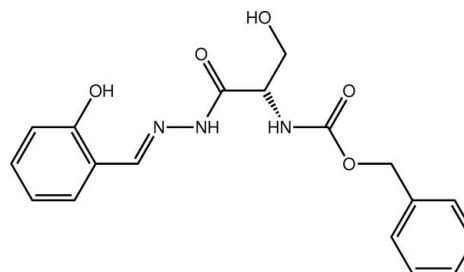


Benzyl *N*-(2-hydroxy-1-[*N'*-(1*E*)-2-hydroxybenzylidene]hydrazinyl)carbamate ethyl



Edward R. T. Tiekink,^{a*} Marcus V. N. de Souza,^b Alessandra C. Pinheiro,^b Solange M. S. V. Wardell^c and James L. Wardell^{d‡}

^aDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, ^bFundação Oswaldo Cruz, Instituto de Tecnologia, em Fármacos – Farmanguinhos, R. Sizenando Nabuco, 100, Manguinhos, 21041-250 Rio de Janeiro, RJ, Brazil, ^cCHEMSOL, 1 Harcourt Road, Aberdeen AB15 5NY, Scotland, and ^dCentro de Desenvolvimento Tecnológico em Saúde (CDTS), Fundação Oswaldo Cruz (FIOCRUZ), Casa Amarela, Campus de Manguinhos, Av. Brasil 4365, 21040-900 Rio de Janeiro, RJ, Brazil

Correspondence e-mail: edward.tiekink@gmail.com

Received 25 June 2011; accepted 26 June 2011

Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.053; wR factor = 0.098; data-to-parameter ratio = 8.2.

The molecule of the title compound, $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_5$, adopts a curved arrangement with the terminal benzene rings lying to the same side. The hydroxylbenzene ring is close to coplanar with the adjacent hydrazine residue [dihedral angle = $11.14(12)^\circ$], an observation which correlates with the presence of an intramolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bond. The benzyl ring forms a dihedral angle of $50.84(13)^\circ$ with the adjacent carbamate group. A twist in the molecule, at the chiral C atom, is reflected in the dihedral angle of $80.21(12)^\circ$ formed between the amide residues. In the crystal, two-dimensional arrays in the *ac* plane are mediated by $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For background to the use of L-serine derivatives in anti-tumour therapy, see: Jiao *et al.* (2009); Yakura *et al.* (2007). For background to *N*-acylhydrazones derivatives from L-serine for anti-tumour testing, see: Pinheiro *et al.* (2010, 2011*a,b*); de Souza *et al.* (2010, 2011); Howie *et al.* (2011).

Experimental

Crystal data

$\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_5$
 $M_r = 357.36$
 Monoclinic, $P2_1$
 $a = 5.0338(5)$ Å
 $b = 31.357(3)$ Å
 $c = 5.5882(6)$ Å
 $\beta = 97.890(3)^\circ$

$V = 873.72(16)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 120$ K
 $0.25 \times 0.05 \times 0.02$ mm

Data collection

Bruker–Nonius Roper CCD camera on κ -goniostat diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2007)
 $T_{\min} = 0.654$, $T_{\max} = 0.746$

8786 measured reflections
 2034 independent reflections
 1485 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.066$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.098$
 $S = 1.06$
 2034 reflections
 247 parameters
 1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1o}\cdots\text{N1}$	0.90 (5)	1.88 (5)	2.648 (4)	143 (4)
$\text{O3}-\text{H3o}\cdots\text{O2}^{\text{i}}$	0.84 (5)	1.79 (5)	2.616 (4)	167 (5)
$\text{N2}-\text{H2n}\cdots\text{O3}^{\text{ii}}$	0.90 (4)	1.87 (4)	2.758 (4)	168 (4)
$\text{N3}-\text{H3n}\cdots\text{O4}^{\text{iii}}$	0.95 (4)	1.97 (4)	2.897 (4)	165 (3)

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

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and DIAMOND (Brandenburg, 2006); software used to prepare material for publication: pubCIF (Westrip, 2010).

The use of the EPSRC X-ray crystallographic service at the University of Southampton, England, and the valuable assistance of the staff there is gratefully acknowledged. JLW acknowledges support from CAPES (Brazil).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5935).

