



Synthesis and crystal structure of 2,2,2-trichloroethyl *N*-{4-[6-(1-hydroxyethyl)-1,2,4,5-tetrazin-3-yl]benzyl}carbamate

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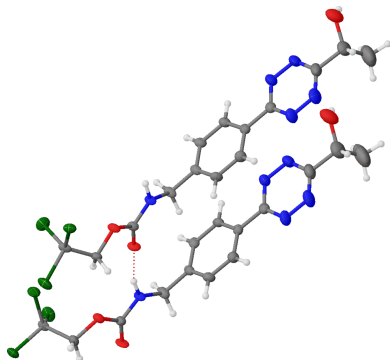
Keywords: crystal structure; 1,2,4,5-tetrazine; carbamate.**CCDC reference:** 2417815**Supporting information:** this article has supporting information at journals.iucr.org/e

An orthogonally addressable 3,6-disubstituted 1,2,4,5-tetrazine, namely 2,2,2-trichloroethyl *N*-{4-[6-(1-hydroxyethyl)-1,2,4,5-tetrazin-3-yl]benzyl}carbamate (C₁₄H₁₄Cl₃N₅O₃), was synthesized and characterized by single-crystal X-ray diffraction. The tetrazine comprises a free hydroxyl and a 2,2,2-trichloroethoxycarbonyl protected amino group, which gives rise to hydrogen-bonding interactions each making the tetrazine highly linked in the solid state. The carbamate moieties form intermolecular hydrogen bonds, stacking the tetrazine molecules above each other, while lateral hydrogen bonds are formed between a tetrazine N atom and a hydroxyl group, the latter interaction being a scarcely explored structural feature of 1,2,4,5-tetrazines.

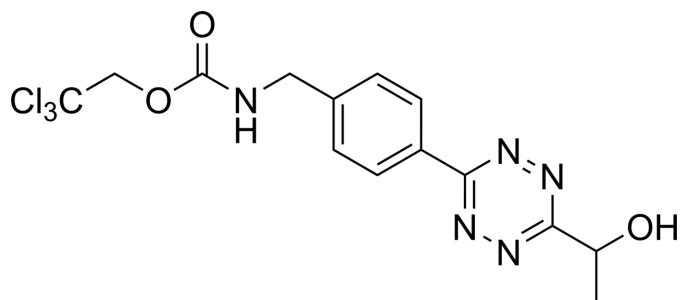
1. Chemical context

The synthesis and structural elucidation of 1,2,4,5-tetrazines goes back to the early reports of Adolf Pinner (Pinner, 1893). Nowadays, over 130 years later, 1,2,4,5-tetrazines (herein further abbreviated as tetrazines) experience their renaissance and have emerged as versatile building blocks in organic and inorganic synthesis, not least because of their distinctive reactivity and bioorthogonal applicability (Zhao *et al.*, 2022). Current research with tetrazines focuses in particular on their extraordinarily fast (click) reaction with activated alkenes and alkynes by an inverse electron-demand Diels–Alder reaction (IEDDA; Mayer & Lang, 2017), thereby spanning second order rate constants of up to 10⁶ M⁻¹ s⁻¹ (Oliveira *et al.*, 2017). This unique and selective reactivity makes the tetrazine ligation applicable *in vivo*, as demonstrated by the early and seminal work of Bertozzi (Agarwal *et al.*, 2015), being encouragingly awarded with the Nobel Prize in Chemistry 2022 for her contributions to click chemistry and bioorthogonal chemistry. In addition to using tetrazines for ligation to biomolecules, they have also been studied *in vivo* as molecular turn-on probes that release drugs selectively into the cellular environment when IEDDA is triggered (van Onzen *et al.*, 2020; Davies *et al.*, 2019; Rossin *et al.*, 2016, 2018). Moreover, tetrazines emerged as useful structural motifs embedded in fluorescent probes (Loredó *et al.*, 2020), metal–organic frameworks (Jiang *et al.*, 2024), metal ligands (Lemes *et al.*, 2018), redox mediators (Beagan *et al.*, 2021), and supramolecular structures (Guo *et al.*, 2020; Roberts *et al.*, 2015).

For many of these applications, tetrazines functionalized in the 3- and 6-position are needed, without compromising high click reaction rates. Herein we disclose the synthesis and characterization of a 3-aryl-6-alkyl-substituted tetrazine, **1**,



with free hydroxyl and 2,2,2-trichloroethoxycarbonyl (Troc) protected amino group.



2. Structural commentary

Tetrazine **1** was obtained starting from the corresponding *N*-tert-butyloxycarbonyl (Boc) and *O*-tetrahydropyranyl (THP) protected tetrazine (van Onzen *et al.*, 2020) through, firstly, acidolysis of both Boc and THP protecting groups and, secondly, *N*-terminal introduction of the Troc group in 61% yield over two steps.

The title compound **1** crystallized as a pseudo-merohedral twin in the triclinic space group $P\bar{1}$ with four units of **1** in the unit cell and the asymmetric unit (ASU) consisting of a hydrogen-bonded dimer of **1** (Fig. 1*a*). Hydroxyl groups (O3 and O6) were disordered in ratios of 84:16 and 78:22, respectively. The phenylene unit shows similar bond lengths for all C–C bonds [1.381 (7)–1.399 (8) Å], a trend that is also

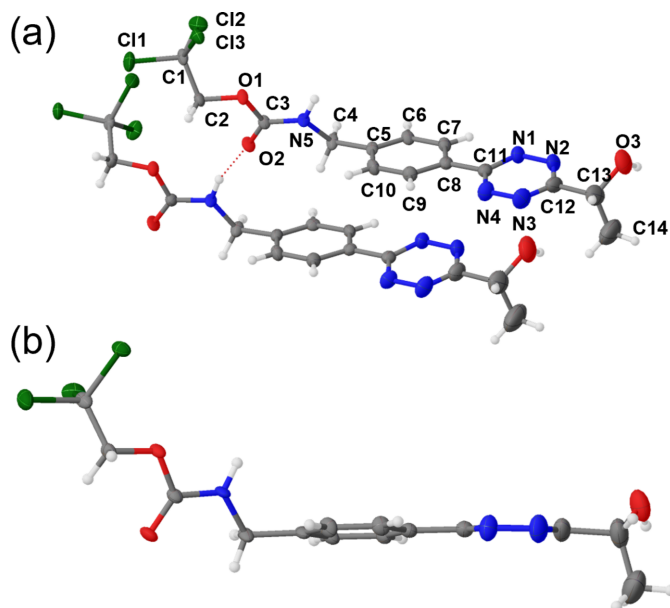


Figure 1

(*a*) Asymmetric unit (ASU) of compound **1** with the atom labelling. Displacement ellipsoids are represented with 50% probability ellipsoids. Only the major occupied hydroxyl group (O3) is depicted. Only one molecule of **1** in the ASU is labelled, and its corresponding lengths and angles are discussed below as they match those described for the second molecule of **1** in the ASU within a 3σ margin of error. (*b*) Side view along the biaryl moiety of **1**, where the normal vector of the plane spanned by the tetrazine core is aligned with the drawing plane.

