

# *N,N'*-[1,4-Phenylenebis(iminocarbonyl)]bis(L-phenylalanine) tetrahydrofuran disolvate

Manuel Stapf\* and Anke Schwarzer

Institut für Organische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Strasse 29, 09599 Freiberg, Germany. \*Correspondence e-mail: manuel.stapf@chemie.tu-freiberg.de

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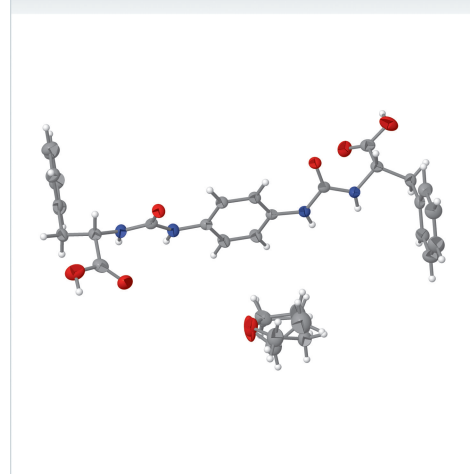
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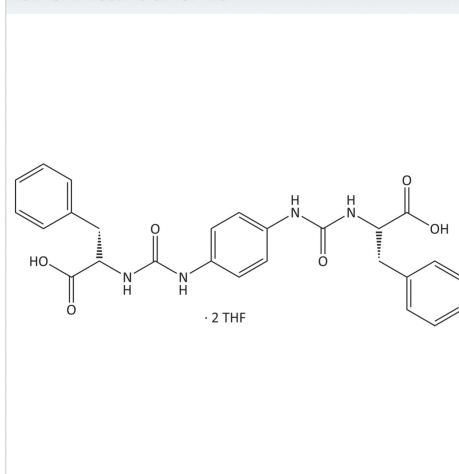
**Keywords:** crystal structure; urea; amino acid; hydrogen bonding; tetrahydrofuran solvate.**CCDC reference:** 2290568**Structural data:** full structural data are available from iucrdata.iucr.org

The title compound,  $C_{26}H_{26}N_4O_6 \cdot 2C_4H_8O$ , representing a bis-urea with terminal phenylalanine units, crystallized with two tetrahydrofuran (THF) molecules. The main molecule is located on a crystallographic twofold axis, while the solvent molecule is disordered over two positions, with occupancies of 0.571 (15) and 0.429 (15). The host molecules are linked by  $N-H \cdots O=C$  hydrogen bonds and  $C-H \cdots O$  contacts with  $R_2^1(6)$  and  $R_2^1(7)$  ring motifs. The THF molecules enclosed in the crystal are connected to the bis-urea compound *via*  $O-H \cdots O$  and  $C-H \cdots O$  interactions.

## 3D view



## Chemical scheme



## Structure description

Bis-urea compounds containing a central 1,4-phenylene unit have been shown to be suitable molecules for anion recognition (Stapf *et al.*, 2015; Casula *et al.*, 2016; Manna *et al.*, 2018; Manna & Das, 2019, 2020; Das *et al.*, 2020). In this context, we introduced compounds combining this scaffold and various amino acids [such as L-valine, L-leucine, L-proline, (*R*)-3-piperidinecarboxylic acid, L-threonine or even L-phenylalanine], whose amino group is part of the urea moiety, among them the title compound, possessing L-phenylalanine units (Stapf *et al.*, 2015). Furthermore, we have already reported the crystal structure of a supramolecular coordination polymer of the title compound with lead(II) (Stapf *et al.*, 2012). In the present article, we describe the crystal structure of the tetrahydrofuran (THF) disolvate.

The title compound was found to crystallize in the tetragonal space group  $I4_1$  with half a molecule of the bis-urea compound and one THF molecule (Fig. 1), which is disordered over two positions (57:43). Within a single molecule possessing a twofold rotation axis, the plane of the phenylene unit includes a dihedral angle with the peripheral arene rings of  $88.4 (1)^\circ$  and with the planes of the urea moieties of  $19.4 (2)^\circ$ . This small angle may be associated with an intramolecular  $C-H \cdots O$  interaction ( $H \cdots O = 2.35 \text{ \AA}$ ) between the phenylene core and the urea moiety. Furthermore, the carboxy group is almost

**Table 1**

Hydrogen-bond geometry (Å, °).

