

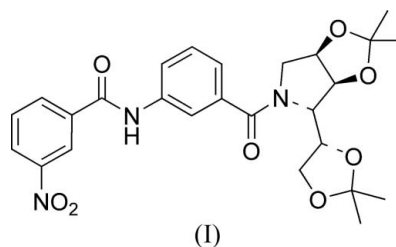
1,4-Dideoxy-2,3-*O*-isopropylidene-*N*-[3-(3-nitrobenzoylamino)benzoyl]-1,4-imino-*D*-talitolChu-Yi Yu^{a,*} and Ying Fu^{a,b}^aBeijing National Laboratory for Molecular Science, Laboratory for Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China, and ^bGraduate University of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China

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Key indicators

Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.066
 wR factor = 0.191
Data-to-parameter ratio = 7.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The title compound, $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_8$, has two molecules in the asymmetric unit. Molecules are linked into chains by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, and $\text{C}-\text{H}\cdots\text{O}$ interactions are observed between chains.

Comment

The title compound, $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_8$, (I) (Fig. 1), is a derivative of 1,4-dideoxy-2,3-*O*-isopropylidene-1,4-imino-*D*-talitol (Fleet *et al.*, 1988). The 3-aminobenzoic acid group can be considered as a β -amino acid with a rigid conformation (Pohl *et al.*, 2001). Thus, the crystal structure of (I) provides information for conformational analysis of this new type of β -peptide mimetic.Two molecules of (I) exist in the asymmetric unit (Fig. 1). Apart from the dimethyldioxolanyl groups, C5/C6/C7/O3/O4/C11/C12 and C31/C32/C33/O13/O21/C37/C38, the molecules are related by pseudo-inversion symmetry. $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are formed between the peptide linkages (Table 1), generating $C_2^2(14)$ chains (Bernstein *et al.*, 1995) propagating along the a direction. Numerous $\text{C}-\text{H}\cdots\text{O}$ interactions are observed between chains (Table 1).

Experimental

The title compound, (I), was prepared from 1,4-dideoxy-2,3-*O*-isopropylidene-1,4-imino-*D*-talitol in three steps, as follows. In the first step, 1,4-dideoxy-2,3-*O*-isopropylidene-1,4-imino-*D*-talitol (4.5 g, 18.5 mmol) was dissolved in a mixture of pyridine (10 ml) and CH_2Cl_2 (20 ml). A solution of 3-nitrobenzoyl chloride (3.7 g, 20 mmol) in CH_2Cl_2 (10 ml) was added slowly to the reaction mixture at 273–278 K (ice bath). After stirring for 2 h, the solvents were removed under reduced pressure and the residue was then dissolved in ethyl acetate (20 ml). The solution was washed with a saturated aqueous solution of NaHCO_3 (20 ml). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2×20 ml). The combined organic layers were dried over MgSO_4 , then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 60:40) to give *N*-(3-nitrobenzoyl)-1,4-dideoxy-2,3:5,6-di-*O*-isopropylidene-1,4-imino-*D*-talitol as a colourless gum (6.8 g, yield 94%).

In the second step, a solution of *N*-(3-nitrobenzoyl)-1,4-dideoxy-2,3,5,6-di-*O*-isopropylidene-1,4-imino-*D*-talitol (1.36 g, 3.5 mmol) in ethanol (20 ml) was stirred under an H₂ atmosphere in the presence of 10% Pd on charcoal (150 mg) at room temperature for 5 h. The reaction mixture was then filtered through celites to remove the catalysts. The filtrate was concentrated under reduced pressure to give the crude aniline, which was directly dissolved in a solution of pyridine (3.5 ml) and CH₂Cl₂ (20 ml) and cooled with an ice–water bath.

In the third step, a solution of 3-nitrobenzoyl chloride (1.0 g, 5.4 mmol) in CH₂Cl₂ (10 ml) was added dropwise under an Ar atmosphere. After stirring for 2 h, the solvents were removed under vacuum and the residue was dissolved in ethyl acetate (20 ml). The resulting solution was washed with a saturated aqueous solution of NaHCO₃ (20 ml). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 20 ml). The organic layers were combined, dried (Na₂SO₄) and evaporated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 1:1) to give the title compound (1.5 g, yield 85%). Suitable single crystals were obtained by slow evaporation of a solution in ethyl acetate (m.p. 456–457 K).