‡ Additional correspondence author: j.wardell@abdn.ac.uk

References

- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Hoof, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Howie, R. A., de Souza, M. V. N., Pinheiro, A. C., Kaiser, C. R., Wardell, J. L. & Wardell, S. M. S. V. (2011). *Z. Kristallogr.* **226**, 483–491.
- Jiao, X., Wang, L., Xiao, Q., Xie, P. & Liang, X. (2009). *J. Asian Nat. Prod. Res.* **11**, 274–280.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Pinheiro, A. C., de Souza, M. V. N., Tiekink, E. R. T., Wardell, J. L. & Wardell, S. M. S. V. (2010). *Acta Cryst.* **E66**, o1004–o1005.
- Pinheiro, A. C., de Souza, M. V. N., Tiekink, E. R. T., Wardell, S. M. S. V. & Wardell, J. L. (2011a). *Acta Cryst.* **E67**, o581–o582.
- Pinheiro, A. C., de Souza, M. V. N., Tiekink, E. R. T., Wardell, S. M. S. V. & Wardell, J. L. (2011b). *Acta Cryst.* **E67**, o1805–o1806.
- Sheldrick, G. M. (2007). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Souza, M. V. N. de, Pinheiro, A. C., Tiekink, E. R. T., Wardell, S. M. S. V. & Wardell, J. L. (2010). *Acta Cryst.* **E66**, o3253–o3254.
- Souza, M. V. N. de, Pinheiro, A. C., Tiekink, E. R. T., Wardell, S. M. S. V. & Wardell, J. L. (2011). *Acta Cryst.* **E67**, hb5927.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yakura, T., Yoshimoto, Y., Ishida, C. & Mabuchi, S. (2007). *Tetrahedron*, **63**, 4429–4438.

supplementary materials

Acta Cryst. (2011). E67, o1866-o1867 [doi:10.1107/S1600536811025128]

Benzyl *N*-(2-hydroxy-1- $\{N'$ -[(1*E*)-2-hydroxybenzylidene]hydrazinecarbonyl}ethyl)carbamate

E. R. T. Tiekink, M. V. N. de Souza, A. C. Pinheiro, S. M. S. V. Wardell and J. L. Wardell

Comment

The known anti-tumour activity of *L*-serine derivatives (Jiao *et al.*, 2009; Yakura *et al.*, 2007) motivates the development of *N*-acylhydrazone derivatives from *L*-serine for anti-tumour testing (Pinheiro *et al.*, 2010; de Souza *et al.*, 2010; Pinheiro *et al.*, 2011*a*; Pinheiro *et al.*, 2011*b*, de Souza *et al.*, 2011; Howie *et al.*, 2011), and led to the analysis of (I).

The absolute structure of (I) could not be determined experimentally but, the assignment of the *S*-configuration at the C9 atom is based on a starting reagent, *L*-serine. The structure of (I), Fig. 1, adopts a curved conformation with both benzene rings lying to the same side of the molecule. The presence of an intramolecular O—H \cdots N hydrogen bond ensures that the hydroxybenzene group is co-planar with the adjacent hydrazine residue with the dihedral angle between the (O2,N1,N2,C7,C8) and (C1–C6) planes being 11.14 (12)°. By contrast, the benzene ring adjacent to the carbamate residue is twisted as seen in the value of the dihedral angle formed between (O4,O5,N3,C11) and (C13–C18) of 50.84 (13)°. The dihedral angle between the two terminal benzene rings is 75.89 (19)°. The molecule is twisted about the chiral centre with the dihedral angle formed between the two amide residues, *i.e.* N2,C8,O2 and N3,C11,O4, being 80.21 (12)°.

Hydrogen bonds dominate the crystal packing, Table 1. Thus, the secondary hydroxyl group forms a O—H \cdots O hydrogen bond to the hydrazine-carbonyl-O2, and accepts a N—H \cdots O hydrogen bond from the hydrazine-amine, leading to chains along the *c* axis. The carbamate-amine forms a N—H \cdots O hydrogen bond to the carbamate-carbonyl-O4, leading to chains along the *a* axis. The result is the formation of a two-dimensional array in the *ac* plane, Fig. 2. The layers stack along the *b* axis, Fig. 3.