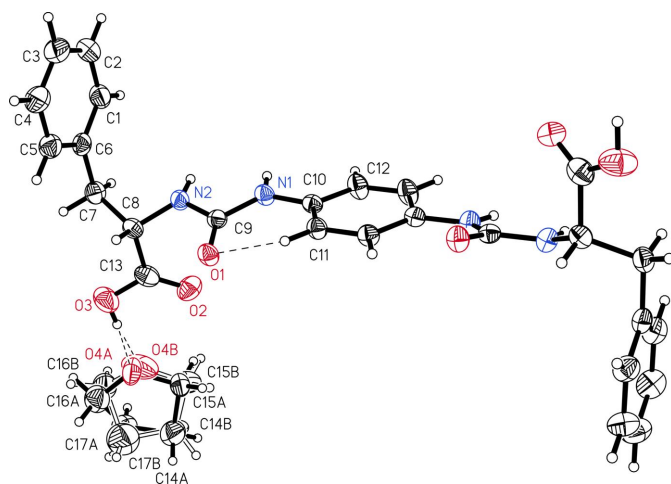
$C_g$  is defined as the centre of gravity of the rings:  $C_{g1}$  is ring C1–C6 and  $C_{g2}$  is C10/C11/C12/C10'/C11'/C12', with primed atoms generated by the symmetry code  $(-x + 1, -y, z)$ .

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1–H1N $\cdots$ O1 <sup>i</sup>	0.84 (4)	2.32 (3)	3.091 (3)	153 (3)
N2–H2N $\cdots$ O1 <sup>i</sup>	0.88 (3)	2.08 (4)	2.937 (3)	163 (3)
O3–H3O $\cdots$ O4A <sup>ii</sup>	0.90 (3)	1.73 (3)	2.623 (7)	175 (7)
C5–H5 $\cdots$ O2 <sup>iii</sup>	0.95	2.55	3.464 (4)	161
C8–H8 $\cdots$ O2 <sup>iii</sup>	1.00	2.70	3.629 (4)	155
C11–H11 $\cdots$ O1	0.95	2.35	2.916 (3)	118
C14A–H14B $\cdots$ O3 <sup>iv</sup>	0.99	2.78	3.581 (18)	139
C16A–H16A $\cdots$ C <sub>g1</sub> <sup>v</sup>	0.99	2.61	3.497 (8)	149
C16B–H16D $\cdots$ C <sub>g1</sub> <sup>v</sup>	0.99	2.82	3.449 (10)	122
C17A–H17B $\cdots$ C <sub>g2</sub> <sup>vi</sup>	0.99	3.00	3.574 (8)	118

Symmetry codes: (i)  $-y + \frac{1}{2}, x, z - \frac{1}{2}$ ; (ii)  $-y, x - \frac{1}{2}, z + \frac{1}{2}$ ; (iii)  $y, -x + \frac{1}{2}, z + \frac{1}{4}$ ; (iv)  $-x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (v)  $x, y + 1, z$ ; (vi)  $y + \frac{1}{2}, -x + 1, z - \frac{1}{4}$ .

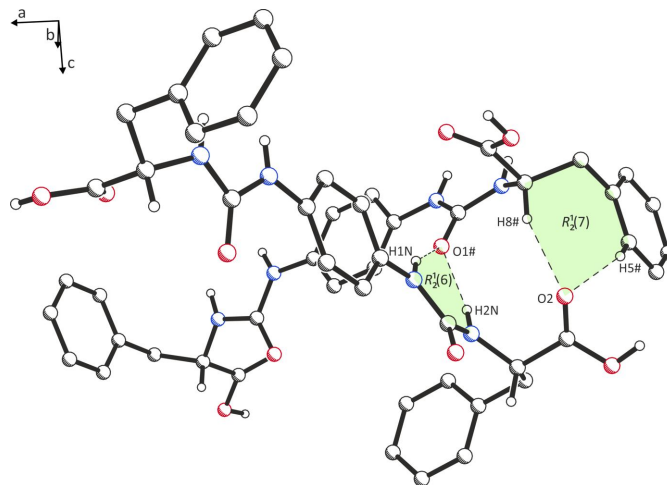
perpendicular to the central aromatic ring, showing a dihedral angle of 82.9 (1)°, and the phenylene units of adjacent molecules are oriented orthogonal with respect to each other.

