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Crystal structure of *meso*-tetrakis(4-nitrophenyl)porphyrin nitrobenzene disolvate

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The porphyrin core of the title centrosymmetric compound, $C_{44}H_{26}N_8O_8 \cdot 2C_6H_5NO_2$, is approximately planar, the maximum deviation being 0.069 (3) Å. The planes of the benzene rings of the nitrophenyl substituents are almost perpendicular to the porphyrin mean plane, making dihedral angles of 73.89 (9) and 89.24 (9)°. The two pyrrole ring H atoms are equally disordered over the four pyrrole ring N atoms. In the crystal, weak C—H⋯O and C—H⋯N hydrogen bonds link the porphyrin molecules into a three-dimensional supramolecular network. The nitrobenzene solvent molecules are linked by weak C—H⋯O hydrogen bonds into supramolecular chains propagating along the *a*-axis direction.

1. Related literature

Porphyrins and metalloporphyrins are of interest as building blocks for molecular cages (Meng *et al.*, 2011), catalysts (Odo *et al.*, 2009) and photofunctional materials (Yan *et al.*, 2009). For related structures, see: Silvers & Tulinsky (1967). For related polymeric complexes, see: Seredyuk *et al.* (2007); Moroz *et al.* (2012); Zha *et al.* (2013). For the synthesis of *meso*-tetrakis(4-nitrophenyl)porphyrin, see: Bettelheim *et al.* (1987).
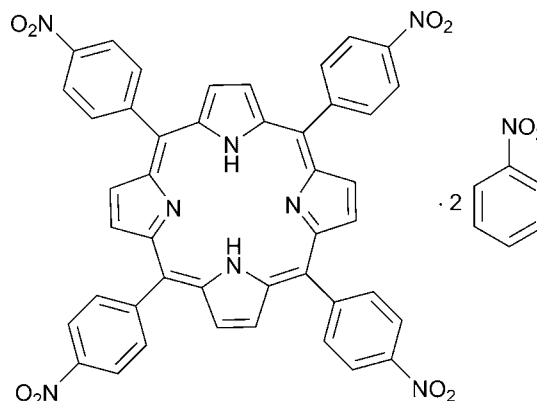
2. Experimental

2.1. Crystal data

$C_{44}H_{26}N_8O_8 \cdot 2C_6H_5NO_2$	$\gamma = 102.17\,(4)°$
$M_r = 1040.95$	$V = 1232.4\,(11)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 7.949\,(4)$ Å	Mo $K\alpha$ radiation
$b = 10.134\,(5)$ Å	$\mu = 0.10$ mm^{-1}
$c = 16.444\,(8)$ Å	$T = 293$ K
$\alpha = 105.43\,(5)°$	$0.13 \times 0.09 \times 0.03$ mm
$\beta = 95.37\,(4)°$	

2.2. Data collection

Agilent Xcalibur κ-axis diffractometer with a Ruby CCD detector	10625 measured reflections
	5284 independent reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)	3437 reflections with $I > 2\sigma(I)$
$T_{min} = 0.981$, $T_{max} = 1.000$	$R_{int} = 0.018$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.086$	9 restraints
$wR(F^2) = 0.275$	H-atom parameters constrained
$S = 1.10$	$\Delta\rho_{max} = 0.60$ e Å^{-3}
5284 reflections	$\Delta\rho_{min} = -0.49$ e Å^{-3}
322 parameters	

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3⋯O1[i]	0.93	2.60	3.519 (4)	171
C11—H11⋯N1[ii]	0.93	2.57	3.426 (4)	152
C15—H15⋯O3[iii]	0.93	2.56	3.453 (5)	161
C18—H18⋯O1[iv]	0.93	2.58	3.455 (5)	157
C26—H26⋯O5[v]	0.93	2.56	3.432 (10)	156

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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supporting information

Crystal structure of *meso*-tetrakis(4-nitrophenyl)porphyrin nitrobenzene disolvate

Maksym Seredyuk, Elzbieta Gumienna–Kontecka, Anna Brzuszkiewicz, Turganbay S. Iskenderov and Valentina A. Kalibabchuk

S1. Introduction

S2. Experimental

S2.1. Synthesis and crystallization

The *meso*-tetrakis[4-nitrophenyl]-porphyrin, synthesized according to Bettelheim *et al.* (1987), was crystallized from boiling nitrobenzene as lustrous violet crystals.