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O3-H3\cdots N9^i$	0.84	2.64	3.271 (10)	133
$O3B-H3B\cdots O6B^{ii}$	0.84	2.46	2.63 (4)	92
$N5-H5\cdots O5^{iii}$	0.88 (5)	1.98 (5)	2.861 (6)	175 (6)
$O6-H6A\cdots N4^{iv}$	0.84	2.74	3.394 (11)	136
$N10-H10A\cdots O2$	0.87 (5)	2.00 (6)	2.844 (6)	163 (6)

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

observed for all C–N and N–N bonds of the tetrazine unit [1.322 (7)–1.353 (8) Å], indicating the aromatic character of both. The observed bond angles are in line with values reported for structurally similar 3-aryl-6-alkyl-substituted tetrazines (Hu & Xu, 2008; Xu & Hu, 2007*a,b*, 2006). The two rings are nearly coplanar (Fig. 1*b*), as indicated by twist angles between 6.34 (19) and 9.17 (19)° of the two molecules in the ASU, respectively. The carbamate moiety is *s-trans* configured (Fausto *et al.*, 1989).

3. Supramolecular features

In the supramolecular assembly, molecules of **1** stack above each other, directed by the hydrogen-bonding interactions (Table 1) between carbamate protons and carbonyl O atoms of

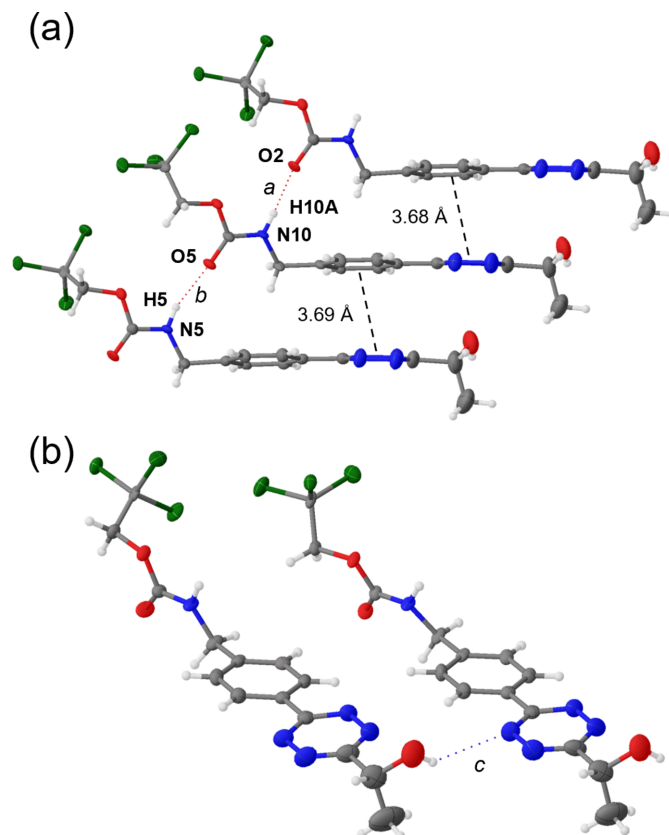


Figure 2

(*a*) Hydrogen-bonded molecules of **1** stacked above each other with calculated distances between phenyl and tetrazine ring centroids. (*b*) Lateral hydrogen bonds involving a tetrazine N atom. Displacement ellipsoid representation with 50% probability ellipsoids.

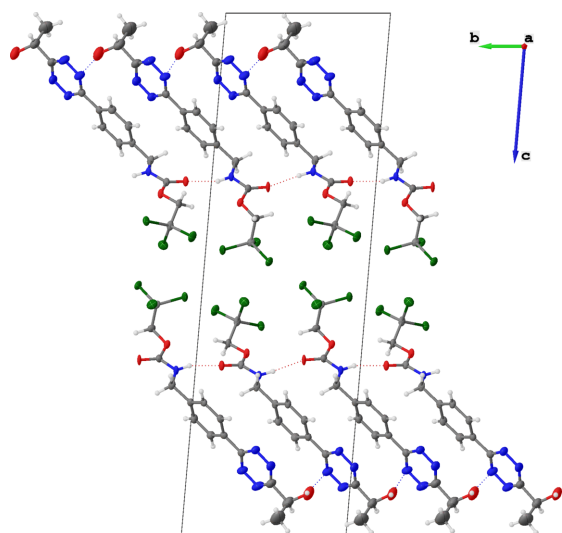


Figure 3
The three-dimensional molecular packing of compound **1** along the crystallographic *a* axis with highlighted unit cell.

the two independent molecules of **1** in the ASU (Fig. 2*a*). Donor–acceptor distances are between 2.844 (6) and 2.861 (6) Å, both with nearly linear arrangements of N, H and O [$\text{N}–\text{H}\cdots\text{O} = 163$ (6)– 175 (6) $^\circ$]. The two aromatic rings are stacked above each other but slightly slipped, with calculated distances between the phenyl/phenyl ring centroids and tetrazine/tetrazine ring centroids of 4.781 (3) Å [slippage between 3.272 (8) and 3.577 (8) Å] and 5.018 (3) Å [slippage between 3.244 (10) and 3.536 (10) Å], respectively, making π – π interactions unlikely. However, the calculated distance between centroids of a tetrazine and a phenyl ring are between 3.677 (3) and 3.689 (3) Å [with a slippage between 1.408 (10) and 1.496 (10) Å], which could indicate weak π – π stacking, also being favored by an increased dipole moment between the phenyl and tetrazine core (Huber *et al.*, 2014).