The dominant intermolecular interactions between urea moieties of neighbouring molecules are inverse bifurcated hydrogen bonds of the N–H $\cdots$ O=C type [ $H \cdots O = 2.08$  (4) and 2.32 (3) Å; Table 1], which can be described by the graph set  $R_2^1(6)$  (Etter, 1990; Fig. 2). Unlike in the previously published coordination polymer (Stapf *et al.*, 2012), in which the urea groups form two-dimensional hydrogen-bridged ribbons ( $H \cdots O = 2.06$ – $2.26$  Å), the structure presented here is characterized by supramolecular chains [graph set  $C(4)$ ]. The angle between the planes of adjacent urea moieties is 83.7 (1)°, thus they are nearly perpendicular to one other. Such a motif is also well known in the literature (for examples, see: Albrecht *et al.*, 2002; Berkessel *et al.*, 2006; Saxena *et al.*,



**Figure 1**

The molecular structure of the title compound, including the atom-numbering scheme. Atoms are drawn with displacement ellipsoids at the 50% probability level. The intramolecular C–H $\cdots$ O interaction, as well as the intermolecular hydrogen bonding between the carboxy group and the THF molecule, are shown as dashed lines. Both disordered parts (57:43) of the THF molecule are displayed. Unlabelled atoms are generated by the symmetry operation  $-x + 1, -y, z$ .



**Figure 2**

Excerpt of the crystal packing showing the  $R_2^1(6)$  and  $R_2^1(7)$  ring motifs of the N–H $\cdots$ O=C and C–H $\cdots$ O=C(OH) interactions drawn as dashed lines. The THF molecules and the H atoms not involved in the interactions have been omitted for clarity.

2014; Shugrue *et al.*, 2019). The N atoms do not act as acceptors for hydrogen bonds. Instead, the linkage of two adjacent molecules is supported by the formation of C–H $\cdots$ O=C contacts ( $H \cdots O = 2.55$  and 2.70 Å) between the C–H groups of phenylalanine and an O atom of a carboxy group which acts as a bifurcated acceptor [graph set  $R_2^1(7)$ ; Fig. 2].

The crystal structure exhibits cavities which are occupied by THF molecules requiring about 961 Å<sup>3</sup> (corresponding to about 29% of the unit-cell volume). The cavities are bounded by the nonpolar phenylene and arene units of the title compound. In addition, the carboxy groups point into the interior of these cavities and form O–H $\cdots$ O hydrogen bonds with the THF O atom [ $H \cdots O = 1.73$  (3) Å]. Further stabilization of the molecular network, each involving the THF molecules, is realized by C–H $\cdots$ O contacts with the carboxy group of an adjacent molecule ( $H \cdots O = 2.78$  Å) and weak C–H $\cdots$ π contacts ( $H \cdots C_g = 2.61$ – $3.00$  Å) with the central benzene core or peripheral arene substituents.

### Synthesis and crystallization

The synthetic and spectroscopic details for the title compound have been reported previously (Stapf *et al.*, 2012, 2015). Single crystals suitable for X-ray analysis were obtained as colourless prisms by slow evaporation of a saturated solution of the bis-urea compound in tetrahydrofuran.

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms at N1 and N2 were located in a difference Fourier map and refined freely. The H atom at O3 was also located in the difference Fourier map but refined using a DFIX restraint at 0.84 (2) Å. Other H atoms were included using a riding model starting from calculated

positions (aromatic C–H = 0.95 Å, methylene C–H = 0.99 Å, and alkyl C–H = 1.00 Å). The  $U_{\text{iso}}(\text{H})$  values were fixed at 1.2 times the equivalent  $U_{\text{eq}}$  value of the parent C atoms. The THF solvent molecule is disordered over at least two positions [refined occupancies 0.571 (15) and 0.429 (15)]. Therefore, the solvent molecule was refined using ISOR for C16A, C16B, C17A and C17B (approximate isotropic behaviour) and SADI (same distances over pairs of bonded atoms) restraints (Sheldrick, 2015b). The absolute structure of the title compound has been assigned by reference to an unchanging chiral centre in the synthetic procedure, not by anomalous dispersion effects in the diffraction experiment.

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**Table 2**

Experimental details.