S2.2. Refinement

H atoms were placed in calculated positions with C—H = 0.93 Å and N—H = 0.86 Å, and refined in riding mode with $U_{iso}(H) = 1.2\ U_{eq}(N,C)$. Each amino H atom is equally disordered over two positions.

S3. Results and discussion

Porphyrins and metalloporphyrins attract attention of the researchers in many aspects, such as building blocks for molecular cages (Meng *et al.*, 2011), catalysts (Odo *et al.*, 2009) or photofunctional materials (Yan *et al.*, 2009). Having continuing interest in study of polynuclear complexes (see, for example, Seredyuk *et al.*, 2007, Moroz *et al.* 2012), in this paper we report the structure of *meso*-tetrakis(4-nitrophenyl)porphyrin, a precursor for polytopic bridging ligands (for example, Zha *et al.*, 2013).

The 24-membered porphyrin moiety of the title compound is planar with a maximum deviation of C2 atom equal to ±0.130 (3) Å. The angle between adjacent pyrrole ring planes (C1–C4/N1 and C5–C13/N3) is 7.190 (11), and bond lengths and angles are close to those found for tetraphenylporphyrin (Silvers & Tulinsky, 1967). This suggests that the nitrophenyl substituents and/or packing effects influence the geometry of the porphyne ring.

The molecule of porphyrin contains two structurally different pairs of pyrrole rings. Despite two hydrogen atoms are disordered over four pyrrole rings, the two structurally non-equivalent pyrrole rings have somewhat different angles C—N—C equal to 107.20 (20)° and 108.30 (20)°.

The 4-nitrophenyl groups are rotated at angles of 73.89 (9)° and 89.24 (9)° with respect to the porphyrin mean plane, due to steric hindrance with the pyrrole-H atoms of the macrocycle.

The unit-cell packing along the *a* axis is shown in Fig. 2. There are no significant π-π interactions between the porphyrins. The 4-nitrobenzene groups around the porphyrin core apparently hinder interactions between the porphyrins. The channels formed due to loose packing of porphyrins are occupied by nitrobenzene molecules.
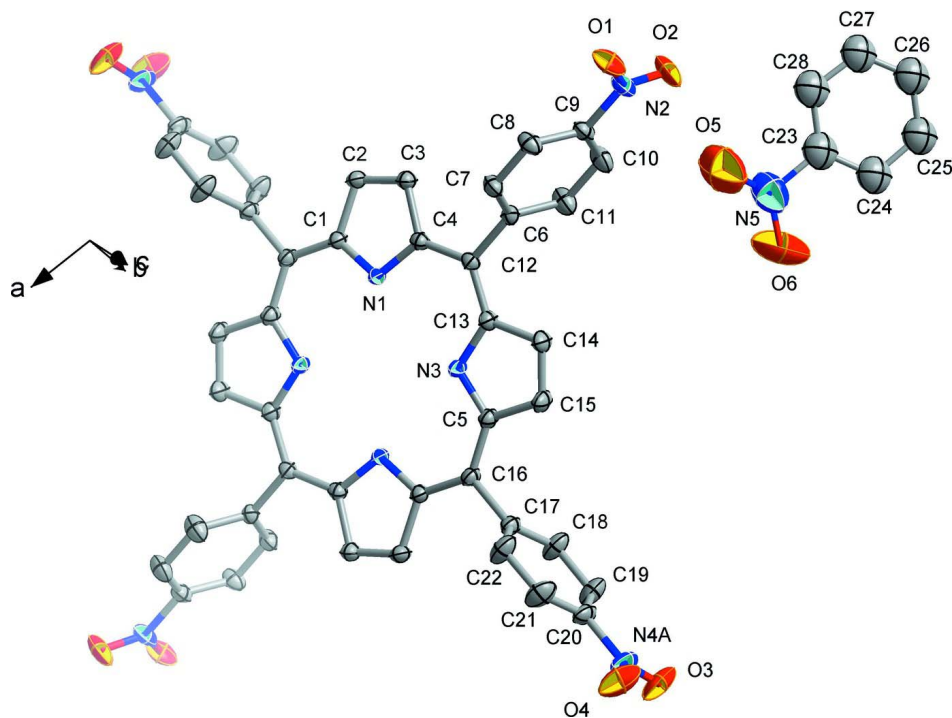
Figure 1