Experimental

To a stirred solution of methyl (2*S*)-2-[(benzyloxycarbonyl)amino]-3-hydroxypropanoate (0.3 g, 1.17 mmol), prepared from (2*S*)-2-amino-3-hydroxypropanoate hydrochloride and benzyl chloroformate (21 ml, 0.15 mol), in ethanol (10 ml) was added N₂H₄·H₂O (80%, 5.5 mmol). The reaction mixture was stirred for 24 h at room temperature, rotary evaporated and the residue washed with cold ethanol (3 x 10 ml) to give benzyl (1*S*)-2-hydrazino-1-(hydroxymethyl)-2-oxoethylcarbamate in 78% yield, which was used as such for the next stage. To a stirred solution of (*S*)-PhCH₂OCONHCH(CH₂OH)CONHNH₂ (1.0 mmol) in ethanol (10 ml) at room temperature was added 2-hydroxybenzaldehyde (1.05 mmol). The reaction mixture was refluxed for 4 h, rotary evaporated and the residue purified by washing with cold ethanol (3 x 10 ml), affording the title compound, *M.pt.* 433 K, yield 89%. The sample for the structure determination was recrystallized from EtOH to yield colourless laths. ¹H NMR (500 MHz, DMSO-*d*₆) δ (p.p.m.): 11.79 (1*H*, s, NHN), 11.12 (1*H*, s, Ph—OH), 8.46 (1*H*, s, N=CH, (*E*)-diastereomer), 7.52 (1*H*, dd, *J* = 7.8 and *J* = 1.5, H6), 7.48 (1*H*, d, *J* = 7.8, NHCH), 7.40–7.20 (6*H*, m, Ph and (H4 or H5)), 6.93–6.84 (2*H*, m, H3 and (H4 or H5)), 5.05 (3*H*, m, CH₂Ph and OH), 4.13 (1*H*, m, CH), 3.80–3.60 (2*H*, m, CH₂OH). ¹³C NMR (125 MHz, DMSO-*d*₆) δ (p.p.m.): 171.6, 157.8, 156.4, 141.2, 137.4, 131.9, 131.6, 129.8, 128.8, 128.3, 128.2, 126.7, 119.9, 119.1, 116.6, 65.9, 61.5, 55.0. IR (cm⁻¹, KBr): 3312 ν (O—H), 1681 ν (COCH and COO). MS/ESI: [M—H]: 356.3.

Refinement

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. The O- and N-bound H atoms were located from a difference map and refined with the distance restraints O–H = 0.84 ± 0.01 and N–H = 0.88 ± 0.01 Å, and with $U_{\text{iso}}(\text{H}) = zU_{\text{eq}}(\text{carrier atom})$; $z = 1.5$ for O and $z = 1.2$ for N. In the absence of significant anomalous scattering effects, 1896 Friedel pairs were averaged in the final refinement. However, the absolute configuration was assigned on the basis of the chirality of the *L*-serine starting material.

Figures

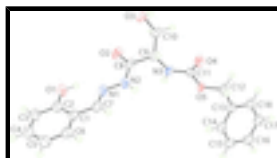


Fig. 1. The molecular structure of (I) showing displacement ellipsoids at the 50% probability level.

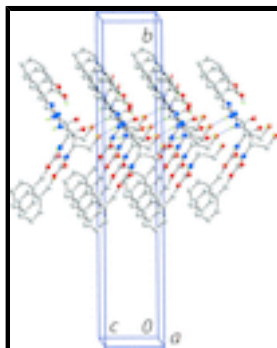


Fig. 2. A view of the supramolecular array in the *ac* plane in (I) with the O—H...O and N—H...O hydrogen bonding shown as orange and blue dashed lines, respectively. Hydrogen atoms not participating in the hydrogen bonding scheme are omitted for reasons of clarity.

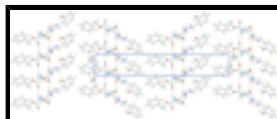


Fig. 3. A view in projection down the *c* axis of the stacking of 2-D supramolecular arrays along the *b* axis in (I), and with the O—H...O and N—H...O hydrogen bonding shown as orange and blue dashed lines, respectively.