Crystal data	
Chemical formula	C <sub>26</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> ·2C <sub>4</sub> H <sub>8</sub> O
$M_r$	634.71
Crystal system, space group	Tetragonal, $I4_1$
Temperature (K)	153
$a, c$ (Å)	13.632 (4), 17.507 (6)
$V$ (Å <sup>3</sup> )	3253 (2)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.09
Crystal size (mm)	0.10 × 0.05 × 0.04
Data collection	
Diffractometer	Stoe IPDS 2T
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	25670, 3554, 3269
$R_{\text{int}}$	0.028
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.040, 0.107, 1.05
No. of reflections	3554
No. of parameters	266
No. of restraints	95
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.31, -0.20

Computer programs: *X-AREA* (Stoe & Cie, 2009), *X-RED* (Stoe & Cie, 2009), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *XP* (Sheldrick, 2008), *WinGX* (Farrugia, 2012), *publCIF* (Westrip, 2010) and *shelXle* (Hübschle *et al.*, 2011).

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## full crystallographic data

*IUCrData* (2023). **8**, x230743 [https://doi.org/10.1107/S2414314623007435]

## *N,N'*-[1,4-Phenylenebis(iminocarbonyl)]bis(*L*-phenylalanine) tetrahydrofuran disolvate

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*N,N'*-[1,4-Phenylenebis(iminocarbonyl)]bis(*L*-phenylalanine) tetrahydrofuran disolvate

### Crystal data

$C_{26}H_{26}N_4O_6 \cdot 2C_4H_8O$

$M_r = 634.71$

Tetragonal,  $I4_1$

$a = 13.632$  (4) Å

$c = 17.507$  (6) Å

$V = 3253$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 1352$

$D_x = 1.296$  Mg m<sup>-3</sup>

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

Cell parameters from 1266 reflections

$\theta = 3.1$ – $26.7^\circ$

$\mu = 0.09$  mm<sup>-1</sup>

$T = 153$  K

Chunk, colourless

$0.10 \times 0.05 \times 0.04$  mm

### Data collection

STOE IPDS 2T

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm<sup>-1</sup>

rotation method scans

25670 measured reflections

3554 independent reflections

3269 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.028$

$\theta_{max} = 27.0^\circ$ ,  $\theta_{min} = 3.0^\circ$

$h = -17 \rightarrow 17$

$k = -17 \rightarrow 17$

$l = -22 \rightarrow 22$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.107$

$S = 1.05$

3554 reflections

266 parameters

95 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

$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 2.0532P]$

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

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.31$  e Å<sup>-3</sup>

$\Delta\rho_{min} = -0.20$  e Å<sup>-3</sup>

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}^*/U_{eq}$	Occ. (<1)
N1	0.38152 (16)	0.16933 (16)	0.54757 (12)	0.0285 (4)	
H1N	0.376 (2)	0.194 (2)	0.504 (2)	0.030 (8)*	
N2	0.27971 (16)	0.29428 (15)	0.58122 (12)	0.0278 (4)	