Molecular structure of the title compound with the atom-labeling scheme and 25% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.
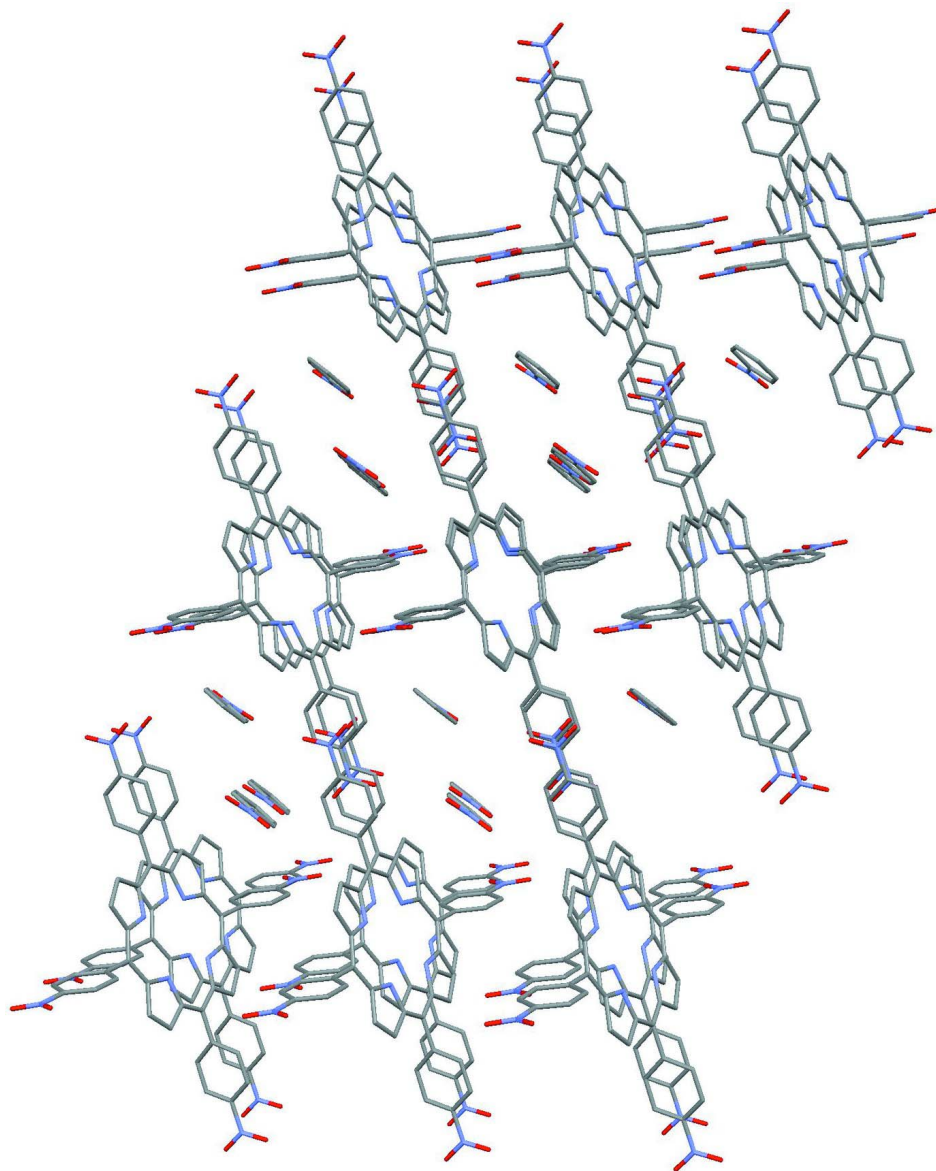
Figure 2

Projection of the crystal packing along *a* axis.

***meso*-Tetrakis(4-nitrophenyl)porphyrin nitrobenzene disolvate**

Crystal data

$C_{44}H_{26}N_8O_8 \cdot 2C_6H_5NO_2$	$Z = 1$
$M_r = 1040.95$	$F(000) = 538$
Triclinic, $P\bar{1}$	$D_x = 1.403$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.949$ (4) Å	Cell parameters from 3566 reflections
$b = 10.134$ (5) Å	$\theta = 2.8$–28.7°
$c = 16.444$ (8) Å	$\mu = 0.10$ mm^{-1}
$\alpha = 105.43$ (5)°	$T = 293$ K
$\beta = 95.37$ (4)°	Plate, violet
$\gamma = 102.17$ (4)°	$0.13 \times 0.09 \times 0.03$ mm
$V = 1232.4$ (11) Å^3	

