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Crystal structures and supramolecular features of 9,9-dimethyl-3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraone, 3,7-diazaspiro[bicyclo[3.3.1]-nonane-9,1′-cyclopentane]-2,4,6,8-tetraone and 9-methyl-9-phenyl-3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraone dimethylformamide monosolvate

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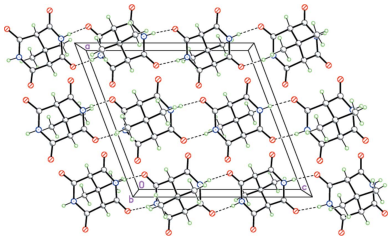
Compounds (I), $C_9H_{10}N_2O_4$, (II), $C_{11}H_{12}N_2O_4$, and (III), $C_{14}H_{12}N_2O_4{\cdot}C_3H_7NO$ represent 9,9-disubstituted-3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraone derivatives with very similar molecular geometries for the bicyclic framework: the dihedral angle between the planes of the imide groups is 74.87 (6), 73.86 (3) and 74.83 (6)° in (I)–(III), respectively. The dimethyl derivative (I) is positioned on a crystallographic twofold axis and its overall geometry deviates only slightly from idealized C_{2v} symmetry. The spiro-cyclopentane derivative (II) and the phenyl/methyl analog (III) retain only internal C_s symmetry, which in the case of (II) coincides with crystallographic mirror symmetry. The cyclopentane moiety in (II) adopts an envelope conformation, with the spiro C atom deviating from the mean plane of the rest of the ring by 0.548 (2) Å. In compound (III), an N—H···O hydrogen bond is formed with the dimethylformamide solvent molecule. In the crystal, both (I) and (II) form similar zigzag hydrogen-bonded ribbons through double intermolecular N—H···O hydrogen bonds. However, whereas in (I) the ribbons are formed by two *trans*-arranged O═C—N—H amide fragments, the amide fragments are *cis*-positioned in (II). The formation of ribbons in (III) is apparently disrupted by participation of one of its N—H groups in hydrogen bonding with the solvent molecule. As a result, the molecules of (III) form zigzag chains rather than the ribbons through intermolecular N—H···O hydrogen bonds. The crystal of (I) was a pseudo-merohedral twin.



1. Chemical context

Diazabicyclononane-tetraones are used in the synthesis of the sparteine subgroup of lupine alcaloids (Norcross *et al.*, 2008) and are precursors in obtaining 3,7-diazabicyclo[3.3.1]nonanes which have been studied in computer models as serine protease inhibitors (Vatsadze *et al.*, 2016). They also have value as building blocks in the design of other biologically active compounds (Kudryavtsev *et al.*, 2014), and in the synthesis of imaging agents for positron emission tomography (Medved'ko *et al.*, 2016). In addition, they are good chelating ligands for 3*d* transition metals (Vatsadze *et al.*, 2005) including Cu (Vatsadze *et al.*, 2014).

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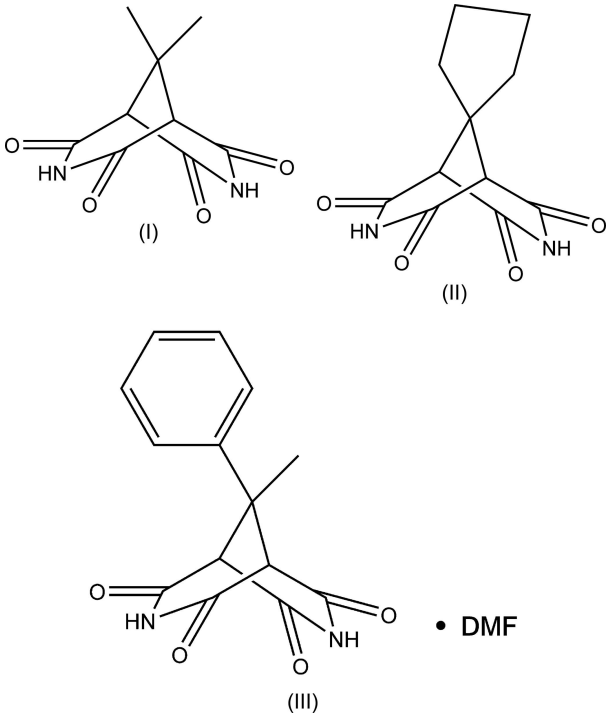

