research communications

CrossMark

Different hydrogen-bonded chains in the crystal structures of three alkyl N-[(E)-1-(2-benzylidene-1-methylhydrazinyl)-3-hydroxy-1-oxopropan-2-yl]-carbamates

Thais C. M. Noguiera,[a] Alessandra C. Pinheiro,[a] James L. Wardell,[a,b] Marcus V. N. de Souza,[a] Jordan P. Abberley[b] and William T. A. Harrison[b]*

[a]Fundação Oswaldo Cruz, Instituto de Tecnologia em Fármacos–FarManguinhos, Rua Sizenando Nabuco, 100, Manguinhos, 21041-250 Rio de Janeiro, RJ, Brazil, and [b]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland. *Correspondence e-mail: w.harrison@abdn.ac.uk

The crystal structures of three methylated hydrazine carbamate derivatives prepared by multi-step syntheses from L-serine are presented, namely benzyl N-{(E)-1-[2-(4-cyanobenzylidene)-1-methylhydrazinyl]-3-hydroxy-1-oxopropan-2-yl}carbamate, $C_{20}H_{20}N_4O_4$, tert-butyl N-{(E)-1-[2-(4-cyanobenzylidene)-1-methylhydrazinyl]-3-hydroxy-1-oxopropan-2-yl}carbamate, $C_{17}H_{22}N_4O_4$, and tert-butyl N-[(E)-1-(2-benzylidene-1-methylhydrazinyl)-3-hydroxy-1-oxopropan-2-yl]-carbamate, $C_{16}H_{23}N_3O_4$. One of them shows that an unexpected racemization has occurred during the mild-condition methylation reaction. In each crystal structure, the molecules are linked into chains by O—H···O hydrogen bonds, but with significant differences between them.

1. Chemical context

As part of our ongoing studies of hydrazine carbamates derived from L-serine with possible anti-tubercular activity (Pinheiro *et al.*, 2011), we now describe the syntheses and structures of three methylated derivatives, *viz*: benzyl (*E*)-3-hydroxy-1-[2-(4-cyanobenzyldene)-1-methylhydrazinyl]-1-oxopropan-2-ylcarbamate (I), tert-butyl (*E*)-3-hydroxy-1-[2-(4-cyanobenzylidene)-1-methylhydrazinyl]-1-oxopropan-2-yl-carbamate (II) and tert-butyl (*E*)-3-hydroxy-1-[2-benzylidene-1-methylhydrazinyl]-1-oxopropan-2-ylcarbamate (III), formed by the reaction of the corresponding (*E*)-(*S*)-*R*OCONHCH(CH₂OH)CONHN=CH-benzene (*R* = *t*-Bu or PhCH₂) compound (Noguiera *et al.*, 2013) with potassium carbonate and methyl iodide.
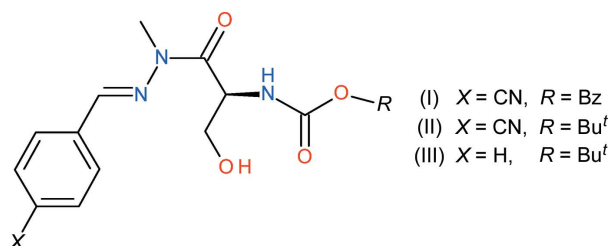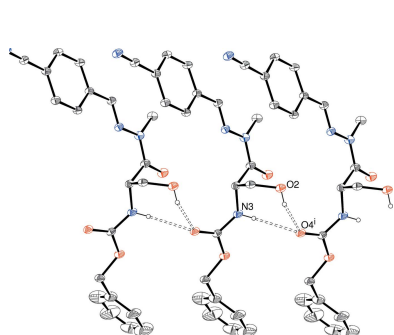
In general, the tertiary butyl compounds form simple methylated products as described here, whereas the benzyl compounds lead to cyclized oxazolidin-2-one products (Noguiera *et al.*, 2013). However, compound (I) described herein has not cyclized. As described below, compound (III) has undergone an unexpected racemization during the methylation step. The acidity of the α-hydrogen atom in serine

(I) X = CN, R = Bz
(II) X = CN, R = Bu^t
(III) X = H,   R = Bu^t
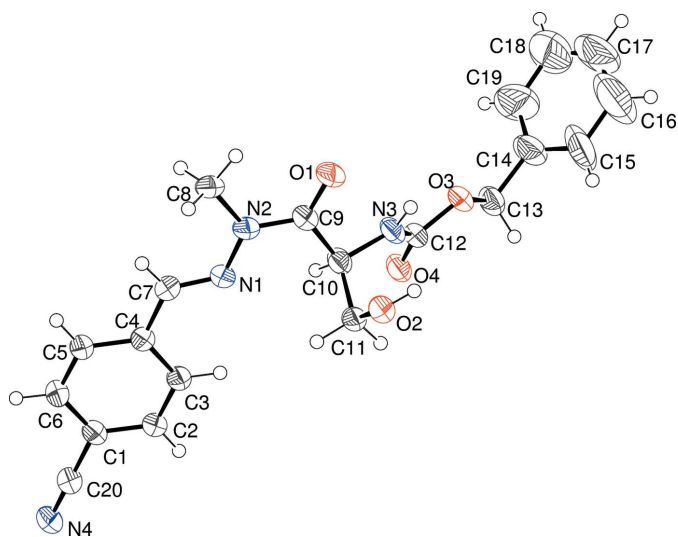
Figure 1
The molecular structure of (I) showing 50% displacement ellipsoids.

derivatives has been variously reported (*e.g.*, Blaskovich & Lajoie, 1993; Kovacs *et al.*, 1984), and apparently can result in racemization in the presence of even a very weak base such as the carbonate ion. Similar racemizations have been observed in the cyclized oxazolidin-2-one products (Noguiera *et al.*, 2015).

2. Structural commentary

The molecular structure of (I) is shown in Fig. 1, which confirms that methylation has occurred at N2 but no cyclization to an oxazolidin-2-one has occurred (Noguiera *et al.*, 2015). Compound (I) crystallizes in a chiral space group but its absolute structure was indeterminate in the present experiment and C10 was assumed to have an *S* configuration to match the corresponding atom in the L-serine starting material. The atoms of the C14 benzene ring show notably larger
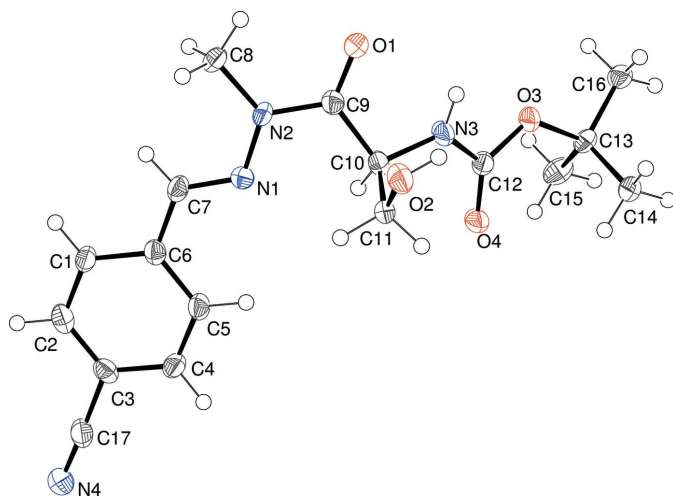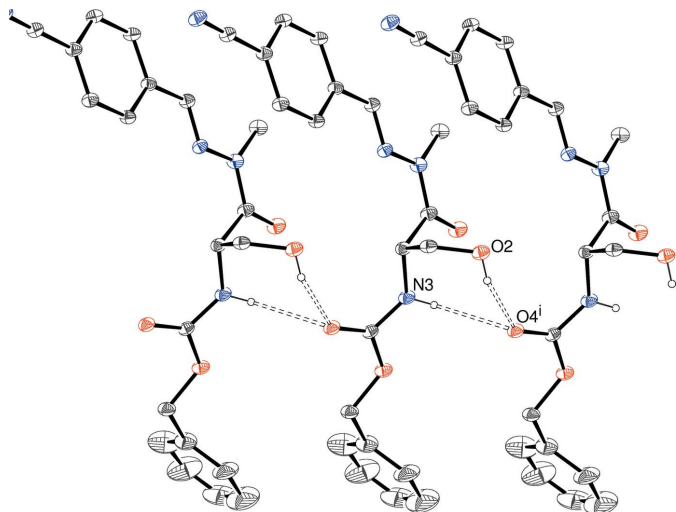