Data collection

Agilent Xcalibur *κ*-axis diffractometer with a Ruby CCD detector	10625 measured reflections
	5284 independent reflections
Radiation source: fine-focus sealed tube	3437 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.018$
ω scans	$\theta_{max} = 27.0°$, $\theta_{min} = 2.8°$
Absorption correction: multi-scan	$h = -10\rightarrow10$
(*CrysAlis PRO*; Agilent, 2011)	$k = -12\rightarrow12$
$T_{min} = 0.981$, $T_{max} = 1.000$	$l = -20\rightarrow20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.086$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.275$	
$S = 1.10$	H-atom parameters constrained
5284 reflections	$w = 1/[\sigma^2(F_o^2) + (0.1381P)^2 + 0.6248P]$
322 parameters	where $P = (F_o^2 + 2F_c^2)/3$
9 restraints	$(\Delta/\sigma)_{max} = 0.002$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.60$ e Å⁻³
	$\Delta\rho_{min} = -0.49$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	1.0682 (3)	1.0348 (3)	−0.1297 (2)	0.0828 (9)	
O2	1.1718 (4)	0.8612 (4)	−0.1166 (3)	0.1000 (11)	
N1	0.2102 (3)	0.6614 (2)	0.06866 (14)	0.0365 (5)	
H1N	0.1178	0.6023	0.0377	0.044*	0.50
N2	1.0538 (4)	0.9210 (4)	−0.11673 (19)	0.0624 (8)	
C1	0.2304 (4)	0.7297 (3)	0.15411 (17)	0.0389 (6)	
C2	0.4064 (4)	0.8181 (3)	0.18213 (19)	0.0470 (7)	
H2	0.4545	0.8742	0.2375	0.056*	
C3	0.4871 (4)	0.8038 (3)	0.11299 (18)	0.0447 (7)	
H3	0.6008	0.8495	0.1116	0.054*	
C4	0.3650 (3)	0.7047 (3)	0.04161 (17)	0.0365 (6)	
C5	0.0641 (4)	0.3740 (3)	−0.18184 (17)	0.0419 (7)	
C6	0.5738 (3)	0.7244 (3)	−0.06002 (17)	0.0374 (6)	
C7	0.6008 (4)	0.8585 (3)	−0.0698 (2)	0.0485 (7)	
H7	0.5121	0.9057	−0.0639	0.058*	
C8	0.7578 (4)	0.9233 (3)	−0.0882 (2)	0.0515 (8)	

H8	0.7754	1.0134	−0.0946	0.062*
C9	0.8864 (4)	0.8526 (3)	−0.09695 (19)	0.0464 (7)
C10	0.8646 (5)	0.7199 (4)	−0.0880 (3)	0.0639 (10)
H10	0.9540	0.6736	−0.0939	0.077*
C11	0.7068 (5)	0.6564 (4)	−0.0701 (3)	0.0628 (10)
H11	0.6898	0.5656	−0.0648	0.075*
O3	−0.2626 (6)	−0.1809 (4)	−0.5712 (2)	0.1246 (15)
O4	−0.3322 (7)	−0.0114 (5)	−0.6082 (2)	0.1343 (16)
N3	0.1296 (3)	0.4707 (2)	−0.10375 (14)	0.0398 (6)
H3N	0.0770	0.4832	−0.0599	0.048*	0.50
N4A	−0.2790 (5)	−0.0618 (4)	−0.5550 (2)	0.0833 (11)
C12	0.4023 (4)	0.6543 (3)	−0.04098 (17)	0.0373 (6)
C13	0.2928 (4)	0.5441 (3)	−0.10724 (17)	0.0397 (6)
C14	0.3327 (4)	0.4883 (3)	−0.1909 (2)	0.0517 (8)
H14	0.4360	0.5183	−0.2104	0.062*
C15	0.1940 (4)	0.3851 (3)	−0.2362 (2)	0.0535 (8)
H15	0.1843	0.3306	−0.2925	0.064*
C16	−0.1031 (4)	0.2835 (3)	−0.20674 (17)	0.0398 (6)
C17	−0.1495 (4)	0.1928 (3)	−0.29832 (18)	0.0439 (7)
C18	−0.1154 (6)	0.0617 (4)	−0.3218 (2)	0.0667 (10)
H18	−0.0624	0.0291	−0.2808	0.080*
C19	−0.1593 (6)	−0.0226 (4)	−0.4062 (2)	0.0733 (11)
H19	−0.1383	−0.1122	−0.4218	0.088*
C20	−0.2330 (5)	0.0277 (4)	−0.4652 (2)	0.0590 (9)
C21	−0.2655 (6)	0.1580 (5)	−0.4446 (2)	0.0796 (12)
H21	−0.3136	0.1917	−0.4863	0.095*
C22	−0.2252 (6)	0.2392 (4)	−0.3599 (2)	0.0731 (11)
H22	−0.2502	0.3273	−0.3445	0.088*
O5	0.9853 (9)	0.2373 (9)	0.3161 (7)	0.233 (4)
O6	1.0580 (9)	0.4623 (10)	0.3993 (6)	0.233 (4)
N5	0.9530 (10)	0.3478 (10)	0.3562 (6)	0.160 (3)
C23	0.7681 (10)	0.3458 (8)	0.3540 (4)	0.1216 (9)
C24	0.7255 (9)	0.4653 (7)	0.4008 (4)	0.1216 (9)
H24	0.8110	0.5438	0.4341	0.146*
C25	0.5530 (9)	0.4635 (8)	0.3964 (4)	0.1216 (9)
H25	0.5192	0.5424	0.4267	0.146*
C26	0.4316 (9)	0.3488 (7)	0.3485 (4)	0.1216 (9)
H26	0.3142	0.3487	0.3468	0.146*
C27	0.4768 (9)	0.2347 (8)	0.3033 (4)	0.1216 (9)
H27	0.3897	0.1569	0.2705	0.146*
C28	0.6424 (9)	0.2289 (8)	0.3038 (4)	0.1216 (9)
H28	0.6724	0.1493	0.2716	0.146*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0524 (16)	0.099 (2)	0.104 (2)	−0.0040 (15)	0.0200 (15)	0.0572 (19)
O2	0.0414 (15)	0.127 (3)	0.145 (3)	0.0250 (17)	0.0367 (17)	0.050 (2)