Benzyl *N*-(2-hydroxy-1- $\{N'$ -[(*E*)-2-hydroxybenzylidene]hydrazinecarbonyl)ethyl)carbamate

Crystal data

$\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_5$

$M_r = 357.36$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 5.0338$ (5) Å

$b = 31.357$ (3) Å

$c = 5.5882$ (6) Å

$\beta = 97.890$ (3)°

$V = 873.72$ (16) Å³

$Z = 2$

$F(000) = 376$

$D_x = 1.358$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 11033 reflections

$\theta = 2.9\text{--}27.5^\circ$

$\mu = 0.10$ mm⁻¹

$T = 120$ K

Lath, colourless

$0.25 \times 0.05 \times 0.02$ mm

Data collection

Bruker–Nonius Roper CCD camera on κ -goniostat diffractometer	2034 independent reflections
Radiation source: Bruker–Nonius FR591 rotating anode	1485 reflections with $I > 2\sigma(I)$
graphite	$R_{\text{int}} = 0.066$
Detector resolution: 9.091 pixels mm^{-1}	$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.7^\circ$
φ & ω scans	$h = -6 \rightarrow 6$
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)	$k = -40 \rightarrow 40$
$T_{\text{min}} = 0.654$, $T_{\text{max}} = 0.746$	$l = -7 \rightarrow 7$
8786 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.053$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.098$	$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 0.1614P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
2034 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
247 parameters	$\Delta\rho_{\text{max}} = 0.17 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\text{min}} = -0.20 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Absolute structure: nd

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.7558 (5)	0.24963 (8)	0.4299 (5)	0.0409 (7)
H1O	0.629 (9)	0.2299 (15)	0.440 (9)	0.061*
O2	0.2652 (5)	0.16299 (9)	0.6800 (5)	0.0427 (7)

supplementary materials

O3	-0.2389 (5)	0.15356 (10)	0.8847 (5)	0.0443 (7)
H3O	-0.401 (10)	0.1591 (16)	0.838 (8)	0.066*
O4	-0.5493 (5)	0.07490 (8)	0.2844 (5)	0.0404 (7)
O5	-0.2450 (4)	0.03271 (7)	0.1329 (4)	0.0303 (6)
N1	0.3164 (6)	0.20615 (9)	0.2693 (6)	0.0343 (7)
N2	0.1183 (6)	0.17580 (9)	0.2843 (6)	0.0331 (7)
H2N	-0.011 (8)	0.1717 (13)	0.159 (7)	0.040*
N3	-0.1010 (6)	0.08812 (9)	0.3608 (5)	0.0274 (7)
H3N	0.069 (7)	0.0788 (11)	0.327 (6)	0.033*
C1	0.4747 (7)	0.26400 (11)	0.0505 (7)	0.0353 (9)
C2	0.6973 (7)	0.27309 (12)	0.2247 (8)	0.0366 (9)
C3	0.8652 (8)	0.30728 (12)	0.1904 (8)	0.0412 (9)
H3	1.0135	0.3136	0.3093	0.049*
C4	0.8165 (9)	0.33195 (13)	-0.0161 (8)	0.0472 (11)
H4	0.9325	0.3551	-0.0386	0.057*
C5	0.5994 (9)	0.32322 (14)	-0.1910 (8)	0.0506 (11)
H5	0.5663	0.3403	-0.3322	0.061*
C6	0.4311 (8)	0.28924 (13)	-0.1577 (8)	0.0439 (10)
H6	0.2841	0.2830	-0.2783	0.053*
C7	0.2850 (7)	0.22982 (12)	0.0788 (8)	0.0366 (9)
H7	0.1376	0.2250	-0.0437	0.044*
C8	0.1053 (6)	0.15684 (11)	0.4959 (6)	0.0304 (8)
C9	-0.1351 (7)	0.12663 (11)	0.4999 (6)	0.0287 (8)
H9	-0.2995	0.1417	0.4215	0.034*
C10	-0.1744 (7)	0.11639 (12)	0.7568 (7)	0.0367 (9)
H10A	-0.3207	0.0953	0.7555	0.044*
H10B	-0.0082	0.1035	0.8416	0.044*
C11	-0.3170 (7)	0.06639 (11)	0.2608 (6)	0.0292 (8)
C12	-0.4669 (8)	0.00648 (12)	0.0233 (8)	0.0430 (10)
H12A	-0.6019	0.0244	-0.0757	0.052*
H12B	-0.5545	-0.0076	0.1503	0.052*
C13	-0.3575 (7)	-0.02651 (11)	-0.1330 (7)	0.0334 (9)
C14	-0.1860 (8)	-0.01563 (12)	-0.2975 (7)	0.0384 (9)
H14	-0.1289	0.0131	-0.3075	0.046*
C15	-0.0973 (9)	-0.04597 (13)	-0.4467 (7)	0.0451 (10)
H15	0.0198	-0.0380	-0.5587	0.054*
C16	-0.1781 (8)	-0.08796 (12)	-0.4336 (7)	0.0435 (10)
H16	-0.1178	-0.1089	-0.5368	0.052*
C17	-0.3479 (8)	-0.09931 (13)	-0.2687 (7)	0.0445 (10)
H17	-0.4039	-0.1281	-0.2588	0.053*
C18	-0.4360 (8)	-0.06899 (12)	-0.1191 (7)	0.0414 (10)
H18	-0.5510	-0.0771	-0.0057	0.050*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0346 (15)	0.0338 (15)	0.0538 (17)	-0.0029 (12)	0.0040 (13)	0.0000 (14)
O2	0.0275 (13)	0.0537 (18)	0.0434 (15)	0.0004 (12)	-0.0074 (12)	-0.0141 (13)