However, the crystal structures of this class of compounds have not been adequately characterized so far, as shown by a small number (eight) of similar structures found in the Cambridge Structural Database (CSD; Groom *et al.*, 2016). Moreover, their ability to form different supramolecular structures depending on the substituents at the 9-position in the heterocycle, which we report in this work, has not been not reported before. A search in the CSD for the substructure 3,7-diaza-2,4,6,8-tetraoxobicyclo[3.3.1]nonane yielded eight hits. Although there is a similarity in chemical structure of known related compounds (Horlein *et al.*, 1981; Norcross *et al.*, 2008), their supramolecular features are significantly different because of the impact of substituents and solvatation.

In this work, we have synthesized three 9,9-disubstituted-3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraones and show how groups bound to C9 as well as the presence of solvate molecules affect their ability to form different hydrogen-bonding systems.

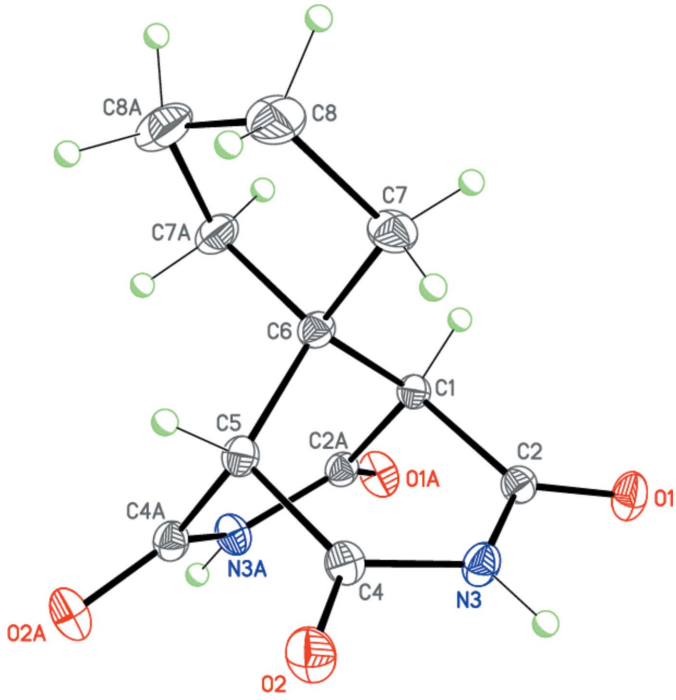

Figure 2
The molecular structure of (II). Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius. [Symmetry code: (A) $x, \frac{1}{2} - y, z$.]

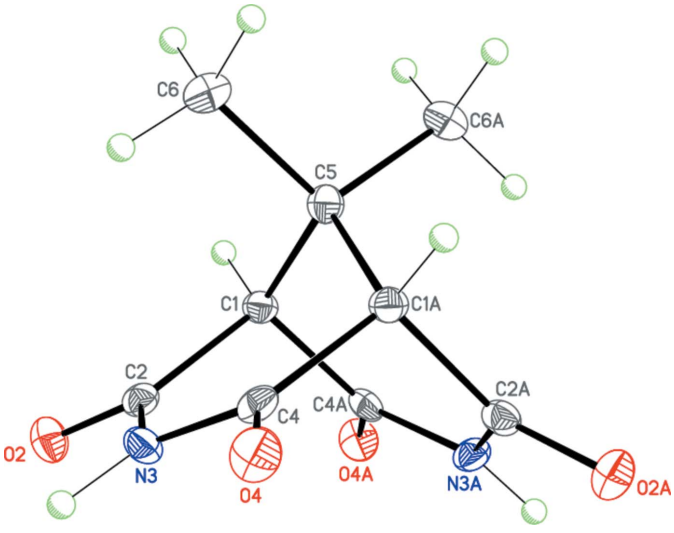

Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius. [Symmetry code: (A) $1 + x, y, -z + \frac{1}{2}$.]