N1	0.0361 (12)	0.0349 (11)	0.0321 (11)	0.0014 (9)	0.0077 (9)	0.0039 (9)
N2	0.0354 (15)	0.089 (2)	0.0634 (19)	0.0058 (15)	0.0115 (13)	0.0285 (17)
C1	0.0405 (15)	0.0338 (13)	0.0354 (14)	0.0018 (11)	0.0061 (11)	0.0042 (11)
C2	0.0429 (17)	0.0450 (16)	0.0393 (16)	−0.0023 (13)	0.0003 (12)	0.0017 (12)
C3	0.0404 (16)	0.0429 (15)	0.0416 (16)	−0.0006 (12)	0.0056 (12)	0.0057 (12)
C4	0.0353 (14)	0.0331 (13)	0.0382 (14)	0.0038 (11)	0.0064 (11)	0.0093 (11)
C5	0.0469 (17)	0.0419 (15)	0.0324 (14)	0.0054 (13)	0.0103 (12)	0.0061 (11)
C6	0.0349 (14)	0.0410 (14)	0.0348 (14)	0.0072 (11)	0.0076 (11)	0.0093 (11)
C7	0.0362 (16)	0.0450 (16)	0.068 (2)	0.0103 (13)	0.0155 (14)	0.0203 (15)
C8	0.0422 (17)	0.0471 (17)	0.071 (2)	0.0068 (14)	0.0139 (15)	0.0280 (16)
C9	0.0315 (15)	0.0611 (19)	0.0457 (17)	0.0052 (14)	0.0086 (12)	0.0180 (14)
C10	0.0454 (19)	0.070 (2)	0.091 (3)	0.0261 (17)	0.0242 (18)	0.035 (2)
C11	0.053 (2)	0.0543 (19)	0.097 (3)	0.0200 (16)	0.0247 (19)	0.0391 (19)
O3	0.189 (4)	0.089 (2)	0.065 (2)	0.023 (3)	0.023 (2)	−0.0227 (18)
O4	0.194 (5)	0.139 (3)	0.0400 (17)	0.018 (3)	−0.016 (2)	0.0073 (19)
N3	0.0421 (13)	0.0399 (12)	0.0305 (12)	0.0017 (10)	0.0091 (9)	0.0044 (9)
N4A	0.089 (3)	0.088 (3)	0.0426 (19)	−0.008 (2)	0.0128 (17)	−0.0086 (18)
C12	0.0371 (15)	0.0358 (13)	0.0384 (14)	0.0052 (11)	0.0097 (11)	0.0117 (11)
C13	0.0418 (16)	0.0400 (14)	0.0354 (14)	0.0037 (12)	0.0112 (11)	0.0110 (12)
C14	0.0487 (18)	0.0564 (18)	0.0428 (17)	0.0009 (15)	0.0197 (14)	0.0077 (14)
C15	0.059 (2)	0.0539 (18)	0.0362 (15)	0.0014 (15)	0.0201 (14)	−0.0002 (13)
C16	0.0465 (16)	0.0376 (14)	0.0298 (13)	0.0058 (12)	0.0077 (11)	0.0035 (11)
C17	0.0445 (16)	0.0445 (15)	0.0337 (14)	0.0004 (13)	0.0088 (12)	0.0040 (12)
C18	0.102 (3)	0.054 (2)	0.0382 (17)	0.025 (2)	0.0027 (18)	0.0029 (15)
C19	0.102 (3)	0.056 (2)	0.050 (2)	0.019 (2)	0.013 (2)	−0.0049 (17)
C20	0.061 (2)	0.064 (2)	0.0318 (16)	−0.0046 (17)	0.0078 (14)	−0.0035 (14)
C21	0.107 (3)	0.080 (3)	0.042 (2)	0.020 (2)	−0.007 (2)	0.0106 (18)
C22	0.106 (3)	0.064 (2)	0.0422 (19)	0.030 (2)	0.0006 (19)	0.0017 (16)
O5	0.164 (6)	0.203 (7)	0.357 (12)	0.088 (6)	0.022 (6)	0.098 (8)
O6	0.134 (5)	0.259 (9)	0.256 (8)	−0.048 (6)	−0.039 (5)	0.089 (7)
N5	0.129 (6)	0.158 (6)	0.217 (8)	0.055 (5)	0.040 (5)	0.078 (6)
C23	0.128 (2)	0.138 (2)	0.106 (2)	0.0241 (19)	0.0334 (17)	0.0501 (17)
C24	0.128 (2)	0.138 (2)	0.106 (2)	0.0241 (19)	0.0334 (17)	0.0501 (17)
C25	0.128 (2)	0.138 (2)	0.106 (2)	0.0241 (19)	0.0334 (17)	0.0501 (17)
C26	0.128 (2)	0.138 (2)	0.106 (2)	0.0241 (19)	0.0334 (17)	0.0501 (17)
C27	0.128 (2)	0.138 (2)	0.106 (2)	0.0241 (19)	0.0334 (17)	0.0501 (17)
C28	0.128 (2)	0.138 (2)	0.106 (2)	0.0241 (19)	0.0334 (17)	0.0501 (17)