O3	0.0277 (13)	0.0647 (19)	0.0378 (15)	0.0139 (14)	-0.0050 (11)	-0.0248 (14)
O4	0.0199 (12)	0.0454 (16)	0.0569 (17)	-0.0006 (11)	0.0091 (12)	-0.0179 (14)
O5	0.0221 (12)	0.0292 (14)	0.0398 (14)	-0.0031 (10)	0.0048 (11)	-0.0104 (11)
N1	0.0247 (15)	0.0287 (16)	0.049 (2)	-0.0013 (13)	0.0051 (14)	-0.0106 (16)
N2	0.0261 (16)	0.0280 (16)	0.044 (2)	-0.0023 (13)	0.0009 (14)	-0.0070 (14)
N3	0.0178 (14)	0.0290 (16)	0.0353 (16)	0.0022 (12)	0.0032 (13)	-0.0097 (13)
C1	0.035 (2)	0.030 (2)	0.044 (2)	0.0020 (16)	0.0139 (18)	-0.0081 (17)
C2	0.033 (2)	0.0279 (19)	0.051 (2)	0.0053 (16)	0.0136 (18)	-0.0052 (19)
C3	0.034 (2)	0.030 (2)	0.060 (3)	-0.0013 (18)	0.0095 (19)	-0.005 (2)
C4	0.044 (2)	0.033 (2)	0.069 (3)	0.0024 (18)	0.023 (2)	-0.005 (2)
C5	0.056 (3)	0.042 (2)	0.057 (3)	0.007 (2)	0.021 (2)	0.001 (2)
C6	0.047 (2)	0.042 (2)	0.045 (2)	0.0035 (19)	0.014 (2)	-0.0073 (19)
C7	0.032 (2)	0.030 (2)	0.049 (2)	0.0038 (15)	0.0080 (18)	-0.0136 (19)
C8	0.0210 (17)	0.0295 (19)	0.039 (2)	0.0042 (15)	-0.0030 (15)	-0.0110 (17)
C9	0.0230 (17)	0.0299 (19)	0.0321 (19)	0.0057 (15)	-0.0003 (15)	-0.0035 (15)
C10	0.0291 (19)	0.046 (2)	0.034 (2)	0.0114 (17)	0.0007 (16)	-0.0069 (18)
C11	0.0248 (19)	0.0317 (19)	0.0318 (19)	-0.0024 (15)	0.0066 (15)	-0.0072 (16)
C12	0.028 (2)	0.040 (2)	0.061 (3)	-0.0096 (17)	0.006 (2)	-0.022 (2)
C13	0.0280 (19)	0.029 (2)	0.042 (2)	-0.0010 (15)	0.0006 (17)	-0.0080 (17)
C14	0.042 (2)	0.030 (2)	0.042 (2)	-0.0026 (17)	0.0029 (18)	-0.0054 (17)
C15	0.059 (3)	0.037 (2)	0.041 (2)	-0.003 (2)	0.013 (2)	-0.0047 (19)
C16	0.057 (3)	0.031 (2)	0.043 (2)	0.0049 (18)	0.006 (2)	-0.0081 (19)
C17	0.052 (2)	0.029 (2)	0.053 (3)	-0.0063 (19)	0.010 (2)	-0.0085 (19)
C18	0.042 (2)	0.039 (2)	0.045 (2)	-0.0071 (18)	0.0127 (19)	-0.0061 (19)

