Crystal structure of (1*S*, 4*S*, 5*S*, 8*R*)-8-nitrooxy-2,6-dioxabicyclo[3.3.0] octan-4-yl-3-(4-acetoxyphenyl)acrylate, $C_{17}H_{17}NO_9$

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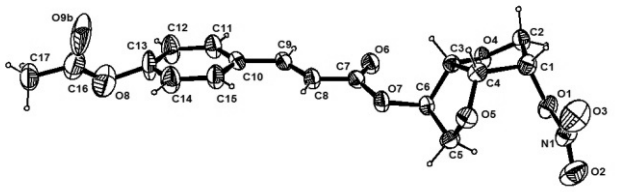

Abstract

$C_{17}H_{17}NO_9$, orthorhombic, $P2_12_12_1$ (no. 19), a = 5.386(3) Å, b = 10.682(6) Å, c = 30.88(2) Å, V = 1776.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.0636, $wR_{ref}(F^2)$ = 0.1800, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.21×0.22×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.17 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6247, 3242
$N(param)_{refined}$:	255
Programs:	SHELXS-97 [5], ORTEP-3 [6]

Source of material

The title compound was synthesized according to the literature [1]. 3-(4-acetoxyphenyl)acrylic acid (2.06 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: 3.1 g (82%). Single crystals of the title compound suitable for *X*-ray diffraction were recrystallized from hexane/ethyl acetate (3:1).

Experimental details

In the structure all of 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.The disordered O atoms (O9A and O9B) were refined using a split model involving two sites, with a total occupancy of 1.

Discussion

The molecule is built up from the isosorbide mononitrate skeleton substituted on C6 by the 3-(4-acetoxyphenyl)acrylic acid. The two fused furanose rings have slightly different conformation. The puckering parameters [2] for the C1–C2–O4–C3–C4 ring are $Q(2)$ = 0.356(4)Å and $\varphi(2)$ = 208.6(7)° whereas those for the C3–C4–O5–C6–C7 ring are $Q(2)$ = 0.304(4)Å and $\varphi(2)$ = 143.5(9)°. These values indicate that these two rings have different extent of puckering caused by the different substituent group in the ring. The pseudorotation parameters [3] for C1–C2–O4–C3–C4 ring are P = 296.4(4)° & $\tau(M)$ = 39.3(3)° for the C1–C4 reference bond with the closest pucker descriptor being enveloped on C(2) and those for C5–O6–C7–C8–C1 ring are P = 235.9(4)° and $\tau(M)$ = 33.5(3)° for the C3–C6 reference bond with the closest puckering descriptor being enveloped on C(5). There is a disorder in the terminal ester group. 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.

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*a*	0.0998	0.0483	0.2552	0.068
H(2A)	4*a*	0.4133	0.1639	0.2859	0.072
H(2B)	4*a*	0.5521	0.0356	0.2785	0.072
H(3)	4*a*	0.4488	0.3161	0.2120	0.057
H(4)	4*a*	0.0873	0.2148	0.2100	0.062
H(5A)	4*a*	0.4139	0.1153	0.1088	0.073
H(5B)	4*a*	0.5130	0.0293	0.1465	0.073
H(6)	4*a*	0.7532	0.1976	0.1582	0.060
H(8)	4*a*	0.4613	0.5240	0.0945	0.073
H(9)	4*a*	0.8534	0.6426	0.1326	0.070
H(11)	4*a*	0.9819	0.8439	0.1044	0.088
H(12)	4*a*	0.9537	1.0044	0.0551	0.124
H(14)	4*a*	0.3389	0.8539	0.0072	0.108
H(15)	4*a*	0.3657	0.6913	0.0560	0.090
H(17A)	4*a*	0.6522	1.2446	–0.0487	0.154
H(17B)	4*a*	0.3640	1.2329	–0.0546	0.154
H(17C)	4*a*	0.5420	1.1408	–0.0790	0.154