Geometric parameters (Å, º)

O1—N2	1.212 (4)	C12—C13	1.399 (4)
O2—N2	1.220 (4)	C13—C14	1.435 (4)
N1—C1	1.369 (3)	C14—C15	1.345 (5)
N1—C4	1.372 (3)	C14—H14	0.9300
N1—H1N	0.8600	C15—H15	0.9300
N2—C9	1.472 (4)	C16—C1^i	1.399 (4)
C1—C16^i	1.399 (4)	C16—C17	1.505 (4)
C1—C2	1.451 (4)	C17—C22	1.366 (5)

C2—C3	1.347 (4)	C17—C18	1.374 (5)
C2—H2	0.9300	C18—C19	1.390 (5)
C3—C4	1.441 (4)	C18—H18	0.9300
C3—H3	0.9300	C19—C20	1.353 (6)
C4—C12	1.401 (4)	C19—H19	0.9300
C5—N3	1.367 (4)	C20—C21	1.359 (6)
C5—C16	1.400 (4)	C21—C22	1.384 (5)
C5—C15	1.433 (4)	C21—H21	0.9300
C6—C11	1.379 (4)	C22—H22	0.9300
C6—C7	1.386 (4)	O5—N5	1.230 (9)
C6—C12	1.500 (4)	O6—N5	1.260 (9)
C7—C8	1.382 (4)	N5—C23	1.462 (10)
C7—H7	0.9300	C23—C24	1.378 (8)
C8—C9	1.363 (4)	C23—C28	1.382 (8)
C8—H8	0.9300	C24—C25	1.363 (8)
C9—C10	1.368 (5)	C24—H24	0.9300
C10—C11	1.379 (5)	C25—C26	1.342 (8)
C10—H10	0.9300	C25—H25	0.9300
C11—H11	0.9300	C26—C27	1.337 (8)
O3—N4A	1.203 (5)	C26—H26	0.9300
O4—N4A	1.210 (5)	C27—C28	1.329 (8)
N3—C13	1.367 (4)	C27—H27	0.9300
N3—H3N	0.8600	C28—H28	0.9300
N4A—C20	1.477 (4)		
C1—N1—C4	107.2 (2)	C12—C13—C14	125.8 (3)
C1—N1—H1N	126.4	C15—C14—C13	107.8 (3)
C4—N1—H1N	126.4	C15—C14—H14	126.1
O1—N2—O2	123.8 (3)	C13—C14—H14	126.1
O1—N2—C9	118.5 (3)	C14—C15—C5	107.6 (3)
O2—N2—C9	117.7 (3)	C14—C15—H15	126.2
N1—C1—C16^i	126.0 (3)	C5—C15—H15	126.2
N1—C1—C2	109.0 (2)	C1^i—C16—C5	125.8 (3)
C16^i—C1—C2	125.0 (3)	C1^i—C16—C17	117.4 (3)
C3—C2—C1	107.1 (3)	C5—C16—C17	116.9 (2)
C3—C2—H2	126.4	C22—C17—C18	118.6 (3)
C1—C2—H2	126.4	C22—C17—C16	120.9 (3)
C2—C3—C4	107.4 (3)	C18—C17—C16	120.5 (3)
C2—C3—H3	126.3	C17—C18—C19	120.6 (3)
C4—C3—H3	126.3	C17—C18—H18	119.7
N1—C4—C12	125.5 (2)	C19—C18—H18	119.7
N1—C4—C3	109.2 (2)	C20—C19—C18	118.9 (3)
C12—C4—C3	125.2 (3)	C20—C19—H19	120.6
N3—C5—C16	126.6 (3)	C18—C19—H19	120.6
N3—C5—C15	108.2 (3)	C19—C20—C21	122.1 (3)
C16—C5—C15	125.2 (3)	C19—C20—N4A	118.8 (4)
C11—C6—C7	118.3 (3)	C21—C20—N4A	119.1 (4)
C11—C6—C12	121.2 (3)	C20—C21—C22	118.3 (4)