H2N	0.285 (2)	0.310 (2)	0.533 (2)	0.034 (8)*	
O1	0.31329 (14)	0.17368 (13)	0.66808 (10)	0.0302 (4)	
O2	0.11068 (16)	0.19008 (15)	0.57508 (14)	0.0445 (5)	
O3	0.02642 (16)	0.30373 (19)	0.63921 (15)	0.0529 (6)	
H3O	-0.023 (4)	0.263 (4)	0.627 (5)	0.14 (3)*	
C1	0.3225 (2)	0.5393 (2)	0.54681 (18)	0.0389 (6)	
H1	0.302627	0.524528	0.496096	0.047*	
C2	0.4061 (2)	0.5960 (2)	0.55894 (19)	0.0460 (7)	
H2A	0.442763	0.619510	0.516591	0.055*	
C3	0.4360 (2)	0.6185 (2)	0.6331 (2)	0.0497 (8)	
H3	0.493013	0.657049	0.641531	0.060*	
C4	0.3818 (3)	0.5840 (2)	0.69431 (19)	0.0466 (7)	
H4	0.401726	0.599088	0.744967	0.056*	
C5	0.2986 (2)	0.5276 (2)	0.68217 (16)	0.0380 (6)	
H5	0.262005	0.504595	0.724742	0.046*	
C6	0.26774 (19)	0.50397 (18)	0.60822 (16)	0.0313 (5)	
C7	0.17887 (19)	0.44008 (19)	0.59624 (15)	0.0327 (6)	
H7A	0.161232	0.440197	0.541378	0.039*	
H7B	0.122863	0.467660	0.625126	0.039*	
C8	0.19711 (18)	0.33349 (18)	0.62249 (14)	0.0283 (5)	
H8	0.213017	0.333795	0.678256	0.034*	
C9	0.32327 (17)	0.20934 (17)	0.60329 (13)	0.0252 (5)	
C10	0.43982 (17)	0.08384 (17)	0.55283 (14)	0.0250 (5)	
C11	0.47052 (18)	0.04159 (18)	0.62133 (14)	0.0275 (5)	
H11	0.450935	0.069967	0.668486	0.033*	
C12	0.4700 (2)	0.0413 (2)	0.48385 (14)	0.0341 (6)	
H12	0.449394	0.068988	0.436734	0.041*	
C13	0.1072 (2)	0.2663 (2)	0.60914 (15)	0.0370 (6)	
O4A	0.6924 (5)	0.1252 (4)	0.3577 (7)	0.048 (2)	0.571 (15)
C14A	0.5578 (8)	0.2254 (9)	0.3317 (12)	0.062 (5)	0.571 (15)
H14A	0.519420	0.224367	0.379670	0.074*	0.571 (15)
H14B	0.515206	0.247603	0.289262	0.074*	0.571 (15)
C15A	0.6031 (10)	0.1256 (10)	0.3148 (10)	0.046 (4)	0.571 (15)
H15A	0.559079	0.071968	0.331644	0.055*	0.571 (15)
H15B	0.616352	0.118003	0.259558	0.055*	0.571 (15)
C16A	0.7185 (6)	0.2206 (5)	0.3801 (6)	0.057 (2)	0.571 (15)
H16A	0.787187	0.234862	0.365513	0.068*	0.571 (15)
H16B	0.711966	0.228135	0.436102	0.068*	0.571 (15)
C17A	0.6488 (4)	0.2893 (4)	0.3391 (4)	0.0483 (19)	0.571 (15)
H17A	0.674677	0.308654	0.288402	0.058*	0.571 (15)
H17B	0.635496	0.348937	0.369627	0.058*	0.571 (15)
O4B	0.6865 (10)	0.1184 (7)	0.3439 (12)	0.081 (5)	0.429 (15)
C14B	0.5595 (10)	0.2278 (11)	0.3178 (12)	0.043 (4)	0.429 (15)
H14C	0.491571	0.225648	0.337787	0.052*	0.429 (15)
H14D	0.560401	0.268410	0.270882	0.052*	0.429 (15)
C15B	0.5969 (15)	0.1248 (10)	0.3012 (13)	0.046 (4)	0.429 (15)
H15C	0.549184	0.074772	0.318503	0.056*	0.429 (15)
H15D	0.609168	0.115831	0.245904	0.056*	0.429 (15)