Additional weak intermolecular hydrogen bonds occur between the hydroxyl proton and an N atom of the tetrazine ring (Fig. 2*b*). The involved atoms are aligned in a kinked geometry [$\text{O}–\text{H}\cdots\text{N} = 133$ – 136°] with $\text{N}\cdots\text{H}$ distances between 2.64 and 2.74 Å, leading to a hydrogen-bonded network (Fig. 3). Tetrazine N atoms involved in intermolecular hydrogen bonds have only been described for few and mostly symmetrical tetrazines such as 3,6-diaminotetrazine ($\text{N}\cdots\text{H} = 2.16$ – 2.20 Å; Krieger *et al.*, 1987), 3,6-dihydrazinotetrazine ($\text{N}\cdots\text{H} = 2.12$ – 2.45 Å; Klapötke *et al.*, 2013), tri(tetrazin-3-yl)-amine ($\text{N}\cdots\text{H} = 2.51$ – 2.73 Å; Liu *et al.*, 2019), 4,4'-(diazene-1,2-diyl)bis(*N*-(tetrazin-3-yl)-1,2,5-oxadiazol-3-amine ($\text{N}\cdots\text{H} = 2.24$ Å; Liu *et al.*, 2019), and 3-amino-6-(3,5-diamino-1,2,4-triazol-1-yl)-tetrazine dihydrate ($\text{N}\cdots\text{H} = 2.13$ Å; Klapötke *et al.*, 2013).

4. Database survey

Searching in the Cambridge Structural Database (CSD version 5.45, June 2024; Groom *et al.*, 2016) using ConQuest (version 2024.1.0), the herein discussed tetrazine **1** was not

found. A search using the molecular formula did not yield a result. In addition, at the time of submission, there were no related structures with a 1-hydroxyethyl-1-yl substituent at the tetrazine ring and an aminomethyl substituent at the phenyl ring found. Seven reports for 3-aryl-6-alkyl-1,2,4,5-tetrazines were found, for example including CICPOU (Hu & Xu, 2008), VIDMEB (Xu & Hu, 2007*a*), REWDUT (Xu & Hu, 2007*b*) and YESCEF (Xu & Hu, 2006).

5. Synthesis and crystallization

5.1. Materials and methods

Solvents and starting materials were used without further purification, unless noted otherwise. The solvents used for extraction and chromatography were of technical grade and were distilled prior to use. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (Merck, F254) using UV light (254 nm) for visualization. *tert*-Butyl [4-(6-{1-[(tetrahydropyran-2-yl)oxy]ethyl}-1,2,4,5-tetrazin-3-yl)benzyl] carbamate was used as starting material and synthesized following the literature procedure (van Onzen *et al.*, 2020), however, omitting the THP deprotection.

5.2. Analytical devices

Nuclear magnetic resonance (NMR) spectra were recorded on an Avance 500 spectrometer (Bruker) at 298 K using the residual protonated solvent signal [$\delta(^1\text{H}$ of CHCl_3) = 7.26 ppm, $\delta(^{13}\text{C}$ of CDCl_3) = 77.36 ppm] (Fulmer *et al.*, 2010) as internal standard. High-resolution mass spectrometry measurements (HR-MS) were performed on a quadrupole ion-mobility time-of-flight mass spectrometer Synapt G2Si (Waters) in resolution mode, interfaced to a nano-electrospray ionization (ESI) source. Determination of exact masses were performed using centroided data.

5.3. Synthesis of compound **1**

tert-Butyl [4-(6-{1-[(tetrahydropyran-2-yl)oxy]ethyl}-1,2,4,5-tetrazin-3-yl)benzyl] carbamate (357 mg, 859 μmol) was dissolved in a solution of HCl in 1,4-dioxane (4 *M*, 21.5 mL). After stirring at 273 K for an hour, analysis by TLC (pentane/ Et_2O , 3:2, *v/v*, $R_f = 0.00$) indicated complete cleavage of the Boc and THP protecting groups. The pink solution was evaporated under reduced pressure at 298 K. The residual pink solid was taken up in H_2O (30 mL) and Et_2O (30 mL), the layers were separated, and the aqueous layer was washed with Et_2O (3 \times 30 mL). The aqueous layer was freeze-dried to yield a voluminous pink solid, which was suspended in CHCl_3 (30 mL) and the solution was cooled to 273 K. $i\text{Pr}_2\text{NET}$ (937 μL , 5.28 mmol) was added dropwise at 273 K, while the red suspension was becoming a solution. 2,2,2-Trichloroethyl chloroformate (148 μL , 1.08 mmol) was added and the red solution was stirred at 273 K for 85 minutes. H_2O (50 mL) and CHCl_3 (30 mL) were added and the layers were separated. The organic layer was washed with an aqueous solution of NaHCO_3 (10 wt%, 50 mL), an aqueous solution of KHSO_4 (5 wt%, 50 mL) and brine (50 mL), dried over Na_2SO_4 ,

filtered, and evaporated to yield a dark-red oil. Purification by column chromatography (diameter = 3.5 cm, length = 30 cm) using CH₂Cl₂/MeOH (95:5, v/v) to yield compound **1** (211 mg, 520 μmol, 61%) as a pink solid. *R*_f (CH₂Cl₂/MeOH, 95:5, v/v) = 0.38. ¹H NMR (500 MHz, CDCl₃, rotamers were observed in the molar ratio of 9:1) δ [ppm]: 8.59 (*m*, 2H, C^{aryl}H *ortho* to tetrazine), 7.54 (*m*, 2H, C^{aryl}H *ortho* to CH₂), 5.55–5.44 (*m*, 1.9H, CHCH₃ and NH, major rotamer), 5.32 (*m*, 0.1H, NH, minor rotamer), 4.79 (*s*, 2H, CH₂CCl₃), 4.56 (*d*, ³*J* = 6.2 Hz, 2H, CH₂NH), 3.40 (*d*, ³*J* = 4.4 Hz, 1H, OH), 1.82 (*d*, ³*J* = 6.7 Hz, 3H, CH₃). ¹³C{¹H}NMR (125 MHz {500 MHz}, CDCl₃) δ [ppm]: 170.4 (C^{aryl}CHCH₃), 165.0 (C^{aryl}=N–N=C^{aryl}CHCH₃), 154.9 (C=O), 143.3 (C^{aryl}CH₂), 131.0 (C^{aryl} attached to tetrazine), 128.8 (C^{aryl} *ortho* to tetrazine), 128.4 (C^{aryl} *ortho* to CH₂), 95.6 (CCl₃), 74.9 (CH₂CCl₃), 68.7 (CHCH₃), 45.1 (C^{aryl}CH₂), 22.9 (CH₃). HR-MS (ESI, negative): *m/z* calculated for [C₁₄H₁₄Cl₃N₅O₃+Cl][−]: 439.9856; found: 439.9852.