Geometric parameters (Å, °)

O1—C2	1.360 (5)	C5—C6	1.389 (6)
O1—H10	0.89 (5)	C5—H5	0.9500
O2—C8	1.231 (4)	C6—H6	0.9500
O3—C10	1.428 (4)	C7—H7	0.9500
O3—H3O	0.84 (5)	C8—C9	1.540 (5)
O4—C11	1.224 (4)	C9—C10	1.510 (5)
O5—C11	1.352 (4)	C9—H9	1.0000
O5—C12	1.453 (4)	C10—H10A	0.9900
N1—C7	1.290 (5)	C10—H10B	0.9900
N1—N2	1.389 (4)	C12—C13	1.506 (5)
N2—C8	1.333 (5)	C12—H12A	0.9900
N2—H2N	0.90 (4)	C12—H12B	0.9900
N3—C11	1.339 (4)	C13—C14	1.387 (6)
N3—C9	1.459 (4)	C13—C18	1.395 (5)
N3—H3N	0.95 (4)	C14—C15	1.379 (5)
C1—C6	1.400 (5)	C14—H14	0.9500
C1—C2	1.409 (5)	C15—C16	1.383 (6)
C1—C7	1.458 (5)	C15—H15	0.9500
C2—C3	1.394 (5)	C16—C17	1.387 (6)
C3—C4	1.383 (6)	C16—H16	0.9500
C3—H3	0.9500	C17—C18	1.379 (5)
C4—C5	1.390 (6)	C17—H17	0.9500

supplementary materials

C4—H4	0.9500	C18—H18	0.9500
C2—O1—H1O	111 (3)	N3—C9—H9	108.0
C10—O3—H3O	107 (3)	C10—C9—H9	108.0
C11—O5—C12	114.7 (2)	C8—C9—H9	108.0
C7—N1—N2	115.9 (3)	O3—C10—C9	111.8 (3)
C8—N2—N1	118.8 (3)	O3—C10—H10A	109.3
C8—N2—H2N	121 (3)	C9—C10—H10A	109.3
N1—N2—H2N	120 (3)	O3—C10—H10B	109.3
C11—N3—C9	119.7 (3)	C9—C10—H10B	109.3
C11—N3—H3N	118 (2)	H10A—C10—H10B	107.9
C9—N3—H3N	122 (2)	O4—C11—N3	125.3 (3)
C6—C1—C2	118.6 (3)	O4—C11—O5	123.8 (3)
C6—C1—C7	118.4 (4)	N3—C11—O5	110.9 (3)
C2—C1—C7	123.0 (4)	O5—C12—C13	108.2 (3)
O1—C2—C3	117.8 (4)	O5—C12—H12A	110.1
O1—C2—C1	122.2 (3)	C13—C12—H12A	110.1
C3—C2—C1	120.0 (4)	O5—C12—H12B	110.1
C4—C3—C2	120.2 (4)	C13—C12—H12B	110.1
C4—C3—H3	119.9	H12A—C12—H12B	108.4
C2—C3—H3	119.9	C14—C13—C18	118.6 (3)
C3—C4—C5	120.6 (4)	C14—C13—C12	121.7 (3)
C3—C4—H4	119.7	C18—C13—C12	119.7 (4)
C5—C4—H4	119.7	C15—C14—C13	120.9 (4)
C4—C5—C6	119.5 (4)	C15—C14—H14	119.5
C4—C5—H5	120.3	C13—C14—H14	119.5
C6—C5—H5	120.3	C14—C15—C16	120.2 (4)
C5—C6—C1	121.1 (4)	C14—C15—H15	119.9
C5—C6—H6	119.5	C16—C15—H15	119.9
C1—C6—H6	119.5	C15—C16—C17	119.5 (4)
N1—C7—C1	120.3 (3)	C15—C16—H16	120.3
N1—C7—H7	119.8	C17—C16—H16	120.3
C1—C7—H7	119.8	C18—C17—C16	120.3 (4)
O2—C8—N2	124.4 (3)	C18—C17—H17	119.8
O2—C8—C9	120.6 (3)	C16—C17—H17	119.8
N2—C8—C9	114.9 (3)	C17—C18—C13	120.5 (4)
N3—C9—C10	111.8 (3)	C17—C18—H18	119.7
N3—C9—C8	110.6 (3)	C13—C18—H18	119.7
C10—C9—C8	110.5 (3)		
C7—N1—N2—C8	-165.5 (3)	N2—C8—C9—N3	71.1 (4)
C6—C1—C2—O1	-178.9 (3)	O2—C8—C9—C10	13.6 (4)
C7—C1—C2—O1	2.0 (5)	N2—C8—C9—C10	-164.7 (3)
C6—C1—C2—C3	1.5 (5)	N3—C9—C10—O3	-173.2 (3)
C7—C1—C2—C3	-177.6 (3)	C8—C9—C10—O3	63.2 (3)
O1—C2—C3—C4	179.4 (3)	C9—N3—C11—O4	-3.6 (5)
C1—C2—C3—C4	-1.0 (5)	C9—N3—C11—O5	177.9 (3)
C2—C3—C4—C5	0.4 (6)	C12—O5—C11—O4	-0.2 (5)
C3—C4—C5—C6	-0.3 (6)	C12—O5—C11—N3	178.3 (3)
C4—C5—C6—C1	0.8 (6)	C11—O5—C12—C13	174.0 (3)