C16B	0.7256 (7)	0.2178 (7)	0.3503 (8)	0.053 (3)	0.429 (15)
H16C	0.748952	0.243547	0.300663	0.064*	0.429 (15)
H16D	0.778608	0.222487	0.388781	0.064*	0.429 (15)
C17B	0.6294 (8)	0.2691 (10)	0.3774 (10)	0.088 (4)	0.429 (15)
H17C	0.610777	0.249281	0.429818	0.105*	0.429 (15)
H17D	0.634210	0.341453	0.374449	0.105*	0.429 (15)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0345 (11)	0.0309 (10)	0.0202 (9)	0.0040 (9)	0.0040 (8)	0.0030 (8)
N2	0.0338 (11)	0.0261 (10)	0.0235 (10)	0.0025 (8)	0.0050 (8)	0.0009 (8)
O1	0.0355 (10)	0.0342 (9)	0.0209 (8)	0.0044 (7)	0.0033 (7)	0.0026 (7)
O2	0.0431 (11)	0.0363 (11)	0.0540 (13)	-0.0057 (8)	-0.0076 (10)	-0.0039 (9)
O3	0.0357 (11)	0.0657 (15)	0.0574 (14)	-0.0110 (10)	0.0096 (10)	-0.0175 (12)
C1	0.0424 (15)	0.0388 (14)	0.0355 (13)	0.0037 (12)	0.0062 (12)	-0.0026 (12)
C2	0.0465 (17)	0.0469 (17)	0.0445 (17)	-0.0021 (13)	0.0145 (14)	-0.0026 (13)
C3	0.0425 (16)	0.0437 (17)	0.063 (2)	-0.0089 (13)	0.0042 (15)	-0.0104 (15)
C4	0.0492 (18)	0.0451 (17)	0.0454 (16)	-0.0092 (14)	-0.0022 (13)	-0.0104 (13)
C5	0.0451 (16)	0.0353 (14)	0.0337 (14)	-0.0013 (12)	0.0016 (12)	-0.0016 (11)
C6	0.0337 (13)	0.0249 (11)	0.0353 (13)	0.0066 (10)	0.0010 (10)	-0.0003 (10)
C7	0.0294 (12)	0.0328 (13)	0.0360 (14)	0.0061 (10)	-0.0019 (10)	0.0012 (11)
C8	0.0277 (11)	0.0333 (12)	0.0240 (11)	0.0004 (10)	0.0008 (9)	0.0005 (9)
C9	0.0268 (11)	0.0263 (11)	0.0224 (11)	-0.0041 (9)	0.0001 (9)	-0.0019 (9)
C10	0.0250 (11)	0.0284 (11)	0.0218 (10)	-0.0018 (9)	0.0011 (9)	0.0006 (9)
C11	0.0309 (11)	0.0306 (12)	0.0210 (11)	0.0013 (10)	0.0007 (9)	-0.0018 (9)
C12	0.0396 (14)	0.0427 (15)	0.0199 (11)	0.0115 (12)	0.0000 (10)	0.0012 (10)
C13	0.0344 (13)	0.0479 (16)	0.0289 (13)	-0.0011 (12)	0.0001 (11)	0.0060 (11)
O4A	0.038 (3)	0.034 (3)	0.072 (5)	-0.003 (2)	-0.021 (3)	-0.001 (2)
C14A	0.048 (6)	0.054 (7)	0.083 (9)	0.003 (5)	-0.003 (5)	-0.012 (5)
C15A	0.037 (5)	0.059 (7)	0.043 (5)	-0.006 (4)	-0.002 (3)	-0.015 (4)
C16A	0.057 (3)	0.055 (3)	0.059 (3)	0.003 (2)	-0.009 (2)	-0.002 (2)
C17A	0.049 (3)	0.038 (2)	0.058 (3)	0.0014 (19)	0.006 (2)	0.000 (2)
O4B	0.113 (10)	0.064 (6)	0.065 (6)	0.058 (6)	-0.020 (5)	-0.008 (5)
C14B	0.040 (7)	0.047 (7)	0.042 (5)	0.024 (5)	-0.003 (4)	-0.003 (4)
C15B	0.056 (8)	0.025 (6)	0.058 (9)	0.009 (5)	0.011 (5)	0.010 (5)
C16B	0.052 (3)	0.053 (3)	0.055 (4)	0.001 (2)	-0.007 (3)	-0.003 (3)
C17B	0.088 (5)	0.087 (5)	0.089 (5)	0.009 (3)	-0.004 (3)	-0.004 (3)

*Geometric parameters (Å, °)*

N1—C9	1.371 (3)	C11—H11	0.9500
N1—C10	1.413 (3)	C12—C12 <sup>i</sup>	1.390 (5)
N1—H1N	0.84 (4)	C12—H12	0.9500
N2—C9	1.357 (3)	O4A—C16A	1.405 (8)
N2—C8	1.441 (3)	O4A—C15A	1.430 (8)
N2—H2N	0.88 (3)	C14A—C15A	1.522 (9)
O1—C9	1.241 (3)	C14A—C17A	1.522 (10)