Figure 2
The molecular structure of (II) showing 50% displacement ellipsoids.
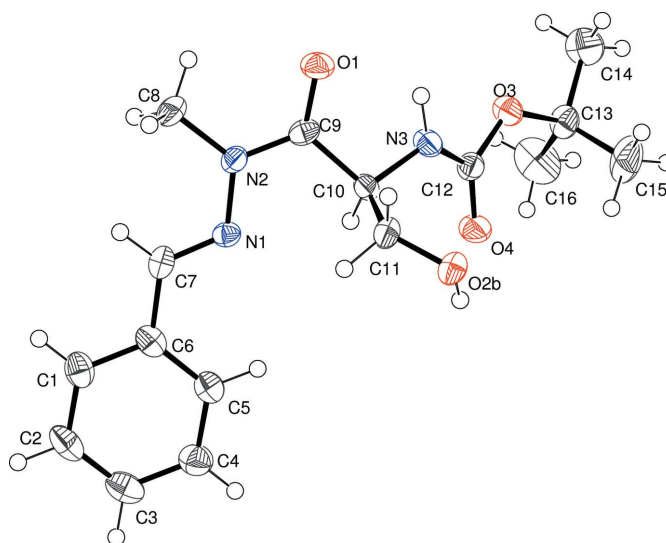
Figure 3
The molecular structure of (III) showing 50% displacement ellipsoids. Only one orientation of the disordered O2—H2 group is shown.

displacement ellipsoids than the rest of the molecule, but attempts to model this as disorder did not lead to a significant improvement in fit. Atom N2 is statistically planar (bond-angle sum = 360°), which implies sp^2 hybridization for this atom. The C9—N2 bond length of 1.358 (6)Å is typical of an amide and the N1—N2 bond length of 1.374 (5) is shorter than the reference value of 1.40 Å for a nominal $N(sp^2)$—$N(sp^2)$ single bond. This suggests at least some electronic conjugation over the almost planar C7/N1/N2/C9/O1 grouping (r.m.s. deviation = 0.010 Å): the C1 benzene ring is twisted by 6.1 (2)° with respect to these atoms. The C7—N1—N2—C8 torsion angle of −1.9 (6)° shows that the carbon atoms are almost eclipsed with respect to the N—N bond whereas the C9—C10—C11—O2 torsion angle of −50.9 (5)° indicates a gauche conformation about the C10—C11 bond. The C9—C10—N3—H3A torsion angle is 38° and the separation between H2A (bonded to O2) and H3A is 2.5 Å.

The molecular structure of (II) can be seen in Fig. 2: again the methylation of N2 has occurred as expected. Because the absolute structure was indeterminate, the configuration of C10 (*S*) was assumed to be the same as that of the corresponding atom in the L-serine starting material. In terms of the C7/N1/N2/C9/O1 grouping in (II), the C9—N2 and N1—N2 bond lengths are 1.385 (6) and 1.388 (5) Å, respectively, which are both notably longer than the corresponding bonds in (I), and the r.m.s. deviation from planarity of 0.049 Å for these five atoms is also larger than the corresponding value for (I). The dihedral angle between C7/N1/N2/C9/O1 and the C1-benzene ring in (II) is 10.5 (3)°. The C7—N1—N2—C8 torsion angle is 1.2 (7)° and the C9—C10—C11—O2 torsion angle is −47.4 (6)°, which are similar to the equivalent data for (I). The C9—C10—N3—H3 torsion angle in (II) is 30° and the separation between H2A and H3 is 2.7 Å. These values are evidently sufficiently different from the corresponding data for (I) to lead to a different hydrogen-bonding pattern in the crystal (see below).

Figure 4
Fragment of a [100] hydrogen-bonded chain in the crystal of (I). Symmetry code: (i) $1 + x, y, z$. All C-bound H atoms are omitted for clarity.

Compound (III), shown in Fig. 3, crystallizes in a centrosymmetric space group, indicating that racemization of C10 has occurred during the methylation of N2: the C10 atom in the asymmetric unit was arbitrarily assigned an S configuration. The O2—H2 hydroxy group is disordered over two orientations in a 0.802 (7):0.198 (7) ratio. The geometric parameters for (III) are largely consistent with those for (I) and (II): the C7/N1/N2/C9/O1 grouping (r.m.s. deviation = 0.014 Å) subtends a dihedral angle of 1.9 (4)° with the C1–C6 benzene ring and the C9—N2 and N1—N2 bond lengths are 1.358 (5) and 1.381 (4) Å, respectively. The C7—N1—N2—C8 torsion angle is 0.8 (5)° and the C9—C10—C11—O2A (major disorder component) torsion angle is −54.9 (4)°. The C9—
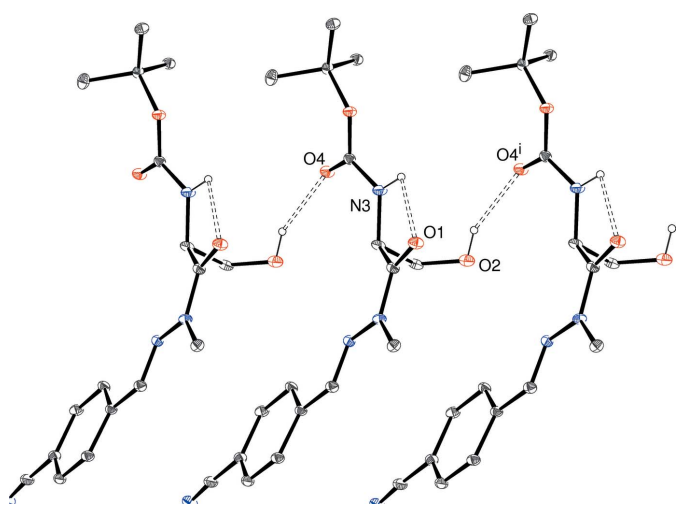
Figure 5
Fragment of a [100] hydrogen-bonded chain in the crystal of (II). Symmetry code: (i) $1 + x, y, z$. All C-bound H atoms are omitted for clarity.

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$Cg2$ is the centroid of the C14–C19 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$A\cdots$O4^i	0.88	2.40	3.091 (6)	135
O2—H2$A\cdots$O4^i	0.84	2.08	2.873 (5)	158
C16—H16$\cdots Cg2^{ii}$	0.95	2.78	3.558 (18)	140
C19—H19$\cdots Cg2^{iii}$	0.95	2.86	3.598 (13)	135

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 2, y + \frac{1}{2}, -z + 1$; (iii) $-x + 1, y - \frac{1}{2}, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$\cdots$O1	0.88	2.27	2.620 (6)	104
O2—H2$A\cdots$O4^i	0.84	2.09	2.877 (5)	156
C4—H4$\cdots$N4^{ii}	0.95	2.61	3.549 (8)	168

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x - 1, y - \frac{1}{2}, -z + 1$.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H1$N\cdots$O1	0.88 (4)	2.11 (4)	2.623 (4)	116 (3)
O2A—H2$A\cdots$O4^i	0.84	2.09	2.852 (4)	150
O2B—H2$B\cdots$O1^{ii}	0.84	2.18	2.966 (13)	156
C7—H7$\cdots$O2A^{iii}	0.95	2.45	3.229 (5)	140

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

C10—C11—O2B torsion angle for the minor disorder component is −156.7 (8)°, which has a significant role to play in the hydrogen-bonding pattern in the crystal of (III).

3. Supramolecular features

In the extended structure of (I), the molecules are linked by short O2—H2$A\cdots$O4^i (i = 1 + x, y, z) and much longer N3—H3$A\cdots$O4^i hydrogen bonds (Table 1, Fig. 4) to the same acceptor oxygen atom, generating [100] chains, with adjacent molecules related by simple translation in the a-axis direction. An unusual $R_2^1(7)$ loop arises from these hydrogen bonds; alternately, this could be described as combined $C(7)$ O—H$\cdots$O and $C(4)$ N—H$\cdots$O chains. A pair of weak C—H$\cdots\pi$ interactions are also observed but there is no aromatic π–π stacking (shortest centroid–centroid separation > 4.7 Å).

The extended structure of (II) also features [100] chains (Fig. 5) with adjacent molecules related by translation, but in this case the molecules are only linked by $C(7)$ O2—H2$A\cdots$O4^i (i = 1 + x, y, z) hydrogen bonds (Table 2) with almost the same local geometry as seen in (I). The N3—H3 grouping in (II) is twisted far enough away from O4^i to not form an intermolecular hydrogen bond (H3$\cdots$O4^i = 3.2 Å), but instead forms an intramolecular link to O1. A very long intermolecular C—H$\cdots$N interaction is observed but there is

no π–π stacking in (II), as the shortest centroid–centroid separation is greater than 5.3 Å.

The packing in the centrosymmetric structure of (III) leads to [010] chains (Fig. 6) with adjacent molecules related by the 2_1 screw axis, so that the C1-benzene ring is 'flipped' from one side of the chain to the other in adjacent molecules. As noted above, the hydroxyl group is disordered over two orientations. The hydrogen bond from the major orientation of O2A—H2A is still a bond to O4^i (Table 3), where i = $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$. The minor disorder component (O2B—H2B) forms an O—H···O hydrogen bond in the opposite chain direction to O1^{ii} (ii = $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$): O1 also accepts an intramolecular N—H···O hydrogen bond, as seen in (II). Once again, no aromatic π–π stacking is observed in the crystal of (III), as the minimum centroid–centroid separation is greater than 4.6 Å.