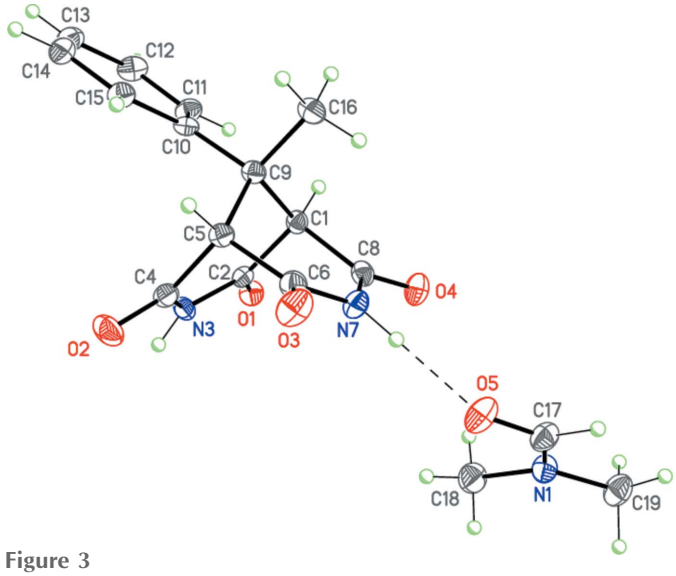

Figure 3
The molecular structure of (III)·DMF. Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius. Dashed line indicates the intramolecular N—H···O hydrogen bond.

2. Structural commentary

Compounds (I), $C_9H_{10}N_2O_4$, (II), $C_{11}H_{12}N_2O_4$, and (III), $C_{14}H_{12}N_2O_4{\cdot}C_3H_7NO$ represent 9,9-disubstituted-3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraone derivatives and have very similar molecular geometries (Figs. 1–3). In general, the 3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraone skeleton exhibits idealized C_{2v} ($mm2$) symmetry. The molecule of (I), containing two 9-methyl substituents, occupies a special position on a twofold axis [C_2 (2)], and its geometry deviates only slightly from the perfectly symmetrical C_{2v}. As a result of the presence of spiro-9-cyclopentane [in the case of (II)] and 9-phenyl and 9-methyl [in the case of (III)] substituents, the overall symmetry of these molecules decreases to C_s (m). However, in the crystal, the intrinsic C_s symmetry remains only for the molecule of (II), which occupies a special position on a mirror plane. Compound (III) crystallizes as a dimethyl formamide monosolvate, with the main molecule occupying a general position.

The two imide fragments in the molecules of (I)–(III) are almost planar (r.m.s. deviations are 0.013, 0.009 and 0.009/0.036 Å, respectively). The dihedral angles between the imide planes are 74.87 (6), 73.86 (3) and 74.83 (6)° for (I)–(III), respectively. Moreover, the four carbonyl carbon atoms in (I)–(III) are each coplanar with r.m.s. deviations of 0.018, 0.000, and 0.031 Å, respectively; the bridged carbon atom lies by 1.854 (3), 1.846 (1), and 1.858 (2) Å, respectively, above this plane in (I)–(III). The cyclopentane substituent in (II) adopts an envelope conformation, with the C6 spiro-carbon atom deviating from the mean plane through the other ring atoms by 0.548 (2) Å.

Importantly, in (III) the main molecule forms a strong N7—H7···O5 hydrogen bond with the dimethyl formamide solvate molecule (Table 3, Fig. 3).