Compound **1** was crystallized by diffusion of *n*-pentane into a concentrated solution of **1** in dichloromethane at room temperature.

6. Refinement

The crystal studied was a pseudo-merohedral twin, component 2 rotated by 180.0° around [0.00 – 0.00 1.00] (reciprocal) or [−0.22 – 0.25 0.94] (direct), in a ratio 88:12. The two hydroxyl groups (O3 and O6) were disordered in ratios of 84:16 and 78:22, respectively; suitable restraints were applied. Hydrogen atoms were refined using a riding model except the fully occupied donor hydrogen atoms H5 and H10A, which were refined isotropically. Crystal data, data collection and structure refinement details are summarized in Table 2.

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Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₁₄ Cl ₃ N ₅ O ₃
<i>M</i> _r	406.65
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.68120 (9), 9.79735 (16), 30.9679 (7)
α , β , γ (°)	84.8340 (16), 86.9814 (16), 83.8568 (14)
<i>V</i> (Å ³)	1705.22 (5)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ^{−1})	5.11
Crystal size (mm)	0.23 × 0.14 × 0.01
Data collection	
Diffractometer	SuperNova, Dual, Cu at home/ near, Atlas
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2022)
<i>T</i> _{min} , <i>T</i> _{max}	0.465, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections (<i>sin</i> θ / λ) _{max} (Å ^{−1})	7450, 7450, 7177 0.630
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.069, 0.206, 1.05
No. of reflections	7450
No. of parameters	486
No. of restraints	19
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{−3})	0.77, −0.91

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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Computing details

2,2,2-Trichloroethyl *N*-{4-[6-(1-hydroxyethyl)-1,2,4,5-tetrazin-3-yl]benzyl}carbamate

Crystal data

$C_{14}H_{14}Cl_3N_5O_3$

$M_r = 406.65$

Triclinic, $P\bar{1}$

$a = 5.68120$ (9) Å

$b = 9.79735$ (16) Å

$c = 30.9679$ (7) Å

$\alpha = 84.8340$ (16)°

$\beta = 86.9814$ (16)°

$\gamma = 83.8568$ (14)°

$V = 1705.22$ (5) Å³

$Z = 4$

$F(000) = 832$

$D_x = 1.584$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 17243 reflections

$\theta = 4.3$ – 76.3 °

$\mu = 5.11$ mm⁻¹

$T = 100$ K

Plate, clear red

$0.23 \times 0.14 \times 0.01$ mm

Data collection

SuperNova, Dual, Cu at home/near, Atlas diffractometer

Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 5.3114 pixels mm⁻¹

ω scans

Absorption correction: gaussian

(CrysAlisPro; Rigaku OD, 2022)

$T_{\min} = 0.465$, $T_{\max} = 1.000$

7450 measured reflections

7450 independent reflections

7177 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 76.4$ °, $\theta_{\min} = 4.3$ °

$h = -7 \rightarrow 7$

$k = -12 \rightarrow 12$

$l = -38 \rightarrow 38$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.069$

$wR(F^2) = 0.206$

$S = 1.05$

7450 reflections

486 parameters

19 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1045P)^2 + 9.5963P]$

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

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.77$ e Å⁻³

$\Delta\rho_{\min} = -0.90$ e Å⁻³

Special details

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

Refinement. Crystal was a pseudo-merohedral twin, component 2 rotated by 180.0 deg. around [0.00 -0.00 1.00] (reciprocal) or [-0.22 -0.25 0.94] (direct, ratio 88:12. Disorder of two hydroxyl groups (O3 and O6), suitable restraints were applied.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C11	1.1322 (2)	0.08824 (14)	0.42925 (5)	0.0329 (3)	
C12	0.6950 (2)	0.26123 (16)	0.44550 (5)	0.0321 (3)	
C13	1.0931 (2)	0.37599 (12)	0.39919 (4)	0.0234 (3)	
O1	0.7048 (6)	0.3022 (4)	0.34668 (12)	0.0211 (7)	
O2	0.4640 (7)	0.1570 (4)	0.32311 (13)	0.0251 (8)	
O3	-0.3128 (14)	1.2598 (7)	0.0771 (2)	0.058 (2)	0.837 (12)
H3	-0.457723	1.253027	0.074885	0.087*	0.837 (12)
O3B	0.041 (5)	1.181 (3)	0.0326 (10)	0.057 (2)	0.163 (12)
H3B	0.062683	1.132429	0.011423	0.085*	0.163 (12)
N1	-0.2060 (10)	0.9150 (5)	0.15838 (16)	0.0342 (11)	
N2	-0.2588 (12)	1.0152 (6)	0.12785 (17)	0.0410 (13)	
N3	0.1015 (12)	0.9577 (7)	0.08992 (18)	0.0465 (15)	
N4	0.1566 (10)	0.8561 (6)	0.11993 (17)	0.0386 (12)	
N5	0.4121 (8)	0.3882 (4)	0.30433 (14)	0.0200 (8)	
H5	0.425 (11)	0.471 (6)	0.3121 (19)	0.021 (15)*	
C1	0.9349 (9)	0.2284 (5)	0.40819 (18)	0.0222 (10)	
C2	0.8490 (9)	0.1865 (5)	0.36602 (17)	0.0210 (10)	
H2A	0.985741	0.160333	0.346223	0.025*	
H2B	0.755748	0.106562	0.371964	0.025*	
C3	0.5192 (9)	0.2743 (5)	0.32447 (16)	0.0191 (9)	
C4	0.1921 (9)	0.3815 (5)	0.28271 (18)	0.0228 (10)	
H4A	0.058991	0.380919	0.304661	0.027*	
H4B	0.202155	0.294306	0.268512	0.027*	
C5	0.1427 (9)	0.5008 (5)	0.24926 (17)	0.0204 (10)	
C6	-0.0741 (9)	0.5793 (5)	0.24949 (17)	0.0220 (10)	
H6	-0.191793	0.558846	0.271351	0.026*	
C7	-0.1219 (10)	0.6876 (5)	0.21823 (17)	0.0233 (10)	
H7	-0.271988	0.740636	0.218868	0.028*	
C8	0.0472 (10)	0.7192 (5)	0.18602 (16)	0.0224 (10)	
C9	0.2680 (10)	0.6410 (6)	0.18550 (18)	0.0265 (11)	
H9	0.386199	0.662407	0.163834	0.032*	
C10	0.3137 (9)	0.5320 (6)	0.21675 (18)	0.0255 (11)	
H10	0.462872	0.477978	0.216052	0.031*	
C11	-0.0040 (10)	0.8342 (6)	0.15300 (17)	0.0252 (11)	
C12	-0.1062 (16)	1.0318 (7)	0.0945 (2)	0.0441 (17)	
C13	-0.1735 (18)	1.1430 (8)	0.0587 (2)	0.056 (2)	