Figure 6
Fragment of an [010] hydrogen-bonded chain in the crystal of (III). Both disorder components of the OH group are shown. Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$. All C-bound H atoms are omitted for clarity.
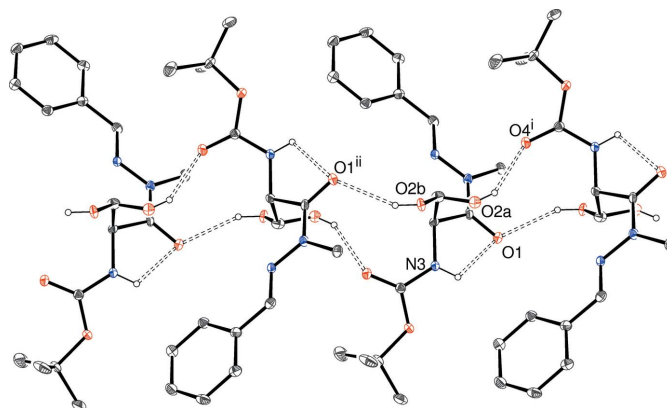
4. Database survey

There are no –OCONHCH(CH$_2$OH)CON(CH$_3$)N=CH– fragments reported in Version 5.36 of the Cambridge Structural Database (Groom & Allen, 2014) but there are 14 unmethylated –OCONHCH(CH$_2$OH)CONHN=CH– groupings with different substituents at each end of the fragment, all of which have been reported by us in the last few years (Howie et al., 2011 and references therein). All of these materials crystallize in chiral space groups.

5. Synthesis and crystallization

Potassium carbonate (1.76 mmol) was added to a solution of the appropriate (E)-(S)-ROCONHCH(CH$_2$OH)-CONHN=CH-benzene compound (Noguiera et al., 2013) in acetone (10 ml) and the reaction mixture was vigorously stirred at room temperature for 5 minutes, before adding methyl iodide (1.80 mmol). The reaction mixture was stirred at 323 K for 24–48 h and the solvent removed by rotary

Table 4
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	C$_{20}$H$_{20}$N$_4$O$_4$	C$_{17}$H$_{22}$N$_4$O$_4$	C$_{16}$H$_{23}$N$_3$O$_4$
M_r	380.40	346.39	321.37
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1$	Monoclinic, $P2_1/c$
Temperature (K)	100	100	100
a, b, c (Å)	4.995 (6), 8.172 (8), 22.94 (3)	5.348 (3), 7.883 (5), 20.903 (14)	10.454 (7), 10.571 (7), 15.664 (11)
β (°)	93.48 (3)	92.763 (1)	101.172 (12)
V (Å^3)	934.7 (19)	880.2 (10)	1698 (2)
Z	2	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.10	0.10	0.09
Crystal size (mm)	0.14 × 0.03 × 0.01	0.08 × 0.08 × 0.02	0.16 × 0.05 × 0.01
Data collection			
Diffractometer	Rigaku Mercury CCD	Rigaku Mercury CCD	Rigaku Mercury CCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13928, 4691, 3270	3672, 2483, 2143	8546, 3319, 2716
R_{int}	0.070	0.023	0.048
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.734	0.617	0.617
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.095, 0.278, 1.10	0.057, 0.194, 1.13	0.104, 0.197, 1.23
No. of reflections	4691	2483	3319
No. of parameters	255	231	220
No. of restraints	1	1	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.35	0.31, −0.36	0.44, −0.26

Computer programs: CrystalClear (Rigaku, 2012), SHELXS97 and SHELXL97 (Sheldrick, 2008), ORTEP-3 for Windows (Farrugia, 2012) and publCIF (Westrip, 2010).

evaporation. The residue was subjected to column chromatography on silica gel, using a chloroform:methanol (100 → 95%) gradient. The colourless crystals used in the structure determinations were recrystallized from ethanol solution at room temperature. For further details and spectroscopic data, see: Noguiera *et al.* (2013).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The crystal of (I) gave a poor diffraction pattern and indexing initially established a large triclinic unit cell [a = 9.512 (12), b = 13.003 (19), c = 22.94 (3) Å, α = 92.93 (2), β = 91.48 (3), γ = 98.13 (3)°, V = 2804 (7) Å^3]. An atomic model could be developed in space group $P1$ with Z = 6, but a *PLATON* (Spek, 2009) symmetry check indicated that the smaller monoclinic cell reported above was more appropriate and the unit cell transformed by the matrix ($-\frac{1}{3}$ $-\frac{1}{3}$ 0 / $-\frac{2}{3}$ $\frac{1}{3}$ 0 / 0 0 -1). It is notable that the aromatic rings of the benzyl groups of all six molecules in the triclinic supercell showed a high degree of thermal motion. The transformation to monoclinic symmetry resulted in a rather low data completion percentage of 92%, but we consider that the refinement is satisfactory and a good geometrical precision results. For each structure, the O- and N-bound H atoms were located in difference maps, repositioned in idealized locations and refined as riding atoms [H1N was freely refined in structure (III)]. The C-bound H atoms were placed geometrically (C—H = 0.95–1.00 Å) and refined as riding atoms. The constraint U_{iso}(H) = 1.2U_{eq}(carrier) or 1.5U_{eq}(methyl carrier) was applied in all cases. The H atoms of the hydroxyl groups were allowed to rotate about their C—O bond (*SHELXL* HFIX 83 instruction with O—H = 0.84 Å and C—O—H = 109.5°) to best fit the electron density. The methyl groups were allowed to rotate, but not to tip, to best fit the electron density (AFIX 137 instruction).

References

Blaskovich, M. A. & Lajoie, G. A. (1993). *J. Am. Chem. Soc.* **115**, 5021–5030.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
Howie, R. A., de Souza, M. V. N., Pinheiro, A., Kaiser, C. R., Wardell, J. L. & Wardell, S. M. S. V. (2011). *Z. Kristallogr.* **226**, 483–491.
Kovacs, J., Jham, G. N., Hui, K. Y., Holleran, E. M., Kim, S. E. & Canavan, T. (1984). *Int. J. Peptide Protein Res.* **24**, 161–167.
Noguiera, T. C. M., Pinheiro, A. C., Kaiser, C., Wardell, J. L., Wardell, S. M. S. V. & de Souza, M. V. N. (2013). *Lett. Org. Chem.* **10**, 626–631.
Noguiera, T. C. M., Pinheiro, A. C., Wardell, J. L., de Souza, M. V. N., Abberley, J. P. & Harrison, W. T. A. (2015). *Acta Cryst.* C**71**. Submitted.
Pinheiro, A. C., Kaiser, C. R., Noguiera, T. C. M., Carvalho, S. A., Silva, E. F., Feitosa, L. O., Henriques, M. O., Candéa, L. P., Lourenço, M. C. S. & Souza, M. V. N. (2011). *Med. Chem.* **7**, 611–623.
Rigaku (2012). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Different hydrogen-bonded chains in the crystal structures of three alkyl N-[(E)-1-(2-benzylidene-1-methylhydrazinyl)-3-hydroxy-1-oxopropan-2-yl]carbamates

Thais C. M. Noguiera, Alessandra C. Pinheiro, James L. Wardell, Marcus V. N. de Souza, Jordan P. Abberley and William T. A. Harrison

Computing details

For all compounds, data collection: *CrystalClear* (Rigaku, 2012); cell refinement: *CrystalClear* (Rigaku, 2012); data reduction: *CrystalClear* (Rigaku, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(I) Benzyl N-{(E)-1-[2-(4-cyanobenzylidene)-1-methylhydrazinyl]-3-hydroxy-1-oxopropan-2-yl}carbamate

Crystal data

$C_{20}H_{20}N_4O_4$	$F(000) = 400$
$M_r = 380.40$	$D_x = 1.352$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 5405 reflections
$a = 4.995$ (6) Å	$\theta = 2.2$–$31.3°$
$b = 8.172$ (8) Å	$\mu = 0.10$ mm^{-1}
$c = 22.94$ (3) Å	$T = 100$ K
$\beta = 93.48$ (3)°	Chip, colourless
$V = 934.7$ (19) Å^3	$0.14 \times 0.03 \times 0.01$ mm
$Z = 2$	

Data collection

Rigaku Mercury CCD diffractometer	3270 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.070$
Graphite monochromator	$\theta_{max} = 31.5°$, $\theta_{min} = 2.7°$
ω scans	$h = -7 \rightarrow 7$
13928 measured reflections	$k = -11 \rightarrow 7$
4691 independent reflections	$l = -32 \rightarrow 33$

Refinement

Refinement on F^2	1 restraint
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.095$	
$wR(F^2) = 0.278$	Secondary atom site location: difference Fourier map
$S = 1.10$	
4691 reflections	Hydrogen site location: inferred from neighbouring sites
255 parameters	

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1373P)^2 + 0.3363P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.005$