C2—C1—C6—C5	-1.4 (5)	O5—C12—C13—C14	-48.4 (5)
C7—C1—C6—C5	177.7 (3)	O5—C12—C13—C18	133.7 (4)
N2—N1—C7—C1	177.1 (3)	C18—C13—C14—C15	0.9 (6)
C6—C1—C7—N1	-179.2 (3)	C12—C13—C14—C15	-177.1 (4)
C2—C1—C7—N1	-0.2 (5)	C13—C14—C15—C16	-0.2 (6)
N1—N2—C8—O2	-3.2 (5)	C14—C15—C16—C17	-0.3 (6)
N1—N2—C8—C9	174.9 (3)	C15—C16—C17—C18	0.1 (7)
C11—N3—C9—C10	82.9 (4)	C16—C17—C18—C13	0.6 (6)
C11—N3—C9—C8	-153.6 (3)	C14—C13—C18—C17	-1.0 (6)
O2—C8—C9—N3	-110.7 (4)	C12—C13—C18—C17	177.0 (4)

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1o \cdots N1	0.90 (5)	1.88 (5)	2.648 (4)	143 (4)
O3—H3o \cdots O2 ⁱ	0.84 (5)	1.79 (5)	2.616 (4)	167 (5)
N2—H2n \cdots O3 ⁱⁱ	0.90 (4)	1.87 (4)	2.758 (4)	168 (4)
N3—H3n \cdots O4 ⁱⁱⁱ	0.95 (4)	1.97 (4)	2.897 (4)	165 (3)