H13	-0.026605	1.174380	0.043490	0.068*	0.837 (12)
H13A	-0.262563	1.225676	0.070826	0.068*	0.163 (12)
C14	-0.315 (3)	1.0854 (13)	0.0276 (4)	0.095 (4)	
H14A	-0.466918	1.064440	0.041722	0.143*	
H14B	-0.228721	1.000804	0.017905	0.143*	
H14C	-0.343324	1.152675	0.002581	0.143*	
C14	0.3166 (2)	-0.29716 (16)	0.44065 (5)	0.0315 (3)	
C15	0.7664 (2)	-0.39206 (13)	0.47735 (4)	0.0249 (3)	
C16	0.6449 (3)	-0.10273 (13)	0.45496 (4)	0.0301 (3)	
O4	0.6305 (6)	-0.1854 (4)	0.36372 (12)	0.0223 (7)	
O5	0.4424 (8)	-0.3461 (4)	0.33389 (14)	0.0329 (10)	
O6	-0.2967 (16)	0.7521 (8)	0.0779 (3)	0.066 (3)	0.781 (12)
H6A	-0.441892	0.742144	0.078460	0.100*	0.781 (12)
O6B	0.066 (4)	0.669 (3)	0.0397 (8)	0.065 (3)	0.219 (12)
H6B	0.073883	0.650586	0.013651	0.097*	0.219 (12)
N6	-0.1979 (10)	0.4068 (6)	0.16096 (16)	0.0353 (12)	
N7	-0.2464 (11)	0.5074 (6)	0.13041 (18)	0.0408 (13)	
N8	0.1101 (12)	0.4390 (7)	0.09173 (18)	0.0471 (15)	
N9	0.1614 (10)	0.3370 (6)	0.12202 (16)	0.0379 (12)	
N10	0.3659 (8)	-0.1176 (4)	0.31429 (15)	0.0230 (9)	
H10A	0.396 (12)	-0.039 (6)	0.323 (2)	0.024 (16)*	
C15	0.6236 (8)	-0.2704 (5)	0.43975 (16)	0.0193 (9)	
C16	0.7363 (10)	-0.2879 (6)	0.39447 (16)	0.0246 (11)	
H16A	0.908502	-0.280039	0.394745	0.030*	
H16B	0.714738	-0.380646	0.385943	0.030*	
C17	0.4739 (10)	-0.2264 (5)	0.33665 (16)	0.0226 (10)	
C18	0.1770 (10)	-0.1350 (6)	0.28555 (18)	0.0263 (11)	
H18A	0.028851	-0.147025	0.303129	0.032*	
H18B	0.220077	-0.219402	0.270328	0.032*	
C19	0.1346 (10)	-0.0128 (5)	0.25238 (16)	0.0228 (10)	
C20	-0.0829 (9)	0.0671 (5)	0.25217 (16)	0.0215 (10)	
H20	-0.203089	0.046435	0.273515	0.026*	
C21	-0.1259 (9)	0.1770 (5)	0.22099 (17)	0.0230 (10)	
H21	-0.274288	0.231891	0.221342	0.028*	
C22	0.0482 (10)	0.2067 (5)	0.18928 (16)	0.0219 (10)	
C23	0.2663 (11)	0.1270 (6)	0.18944 (18)	0.0277 (11)	
H23	0.386184	0.146932	0.167935	0.033*	
C24	0.3089 (10)	0.0183 (6)	0.22100 (18)	0.0266 (11)	
H24	0.458556	-0.035162	0.221115	0.032*	
C25	0.0020 (10)	0.3216 (6)	0.15551 (17)	0.0258 (11)	
C26	-0.0929 (15)	0.5181 (8)	0.0967 (2)	0.0458 (17)	
C27	-0.1601 (19)	0.6313 (9)	0.0606 (3)	0.064 (2)	
H27	-0.013816	0.659602	0.044318	0.077*	0.781 (12)
H27A	-0.246526	0.713110	0.073622	0.077*	0.219 (12)
C28	-0.316 (3)	0.5772 (14)	0.0307 (4)	0.111 (5)	
H28A	-0.239850	0.489798	0.021050	0.167*	
H28B	-0.342077	0.643866	0.005394	0.167*	
H28C	-0.467882	0.562106	0.045729	0.167*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0285 (7)	0.0247 (6)	0.0446 (7)	-0.0008 (5)	-0.0148 (6)	0.0072 (5)
Cl2	0.0234 (6)	0.0390 (8)	0.0352 (7)	-0.0087 (5)	0.0066 (5)	-0.0073 (6)
Cl3	0.0175 (5)	0.0184 (5)	0.0351 (6)	-0.0027 (4)	-0.0045 (4)	-0.0048 (5)
O1	0.0167 (16)	0.0132 (16)	0.0344 (19)	-0.0039 (13)	-0.0087 (14)	-0.0001 (14)
O2	0.0271 (19)	0.0122 (17)	0.037 (2)	-0.0049 (14)	-0.0076 (15)	-0.0027 (15)