$\Delta\rho_{max} = 0.39$ e Å^{-3}

$\Delta\rho_{min} = -0.35$ e Å^{-3}

Extinction correction: *SHELXL*,

$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.079 (13)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.1557 (8)	−0.2306 (6)	0.04534 (16)	0.0387 (8)
C2	−0.0584 (9)	−0.0833 (5)	0.06903 (16)	0.0389 (9)
H2	−0.1380	0.0174	0.0567	0.047*
C3	0.1564 (8)	−0.0847 (5)	0.11093 (16)	0.0371 (8)
H3	0.2225	0.0153	0.1273	0.044*
C4	0.2746 (8)	−0.2330 (5)	0.12891 (15)	0.0358 (8)
C5	0.1737 (9)	−0.3795 (5)	0.10501 (16)	0.0393 (9)
H5	0.2541	−0.4802	0.1171	0.047*
C6	−0.0422 (9)	−0.3803 (6)	0.06378 (18)	0.0404 (9)
H6	−0.1116	−0.4806	0.0483	0.048*
C7	0.5009 (8)	−0.2375 (6)	0.17309 (16)	0.0378 (8)
H7	0.5872	−0.3388	0.1820	0.045*
C8	0.9329 (10)	−0.2648 (6)	0.25743 (18)	0.0443 (10)
H8A	1.0041	−0.3156	0.2229	0.066*
H8B	0.8063	−0.3400	0.2745	0.066*
H8C	1.0808	−0.2409	0.2862	0.066*
C9	0.8664 (10)	0.0289 (6)	0.26783 (18)	0.0416 (9)
C10	0.7063 (9)	0.1831 (5)	0.24991 (18)	0.0388 (9)
H10	0.5107	0.1563	0.2457	0.047*
C11	0.7983 (9)	0.2508 (5)	0.19144 (16)	0.0396 (9)
H11A	0.7380	0.1753	0.1595	0.048*
H11B	0.7112	0.3580	0.1835	0.048*
C12	0.5656 (8)	0.4037 (6)	0.31560 (16)	0.0379 (8)
C13	0.4928 (10)	0.6097 (6)	0.3865 (2)	0.0477 (11)
H13A	0.3119	0.5643	0.3916	0.057*
H13B	0.4753	0.7055	0.3602	0.057*
C14	0.6244 (14)	0.6577 (9)	0.4441 (2)	0.0688 (17)
C15	0.8449 (18)	0.7581 (12)	0.4483 (4)	0.105 (3)
H15	0.9131	0.8020	0.4139	0.126*
C16	0.970 (3)	0.796 (2)	0.5025 (7)	0.163 (5)

H16	1.1220	0.8664	0.5053	0.195*
C17	0.871 (3)	0.7322 (17)	0.5505 (4)	0.141 (5)
H17	0.9569	0.7613	0.5872	0.169*
C18	0.671 (3)	0.6355 (18)	0.5509 (4)	0.149 (5)
H18	0.6174	0.5882	0.5862	0.179*
C19	0.531 (3)	0.6011 (13)	0.4962 (3)	0.125 (4)
H19	0.3715	0.5381	0.4954	0.150*
C20	−0.3731 (8)	−0.2306 (6)	0.00082 (17)	0.0411 (9)
N1	0.5835 (7)	−0.1082 (5)	0.19964 (14)	0.0360 (7)
N2	0.7956 (8)	−0.1136 (5)	0.24061 (15)	0.0407 (8)
N3	0.7554 (7)	0.2999 (5)	0.29708 (15)	0.0422 (8)
H3A	0.9170	0.3037	0.3146	0.051*
N4	−0.5474 (8)	−0.2307 (6)	−0.03581 (15)	0.0480 (9)
O1	1.0542 (7)	0.0348 (4)	0.30583 (13)	0.0503 (9)
O2	1.0784 (6)	0.2702 (4)	0.19126 (12)	0.0445 (7)
H2A	1.1303	0.3363	0.2176	0.067*
O3	0.6668 (7)	0.4855 (4)	0.36255 (12)	0.0440 (8)
O4	0.3405 (6)	0.4203 (4)	0.29257 (13)	0.0443 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.046 (2)	0.038 (2)	0.0309 (16)	−0.0001 (19)	−0.0025 (14)	−0.0043 (17)
C2	0.048 (2)	0.035 (2)	0.0324 (17)	−0.0014 (19)	−0.0040 (15)	0.0005 (16)
C3	0.044 (2)	0.032 (2)	0.0344 (17)	0.0029 (18)	−0.0044 (15)	−0.0008 (15)
C4	0.043 (2)	0.0313 (19)	0.0324 (16)	0.0012 (18)	−0.0016 (14)	−0.0003 (16)
C5	0.053 (2)	0.031 (2)	0.0333 (18)	−0.0002 (18)	−0.0037 (16)	−0.0020 (15)
C6	0.049 (2)	0.035 (2)	0.0365 (19)	−0.0059 (18)	−0.0001 (16)	−0.0050 (16)
C7	0.044 (2)	0.0329 (19)	0.0360 (17)	−0.0007 (18)	−0.0012 (15)	0.0032 (16)
C8	0.060 (3)	0.040 (2)	0.0316 (17)	0.005 (2)	−0.0073 (17)	0.0056 (16)
C9	0.050 (2)	0.039 (2)	0.0346 (18)	−0.0028 (19)	−0.0080 (16)	−0.0021 (17)
C10	0.039 (2)	0.036 (2)	0.0397 (19)	0.0014 (17)	−0.0100 (16)	−0.0058 (16)
C11	0.052 (2)	0.030 (2)	0.0355 (18)	0.0038 (18)	−0.0102 (16)	−0.0012 (15)
C12	0.043 (2)	0.037 (2)	0.0324 (17)	−0.0061 (18)	−0.0066 (15)	−0.0023 (16)
C13	0.057 (3)	0.044 (3)	0.042 (2)	0.000 (2)	−0.0026 (19)	−0.0129 (19)
C14	0.092 (4)	0.071 (4)	0.042 (2)	0.003 (3)	−0.009 (3)	−0.016 (3)
C15	0.116 (6)	0.087 (6)	0.107 (6)	−0.015 (5)	−0.035 (5)	−0.048 (5)
C16	0.189 (11)	0.144 (11)	0.145 (9)	−0.013 (10)	−0.080 (9)	−0.057 (9)
C17	0.232 (15)	0.110 (9)	0.075 (6)	0.032 (9)	−0.048 (8)	−0.044 (6)
C18	0.242 (16)	0.140 (11)	0.066 (5)	−0.048 (11)	0.006 (7)	−0.020 (6)
C19	0.207 (11)	0.113 (8)	0.054 (4)	0.005 (8)	0.005 (5)	−0.011 (5)
C20	0.046 (2)	0.038 (2)	0.0390 (18)	−0.0037 (19)	−0.0011 (16)	−0.0022 (18)
N1	0.0400 (17)	0.0363 (18)	0.0308 (14)	−0.0027 (15)	−0.0057 (12)	0.0015 (13)
N2	0.050 (2)	0.0362 (19)	0.0343 (15)	0.0043 (16)	−0.0108 (14)	0.0038 (14)
N3	0.0452 (18)	0.042 (2)	0.0372 (16)	−0.0023 (16)	−0.0142 (13)	−0.0077 (14)
N4	0.053 (2)	0.047 (2)	0.0423 (18)	−0.0066 (19)	−0.0120 (15)	−0.0048 (18)
O1	0.058 (2)	0.0464 (19)	0.0429 (16)	0.0028 (16)	−0.0232 (14)	0.0009 (14)
O2	0.0532 (17)	0.0387 (16)	0.0403 (14)	−0.0021 (14)	−0.0072 (12)	−0.0024 (13)

| O3 | 0.0546 (19) | 0.0439 (17) | 0.0321 (13) | −0.0040 (14) | −0.0090 (12) | −0.0074 (12) |
| O4 | 0.0466 (16) | 0.0429 (18) | 0.0421 (15) | −0.0021 (14) | −0.0093 (12) | −0.0093 (13) |

Geometric parameters (Å, º)

C1—C2	1.395 (6)	C11—H11A	0.9900
C1—C6	1.404 (7)	C11—H11B	0.9900
C1—C20	1.445 (5)	C12—O4	1.221 (5)
C2—C3	1.397 (6)	C12—O3	1.340 (5)
C2—H2	0.9500	C12—N3	1.359 (6)
C3—C4	1.399 (6)	C13—O3	1.465 (6)
C3—H3	0.9500	C13—C14	1.492 (7)
C4—C5	1.398 (6)	C13—H13A	0.9900
C4—C7	1.472 (5)	C13—H13B	0.9900
C5—C6	1.391 (6)	C14—C15	1.372 (11)
C5—H5	0.9500	C14—C19	1.386 (11)
C6—H6	0.9500	C15—C16	1.391 (12)
C7—N1	1.276 (6)	C15—H15	0.9500
C7—H7	0.9500	C16—C17	1.34 (2)
C8—N2	1.454 (6)	C16—H16	0.9500
C8—H8A	0.9800	C17—C18	1.274 (17)
C8—H8B	0.9800	C17—H17	0.9500
C8—H8C	0.9800	C18—C19	1.428 (16)
C9—O1	1.242 (5)	C18—H18	0.9500
C9—N2	1.358 (6)	C19—H19	0.9500
C9—C10	1.535 (6)	C20—N4	1.173 (5)
C10—N3	1.453 (5)	N1—N2	1.374 (5)
C10—C11	1.546 (6)	N3—H3A	0.8800
C10—H10	1.0000	O2—H2A	0.8400
C11—O2	1.409 (6)		
C2—C1—C6	120.6 (3)	C10—C11—H11B	109.0
C2—C1—C20	120.3 (4)	H11A—C11—H11B	107.8
C6—C1—C20	119.0 (4)	O4—C12—O3	125.8 (4)
C1—C2—C3	119.7 (4)	O4—C12—N3	125.2 (4)
C1—C2—H2	120.1	O3—C12—N3	109.0 (3)
C3—C2—H2	120.1	O3—C13—C14	106.0 (4)
C2—C3—C4	120.2 (4)	O3—C13—H13A	110.5
C2—C3—H3	119.9	C14—C13—H13A	110.5
C4—C3—H3	119.9	O3—C13—H13B	110.5
C5—C4—C3	119.4 (3)	C14—C13—H13B	110.5
C5—C4—C7	119.5 (4)	H13A—C13—H13B	108.7
C3—C4—C7	121.2 (4)	C15—C14—C19	116.6 (8)
C6—C5—C4	121.2 (4)	C15—C14—C13	121.9 (6)
C6—C5—H5	119.4	C19—C14—C13	121.5 (8)
C4—C5—H5	119.4	C14—C15—C16	120.8 (11)
C5—C6—C1	118.9 (4)	C14—C15—H15	119.6
C5—C6—H6	120.6	C16—C15—H15	119.6