C7—C6—C12	120.5 (2)	C20—C21—H21	120.9
C8—C7—C6	120.9 (3)	C22—C21—H21	120.9
C8—C7—H7	119.5	C17—C22—C21	121.5 (4)
C6—C7—H7	119.5	C17—C22—H22	119.2
C9—C8—C7	118.9 (3)	C21—C22—H22	119.2
C9—C8—H8	120.6	O5—N5—O6	128.7 (9)
C7—C8—H8	120.6	O5—N5—C23	115.7 (9)
C8—C9—C10	122.0 (3)	O6—N5—C23	115.6 (8)
C8—C9—N2	119.1 (3)	C24—C23—C28	121.9 (7)
C10—C9—N2	118.9 (3)	C24—C23—N5	117.8 (7)
C9—C10—C11	118.5 (3)	C28—C23—N5	120.3 (7)
C9—C10—H10	120.8	C25—C24—C23	117.2 (7)
C11—C10—H10	120.8	C25—C24—H24	121.4
C6—C11—C10	121.5 (3)	C23—C24—H24	121.4
C6—C11—H11	119.3	C26—C25—C24	120.6 (7)
C10—C11—H11	119.3	C26—C25—H25	119.7
C13—N3—C5	108.3 (2)	C24—C25—H25	119.7
C13—N3—H3N	125.8	C27—C26—C25	120.9 (7)
C5—N3—H3N	125.8	C27—C26—H26	119.5
O3—N4A—O4	123.5 (4)	C25—C26—H26	119.5
O3—N4A—C20	118.4 (4)	C28—C27—C26	122.0 (8)
O4—N4A—C20	118.2 (4)	C28—C27—H27	119.0
C13—C12—C4	125.4 (3)	C26—C27—H27	119.0
C13—C12—C6	117.2 (2)	C27—C28—C23	117.4 (7)
C4—C12—C6	117.3 (2)	C27—C28—H28	121.3
N3—C13—C12	126.2 (2)	C23—C28—H28	121.3
N3—C13—C14	108.1 (2)		
C4—N1—C1—C16[i]	179.5 (3)	N3—C13—C14—C15	0.8 (4)
C4—N1—C1—C2	−0.9 (3)	C12—C13—C14—C15	−179.2 (3)
N1—C1—C2—C3	1.3 (3)	C13—C14—C15—C5	0.1 (4)
C16[i]—C1—C2—C3	−179.1 (3)	N3—C5—C15—C14	−1.0 (4)
C1—C2—C3—C4	−1.2 (3)	C16—C5—C15—C14	176.5 (3)
C1—N1—C4—C12	176.6 (3)	N3—C5—C16—C1[i]	−3.9 (5)
C1—N1—C4—C3	0.2 (3)	C15—C5—C16—C1[i]	179.1 (3)
C2—C3—C4—N1	0.7 (3)	N3—C5—C16—C17	176.0 (3)
C2—C3—C4—C12	−175.8 (3)	C15—C5—C16—C17	−1.0 (5)
C11—C6—C7—C8	−0.8 (5)	C1[i]—C16—C17—C22	89.5 (4)
C12—C6—C7—C8	−179.3 (3)	C5—C16—C17—C22	−90.4 (4)
C6—C7—C8—C9	0.2 (5)	C1[i]—C16—C17—C18	−90.9 (4)
C7—C8—C9—C10	0.0 (5)	C5—C16—C17—C18	89.2 (4)
C7—C8—C9—N2	179.9 (3)	C22—C17—C18—C19	−0.9 (6)
O1—N2—C9—C8	−4.4 (5)	C16—C17—C18—C19	179.5 (3)
O2—N2—C9—C8	173.5 (3)	C17—C18—C19—C20	1.3 (6)
O1—N2—C9—C10	175.5 (3)	C18—C19—C20—C21	0.0 (6)
O2—N2—C9—C10	−6.6 (5)	C18—C19—C20—N4A	179.8 (4)
C8—C9—C10—C11	0.4 (6)	O3—N4A—C20—C19	6.1 (6)
N2—C9—C10—C11	−179.5 (3)	O4—N4A—C20—C19	−174.3 (4)