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

Atom	Site	*Occ.*	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*a*		0.2508(8)	0.0576(4)	0.2378(1)	0.049(3)	0.056(3)	0.065(3)	–0.010(2)	0.002(2)	0.002(2)
C(2)	4*a*		0.4678(9)	0.1044(4)	0.2642(1)	0.062(3)	0.064(3)	0.054(2)	–0.015(3)	–0.004(2)	0.012(2)
C(3)	4*a*		0.4707(8)	0.2282(4)	0.2037(1)	0.049(2)	0.044(2)	0.048(2)	0.002(2)	–0.002(2)	0.002(2)
C(4)	4*a*		0.2234(8)	0.1579(4)	0.2026(1)	0.044(2)	0.052(3)	0.059(2)	0.005(2)	–0.004(2)	–0.001(2)
C(5)	4*a*		0.4299(9)	0.1077(4)	0.1400(1)	0.076(3)	0.050(3)	0.057(2)	0.007(3)	–0.008(3)	–0.005(2)
C(6)	4*a*		0.5747(9)	0.2153(4)	0.1579(1)	0.051(3)	0.052(2)	0.048(2)	0.002(2)	–0.003(2)	0.013(2)
C(7)	4*a*		0.667(1)	0.4275(5)	0.1402(1)	0.065(3)	0.059(3)	0.046(2)	0.007(3)	0.002(2)	0.005(2)
C(8)	4*a*		0.598(1)	0.5317(4)	0.1126(1)	0.069(3)	0.059(3)	0.055(2)	–0.005(3)	–0.009(2)	0.014(2)
C(9)	4*a*		0.725(1)	0.6366(4)	0.1126(1)	0.071(3)	0.059(3)	0.045(2)	–0.005(3)	–0.001(2)	0.007(2)
C(10)	4*a*		0.686(1)	0.7465(4)	0.0842(1)	0.067(3)	0.060(3)	0.042(2)	–0.002(3)	0.004(2)	0.009(2)
C(11)	4*a*		0.853(1)	0.8439(5)	0.0842(2)	0.077(4)	0.072(3)	0.072(3)	–0.016(3)	–0.021(3)	0.022(3)
C(12)	4*a*		0.836(1)	0.9410(6)	0.0554(2)	0.116(5)	0.082(4)	0.111(4)	–0.044(4)	–0.027(4)	0.039(4)
C(13)	4*a*		0.643(2)	0.9428(6)	0.0272(2)	0.141(6)	0.067(4)	0.098(4)	–0.027(4)	–0.042(4)	0.049(3)
C(14)	4*a*		0.469(1)	0.8509(5)	0.0269(2)	0.101(5)	0.079(4)	0.089(4)	–0.012(4)	–0.038(3)	0.021(3)
C(15)	4*a*		0.487(1)	0.7532(5)	0.0557(2)	0.094(4)	0.060(3)	0.071(3)	–0.019(3)	–0.020(3)	0.018(2)
C(16)	4*a*		0.507(2)	1.1030(7)	–0.0171(3)	0.141(9)	0.072(4)	0.132(7)	0.007(6)	–0.027(6)	0.019(5)
C(17)	4*a*		0.517(2)	1.1872(6)	–0.0528(2)	0.146(6)	0.068(3)	0.093(4)	–0.001(4)	–0.025(4)	0.027(3)
N(1)	4*a*		0.137(1)	–0.1305(4)	0.2008(2)	0.088(4)	0.054(3)	0.085(3)	–0.015(3)	–0.044(3)	0.006(2)
O(1)	4*a*		0.3305(6)	–0.0594(3)	0.21891(9)	0.057(2)	0.051(2)	0.079(2)	–0.005(2)	–0.016(2)	0.007(2)
O(2)	4*a*		0.215(1)	–0.2122(4)	0.1770(1)	0.141(4)	0.066(2)	0.108(3)	0.010(3)	–0.058(3)	–0.011(2)
O(3)	4*a*		–0.0712(8)	–0.1084(4)	0.2111(2)	0.059(3)	0.107(3)	0.155(4)	–0.030(3)	–0.017(3)	–0.008(3)
O(4)	4*a*		0.6261(5)	0.1629(3)	0.23342(8)	0.042(2)	0.062(2)	0.051(1)	–0.009(2)	–0.010(1)	0.016(1)
O(5)	4*a*		0.1904(6)	0.1109(3)	0.16008(9)	0.054(2)	0.065(2)	0.061(2)	–0.002(2)	–0.013(2)	–0.001(2)
O(6)	4*a*		0.8325(7)	0.4256(3)	0.1666(1)	0.077(2)	0.070(2)	0.061(2)	–0.009(2)	–0.009(2)	0.009(2)
O(7)	4*a*		0.5192(6)	0.3277(3)	0.13318(9)	0.065(2)	0.054(2)	0.055(2)	–0.002(2)	–0.010(2)	0.016(1)
O(8)	4*a*		0.674(1)	1.0258(5)	–0.0124(2)	0.137(5)	0.114(4)	0.168(5)	0.026(4)	0.006(5)	0.037(4)
O(9A)	4*a*	0.4	0.513(5)	1.079(2)	0.0181(4)	0.180(2)	0.130(1)	0.079(9)	0.040(1)	–0.010(1)	0.023(8)
O(9B)	4*a*	0.4	0.336(3)	1.118(1)	0.0105(5)	0.170(1)	0.170(1)	0.240(1)	0.126(9)	0.130(1)	0.133(9)

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References

1. C. Velázquez, P. N. Praveen Rao, E. E. Knaus, M. L. Citro, L. K. Keefer O^2-Acetoxymethyl-protected diazeniumdiolate-based NSAIDs (NONO–NSAIDs): Synthesis, nitric oxide release, and biological evaluation studies. Bioorg. Med. Chem. **15** (2007) 4767-4774.
2. Cremer, D. & Pople, J. A. General definition of ring puckering coordinates J. Am. Chem. Soc. **97** (1975) 1354-1358.
3. Rao, S. T., Westhof, E. Sundaralingam, M. Exact method for the calculation of pseudorotation parameters P, γ_m and their errors. A comparison of the Altona-Sundaralingam and Cremer-Pople treatment of puckering of five-membered rings. Acta Crystallogr. **A37** (1981) 421-425.
4. Bruker *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA. 2007.
5. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
6. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.