C1—C6—H6	120.6	C17—C16—C15	118.6 (13)
N1—C7—C4	121.3 (4)	C17—C16—H16	120.7
N1—C7—H7	119.3	C15—C16—H16	120.7
C4—C7—H7	119.3	C18—C17—C16	125.1 (10)
N2—C8—H8A	109.5	C18—C17—H17	117.4
N2—C8—H8B	109.5	C16—C17—H17	117.4
H8A—C8—H8B	109.5	C17—C18—C19	117.2 (11)
N2—C8—H8C	109.5	C17—C18—H18	121.4
H8A—C8—H8C	109.5	C19—C18—H18	121.4
H8B—C8—H8C	109.5	C14—C19—C18	121.4 (12)
O1—C9—N2	121.3 (4)	C14—C19—H19	119.3
O1—C9—C10	121.0 (4)	C18—C19—H19	119.3
N2—C9—C10	117.6 (3)	N4—C20—C1	179.2 (4)
N3—C10—C9	106.2 (3)	C7—N1—N2	120.9 (4)
N3—C10—C11	111.4 (4)	C9—N2—N1	117.1 (3)
C9—C10—C11	110.4 (4)	C9—N2—C8	120.1 (3)
N3—C10—H10	109.6	N1—N2—C8	122.7 (3)
C9—C10—H10	109.6	C12—N3—C10	123.6 (3)
C11—C10—H10	109.6	C12—N3—H3A	118.2
O2—C11—C10	113.0 (3)	C10—N3—H3A	118.2
O2—C11—H11A	109.0	C11—O2—H2A	109.5
C10—C11—H11A	109.0	C12—O3—C13	116.3 (4)
O2—C11—H11B	109.0		
C6—C1—C2—C3	0.8 (6)	C14—C15—C16—C17	0 (2)
C20—C1—C2—C3	−178.3 (4)	C15—C16—C17—C18	1 (2)
C1—C2—C3—C4	0.3 (6)	C16—C17—C18—C19	−4 (2)
C2—C3—C4—C5	−0.7 (6)	C15—C14—C19—C18	−4.7 (15)
C2—C3—C4—C7	−179.9 (3)	C13—C14—C19—C18	174.5 (10)
C3—C4—C5—C6	−0.1 (6)	C17—C18—C19—C14	6 (2)
C7—C4—C5—C6	179.1 (3)	C2—C1—C20—N4	94 (37)
C4—C5—C6—C1	1.2 (6)	C6—C1—C20—N4	−85 (37)
C2—C1—C6—C5	−1.6 (6)	C4—C7—N1—N2	−179.7 (3)
C20—C1—C6—C5	177.6 (4)	O1—C9—N2—N1	179.3 (4)
C5—C4—C7—N1	−173.8 (4)	C10—C9—N2—N1	−0.8 (6)
C3—C4—C7—N1	5.4 (6)	O1—C9—N2—C8	2.6 (7)
O1—C9—C10—N3	−19.1 (6)	C10—C9—N2—C8	−177.5 (4)
N2—C9—C10—N3	161.0 (4)	C7—N1—N2—C9	−178.4 (4)
O1—C9—C10—C11	101.8 (5)	C7—N1—N2—C8	−1.8 (6)
N2—C9—C10—C11	−78.1 (5)	O4—C12—N3—C10	−5.8 (7)
N3—C10—C11—O2	66.8 (5)	O3—C12—N3—C10	174.9 (4)
C9—C10—C11—O2	−50.9 (5)	C9—C10—N3—C12	−142.7 (4)
O3—C13—C14—C15	76.1 (8)	C11—C10—N3—C12	97.1 (5)
O3—C13—C14—C19	−103.1 (8)	O4—C12—O3—C13	−2.4 (6)
C19—C14—C15—C16	1.5 (15)	N3—C12—O3—C13	176.9 (4)
C13—C14—C15—C16	−177.6 (10)	C14—C13—O3—C12	168.8 (4)

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of the C14–C19 ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3A⋯O4^i	0.88	2.40	3.091 (6)	135
O2—H2A⋯O4^i	0.84	2.08	2.873 (5)	158
C16—H16⋯$Cg2^{ii}$	0.95	2.78	3.558 (18)	140
C19—H19⋯$Cg2^{iii}$	0.95	2.86	3.598 (13)	135

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

(II) *tert*-Butyl *N*-{(*E*)-1-[2-(4-cyanobenzylidene)-1-methylhydrazinyl]-3-hydroxy-1-oxopropan-2-yl}carbamate

Crystal data

$C_{17}H_{22}N_4O_4$	$F(000) = 368$
$M_r = 346.39$	$D_x = 1.307$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 2232 reflections
$a = 5.348$ (3) Å	$\theta = 2.6–31.2°$
$b = 7.883$ (5) Å	$\mu = 0.10$ mm^{-1}
$c = 20.903$ (14) Å	$T = 100$ K
$\beta = 92.763$ (1)°	Slab, colourless
$V = 880.2$ (10) Å^3	$0.08 \times 0.08 \times 0.02$ mm
$Z = 2$	

Data collection

Rigaku Mercury CCD diffractometer	2143 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.023$
Graphite monochromator	$\theta_{max} = 26.0°$, $\theta_{min} = 2.9°$
ω scans	$h = -6 \rightarrow 5$
3672 measured reflections	$k = -9 \rightarrow 7$
2483 independent reflections	$l = -22 \rightarrow 25$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.057$	H-atom parameters constrained
$wR(F^2) = 0.194$	$w = 1/[\sigma^2(F_o^2) + (0.0993P)^2 + 0.4415P]$
$S = 1.13$	where $P = (F_o^2 + 2F_c^2)/3$
2483 reflections	$(\Delta/\sigma)_{max} < 0.001$
231 parameters	$\Delta\rho_{max} = 0.31$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.35$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: *SHELXL*, Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.027 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1123 (9)	0.5292 (7)	0.3916 (2)	0.0253 (11)
H1	0.1851	0.6345	0.3806	0.030*
C2	−0.0770 (9)	0.5247 (7)	0.4346 (2)	0.0283 (12)
H2	−0.1325	0.6272	0.4532	0.034*
C3	−0.1848 (9)	0.3741 (8)	0.4505 (2)	0.0268 (11)
C4	−0.1071 (10)	0.2210 (7)	0.4233 (2)	0.0273 (12)
H4	−0.1829	0.1170	0.4347	0.033*
C5	0.0802 (9)	0.2224 (7)	0.3799 (2)	0.0260 (12)
H5	0.1300	0.1194	0.3606	0.031*
C6	0.1972 (9)	0.3760 (7)	0.3641 (2)	0.0235 (10)
C7	0.3919 (9)	0.3849 (7)	0.3194 (2)	0.0249 (10)
H7	0.4750	0.4895	0.3127	0.030*
C8	0.7748 (9)	0.4254 (6)	0.2344 (2)	0.0254 (11)
H8A	0.8529	0.4655	0.2750	0.038*
H8B	0.6564	0.5110	0.2174	0.038*
H8C	0.9043	0.4061	0.2036	0.038*
C9	0.6871 (9)	0.1258 (7)	0.2084 (2)	0.0242 (11)
C10	0.5475 (10)	−0.0357 (6)	0.2249 (2)	0.0264 (12)
H10	0.3697	−0.0078	0.2334	0.032*
C11	0.6754 (9)	−0.1158 (7)	0.2847 (2)	0.0279 (11)
H11A	0.6336	−0.0478	0.3226	0.034*
H11B	0.6061	−0.2311	0.2903	0.034*
C12	0.3719 (9)	−0.2554 (7)	0.1527 (2)	0.0234 (11)
C13	0.2467 (9)	−0.4533 (7)	0.0650 (2)	0.0234 (11)
C14	0.3177 (9)	−0.6125 (7)	0.1010 (2)	0.0264 (11)
H14A	0.2701	−0.6018	0.1456	0.040*
H14B	0.4989	−0.6300	0.1001	0.040*
H14C	0.2303	−0.7095	0.0810	0.040*
C15	−0.0334 (9)	−0.4161 (8)	0.0670 (3)	0.0333 (13)
H15A	−0.0711	−0.3082	0.0453	0.050*
H15B	−0.0803	−0.4087	0.1116	0.050*
H15C	−0.1285	−0.5074	0.0453	0.050*
C16	0.3205 (9)	−0.4594 (7)	−0.0040 (2)	0.0278 (12)
H16A	0.2902	−0.3484	−0.0241	0.042*
H16B	0.2205	−0.5458	−0.0272	0.042*
H16C	0.4985	−0.4880	−0.0054	0.042*
C17	−0.3795 (10)	0.3679 (8)	0.4971 (2)	0.0306 (12)
N1	0.4545 (7)	0.2521 (5)	0.28820 (18)	0.0224 (9)
N2	0.6425 (8)	0.2680 (5)	0.24509 (19)	0.0233 (9)
N3	0.5555 (8)	−0.1424 (6)	0.16859 (19)	0.0280 (10)