O2—C13	1.199 (4)	C14A—H14A	0.9900
O3—C13	1.324 (4)	C14A—H14B	0.9900
O3—H3O	0.90 (3)	C15A—H15A	0.9900
C1—C2	1.393 (5)	C15A—H15B	0.9900
C1—C6	1.395 (4)	C16A—C17A	1.515 (8)
C1—H1	0.9500	C16A—H16A	0.9900
C2—C3	1.395 (5)	C16A—H16B	0.9900
C2—H2A	0.9500	C17A—H17A	0.9900
C3—C4	1.383 (5)	C17A—H17B	0.9900
C3—H3	0.9500	O4B—C15B	1.435 (10)
C4—C5	1.387 (4)	O4B—C16B	1.460 (10)
C4—H4	0.9500	C14B—C15B	1.521 (9)
C5—C6	1.399 (4)	C14B—C17B	1.521 (11)
C5—H5	0.9500	C14B—H14C	0.9900
C6—C7	1.507 (4)	C14B—H14D	0.9900
C7—C8	1.544 (3)	C15B—H15C	0.9900
C7—H7A	0.9900	C15B—H15D	0.9900
C7—H7B	0.9900	C16B—C17B	1.560 (10)
C8—C13	1.547 (4)	C16B—H16C	0.9900
C8—H8	1.0000	C16B—H16D	0.9900
C10—C11	1.395 (3)	C17B—H17C	0.9900
C10—C12	1.402 (3)	C17B—H17D	0.9900
C11—C11 <sup>i</sup>	1.390 (5)		
C9—N1—C10	127.4 (2)	O3—C13—C8	111.8 (3)
C9—N1—H1N	116 (2)	C16A—O4A—C15A	111.0 (7)
C10—N1—H1N	116 (2)	C15A—C14A—C17A	101.4 (8)
C9—N2—C8	121.0 (2)	C15A—C14A—H14A	111.5
C9—N2—H2N	117 (2)	C17A—C14A—H14A	111.5
C8—N2—H2N	117 (2)	C15A—C14A—H14B	111.5
C13—O3—H3O	107 (5)	C17A—C14A—H14B	111.5
C2—C1—C6	120.8 (3)	H14A—C14A—H14B	109.3
C2—C1—H1	119.6	O4A—C15A—C14A	104.3 (7)
C6—C1—H1	119.6	O4A—C15A—H15A	110.9
C1—C2—C3	120.2 (3)	C14A—C15A—H15A	110.9
C1—C2—H2A	119.9	O4A—C15A—H15B	110.9
C3—C2—H2A	119.9	C14A—C15A—H15B	110.9
C4—C3—C2	119.4 (3)	H15A—C15A—H15B	108.9
C4—C3—H3	120.3	O4A—C16A—C17A	106.4 (6)
C2—C3—H3	120.3	O4A—C16A—H16A	110.5
C3—C4—C5	120.4 (3)	C17A—C16A—H16A	110.5
C3—C4—H4	119.8	O4A—C16A—H16B	110.5
C5—C4—H4	119.8	C17A—C16A—H16B	110.5
C4—C5—C6	121.0 (3)	H16A—C16A—H16B	108.6
C4—C5—H5	119.5	C16A—C17A—C14A	101.4 (6)
C6—C5—H5	119.5	C16A—C17A—H17A	111.5
C1—C6—C5	118.2 (3)	C14A—C17A—H17A	111.5
C1—C6—C7	121.5 (3)	C16A—C17A—H17B	111.5

