Crystal structure of (1*S*, 4*S*, 5*S*, 8*R*)-8-nitrooxy-2,6-dioxabicyclo[3.3.0] octan-4-yl-4-acetoxybenzoate, $C_{15}H_{15}NO_9$

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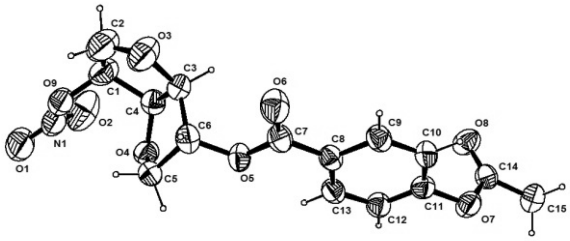

Abstract

$C_{15}H_{15}NO_9$, monoclinic, $P2_1$ (no. 4), a = 9.554(5) Å, b = 6.503(3) Å, c = 13.312(6) Å, β = 99.037(5)°, V = 816.8 Å^3, Z = 2, $R_{gt(F)}$ = 0.0614, $wR_{ref(F^2)}$ = 0.1879, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.21×0.23×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.21 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3612, 2849
$N(param)_{refined}$:	228
Programs:	SHELXS-97 [5], ORTEP-3 [6]

Source of material

The title compound was synthesized according to the literature [1]. 4-acetoxybenzoicacid (1.80 g, 10 mmol), isosorbide mononitrate (1.91 g, 10 mmol, CAS No:16051-77-7, $[\alpha]_D$=168° (c = 1.0, EtOH) and DMAP (0.24 g, 1 mmol) were dissolved in 100 ml of dry THF, then DCC (4.12 g, 10 mmol) was added to the solution at 0°C. The mixture was stirred at room temperature for 5 h. The resulting mixture was filtered and concentrated *in vacuo*. The crude product was purified by column chromatography over silica gel using ethyl acetate/*n*-hexane (7:3) as eluent. Yield: 3.00 g (85%).Single crystals of the title compound suitable for *X*-ray diffraction were recrystallized from hexane/ethylacetate (2:1).

Experimental details

In the structure all the H atoms were positioned geometrically and refined discernible using a riding model, with C–$H_{methine}$ = 0.98 Å; C–H_{methyl} = 0.96 Å; C–$H_{methylene}$ = 0.97 Å; C–H_{aryl} = 0.93 Å. The H atom isotropic displacement parameters were fixed; U_{iso} (H_{aryl}, $H_{methine}$) = 1.2 times U_{eq} of the parent atom; U_{iso} ($H_{methylene}$, H_{methyl}) = 1.5 times $U_{eq}$of the parent atom.

Discussion

The molecule is built up from the isosorbide mononitrate skeleton substituted on C6 by the 4-acetoxybenzoicacid. The two furanose rings have slightly different conformation. The ring C3–C4–C1–C2–O3 is disordered. C2 and to a lesser extent O3 and C1 are in two conformations. The C3–C4–O4–C5–C6 ring distorted envelope conformation. The puckering parameters [2] for the C3–C4–O4–C5–C6 ring are $Q(2)$ = 0.285(6)Å and $\varphi(2)$ = 139.2(12)° and the pseudorotation parameters [3] for C3–C4–O4–C5–C6 ring are P = 232.4(7)° & $\tau(M)$ =31.3(4)° for the C3– C6 reference bond with the closest pucker descriptor being enveloped on C5. Owing to the known absolute configuration of the starting isosorbide mononitrate, the absolute configuration of the title compound could be deduced to be 1*S*, 4*S*, 5*S*, 8*R*. The molecular packing is stabilized by weak non-classical intermolecular C–H···O hydrogen bonds and by intermolecular C–H···π interaction.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*a*	0.2681	0.4172	–0.2171	0.128
H(2A)	2*a*	0.3337	0.7297	–0.1870	0.154
H(2B)	2*a*	0.1903	0.7802	–0.1493	0.154
H(3)	2*a*	0.4505	0.4909	0.0270	0.094
H(4)	2*a*	0.3330	0.2483	–0.0687	0.093
H(5A)	2*a*	0.0960	0.3815	0.1158	0.101
H(5B)	2*a*	0.0660	0.5489	0.0294	0.101
H(6)	2*a*	0.2637	0.6880	0.1177	0.094
H(9)	2*a*	0.6826	0.5786	0.3716	0.089
H(10)	2*a*	0.8022	0.3691	0.4969	0.089
H(12)	2*a*	0.5207	–0.0784	0.4193	0.089
H(13)	2*a*	0.3992	0.1277	0.2939	0.091
H(15A)	2*a*	0.9547	–0.3478	0.6054	0.136
H(15B)	2*a*	0.8396	–0.2546	0.6641	0.136
H(15C)	2*a*	0.9829	–0.1379	0.6630	0.136