H3	0.6837	−0.1335	0.1439	0.034*
N4	−0.5229 (9)	0.3672 (7)	0.5357 (2)	0.0356 (11)
O1	0.8318 (6)	0.1316 (5)	0.16515 (16)	0.0292 (9)
O2	0.9367 (7)	−0.1279 (5)	0.28307 (16)	0.0339 (9)
H2A	0.9742	−0.1874	0.2516	0.041*
O3	0.3944 (6)	−0.3085 (5)	0.09164 (16)	0.0256 (8)
O4	0.2146 (6)	−0.3015 (5)	0.18845 (16)	0.0292 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.032 (3)	0.017 (3)	0.027 (2)	−0.001 (2)	0.000 (2)	−0.002 (2)
C2	0.035 (3)	0.027 (3)	0.023 (2)	0.009 (3)	−0.004 (2)	−0.005 (2)
C3	0.031 (2)	0.031 (3)	0.018 (2)	0.003 (3)	0.0011 (18)	−0.002 (2)
C4	0.036 (3)	0.020 (3)	0.026 (3)	−0.006 (2)	0.000 (2)	0.000 (2)
C5	0.030 (2)	0.020 (3)	0.028 (3)	0.005 (2)	0.002 (2)	−0.002 (2)
C6	0.030 (2)	0.021 (3)	0.019 (2)	0.004 (2)	−0.0026 (18)	−0.001 (2)
C7	0.033 (2)	0.016 (2)	0.026 (2)	0.003 (2)	−0.0020 (19)	0.001 (2)
C8	0.029 (3)	0.018 (3)	0.029 (3)	−0.005 (2)	0.000 (2)	0.002 (2)
C9	0.029 (3)	0.021 (3)	0.022 (2)	0.003 (2)	0.0025 (19)	0.000 (2)
C10	0.031 (3)	0.022 (3)	0.027 (3)	−0.003 (2)	0.010 (2)	−0.007 (2)
C11	0.041 (3)	0.018 (3)	0.025 (2)	0.001 (3)	0.012 (2)	−0.002 (2)
C12	0.023 (2)	0.020 (3)	0.028 (3)	−0.001 (2)	0.0047 (19)	−0.002 (2)
C13	0.022 (2)	0.019 (3)	0.029 (2)	−0.005 (2)	−0.0001 (18)	0.001 (2)
C14	0.030 (2)	0.021 (3)	0.029 (2)	−0.004 (2)	0.0031 (19)	−0.003 (2)
C15	0.028 (3)	0.031 (3)	0.040 (3)	−0.004 (3)	−0.004 (2)	0.008 (2)
C16	0.033 (3)	0.025 (3)	0.025 (3)	−0.007 (2)	0.002 (2)	−0.001 (2)
C17	0.038 (3)	0.025 (3)	0.029 (3)	0.003 (3)	0.001 (2)	−0.006 (3)
N1	0.024 (2)	0.022 (2)	0.021 (2)	0.0006 (19)	0.0028 (15)	0.0007 (17)
N2	0.031 (2)	0.015 (2)	0.024 (2)	−0.0043 (19)	0.0019 (17)	−0.0020 (17)
N3	0.031 (2)	0.027 (2)	0.027 (2)	−0.009 (2)	0.0088 (17)	−0.010 (2)
N4	0.041 (3)	0.031 (3)	0.035 (2)	0.003 (3)	0.012 (2)	−0.002 (2)
O1	0.0357 (19)	0.023 (2)	0.0300 (19)	−0.0063 (17)	0.0086 (15)	−0.0027 (16)
O2	0.044 (2)	0.031 (2)	0.0270 (18)	0.002 (2)	0.0030 (15)	−0.0058 (18)
O3	0.0299 (18)	0.0225 (18)	0.0247 (17)	−0.0042 (16)	0.0039 (13)	−0.0062 (15)
O4	0.0305 (18)	0.028 (2)	0.0304 (19)	−0.0073 (18)	0.0109 (15)	−0.0062 (16)

Geometric parameters (Å, °)

C1—C2	1.386 (7)	C11—O2	1.403 (6)
C1—C6	1.422 (7)	C11—H11A	0.9900
C1—H1	0.9500	C11—H11B	0.9900
C2—C3	1.368 (8)	C12—O4	1.208 (5)
C2—H2	0.9500	C12—O3	1.354 (6)
C3—C4	1.405 (8)	C12—N3	1.355 (6)
C3—C17	1.461 (7)	C13—O3	1.481 (6)
C4—C5	1.384 (7)	C13—C14	1.503 (8)
C4—H4	0.9500	C13—C16	1.514 (6)

C5—C6	1.409 (8)	C13—C15	1.529 (7)
C5—H5	0.9500	C14—H14A	0.9800
C6—C7	1.435 (6)	C14—H14B	0.9800
C7—N1	1.286 (6)	C14—H14C	0.9800
C7—H7	0.9500	C15—H15A	0.9800
C8—N2	1.450 (6)	C15—H15B	0.9800
C8—H8A	0.9800	C15—H15C	0.9800
C8—H8B	0.9800	C16—H16A	0.9800
C8—H8C	0.9800	C16—H16B	0.9800
C9—O1	1.219 (6)	C16—H16C	0.9800
C9—N2	1.385 (6)	C17—N4	1.139 (6)
C9—C10	1.524 (7)	N1—N2	1.388 (5)
C10—N3	1.449 (6)	N3—H3	0.8800
C10—C11	1.532 (7)	O2—H2A	0.8400
C10—H10	1.0000		
C2—C1—C6	119.9 (5)	C10—C11—H11B	108.7
C2—C1—H1	120.1	H11A—C11—H11B	107.6
C6—C1—H1	120.1	O4—C12—O3	125.9 (5)
C3—C2—C1	120.6 (5)	O4—C12—N3	124.3 (4)
C3—C2—H2	119.7	O3—C12—N3	109.8 (4)
C1—C2—H2	119.7	O3—C13—C14	109.7 (4)
C2—C3—C4	120.7 (4)	O3—C13—C16	103.0 (4)
C2—C3—C17	120.9 (5)	C14—C13—C16	112.3 (4)
C4—C3—C17	118.4 (5)	O3—C13—C15	110.3 (4)
C5—C4—C3	119.8 (5)	C14—C13—C15	111.7 (4)
C5—C4—H4	120.1	C16—C13—C15	109.4 (4)
C3—C4—H4	120.1	C13—C14—H14A	109.5
C4—C5—C6	120.2 (5)	C13—C14—H14B	109.5
C4—C5—H5	119.9	H14A—C14—H14B	109.5
C6—C5—H5	119.9	C13—C14—H14C	109.5
C5—C6—C1	118.8 (4)	H14A—C14—H14C	109.5
C5—C6—C7	122.6 (5)	H14B—C14—H14C	109.5
C1—C6—C7	118.6 (5)	C13—C15—H15A	109.5
N1—C7—C6	120.4 (5)	C13—C15—H15B	109.5
N1—C7—H7	119.8	H15A—C15—H15B	109.5
C6—C7—H7	119.8	C13—C15—H15C	109.5
N2—C8—H8A	109.5	H15A—C15—H15C	109.5
N2—C8—H8B	109.5	H15B—C15—H15C	109.5
H8A—C8—H8B	109.5	C13—C16—H16A	109.5
N2—C8—H8C	109.5	C13—C16—H16B	109.5
H8A—C8—H8C	109.5	H16A—C16—H16B	109.5
H8B—C8—H8C	109.5	C13—C16—H16C	109.5
O1—C9—N2	120.9 (5)	H16A—C16—H16C	109.5
O1—C9—C10	122.3 (4)	H16B—C16—H16C	109.5
N2—C9—C10	116.8 (4)	N4—C17—C3	176.4 (6)
N3—C10—C9	105.5 (4)	C7—N1—N2	118.0 (4)
N3—C10—C11	113.2 (5)	C9—N2—N1	115.8 (4)