O3	0.069 (5)	0.034 (3)	0.065 (4)	0.007 (3)	-0.002 (4)	0.012 (3)
O3B	0.092 (7)	0.035 (4)	0.040 (4)	0.002 (4)	-0.001 (4)	0.009 (4)
N1	0.044 (3)	0.025 (2)	0.031 (2)	0.004 (2)	-0.005 (2)	0.003 (2)
N2	0.061 (4)	0.026 (3)	0.033 (3)	0.010 (2)	-0.008 (2)	0.002 (2)
N3	0.060 (4)	0.044 (3)	0.031 (3)	-0.004 (3)	0.002 (3)	0.011 (2)
N4	0.040 (3)	0.042 (3)	0.031 (3)	-0.001 (2)	0.001 (2)	0.009 (2)
N5	0.021 (2)	0.0116 (19)	0.029 (2)	-0.0071 (16)	-0.0087 (17)	-0.0012 (16)
C1	0.012 (2)	0.018 (2)	0.037 (3)	-0.0006 (18)	-0.0072 (19)	0.000 (2)
C2	0.021 (2)	0.014 (2)	0.028 (2)	0.0019 (18)	-0.0043 (19)	-0.0016 (18)
C3	0.015 (2)	0.016 (2)	0.027 (2)	-0.0042 (18)	-0.0016 (18)	-0.0006 (18)
C4	0.017 (2)	0.017 (2)	0.036 (3)	-0.0072 (19)	-0.011 (2)	0.003 (2)
C5	0.019 (2)	0.016 (2)	0.028 (2)	-0.0059 (18)	-0.0092 (19)	-0.0010 (19)
C6	0.020 (2)	0.016 (2)	0.030 (3)	-0.0048 (19)	-0.0027 (19)	-0.002 (2)
C7	0.024 (3)	0.017 (2)	0.029 (3)	-0.0024 (19)	-0.005 (2)	-0.001 (2)
C8	0.026 (3)	0.018 (2)	0.024 (2)	-0.004 (2)	-0.0054 (19)	-0.0029 (19)
C9	0.024 (3)	0.027 (3)	0.028 (3)	-0.003 (2)	0.001 (2)	-0.001 (2)
C10	0.020 (2)	0.022 (3)	0.033 (3)	0.003 (2)	-0.001 (2)	-0.002 (2)
C11	0.031 (3)	0.022 (3)	0.024 (2)	-0.005 (2)	-0.005 (2)	-0.003 (2)
C12	0.076 (5)	0.028 (3)	0.027 (3)	0.001 (3)	-0.010 (3)	0.001 (2)
C13	0.091 (6)	0.035 (4)	0.039 (4)	0.002 (4)	-0.001 (4)	0.009 (3)
C14	0.147 (12)	0.077 (7)	0.061 (6)	0.003 (8)	-0.048 (7)	0.011 (5)
Cl4	0.0147 (5)	0.0430 (8)	0.0375 (7)	-0.0108 (5)	-0.0052 (5)	0.0047 (6)
Cl5	0.0229 (6)	0.0202 (6)	0.0301 (6)	0.0014 (4)	-0.0064 (5)	0.0054 (5)
Cl6	0.0412 (7)	0.0149 (6)	0.0354 (7)	-0.0034 (5)	-0.0113 (5)	-0.0032 (5)
O4	0.0226 (18)	0.0155 (17)	0.0287 (18)	-0.0025 (14)	-0.0065 (14)	0.0020 (14)
O5	0.052 (3)	0.0066 (16)	0.042 (2)	-0.0013 (16)	-0.020 (2)	-0.0033 (15)
O6	0.078 (6)	0.042 (4)	0.074 (5)	0.006 (4)	-0.012 (5)	0.014 (4)
O6B	0.092 (7)	0.049 (5)	0.048 (5)	-0.003 (5)	-0.003 (4)	0.015 (4)
N6	0.047 (3)	0.029 (3)	0.027 (2)	0.005 (2)	-0.005 (2)	0.002 (2)
N7	0.055 (4)	0.030 (3)	0.034 (3)	0.009 (2)	-0.009 (2)	0.002 (2)
N8	0.054 (4)	0.053 (4)	0.032 (3)	-0.007 (3)	-0.005 (2)	0.014 (3)
N9	0.043 (3)	0.043 (3)	0.026 (2)	-0.006 (2)	-0.002 (2)	0.007 (2)
N10	0.029 (2)	0.011 (2)	0.030 (2)	-0.0044 (17)	-0.0138 (18)	-0.0027 (17)
C15	0.008 (2)	0.022 (2)	0.027 (2)	-0.0035 (17)	-0.0035 (17)	0.0039 (19)
C16	0.026 (3)	0.025 (3)	0.022 (2)	0.003 (2)	-0.006 (2)	0.001 (2)
C17	0.028 (3)	0.017 (2)	0.023 (2)	0.000 (2)	-0.007 (2)	-0.0026 (19)
C18	0.029 (3)	0.020 (3)	0.032 (3)	-0.007 (2)	-0.013 (2)	0.002 (2)
C19	0.028 (3)	0.017 (2)	0.024 (2)	-0.002 (2)	-0.010 (2)	-0.0025 (19)
C20	0.026 (3)	0.017 (2)	0.023 (2)	-0.009 (2)	-0.0032 (19)	-0.0024 (19)
C21	0.023 (3)	0.019 (2)	0.027 (2)	0.002 (2)	-0.006 (2)	-0.005 (2)