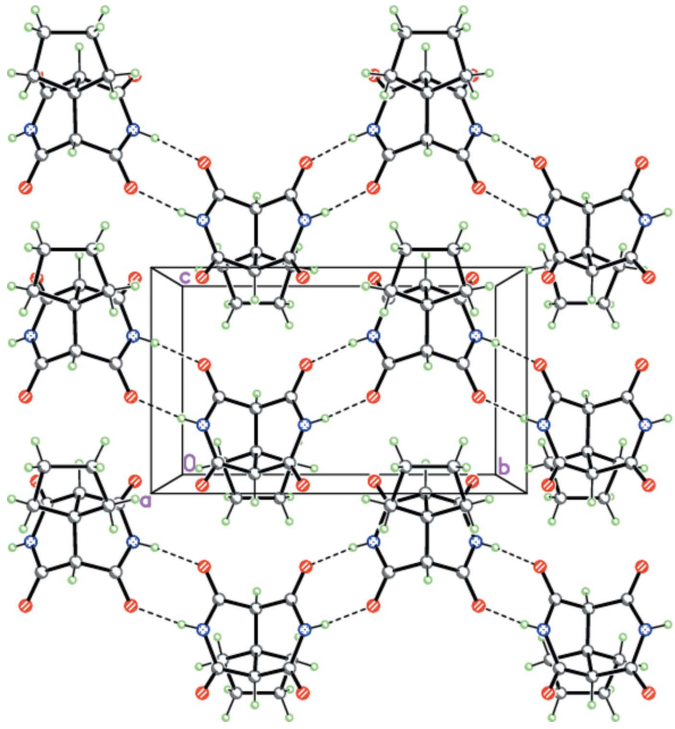

Figure 5
The crystal structure of (II), demonstrating the H-bonded zigzag-like ribbons propagating toward [010]. Dashed lines indicate the intermolecular N—H···O hydrogen bonds.

3. Supramolecular features

In general, any compound of type (I)–(III) could form up to six intermolecular hydrogen bonds utilizing two hydrogen-bond donor NH groups and four hydrogen-bond acceptor carbonyl oxygen atoms. In the literature, even the unsubstituted analogue (refcode GOHHER; Norcross *et al.*, 2008) shows only four intermolecular hydrogen bonds involving both imide fragments of bispidintetraone with the formation of an infinite three-dimensional hydrogen-bonded network. If

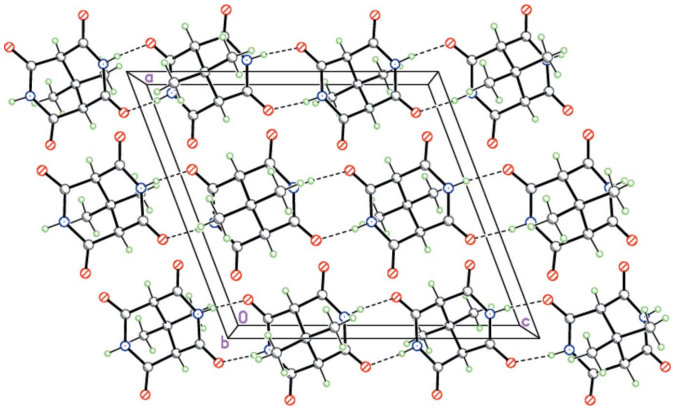

Figure 4
The crystal structure of (I), demonstrating the H-bonded zigzag-like ribbons propagating toward [001]. Dashed lines indicate the intermolecular N—H···O hydrogen bonds.

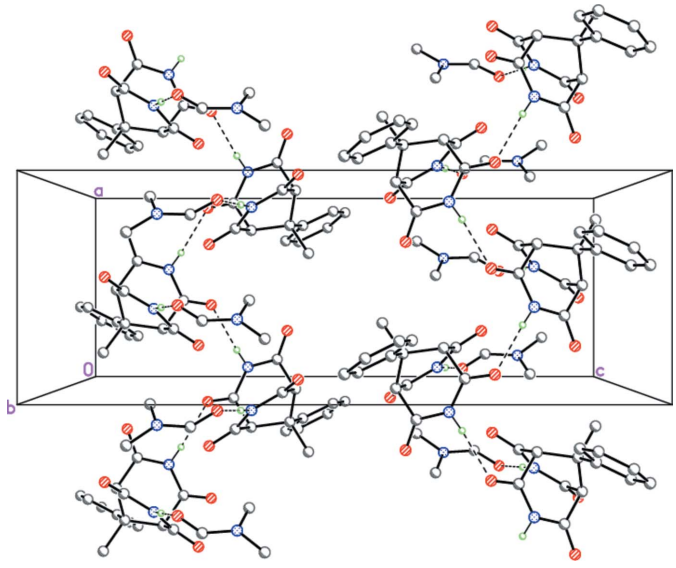

Figure 6
The crystal structure of (III)·DMF, demonstrating the H-bonded zigzag-like chains propagating toward [100]. Dashed lines indicate the intermolecular N—H···O hydrogen bonds.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O2^{i}	0.90 (3)	2.01 (3)	2.906 (2)	173 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O1^{i}	0.855 (14)	2.021 (14)	2.8718 (11)	173.7 (13)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O1^{i}	0.861 (19)	2.12 (2)	2.9650 (19)	168.3 (18)
N7—H7···O5	0.90 (2)	1.86 (2)	2.7682 (19)	178.6 (18)

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

one of the nitrogen atoms is alkylated (for example, refcode BAHFIZ; Horlein *et al.*, 1981), the other one is involved in the formation of a doubly hydrogen-bonded dimer. When both nitrogen atoms are functionalized [refcodes JIMWUY (Hametner *et al.*, 2007), NAWLIH (Mereiter *et al.*, 2014), NAWLON *et al.*, 2014), PILXAK (Hametner *et al.*, 2007), XAZGAH (Blakemore, *et al.*, 2005)], no hydrogen-bonds are observed.