C9—C10—C11	109.0 (4)	C9—N2—C8	120.6 (4)
N3—C10—H10	109.7	N1—N2—C8	123.4 (4)
C9—C10—H10	109.7	C12—N3—C10	122.1 (4)
C11—C10—H10	109.7	C12—N3—H3	119.0
O2—C11—C10	114.4 (4)	C10—N3—H3	119.0
O2—C11—H11A	108.7	C11—O2—H2A	109.5
C10—C11—H11A	108.7	C12—O3—C13	121.5 (4)
O2—C11—H11B	108.7		
C6—C1—C2—C3	−0.5 (7)	C9—C10—C11—O2	−47.4 (6)
C1—C2—C3—C4	−0.5 (7)	C6—C7—N1—N2	179.5 (4)
C1—C2—C3—C17	178.3 (4)	O1—C9—N2—N1	173.2 (4)
C2—C3—C4—C5	0.0 (7)	C10—C9—N2—N1	−6.9 (6)
C17—C3—C4—C5	−178.9 (4)	O1—C9—N2—C8	−2.4 (7)
C3—C4—C5—C6	1.6 (7)	C10—C9—N2—C8	177.5 (4)
C4—C5—C6—C1	−2.5 (7)	C7—N1—N2—C9	−174.2 (4)
C4—C5—C6—C7	−179.9 (4)	C7—N1—N2—C8	1.2 (7)
C2—C1—C6—C5	2.0 (7)	O4—C12—N3—C10	−14.8 (8)
C2—C1—C6—C7	179.4 (4)	O3—C12—N3—C10	165.8 (5)
C5—C6—C7—N1	5.0 (7)	C9—C10—N3—C12	−150.2 (5)
C1—C6—C7—N1	−172.3 (4)	C11—C10—N3—C12	90.7 (6)
O1—C9—C10—N3	−19.4 (7)	O4—C12—O3—C13	−9.9 (8)
N2—C9—C10—N3	160.7 (4)	N3—C12—O3—C13	169.5 (4)
O1—C9—C10—C11	102.5 (5)	C14—C13—O3—C12	−63.4 (5)
N2—C9—C10—C11	−77.5 (5)	C16—C13—O3—C12	176.8 (4)
N3—C10—C11—O2	69.7 (6)	C15—C13—O3—C12	60.1 (6)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3⋯O1	0.88	2.27	2.620 (6)	104
O2—H2A⋯O4[i]	0.84	2.09	2.877 (5)	156
C4—H4⋯N4[ii]	0.95	2.61	3.549 (8)	168

Symmetry codes: (i) $x+1, y, z$; (ii) $−x−1, y−1/2, −z+1$.

(III) *tert*-Butyl *N*-[(*E*)-1-(2-benzylidene-1-methylhydrazinyl)-3-hydroxy-1-oxopropan-2-yl]carbamate

Crystal data

$C_{16}H_{23}N_3O_4$	$F(000) = 688$
$M_r = 321.37$	$D_x = 1.257$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Hall symbol: -P 2ybc	Cell parameters from 3225 reflections
$a = 10.454$ (7) Å	$\theta = 2.0–27.5°$
$b = 10.571$ (7) Å	$\mu = 0.09$ mm^{-1}
$c = 15.664$ (11) Å	$T = 100$ K
$\beta = 101.172$ (12)°	Blade, colourless
$V = 1698$ (2) Å^3	$0.16 \times 0.05 \times 0.01$ mm
$Z = 4$	

Data collection

Rigaku Mercury CCD diffractometer	2716 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.048$
Graphite monochromator	$\theta_{max} = 26.0°$, $\theta_{min} = 2.3°$
ω scans	$h = -11 \rightarrow 12$
8546 measured reflections	$k = -13 \rightarrow 9$
3319 independent reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.104$	
$wR(F^2) = 0.197$	
$S = 1.23$	H atoms treated by a mixture of independent and constrained refinement
3319 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 3.1065P]$
220 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.002$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.44$ e Å^{-3}
	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.7859 (4)	0.4700 (4)	−0.0477 (3)	0.0348 (9)	
H1	0.7784	0.4009	−0.0872	0.042*	
C2	0.8683 (4)	0.5702 (4)	−0.0568 (3)	0.0412 (11)	
H2	0.9170	0.5695	−0.1021	0.049*	
C3	0.8788 (4)	0.6708 (4)	0.0004 (3)	0.0430 (11)	
H3	0.9349	0.7395	−0.0057	0.052*	
C4	0.8078 (4)	0.6721 (4)	0.0669 (3)	0.0386 (10)	
H4	0.8158	0.7415	0.1061	0.046*	
C5	0.7255 (4)	0.5723 (4)	0.0762 (3)	0.0327 (9)	
H5	0.6769	0.5736	0.1215	0.039*	
C6	0.7141 (4)	0.4698 (4)	0.0188 (2)	0.0311 (9)	
C7	0.6264 (4)	0.3627 (4)	0.0243 (2)	0.0296 (9)	
H7	0.6199	0.2956	−0.0166	0.035*	
C8	0.4643 (4)	0.1543 (4)	0.0243 (3)	0.0344 (9)	
H8A	0.4422	0.1880	−0.0350	0.052*	
H8B	0.3956	0.0962	0.0343	0.052*	

H8C	0.5474	0.1087	0.0317	0.052*	
C9	0.4092 (3)	0.2560 (3)	0.1529 (2)	0.0271 (8)	
C10	0.4332 (4)	0.3650 (4)	0.2184 (2)	0.0285 (8)	
H10	0.4347	0.4465	0.1862	0.034*	
C11	0.5617 (4)	0.3500 (4)	0.2828 (3)	0.0362 (10)	
H11A	0.5651	0.2596	0.2995	0.043*	0.198 (7)
H11B	0.5700	0.4247	0.3256	0.043*	0.802 (7)
H11C	0.6349	0.3651	0.2502	0.043*	
C12	0.2675 (4)	0.4729 (4)	0.2834 (2)	0.0281 (8)	
C13	0.0726 (4)	0.5471 (4)	0.3365 (3)	0.0341 (9)	
C14	−0.0564 (4)	0.4811 (5)	0.3367 (3)	0.0520 (13)	
H14A	−0.0411	0.4045	0.3725	0.078*	
H14B	−0.0970	0.4580	0.2770	0.078*	
H14C	−0.1144	0.5381	0.3607	0.078*	
C15	0.1439 (5)	0.5729 (6)	0.4287 (3)	0.0623 (15)	
H15A	0.1576	0.4932	0.4611	0.093*	
H15B	0.0918	0.6303	0.4574	0.093*	
H15C	0.2285	0.6121	0.4273	0.093*	
C16	0.0522 (5)	0.6640 (5)	0.2808 (4)	0.0669 (16)	
H16A	0.1357	0.7076	0.2838	0.100*	
H16B	−0.0093	0.7204	0.3018	0.100*	
H16C	0.0169	0.6401	0.2204	0.100*	
N1	0.5586 (3)	0.3598 (3)	0.08443 (19)	0.0242 (7)	
N2	0.4760 (3)	0.2584 (3)	0.08675 (19)	0.0266 (7)	
N3	0.3211 (3)	0.3649 (3)	0.2618 (2)	0.0314 (8)	
H1N	0.275 (4)	0.295 (4)	0.251 (3)	0.038*	
O1	0.3346 (3)	0.1683 (2)	0.16179 (18)	0.0340 (7)	
O2A	0.5728 (3)	0.2373 (3)	0.3258 (2)	0.0362 (10)*	0.802 (7)
H2A	0.5770	0.1766	0.2917	0.043*	0.802 (7)
O2B	0.5960 (13)	0.4007 (12)	0.3635 (8)	0.029 (4)	0.198 (7)
H2B	0.5934	0.4800	0.3600	0.035*	0.198 (7)
O3	0.1477 (3)	0.4493 (2)	0.29998 (18)	0.0335 (7)	
O4	0.3204 (3)	0.5758 (2)	0.28835 (19)	0.0383 (7)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.034 (2)	0.042 (2)	0.029 (2)	0.0071 (18)	0.0076 (17)	0.0056 (18)
C2	0.032 (2)	0.056 (3)	0.038 (2)	0.001 (2)	0.0133 (18)	0.016 (2)
C3	0.039 (2)	0.040 (3)	0.051 (3)	−0.005 (2)	0.012 (2)	0.012 (2)
C4	0.039 (2)	0.035 (2)	0.043 (2)	−0.0030 (19)	0.0095 (19)	0.0015 (19)
C5	0.033 (2)	0.035 (2)	0.032 (2)	0.0011 (17)	0.0091 (17)	0.0036 (18)
C6	0.027 (2)	0.035 (2)	0.031 (2)	0.0035 (17)	0.0064 (16)	0.0084 (18)
C7	0.034 (2)	0.031 (2)	0.0233 (19)	0.0052 (17)	0.0046 (16)	−0.0030 (16)
C8	0.040 (2)	0.027 (2)	0.036 (2)	−0.0023 (17)	0.0084 (18)	−0.0113 (18)
C9	0.031 (2)	0.0163 (18)	0.034 (2)	0.0006 (15)	0.0040 (16)	−0.0021 (15)
C10	0.035 (2)	0.0245 (19)	0.031 (2)	−0.0056 (16)	0.0168 (17)	−0.0027 (16)
C11	0.036 (2)	0.046 (3)	0.028 (2)	−0.0073 (19)	0.0087 (17)	−0.0123 (19)

