.4689 (3)	0.4071 (22)	0.3334 (9)	0.056 (3)
F1	0.50497 (13)	0.4389 (14)	0.3376 (5)	0.080 (2)
F2	0.4660 (2)	0.1765 (13)	0.3568 (5)	0.079 (2)
F3	0.45766 (15)	0.5144 (14)	0.4169 (5)	0.101 (3)
C9	0.3906 (2)	−0.0221 (20)	0.4426 (7)	0.034 (2)
O9	0.3891 (2)	−0.2122 (12)	0.4005 (5)	0.046 (2)

C10	0.40803 (14)	0.0483 (9)	0.5692 (3)	0.028 (2)
C11	0.40125 (13)	0.2583 (8)	0.6226 (4)	0.045 (3)
C12	0.41792 (15)	0.3057 (8)	0.7409 (4)	0.043 (3)
C13	0.44138 (13)	0.1431 (11)	0.8058 (3)	0.050 (3)
C14	0.44816 (14)	−0.0669 (10)	0.7523 (5)	0.053 (3)
C15	0.4315 (2)	−0.1143 (7)	0.6341 (5)	0.053 (3)
C16	0.2703 (2)	0.4061 (16)	0.2554 (6)	0.028 (2)
C17	0.23979 (12)	0.3290 (9)	0.3233 (4)	0.028 (2)
C18	0.22739 (13)	0.4785 (8)	0.4051 (4)	0.040 (2)
C19	0.19832 (13)	0.4124 (9)	0.4624 (4)	0.044 (2)
C20	0.18165 (11)	0.1967 (10)	0.4379 (4)	0.044 (3)
C21	0.19405 (13)	0.0472 (8)	0.3562 (4)	0.038 (2)
C22	0.22312 (13)	0.1133 (8)	0.2989 (4)	0.042 (2)

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

C1—O1	1.395 (10)	O4—C16	1.414 (9)
C1—O5	1.402 (9)	C5—O5	1.450 (8)
C1—C2	1.547 (10)	C5—C6	1.489 (11)
O1—C7	1.427 (9)	C6—O6	1.439 (8)
C2—O2	1.459 (9)	O6—C16	1.417 (8)
C2—C3	1.527 (10)	S1—O7	1.409 (6)
O2—S1	1.548 (5)	S1—O8	1.409 (7)
C3—O3	1.458 (9)	S1—C8	1.812 (11)
C3—C4	1.519 (10)	C8—F3	1.250 (10)
O3—C9	1.378 (11)	C8—F1	1.328 (11)
C4—O4	1.438 (8)	C8—F2	1.360 (12)
C4—C5	1.549 (10)	C9—O9	1.189 (11)
O1—C1—O5	113.1 (8)	C6—C5—C4	107.1 (7)
O1—C1—C2	104.8 (7)	C1—O5—C5	113.2 (7)
O5—C1—C2	111.3 (7)	O6—C6—C5	108.7 (7)
C1—O1—C7	112.4 (7)	C16—O6—C6	110.8 (6)
O2—C2—C3	107.7 (6)	O7—S1—O8	123.0 (4)
O2—C2—C1	108.9 (7)	O7—S1—O2	111.8 (4)
C3—C2—C1	109.8 (7)	O8—S1—O2	107.4 (4)
C2—O2—S1	119.8 (5)	O7—S1—C8	108.2 (5)
O3—C3—C4	107.9 (7)	O8—S1—C8	103.4 (5)
O3—C3—C2	109.2 (7)	O2—S1—C8	100.4 (4)
C4—C3—C2	109.0 (7)	F3—C8—F1	111.2 (9)
C9—O3—C3	115.4 (7)	F3—C8—F2	106.8 (9)
O4—C4—C3	109.6 (6)	F1—C8—F2	103.9 (10)
O4—C4—C5	104.2 (6)	F3—C8—S1	115.1 (9)
C3—C4—C5	108.7 (7)	F1—C8—S1	109.7 (7)
C16—O4—C4	110.0 (6)	F2—C8—S1	109.5 (7)
O5—C5—C6	110.8 (7)	O9—C9—O3	124.0 (8)
O5—C5—C4	109.3 (6)	O6—C16—O4	111.3 (6)

An area-detector system was used. Cell dimensions were refined from 250 reflections selected from 2 regions 90° apart and 5° wide at $\kappa = 0°$. The phenyl groups were refined as rigid groups with individual isotropic atomic displacement parameters for the C atoms and $U(H) = 1.5U(C)$.

Although there was no intention to derive the absolute configuration from the relatively poor quality data obtained from crystals which were far from ideal, the automatic Flack (1983) calculation in *SHELXL*93 (Sheldrick, 1993) confirmed the expected configuration.

The high value of $R_{\rm int}$ reflects the poor quality and weak diffraction of the available crystals.

Data collection: *MADNESS* (Enraf–Nonius, 1990). Cell refinement: *MADNESS*. Data reduction: *MADNESS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON*92 (Spek, 1992*a*), *PLUTON*92 (Spek, 1992*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6-Amino-4-methoxy-2-methylthiopyrimidine

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Abstract

Molecules of the title compound, $C_6H_9N_3OS$, form base-paired N—H···N hydrogen-bonded dimers in the solid state, with N···N 3.060 (3) Å.

Comment

Derivatives of 6-aminopyrimidines are of interest both because of their biological activity and their use as in-