Crystal data

C₂₆H₂₉N₃O₈ Z = 4
 M_r = 511.52 D_x = 1.294 Mg m⁻³
 Monoclinic, P2₁ Mo Kα radiation
 a = 12.5459 (13) Å μ = 0.10 mm⁻¹
 b = 14.5417 (14) Å T = 294 (2) K
 c = 14.6939 (15) Å Block, colourless
 β = 101.563 (4)° 0.24 × 0.20 × 0.14 mm
 V = 2626.3 (5) Å³

Data collection

Rigaku Saturn CCD area-detector 21856 measured reflections
 diffractometer 5372 independent reflections
 ω scans 3777 reflections with I > 2σ(I)
 Absorption correction: multi-scan R_{int} = 0.043
 Jacobson (1998) θ_{max} = 26.0°
 T_{min} = 0.977, T_{max} = 0.987

Refinement

Refinement on F² w = 1/[σ²(F_o²) + (0.1155P)²]
 R[F² > 2σ(F²)] = 0.066 where P = (F_o² + 2F_c²)/3
 wR(F²) = 0.191 (Δ/σ)_{max} < 0.001
 S = 1.03 Δρ_{max} = 0.41 e Å⁻³
 5372 reflections Δρ_{min} = -0.19 e Å⁻³
 685 parameters Extinction correction: SHELXL97
 H atoms treated by a mixture of (Sheldrick, 1997)
 independent and constrained Extinction coefficient: 0.019 (3)
 refinement

Table 1

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2A...O14 ⁱ	0.87 (6)	2.13 (6)	2.981 (6)	165 (5)
N5—H5A...O5 ⁱⁱ	1.10 (6)	1.90 (6)	2.982 (6)	166 (5)
C24—H24...O13 ⁱⁱⁱ	0.93	2.59	3.489 (7)	162
C25—H25...O8 ^{iv}	0.93	2.52	3.418 (7)	163
C51—H51...O17 ^v	0.93	2.56	3.473 (7)	166
C52—H52...O5 ⁱⁱ	0.93	2.56	3.370 (7)	146

Symmetry codes: (i) -x + 1, y + 1/2, -z + 1; (ii) -x, y - 1/2, -z + 1; (iii) x + 1, y, z + 1; (iv) -x + 2, y + 1/2, -z + 2; (v) -x - 1, y - 1/2, -z.

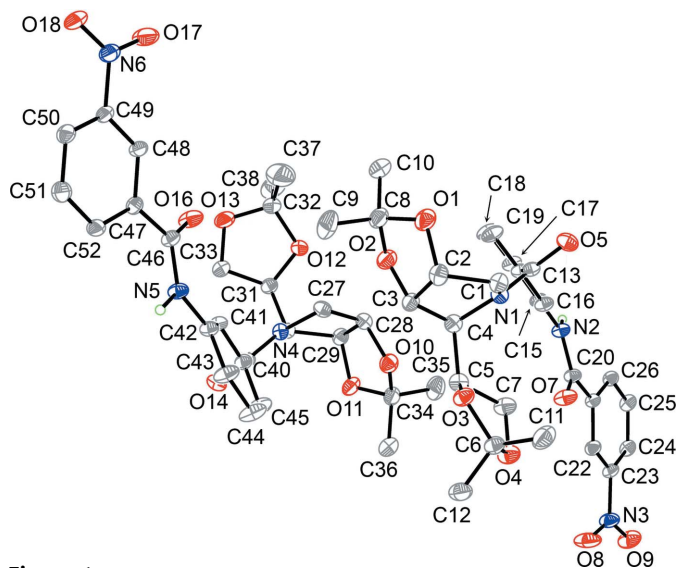


Figure 1

A view of the asymmetric unit of (I), showing displacement ellipsoids at the 30% probability level. H atoms bound to C atoms have been omitted.

H atoms were placed in calculated positions and refined using a riding model, with C—H = 0.93 Å for Csp², 0.98 Å for CH, 0.97 Å for CH₂ and 0.96 Å for CH₃. U_{iso}(H) = 1.2U_{eq}(C), except for the methyl groups, for which U_{iso}(H) = 1.5U_{eq}(C). The H atoms of the N—H groups were located in difference Fourier maps and refined with isotropic displacement parameters. The displacement parameters of atoms C37 and C38 were restrained to approximate isotropic behaviour. In the absence of significant anomalous scattering effects, Friedel pairs were merged as equivalent data for the final cycles of refinement. The absolute configuration was assigned on the basis of the known configuration of the starting material.

Data collection: *CrystalClear* (Rigaku/MS, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997) and *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalStructure* (Rigaku/MS, 2005); software used to prepare material for publication: *CrystalStructure*.

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