Despite the geometrical similarity of compounds (I)-(III), they form different supramolecular structures in the solid state. Thus, in the crystals of (I) and (II), the molecules form the zigzag hydrogen-bonded ribbons by double N—H···O hydrogen bonds (Tables 1 and 2, Figs. 4 and 5). The hydrogen-bonded ribbons in (I) and (II) are distinguished by the binding sites of the 3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraone skeleton. According to symmetry, the ribbons in (I) are formed by the two *trans*-arranged O═C—N—H amide fragments, whereas the binding O═C—N—H amide fragments in (II) are *cis* disposed. As one of the two NH groups in (III) is bonded to the dimethyl formamide solvate molecule, the N—H···O hydrogen bonds form the zigzag chains rather than ribbons (Table 3, Fig. 6).

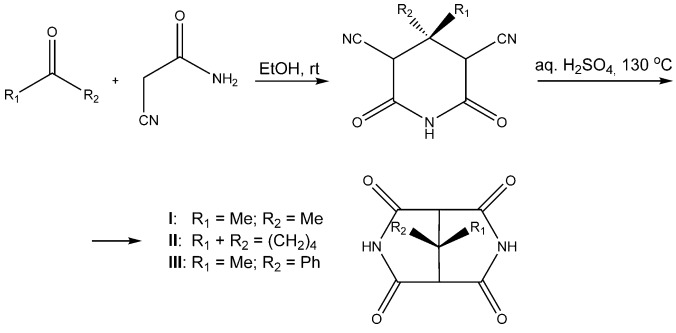

Figure 7
Synthesis of (I)–(III) from 2-cyanoacetamide and ketones.

4. Synthesis and crystallization

The title compounds (I)–(III) were synthesized (Fig. 7) according to the procedure described earlier (Schon *et al.*, 1998).

Dinitrile subproducts were obtained by adding 2-cyanoacetamide to the corresponding ketone [(I) – acetone, (II) – acetophenone, (III) – cyclopentanone] in ethanol at room temperature. Then, the dinitriles were heated to 393–413 K upon stirring in an acidic medium to complete dissolving. After 10–15 min, the mixture was poured into ice–water. The precipitated tetraoxo-compounds were filtered off by suction, recrystallized from ethanol solution and finally dried. Single crystals suitable for X-ray diffraction study were obtained by recrystallization of the crude products from DMF solution.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The hydrogen atoms of the amino groups were localized in the difference-Fourier maps and refined isotropically with fixed displacement parameters [U_{iso}(H) = 1.2U_{eq}(N)]. The other hydrogen atoms were placed in calculated positions with C—H = 0.95–1.00 Å and refined in the riding/rotating model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the CH_3-groups and 1.2U_{eq}(C) for the other groups]. The crystal of (I) was a pseudo-merohedral twin. The twin matrix is ($\bar{1}$ 0 0 0 $\bar{1}$ 0 0.775 0 1), and BASF = 0.180 (1).

Acknowledgements

The synthesis, purification and crystallization of compounds (I)–(III) were funded by RSF (grant No. 16–13-00114). This work was financially supported in part by the Ministry of Education and Science of the Russian Federation (the Agreement number 02.*a*03.21.0008).