C5—C6—C7	120.2 (2)	C14A—C17A—H17B	111.5
C6—C7—C8	111.9 (2)	H17A—C17A—H17B	109.3
C6—C7—H7A	109.2	C15B—O4B—C16B	107.1 (10)
C8—C7—H7A	109.2	C15B—C14B—C17B	105.2 (7)
C6—C7—H7B	109.2	C15B—C14B—H14C	110.7
C8—C7—H7B	109.2	C17B—C14B—H14C	110.7
H7A—C7—H7B	107.9	C15B—C14B—H14D	110.7
N2—C8—C7	109.0 (2)	C17B—C14B—H14D	110.7
N2—C8—C13	108.9 (2)	H14C—C14B—H14D	108.8
C7—C8—C13	112.6 (2)	O4B—C15B—C14B	104.0 (8)
N2—C8—H8	108.8	O4B—C15B—H15C	111.0
C7—C8—H8	108.8	C14B—C15B—H15C	111.0
C13—C8—H8	108.8	O4B—C15B—H15D	111.0
O1—C9—N2	123.1 (2)	C14B—C15B—H15D	111.0
O1—C9—N1	123.9 (2)	H15C—C15B—H15D	109.0
N2—C9—N1	113.0 (2)	O4B—C16B—C17B	97.6 (8)
C11—C10—C12	118.8 (2)	O4B—C16B—H16C	112.2
C11—C10—N1	124.4 (2)	C17B—C16B—H16C	112.2
C12—C10—N1	116.8 (2)	O4B—C16B—H16D	112.2
C11 <sup>i</sup> —C11—C10	120.70 (14)	C17B—C16B—H16D	112.2
C11 <sup>i</sup> —C11—H11	119.7	H16C—C16B—H16D	109.8
C10—C11—H11	119.7	C14B—C17B—C16B	98.8 (10)
C12 <sup>i</sup> —C12—C10	120.52 (15)	C14B—C17B—H17C	112.0
C12 <sup>i</sup> —C12—H12	119.7	C16B—C17B—H17C	112.0
C10—C12—H12	119.7	C14B—C17B—H17D	112.0
O2—C13—O3	124.4 (3)	C16B—C17B—H17D	112.0
O2—C13—C8	123.9 (3)	H17C—C17B—H17D	109.7
C6—C1—C2—C3	-0.1 (5)	C9—N1—C10—C12	161.9 (2)
C1—C2—C3—C4	-0.1 (5)	C12—C10—C11—C11 <sup>i</sup>	-0.4 (4)
C2—C3—C4—C5	0.1 (5)	N1—C10—C11—C11 <sup>i</sup>	-178.7 (3)
C3—C4—C5—C6	0.2 (5)	C11—C10—C12—C12 <sup>i</sup>	-0.4 (5)
C2—C1—C6—C5	0.4 (4)	N1—C10—C12—C12 <sup>i</sup>	178.1 (3)
C2—C1—C6—C7	-178.2 (3)	N2—C8—C13—O2	5.8 (4)
C4—C5—C6—C1	-0.5 (4)	C7—C8—C13—O2	126.8 (3)
C4—C5—C6—C7	178.2 (3)	N2—C8—C13—O3	-173.6 (2)
C1—C6—C7—C8	110.2 (3)	C7—C8—C13—O3	-52.6 (3)
C5—C6—C7—C8	-68.4 (3)	C16A—O4A—C15A—C14A	-16.5 (18)
C9—N2—C8—C7	167.2 (2)	C17A—C14A—C15A—O4A	34.2 (17)
C9—N2—C8—C13	-69.6 (3)	C15A—O4A—C16A—C17A	-8.6 (15)
C6—C7—C8—N2	-57.9 (3)	O4A—C16A—C17A—C14A	29.8 (13)
C6—C7—C8—C13	-178.9 (2)	C15A—C14A—C17A—C16A	-38.3 (15)
C8—N2—C9—O1	-18.6 (4)	C16B—O4B—C15B—C14B	-28 (2)
C8—N2—C9—N1	163.4 (2)	C17B—C14B—C15B—O4B	-6 (2)
C10—N1—C9—O1	-0.6 (4)	C15B—O4B—C16B—C17B	48.8 (18)



C10—N1—C9—N2	177.4 (2)	C15B—C14B—C17B—C16B	34 (2)
C9—N1—C10—C11	-19.7 (4)	O4B—C16B—C17B—C14B	-48.8 (16)

Symmetry code: (i)  $-x+1, -y, z$ .

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$C_g$  is defined as the centre of gravity of the rings:  $C_{g1}$  is C1...C6;  $C_{g2}$  is C10/C11/C12/C10'/C11'/C12' with primed atoms generated by symmetry  $-x+1, -y, z$ .

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N...O1 <sup>ii</sup>	0.84 (4)	2.32 (3)	3.091 (3)	153 (3)
N2—H2N...O1 <sup>ii</sup>	0.88 (3)	2.08 (4)	2.937 (3)	163 (3)
O3—H3O...O4A <sup>iii</sup>	0.90 (3)	1.73 (3)	2.623 (7)	175 (7)
C5—H5...O2 <sup>iv</sup>	0.95	2.55	3.464 (4)	161
C8—H8...O2 <sup>iv</sup>	1.00	2.70	3.629 (4)	155
C11—H11...O1	0.95	2.35	2.916 (3)	118
C14A—H14B...O3 <sup>v</sup>	0.99	2.78	3.581 (18)	139
C16A—H16A...Cg1 <sup>vi</sup>	0.99	2.61	3.497 (8)	149
C16B—H16D...Cg1 <sup>vi</sup>	0.99	2.82	3.449 (10)	122
C17A—H17B...Cg2 <sup>vii</sup>	0.99	3.00	3.574 (8)	118

Symmetry codes: (ii)  $-y+1/2, x, z-1/4$ ; (iii)  $-y, x-1/2, z+1/4$ ; (iv)  $y, -x+1/2, z+1/4$ ; (v)  $-x+1/2, -y+1/2, z-1/2$ ; (vi)  $x, y+1, z$ ; (vii)  $y+1/2, -x+1, z-1/4$ .