C7—C6—C11—C10	1.2 (5)	O3—N4A—C20—C21	−174.1 (4)
C12—C6—C11—C10	179.7 (3)	O4—N4A—C20—C21	5.5 (6)
C9—C10—C11—C6	−1.0 (6)	C19—C20—C21—C22	−1.6 (7)
C16—C5—N3—C13	−176.0 (3)	N4A—C20—C21—C22	178.6 (4)
C15—C5—N3—C13	1.4 (3)	C18—C17—C22—C21	−0.8 (6)
N1—C4—C12—C13	−5.3 (5)	C16—C17—C22—C21	178.8 (4)
C3—C4—C12—C13	170.6 (3)	C20—C21—C22—C17	2.1 (7)
N1—C4—C12—C6	174.7 (2)	O5—N5—C23—C24	177.4 (8)
C3—C4—C12—C6	−9.5 (4)	O6—N5—C23—C24	−2.3 (10)
C11—C6—C12—C13	−71.9 (4)	O5—N5—C23—C28	−4.8 (11)
C7—C6—C12—C13	106.6 (3)	O6—N5—C23—C28	175.5 (7)
C11—C6—C12—C4	108.1 (3)	C28—C23—C24—C25	0.6 (8)
C7—C6—C12—C4	−73.4 (4)	N5—C23—C24—C25	178.3 (6)
C5—N3—C13—C12	178.6 (3)	C23—C24—C25—C26	0.5 (8)
C5—N3—C13—C14	−1.4 (3)	C24—C25—C26—C27	−0.9 (9)
C4—C12—C13—N3	2.5 (5)	C25—C26—C27—C28	0.3 (10)
C6—C12—C13—N3	−177.5 (2)	C26—C27—C28—C23	0.7 (10)
C4—C12—C13—C14	−177.5 (3)	C24—C23—C28—C27	−1.1 (9)
C6—C12—C13—C14	2.5 (4)	N5—C23—C28—C27	−178.8 (6)

Symmetry code: (i) −x, −y+1, −z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O1[ii]	0.93	2.60	3.519 (4)	171
C11—H11···N1[iii]	0.93	2.57	3.426 (4)	152
C15—H15···O3[iv]	0.93	2.56	3.453 (5)	161
C18—H18···O1[v]	0.93	2.58	3.455 (5)	157
C26—H26···O5[vi]	0.93	2.56	3.432 (10)	156

Symmetry codes: (ii) −x+2, −y+2, −z; (iii) −x+1, −y+1, −z; (iv) −x, −y, −z−1; (v) x−1, y−1, z; (vi) x−1, y, z.