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Table 4
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_9H_{10}N_2O_4$	$C_{11}H_{12}N_2O_4$	$C_{14}H_{12}N_2O_4{\cdot}C_3H_7NO$
M_r	210.19	236.23	345.35
Crystal system, space group	Monoclinic, *C*2/*c*	Orthorhombic, *Pnma*	Orthorhombic, *Pbca*
Temperature (K)	100	120	120
a, *b*, *c* (Å)	11.4321 (17), 6.6263 (10), 12.4819 (19)	12.8058 (6), 11.4850 (6), 6.9058 (3)	7.7876 (5), 19.4656 (12), 21.7879 (13)
α, β, γ (°)	90, 110.788 (3), 90	90, 90, 90	90, 90, 90
V (Å^3)	884.0 (2)	1015.67 (8)	3302.8 (4)
Z	4	4	8
Radiation type	Mo *Kα*	Mo *Kα*	Mo *Kα*
μ (mm^{-1})	0.13	0.12	0.10
Crystal size (mm)	0.30 × 0.20 × 0.15	0.30 × 0.20 × 0.20	0.22 × 0.20 × 0.18
Data collection			
Diffractometer	Bruker *SMART* 1K CCD	Bruker *SMART* 1K CCD	Bruker *SMART* 1K CCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2003)	Multi-scan (*SADABS*; Sheldrick, 2003)	Multi-scan (*SADABS*; Sheldrick, 2003)
T_{min}, T_{max}	0.950, 0.970	0.960, 0.970	0.970, 0.975
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4993, 1289, 1165	15297, 2181, 1782	41691, 5056, 3210
R_{int}	0.027	0.031	0.090
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.703	0.802	0.716
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.062, 0.184, 1.06	0.043, 0.119, 1.03	0.051, 0.124, 1.01
No. of reflections	1289	2181	5056
No. of parameters	74	85	235
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.55, −0.54	0.42, −0.23	0.33, −0.26

Computer programs: *APEX2* (Bruker, 2005), *SAINT* (Bruker, 2001), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *SHELXTL* (Sheldrick, 2008).

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supporting information

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Crystal structures and supramolecular features of 9,9-dimethyl-3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraone, 3,7-diazaspiro[bicyclo-[3.3.1]nonane-9,1′-cyclopentane]-2,4,6,8-tetraone and 9-methyl-9-phenyl-3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraone dimethylformamide monosolvate

Sergey Z. Vatsadze, Marina A. Manaenkova, Evgeny V. Vasilev, Nikolai U. Venskovsky and Victor N. Khrustalev

Computing details

For all compounds, data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(I) 9,9-Dimethyl-3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraone

Crystal data

$C_9H_{10}N_2O_4$
M_r = 210.19
Monoclinic, $C2/c$
a = 11.4321 (17) Å
b = 6.6263 (10) Å
c = 12.4819 (19) Å
β = 110.788 (3)°
V = 884.0 (2) Å^3
Z = 4
$F(000)$ = 440
D_x = 1.579 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3269 reflections
θ = 3.5–30.0°
μ = 0.13 mm^{-1}
T = 100 K
Prism, colourless
0.30 × 0.20 × 0.15 mm

Data collection

Bruker SMART 1K CCD diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.950, T_{max} = 0.970
4993 measured reflections
1289 independent reflections
1165 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 30.0°, θ_{min} = 1.8°
$h = -16 \rightarrow 16$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.184
S = 1.06
1289 reflections
74 parameters
0 restraints

Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0846P)^2 + 3.9571P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ 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. Refined as a 2-component twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.39535 (15)	0.3325 (3)	0.25497 (14)	0.0103 (4)
H1	0.3243	0.4158	0.2595	0.012*
C2	0.43977 (16)	0.1911 (3)	0.35793 (14)	0.0110 (4)
O2	0.36911 (13)	0.1256 (2)	0.40357 (12)	0.0156 (3)
N3	0.56404 (14)	0.1339 (2)	0.39595 (13)	0.0119 (4)
H3	0.591 (3)	0.054 (4)	0.458 (2)	0.014*
C4	0.65231 (16)	0.1966 (3)	0.35040 (14)	0.0109 (4)
O4	0.75961 (13)	0.1393 (2)	0.39060 (12)	0.0161 (4)
C5	0.5000	0.4737 (4)	0.2500	0.0107 (5)
C6	0.54703 (18)	0.6086 (3)	0.35697 (16)	0.0147 (4)
H6A	0.6154	0.6941	0.3532	0.022*
H6B	0.5774	0.5239	0.4257	0.022*
H6C	0.4783	0.6939	0.3603	0.022*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0104 (7)	0.0099 (8)	0.0096 (7)	−0.0002 (5)	0.0026 (6)	0.0002 (5)
C2	0.0117 (8)	0.0105 (7)	0.0094 (7)	−0.0007 (6)	0.0021 (6)	−0.0012 (6)
O2	0.0148 (6)	0.0192 (7)	0.0135 (6)	−0.0021 (5)	0.0058 (5)	0.0027 (5)
N3	0.0131 (7)	0.0114 (7)	0.0106 (7)	0.0004 (5)	0.0035 (6)	0.0024 (5)
C4	0.0119 (8)	0.0105 (7)	0.0093 (7)	0.0000 (6)	0.0026 (6)	−0.0020 (6)
O4	0.0131 (7)	0.0200 (7)	0.0139 (7)	0.0037 (5)	0.0031 (5)	0.0006 (5)
C5	0.0107 (10)	0.0100 (10)	0.0114 (10)	0.000	0.0039 (8)	0.000
C6	0.0148 (8)	0.0129 (8)	0.0160 (8)	−0.0011 (6)	0.0049 (6)	−0.0039 (6)