C12	0.029 (2)	0.028 (2)	0.0270 (19)	0.0001 (16)	0.0057 (15)	−0.0018 (16)
C13	0.034 (2)	0.031 (2)	0.040 (2)	0.0102 (17)	0.0119 (18)	−0.0056 (18)
C14	0.035 (2)	0.052 (3)	0.074 (3)	0.009 (2)	0.021 (2)	−0.011 (3)
C15	0.043 (3)	0.089 (4)	0.057 (3)	0.016 (3)	0.014 (2)	−0.033 (3)
C16	0.063 (3)	0.052 (3)	0.091 (4)	0.026 (3)	0.026 (3)	0.022 (3)
N1	0.0251 (16)	0.0186 (15)	0.0286 (16)	−0.0003 (12)	0.0046 (13)	−0.0010 (13)
N2	0.0318 (17)	0.0237 (16)	0.0242 (16)	−0.0026 (14)	0.0053 (13)	−0.0036 (13)
N3	0.0373 (19)	0.0188 (16)	0.043 (2)	−0.0010 (14)	0.0211 (16)	−0.0022 (15)
O1	0.0369 (16)	0.0228 (14)	0.0443 (17)	−0.0052 (12)	0.0125 (13)	−0.0011 (12)
O2B	0.043 (8)	0.017 (7)	0.027 (7)	0.006 (6)	0.005 (6)	0.001 (5)
O3	0.0355 (15)	0.0233 (14)	0.0465 (16)	0.0034 (12)	0.0200 (13)	−0.0026 (12)
O4	0.0441 (17)	0.0231 (14)	0.0529 (18)	−0.0055 (13)	0.0226 (14)	−0.0072 (13)

Geometric parameters (Å, º)

C1—C2	1.389 (6)	C11—H11A	0.9900
C1—C6	1.398 (5)	C11—H11B	1.0278
C1—H1	0.9500	C11—H11C	1.0114
C2—C3	1.382 (6)	C12—O4	1.216 (4)
C2—H2	0.9500	C12—N3	1.344 (5)
C3—C4	1.391 (6)	C12—O3	1.350 (4)
C3—H3	0.9500	C13—O3	1.478 (4)
C4—C5	1.386 (5)	C13—C16	1.504 (6)
C4—H4	0.9500	C13—C15	1.516 (6)
C5—C6	1.398 (6)	C13—C14	1.519 (6)
C5—H5	0.9500	C14—H14A	0.9800
C6—C7	1.470 (5)	C14—H14B	0.9800
C7—N1	1.284 (5)	C14—H14C	0.9800
C7—H7	0.9500	C15—H15A	0.9800
C8—N2	1.462 (5)	C15—H15B	0.9800
C8—H8A	0.9800	C15—H15C	0.9800
C8—H8B	0.9800	C16—H16A	0.9800
C8—H8C	0.9800	C16—H16B	0.9800
C9—O1	1.236 (4)	C16—H16C	0.9800
C9—N2	1.358 (5)	N1—N2	1.381 (4)
C9—C10	1.531 (5)	N3—H1N	0.88 (4)
C10—N3	1.465 (5)	O2A—H11A	0.4685
C10—C11	1.523 (5)	O2A—H2A	0.8421
C10—H10	1.0000	O2B—H11B	0.6548
C11—O2B	1.356 (13)	O2B—H2B	0.8400
C11—O2A	1.363 (5)		
C2—C1—C6	120.7 (4)	O2B—C11—H11C	108.6
C2—C1—H1	119.6	O2A—C11—H11C	112.7
C6—C1—H1	119.6	C10—C11—H11C	107.8
C3—C2—C1	119.5 (4)	H11A—C11—H11C	107.0
C3—C2—H2	120.2	H11B—C11—H11C	103.4
C1—C2—H2	120.2	O4—C12—N3	124.7 (3)

C2—C3—C4	120.4 (4)	O4—C12—O3	125.4 (3)
C2—C3—H3	119.8	N3—C12—O3	109.8 (3)
C4—C3—H3	119.8	O3—C13—C16	112.1 (3)
C5—C4—C3	120.2 (4)	O3—C13—C15	107.2 (3)
C5—C4—H4	119.9	C16—C13—C15	113.1 (4)
C3—C4—H4	119.9	O3—C13—C14	102.6 (3)
C4—C5—C6	120.0 (4)	C16—C13—C14	110.6 (4)
C4—C5—H5	120.0	C15—C13—C14	110.7 (4)
C6—C5—H5	120.0	C13—C14—H14A	109.5
C1—C6—C5	119.1 (4)	C13—C14—H14B	109.5
C1—C6—C7	118.4 (4)	H14A—C14—H14B	109.5
C5—C6—C7	122.4 (3)	C13—C14—H14C	109.5
N1—C7—C6	120.1 (3)	H14A—C14—H14C	109.5
N1—C7—H7	120.0	H14B—C14—H14C	109.5
C6—C7—H7	120.0	C13—C15—H15A	109.5
N2—C8—H8A	109.5	C13—C15—H15B	109.5
N2—C8—H8B	109.5	H15A—C15—H15B	109.5
H8A—C8—H8B	109.5	C13—C15—H15C	109.5
N2—C8—H8C	109.5	H15A—C15—H15C	109.5
H8A—C8—H8C	109.5	H15B—C15—H15C	109.5
H8B—C8—H8C	109.5	C13—C16—H16A	109.5
O1—C9—N2	121.9 (3)	C13—C16—H16B	109.5
O1—C9—C10	121.0 (3)	H16A—C16—H16B	109.5
N2—C9—C10	117.1 (3)	C13—C16—H16C	109.5
N3—C10—C11	112.0 (3)	H16A—C16—H16C	109.5
N3—C10—C9	105.5 (3)	H16B—C16—H16C	109.5
C11—C10—C9	112.0 (3)	C7—N1—N2	118.3 (3)
N3—C10—H10	109.1	C9—N2—N1	116.8 (3)
C11—C10—H10	109.1	C9—N2—C8	120.5 (3)
C9—C10—H10	109.1	N1—N2—C8	122.5 (3)
O2B—C11—O2A	84.4 (6)	C12—N3—C10	121.8 (3)
O2B—C11—C10	128.1 (6)	C12—N3—H1N	121 (3)
O2A—C11—C10	113.4 (3)	C10—N3—H1N	112 (3)
O2B—C11—H11A	98.4	C11—O2A—H11A	30.8
O2A—C11—H11A	14.0	C11—O2A—H2A	111.3
C10—C11—H11A	104.9	H11A—O2A—H2A	81.1
O2B—C11—H11B	27.8	C11—O2B—H11B	47.0
O2A—C11—H11B	111.2	C11—O2B—H2B	109.4
C10—C11—H11B	107.7	H11B—O2B—H2B	63.3
H11A—C11—H11B	125.2	C12—O3—C13	121.8 (3)
C6—C1—C2—C3	−0.2 (6)	C9—C10—C11—O2A	−54.9 (4)
C1—C2—C3—C4	0.1 (6)	C6—C7—N1—N2	179.1 (3)
C2—C3—C4—C5	−0.2 (7)	O1—C9—N2—N1	−178.6 (3)
C3—C4—C5—C6	0.2 (6)	C10—C9—N2—N1	−0.5 (5)
C2—C1—C6—C5	0.3 (6)	O1—C9—N2—C8	−1.7 (5)
C2—C1—C6—C7	178.8 (4)	C10—C9—N2—C8	176.5 (3)
C4—C5—C6—C1	−0.3 (6)	C7—N1—N2—C9	177.7 (3)

C4—C5—C6—C7	−178.7 (4)	C7—N1—N2—C8	0.8 (5)
C1—C6—C7—N1	−179.7 (4)	O4—C12—N3—C10	−17.6 (6)
C5—C6—C7—N1	−1.3 (6)	O3—C12—N3—C10	163.4 (3)
O1—C9—C10—N3	−21.4 (5)	C11—C10—N3—C12	95.9 (4)
N2—C9—C10—N3	160.5 (3)	C9—C10—N3—C12	−141.9 (4)
O1—C9—C10—C11	100.8 (4)	O4—C12—O3—C13	−7.2 (6)
N2—C9—C10—C11	−77.4 (4)	N3—C12—O3—C13	171.8 (3)
N3—C10—C11—O2B	−38.4 (9)	C16—C13—O3—C12	57.0 (5)
C9—C10—C11—O2B	−156.7 (8)	C15—C13—O3—C12	−67.7 (5)
N3—C10—C11—O2A	63.5 (4)	C14—C13—O3—C12	175.7 (3)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H1N⋯O1	0.88 (4)	2.11 (4)	2.623 (4)	116 (3)
O2A—H2A⋯O4[i]	0.84	2.09	2.852 (4)	150
O2B—H2B⋯O1[ii]	0.84	2.18	2.966 (13)	156
C7—H7⋯O2A[iii]	0.95	2.45	3.229 (5)	140

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