C22	0.025 (3)	0.021 (2)	0.021 (2)	-0.005 (2)	-0.0045 (19)	-0.0031 (19)
C23	0.032 (3)	0.025 (3)	0.026 (3)	-0.001 (2)	-0.002 (2)	-0.001 (2)
C24	0.026 (3)	0.020 (3)	0.034 (3)	0.002 (2)	-0.004 (2)	-0.002 (2)
C25	0.033 (3)	0.021 (3)	0.024 (2)	-0.005 (2)	-0.006 (2)	-0.003 (2)
C26	0.068 (5)	0.038 (4)	0.031 (3)	-0.004 (3)	-0.012 (3)	0.007 (3)
C27	0.091 (7)	0.049 (5)	0.047 (4)	-0.002 (4)	-0.004 (4)	0.014 (4)
C28	0.176 (15)	0.079 (8)	0.079 (8)	-0.001 (9)	-0.070 (9)	0.015 (6)

Geometric parameters (Å, °)

C11—C1	1.776 (5)	C14—C15	1.790 (5)
C12—C1	1.762 (6)	C15—C15	1.754 (5)
C13—C1	1.776 (5)	C16—C15	1.767 (5)
O1—C2	1.431 (6)	O4—C16	1.427 (6)
O1—C3	1.353 (6)	O4—C17	1.368 (6)
O2—C3	1.228 (6)	O5—C17	1.216 (7)
O3—H3	0.8400	O6—H6A	0.8400
O3—C13	1.462 (10)	O6—C27	1.471 (11)
O3B—H3B	0.8400	O6B—H6B	0.8400
O3B—C13	1.486 (18)	O6B—C27	1.477 (17)
N1—N2	1.322 (7)	N6—N7	1.321 (7)
N1—C11	1.334 (8)	N6—C25	1.348 (8)
N2—C12	1.323 (10)	N7—C26	1.328 (10)
N3—N4	1.323 (8)	N8—N9	1.327 (8)
N3—C12	1.326 (10)	N8—C26	1.329 (11)
N4—C11	1.353 (8)	N9—C25	1.350 (8)
N5—H5	0.88 (5)	N10—H10A	0.87 (5)
N5—C3	1.332 (6)	N10—C17	1.329 (7)
N5—C4	1.459 (6)	N10—C18	1.463 (6)
C1—C2	1.523 (7)	C15—C16	1.527 (7)
C2—H2A	0.9900	C16—H16A	0.9900
C2—H2B	0.9900	C16—H16B	0.9900
C4—H4A	0.9900	C18—H18A	0.9900
C4—H4B	0.9900	C18—H18B	0.9900
C4—C5	1.503 (7)	C18—C19	1.514 (7)
C5—C6	1.381 (7)	C19—C20	1.390 (8)
C5—C10	1.399 (8)	C19—C24	1.388 (8)
C6—H6	0.9500	C20—H20	0.9500
C6—C7	1.385 (7)	C20—C21	1.390 (7)
C7—H7	0.9500	C21—H21	0.9500
C7—C8	1.386 (8)	C21—C22	1.391 (8)
C8—C9	1.398 (8)	C22—C23	1.392 (8)
C8—C11	1.467 (7)	C22—C25	1.478 (7)
C9—H9	0.9500	C23—H23	0.9500
C9—C10	1.388 (8)	C23—C24	1.389 (8)
C10—H10	0.9500	C24—H24	0.9500
C12—C13	1.516 (9)	C26—C27	1.537 (10)
C13—H13	1.0000	C27—H27	1.0000

C13—H13A	1.0000	C27—H27A	1.0000
C13—C14	1.472 (14)	C27—C28	1.482 (16)
C14—H14A	0.9800	C28—H28A	0.9800
C14—H14B	0.9800	C28—H28B	0.9800
C14—H14C	0.9800	C28—H28C	0.9800
C3—O1—C2	116.7 (4)	C17—O4—C16	117.1 (4)
C13—O3—H3	109.5	C27—O6—H6A	109.5
C13—O3B—H3B	109.5	C27—O6B—H6B	109.5
N2—N1—C11	117.7 (5)	N7—N6—C25	117.8 (5)
N1—N2—C12	118.3 (6)	N6—N7—C26	117.5 (6)
N4—N3—C12	117.8 (6)	N9—N8—C26	117.8 (6)
N3—N4—C11	117.7 (6)	N8—N9—C25	117.1 (6)
C3—N5—H5	123 (4)	C17—N10—H10A	114 (4)
C3—N5—C4	119.5 (4)	C17—N10—C18	120.1 (4)
C4—N5—H5	112 (4)	C18—N10—H10A	125 (4)
C11—C1—C13	108.2 (3)	C15—C15—C14	108.7 (3)
C12—C1—C11	110.2 (3)	C15—C15—C16	109.5 (3)
C12—C1—C13	109.5 (3)	C16—C15—C14	108.2 (3)
C2—C1—C11	106.5 (4)	C16—C15—C14	110.0 (4)
C2—C1—C12	110.7 (3)	C16—C15—C15	109.5 (3)
C2—C1—C13	111.7 (4)	C16—C15—C16	110.9 (4)
O1—C2—C1	107.5 (4)	O4—C16—C15	110.4 (4)
O1—C2—H2A	110.2	O4—C16—H16A	109.6
O1—C2—H2B	110.2	O4—C16—H16B	109.6
C1—C2—H2A	110.2	C15—C16—H16A	109.6
C1—C2—H2B	110.2	C15—C16—H16B	109.6
H2A—C2—H2B	108.5	H16A—C16—H16B	108.1
O2—C3—O1	122.7 (5)	O5—C17—O4	123.8 (5)
O2—C3—N5	125.8 (5)	O5—C17—N10	126.0 (5)
N5—C3—O1	111.5 (4)	N10—C17—O4	110.2 (4)
N5—C4—H4A	109.2	N10—C18—H18A	109.2
N5—C4—H4B	109.2	N10—C18—H18B	109.2
N5—C4—C5	112.1 (4)	N10—C18—C19	111.8 (4)
H4A—C4—H4B	107.9	H18A—C18—H18B	107.9
C5—C4—H4A	109.2	C19—C18—H18A	109.2
C5—C4—H4B	109.2	C19—C18—H18B	109.2
C6—C5—C4	120.6 (5)	C20—C19—C18	120.2 (5)
C6—C5—C10	118.9 (5)	C24—C19—C18	120.6 (5)
C10—C5—C4	120.5 (5)	C24—C19—C20	119.2 (5)
C5—C6—H6	119.6	C19—C20—H20	119.7
C5—C6—C7	120.8 (5)	C19—C20—C21	120.6 (5)
C7—C6—H6	119.6	C21—C20—H20	119.7
C6—C7—H7	119.7	C20—C21—H21	120.0
C6—C7—C8	120.6 (5)	C20—C21—C22	120.0 (5)
C8—C7—H7	119.7	C22—C21—H21	120.0
C7—C8—C9	119.3 (5)	C21—C22—C23	119.6 (5)
C7—C8—C11	120.4 (5)	C21—C22—C25	120.3 (5)