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

Fig. 1

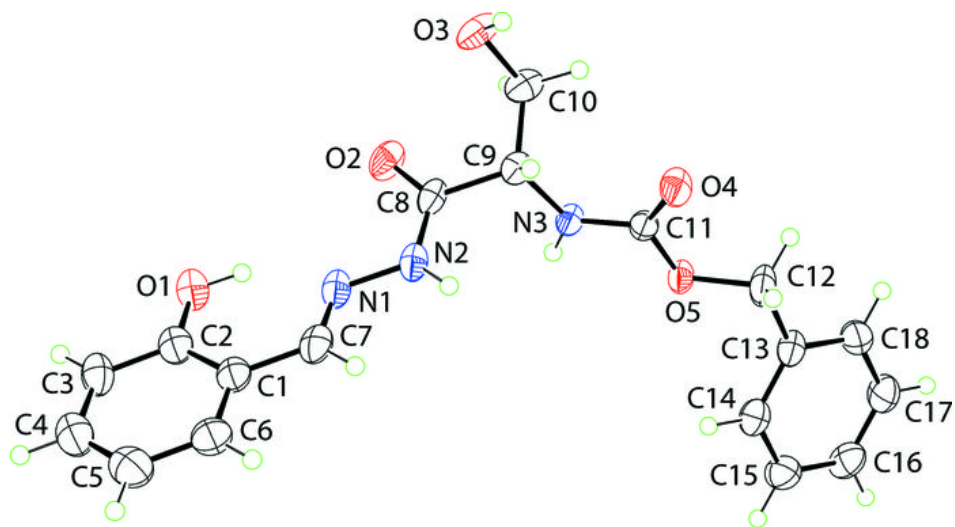


Fig. 2

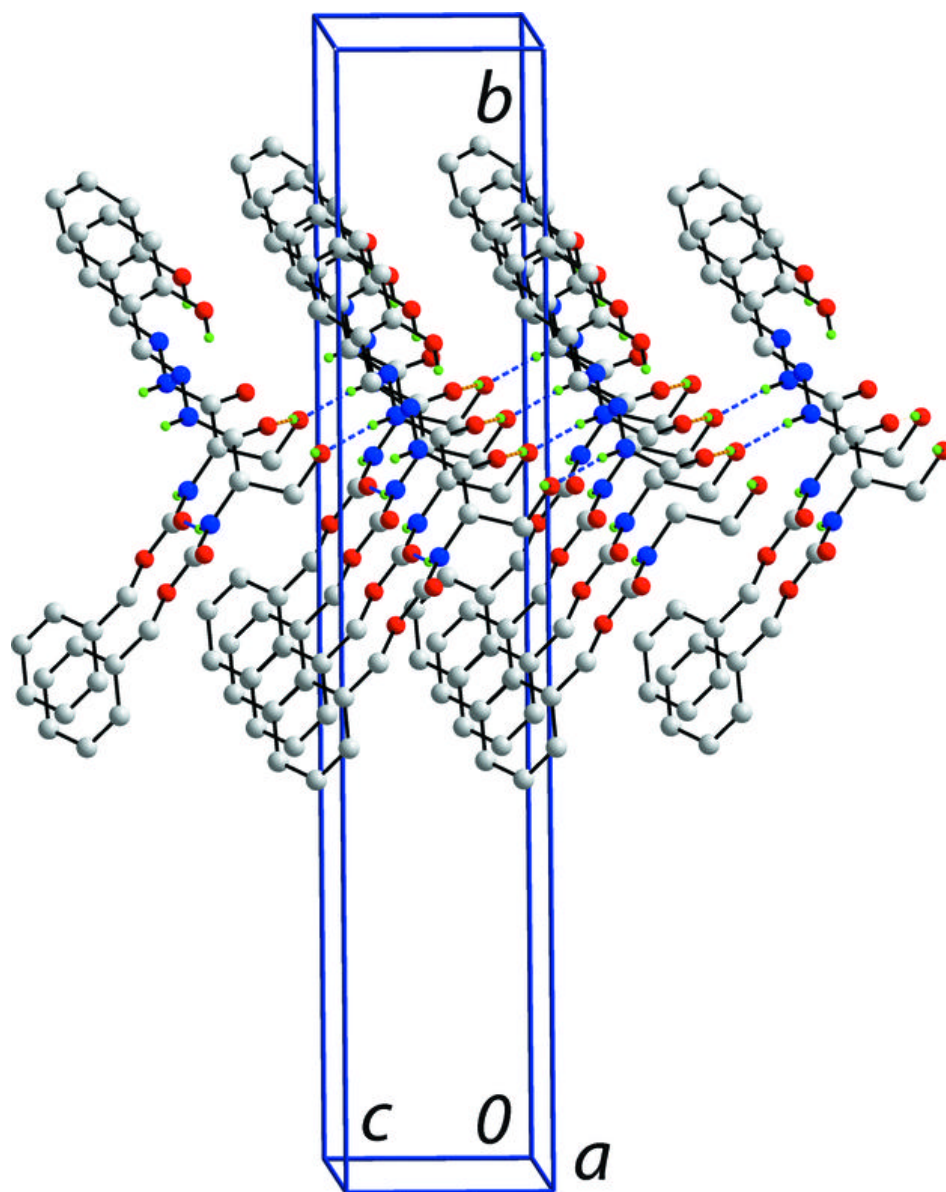


Fig. 3