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*a*	0.2227(8)	0.4770(1)	–0.1627(5)	0.126(4)	0.119(4)	0.075(3)	–0.022(3)	0.014(3)	0.011(3)
C(2)	2*a*	0.2720(1)	0.6890(1)	–0.1393(6)	0.155(4)	0.124(3)	0.100(3)	–0.036(3)	0.000(3)	0.023(3)
C(3)	2*a*	0.3508(6)	0.5286(9)	0.0066(4)	0.077(3)	0.083(4)	0.075(3)	0.004(3)	0.007(3)	0.017(3)
C(4)	2*a*	0.2703(6)	0.3637(9)	–0.0595(4)	0.078(3)	0.078(4)	0.077(3)	0.006(3)	0.013(3)	–0.003(3)
C(5)	2*a*	0.1335(5)	0.4470(1)	0.0601(4)	0.062(3)	0.120(5)	0.071(3)	0.006(3)	0.010(2)	0.010(4)
C(6)	2*a*	0.2743(5)	0.5446(9)	0.0976(4)	0.075(3)	0.081(4)	0.075(3)	0.012(3)	0.001(3)	–0.008(3)
C(7)	2*a*	0.4563(5)	0.5120(1)	0.2383(4)	0.070(3)	0.077(4)	0.078(3)	–0.007(3)	0.001(3)	–0.009(3)
C(8)	2*a*	0.5268(5)	0.3761(9)	0.3191(4)	0.059(3)	0.070(4)	0.066(3)	0.001(3)	0.007(2)	–0.012(3)
C(9)	2*a*	0.6493(5)	0.4467(9)	0.3809(4)	0.065(3)	0.079(4)	0.075(3)	–0.009(3)	0.005(2)	–0.013(3)
C(10)	2*a*	0.7210(5)	0.3220(1)	0.4555(4)	0.065(3)	0.090(4)	0.063(3)	–0.006(3)	–0.003(2)	–0.004(3)
C(11)	2*a*	0.6708(6)	0.1298(9)	0.4674(4)	0.067(3)	0.085(4)	0.065(3)	0.009(3)	0.015(3)	0.006(3)
C(12)	2*a*	0.5522(5)	0.0541(9)	0.4090(4)	0.074(3)	0.071(4)	0.076(3)	–0.004(3)	0.008(3)	0.001(3)
C(13)	2*a*	0.4802(6)	0.1775(9)	0.3346(4)	0.062(3)	0.081(4)	0.082(4)	–0.006(3)	0.004(3)	0.002(3)
C(14)	2*a*	0.8480(5)	–0.1108(8)	0.5305(4)	0.065(3)	0.063(3)	0.073(3)	–0.001(3)	0.003(3)	–0.006(3)
C(15)	2*a*	0.9120(6)	–0.2230(1)	0.6241(4)	0.101(4)	0.094(4)	0.072(3)	0.014(4)	0.001(3)	–0.002(3)
N(1)	2*a*	0.0145(9)	0.3050(1)	–0.2288(5)	0.127(6)	0.121(6)	0.109(5)	–0.023(6)	–0.017(4)	0.042(5)
O(1)	2*a*	–0.1072(7)	0.3140(2)	–0.2529(6)	0.112(4)	0.280(1)	0.229(7)	–0.077(6)	–0.048(4)	0.146(8)
O(2)	2*a*	0.0930(1)	0.1630(1)	–0.2326(5)	0.257(9)	0.120(6)	0.104(4)	–0.022(6)	–0.031(5)	–0.012(4)
O(3)	2*a*	0.3371(6)	0.7134(8)	–0.0498(4)	0.159(4)	0.110(3)	0.098(3)	–0.029(3)	–0.006(3)	0.020(3)
O(4)	2*a*	0.1589(4)	0.2981(7)	–0.0132(3)	0.082(2)	0.097(3)	0.073(2)	–0.025(2)	0.005(2)	0.009(2)
O(5)	2*a*	0.3451(3)	0.4231(6)	0.1806(2)	0.073(2)	0.081(3)	0.068(2)	–0.001(2)	–0.009(2)	–0.000(2)
O(6)	2*a*	0.4945(5)	0.6833(7)	0.2238(3)	0.104(3)	0.079(3)	0.108(3)	–0.016(3)	–0.014(2)	0.002(2)
O(7)	2*a*	0.7394(4)	0.0081(7)	0.5482(3)	0.087(2)	0.111(3)	0.067(2)	0.028(3)	0.016(2)	0.015(2)
O(8)	2*a*	0.8834(4)	–0.1227(7)	0.4500(3)	0.107(3)	0.103(3)	0.079(2)	0.022(2)	0.029(2)	0.004(2)
O(9)	2*a*	0.0754(4)	0.4867(7)	–0.1910(3)	0.096(3)	0.095(4)	0.091(3)	–0.005(3)	0.001(2)	0.022(2)

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