C9—C8—C11	120.3 (5)	C23—C22—C25	120.1 (5)
C8—C9—H9	120.1	C22—C23—H23	120.0
C10—C9—C8	119.7 (5)	C24—C23—C22	120.1 (5)
C10—C9—H9	120.1	C24—C23—H23	120.0
C5—C10—H10	119.6	C19—C24—C23	120.6 (5)
C9—C10—C5	120.7 (5)	C19—C24—H24	119.7
C9—C10—H10	119.6	C23—C24—H24	119.7
N1—C11—N4	123.5 (5)	N6—C25—N9	124.1 (5)
N1—C11—C8	117.2 (5)	N6—C25—C22	116.9 (5)
N4—C11—C8	119.3 (5)	N9—C25—C22	119.0 (5)
N2—C12—N3	124.7 (6)	N7—C26—N8	125.6 (6)
N2—C12—C13	117.9 (7)	N7—C26—C27	116.3 (7)
N3—C12—C13	117.4 (7)	N8—C26—C27	118.1 (7)
O3—C13—C12	109.9 (6)	O6—C27—C26	111.7 (7)
O3—C13—H13	109.5	O6—C27—H27	109.9
O3—C13—C14	109.6 (9)	O6—C27—C28	106.5 (10)
O3B—C13—C12	110.5 (14)	O6B—C27—C26	105.9 (12)
O3B—C13—H13A	111.1	O6B—C27—H27A	109.5
C12—C13—H13	109.5	O6B—C27—C28	113.6 (15)
C12—C13—H13A	111.1	C26—C27—H27	109.9
C14—C13—O3B	104.1 (16)	C26—C27—H27A	109.5
C14—C13—C12	108.7 (7)	C28—C27—C26	108.8 (8)
C14—C13—H13	109.5	C28—C27—H27	109.9
C14—C13—H13A	111.1	C28—C27—H27A	109.5
C13—C14—H14A	109.5	C27—C28—H28A	109.5
C13—C14—H14B	109.5	C27—C28—H28B	109.5
C13—C14—H14C	109.5	C27—C28—H28C	109.5
H14A—C14—H14B	109.5	H28A—C28—H28B	109.5
H14A—C14—H14C	109.5	H28A—C28—H28C	109.5
H14B—C14—H14C	109.5	H28B—C28—H28C	109.5
C11—C1—C2—O1	-175.4 (3)	C14—C15—C16—O4	63.5 (5)
C12—C1—C2—O1	64.8 (5)	C15—C15—C16—O4	-177.1 (3)
C13—C1—C2—O1	-57.5 (5)	C16—C15—C16—O4	-56.2 (5)
N1—N2—C12—N3	-2.3 (11)	N6—N7—C26—N8	-2.5 (11)
N1—N2—C12—C13	177.4 (6)	N6—N7—C26—C27	176.9 (7)
N2—N1—C11—N4	5.3 (9)	N7—N6—C25—N9	3.6 (9)
N2—N1—C11—C8	-177.1 (5)	N7—N6—C25—C22	-177.8 (5)
N2—C12—C13—O3	34.0 (11)	N7—C26—C27—O6	32.5 (12)
N2—C12—C13—O3B	160.4 (16)	N7—C26—C27—O6B	152.9 (14)
N2—C12—C13—C14	-86.0 (10)	N7—C26—C27—C28	-84.7 (11)
N3—N4—C11—N1	-4.7 (9)	N8—N9—C25—N6	-3.4 (9)
N3—N4—C11—C8	177.7 (6)	N8—N9—C25—C22	178.1 (5)
N3—C12—C13—O3	-146.3 (8)	N8—C26—C27—O6	-148.0 (8)
N3—C12—C13—O3B	-19.9 (18)	N8—C26—C27—O6B	-27.7 (16)
N3—C12—C13—C14	93.7 (11)	N8—C26—C27—C28	94.7 (12)
N4—N3—C12—N2	2.9 (12)	N9—N8—C26—N7	2.7 (12)
N4—N3—C12—C13	-176.8 (7)	N9—N8—C26—C27	-176.7 (7)

N5—C4—C5—C6	-128.5 (5)	N10—C18—C19—C20	-117.2 (5)
N5—C4—C5—C10	53.1 (7)	N10—C18—C19—C24	64.9 (7)
C2—O1—C3—O2	5.0 (7)	C16—O4—C17—O5	-9.1 (8)
C2—O1—C3—N5	-173.8 (4)	C16—O4—C17—N10	171.3 (4)
C3—O1—C2—C1	-146.0 (4)	C17—O4—C16—C15	-104.4 (5)
C3—N5—C4—C5	-159.6 (5)	C17—N10—C18—C19	-160.7 (5)
C4—N5—C3—O1	-173.1 (4)	C18—N10—C17—O4	-175.4 (5)
C4—N5—C3—O2	8.1 (8)	C18—N10—C17—O5	5.0 (9)
C4—C5—C6—C7	-178.7 (5)	C18—C19—C20—C21	-178.0 (5)
C4—C5—C10—C9	179.2 (5)	C18—C19—C24—C23	177.2 (5)
C5—C6—C7—C8	0.0 (8)	C19—C20—C21—C22	0.9 (8)
C6—C5—C10—C9	0.7 (8)	C20—C19—C24—C23	-0.7 (8)
C6—C7—C8—C9	-0.4 (8)	C20—C21—C22—C23	-1.0 (8)
C6—C7—C8—C11	-179.9 (5)	C20—C21—C22—C25	178.8 (5)
C7—C8—C9—C10	0.9 (8)	C21—C22—C23—C24	0.2 (8)
C7—C8—C11—N1	7.6 (8)	C21—C22—C25—N6	9.9 (8)
C7—C8—C11—N4	-174.7 (5)	C21—C22—C25—N9	-171.5 (5)
C8—C9—C10—C5	-1.1 (8)	C22—C23—C24—C19	0.6 (9)
C9—C8—C11—N1	-172.0 (5)	C23—C22—C25—N6	-170.4 (5)
C9—C8—C11—N4	5.7 (8)	C23—C22—C25—N9	8.2 (8)
C10—C5—C6—C7	-0.2 (8)	C24—C19—C20—C21	-0.1 (8)
C11—N1—N2—C12	-1.8 (9)	C25—N6—N7—C26	-0.7 (9)
C11—C8—C9—C10	-179.6 (5)	C25—C22—C23—C24	-179.5 (5)
C12—N3—N4—C11	0.6 (10)	C26—N8—N9—C25	0.2 (10)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...N9 ⁱ	0.84	2.64	3.271 (10)	133
O3 <i>B</i> —H3 <i>B</i> ...O6 <i>B</i> ⁱⁱ	0.84	2.46	2.63 (4)	92
N5—H5...O5 ⁱⁱⁱ	0.88 (5)	1.98 (5)	2.861 (6)	175 (6)
O6—H6 <i>A</i> ...N4 ^{iv}	0.84	2.74	3.394 (11)	136
N10—H10 <i>A</i> ...O2	0.87 (5)	2.00 (6)	2.844 (6)	163 (6)

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