Geometric parameters (Å, º)

C1—C2	1.525 (2)	N3—H3	0.90 (3)
C1—C4^{i}	1.527 (2)	C4—O4	1.210 (2)
C1—C5	1.537 (2)	C5—C6	1.537 (2)
C1—H1	1.0000	C6—H6A	0.9800

C2—O2	1.221 (2)	C6—H6B	0.9800
C2—N3	1.382 (2)	C6—H6C	0.9800
N3—C4	1.386 (2)		
C2—C1—C4^{i}	105.89 (14)	O4—C4—C1^{i}	122.81 (16)
C2—C1—C5	112.14 (13)	N3—C4—C1^{i}	116.17 (14)
C4^{i}—C1—C5	111.67 (12)	C6^{i}—C5—C6	108.8 (2)
C2—C1—H1	109.0	C6—C5—C1^{i}	110.59 (9)
C4^{i}—C1—H1	109.0	C6—C5—C1	110.87 (10)
C5—C1—H1	109.0	C1^{i}—C5—C1	105.1 (2)
O2—C2—N3	120.80 (17)	C5—C6—H6A	109.5
O2—C2—C1	122.27 (16)	C5—C6—H6B	109.5
N3—C2—C1	116.90 (15)	H6A—C6—H6B	109.5
C2—N3—C4	125.92 (15)	C5—C6—H6C	109.5
C2—N3—H3	117.3 (18)	H6A—C6—H6C	109.5
C4—N3—H3	116.7 (18)	H6B—C6—H6C	109.5
O4—C4—N3	120.97 (17)		
C4^{i}—C1—C2—O2	−86.7 (2)	C2—N3—C4—C1^{i}	−3.3 (3)
C5—C1—C2—O2	151.29 (17)	C2—C1—C5—C6^{i}	178.06 (14)
C4^{i}—C1—C2—N3	91.29 (17)	C4^{i}—C1—C5—C6^{i}	59.40 (19)
C5—C1—C2—N3	−30.7 (2)	C2—C1—C5—C6	−61.11 (19)
O2—C2—N3—C4	179.35 (16)	C4^{i}—C1—C5—C6	−179.77 (14)
C1—C2—N3—C4	1.3 (3)	C2—C1—C5—C1^{i}	58.38 (11)
C2—N3—C4—O4	179.26 (16)	C4^{i}—C1—C5—C1^{i}	−60.28 (11)

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O2^{ii}	0.90 (3)	2.01 (3)	2.906 (2)	173 (3)

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

(II) 3,7-Diazaspiro[bicyclo[3.3.1]nonane-9,1′-cyclopentane]-2,4,6,8-tetraone

Crystal data

$C_{11}H_{12}N_2O_4$
M_r = 236.23
Orthorhombic, *Pnma*
a = 12.8058 (6) Å
b = 11.4850 (6) Å
c = 6.9058 (3) Å
V = 1015.67 (8) Å^3
Z = 4
F(000) = 496
D_x = 1.545 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4118 reflections
θ = 3.2–33.9°
μ = 0.12 mm^{-1}
T = 120 K
Prism, colourless
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART 1K CCD diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.960, T_{max} = 0.970
15297 measured reflections
2181 independent reflections
1782 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 34.8°, θ_{min} = 3.2°
$h = -19 \rightarrow 19$
$k = -17 \rightarrow 18$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.119
S = 1.03
2181 reflections
85 parameters
0 restraints
Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.338P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
O1	0.40454 (6)	0.09843 (6)	0.57775 (10)	0.01863 (16)
O2	0.56727 (6)	0.10479 (6)	−0.00332 (11)	0.02057 (17)
C1	0.35046 (9)	0.2500	0.35970 (17)	0.0114 (2)
H1	0.2831	0.2500	0.4330	0.014*
C2	0.41314 (6)	0.14320 (7)	0.41787 (12)	0.01265 (16)
N3	0.48223 (6)	0.10060 (7)	0.28341 (11)	0.01450 (16)
H3	0.5177 (10)	0.0407 (13)	0.3159 (19)	0.017*
C4	0.49953 (7)	0.14512 (8)	0.09885 (13)	0.01376 (16)
C5	0.43357 (9)	0.2500	0.04181 (17)	0.0130 (2)
H5	0.4232	0.2500	−0.1017	0.016*
C6	0.32636 (9)	0.2500	0.14282 (17)	0.0130 (2)
C7	0.25898 (8)	0.14463 (9)	0.08181 (14)	0.01871 (19)
H7A	0.3034	0.0757	0.0571	0.022*
H7B	0.2078	0.1251	0.1842	0.022*
C8	0.20315 (9)	0.18259 (12)	−0.10339 (15)	0.0277 (2)
H8A	0.1307	0.1525	−0.1051	0.033*
H8B	0.2403	0.1525	−0.2187	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0241 (3)	0.0172 (3)	0.0146 (3)	0.0043 (2)	0.0040 (2)	0.0046 (2)
O2	0.0232 (3)	0.0186 (3)	0.0199 (3)	0.0043 (2)	0.0081 (3)	−0.0004 (3)
C1	0.0116 (4)	0.0102 (4)	0.0124 (4)	0.000	0.0003 (4)	0.000
C2	0.0135 (3)	0.0113 (3)	0.0131 (3)	−0.0001 (3)	0.0003 (3)	0.0000 (3)
N3	0.0172 (3)	0.0123 (3)	0.0140 (3)	0.0038 (2)	0.0023 (2)	0.0015 (2)
C4	0.0160 (4)	0.0120 (3)	0.0133 (3)	−0.0006 (3)	0.0010 (3)	−0.0007 (3)
C5	0.0149 (5)	0.0135 (5)	0.0105 (4)	0.000	−0.0001 (4)	0.000
C6	0.0130 (5)	0.0137 (5)	0.0124 (5)	0.000	−0.0017 (4)	0.000
C7	0.0170 (4)	0.0213 (4)	0.0179 (4)	−0.0047 (3)	−0.0031 (3)	−0.0026 (3)
C8	0.0248 (5)	0.0397 (6)	0.0187 (4)	−0.0066 (4)	−0.0075 (4)	−0.0015 (4)

Geometric parameters (Å, º)

O1—C2	1.2230 (11)	C5—C6	1.5399 (17)
O2—C4	1.2103 (11)	C5—H5	1.0000
C1—C2	1.5200 (11)	C6—C7	1.5448 (12)
C1—C6	1.5292 (17)	C7—C8	1.5287 (14)
C1—H1	1.0000	C7—H7A	0.9900
C2—N3	1.3727 (11)	C7—H7B	0.9900
N3—C4	1.3910 (11)	C8—C8^{i}	1.549 (3)
N3—H3	0.855 (14)	C8—H8A	0.9900
C4—C5	1.5231 (11)	C8—H8B	0.9900
C2^{i}—C1—C2	107.61 (9)	C1—C6—C5	105.29 (10)
C2—C1—C6	111.43 (6)	C1—C6—C7	112.32 (7)
C2—C1—H1	108.8	C5—C6—C7	111.99 (7)
C6—C1—H1	108.8	C7^{i}—C6—C7	103.14 (10)
O1—C2—N3	121.26 (8)	C8—C7—C6	105.43 (9)
O1—C2—C1	122.03 (8)	C8—C7—H7A	110.7
N3—C2—C1	116.69 (8)	C6—C7—H7A	110.7
C2—N3—C4	126.26 (8)	C8—C7—H7B	110.7
C2—N3—H3	116.9 (9)	C6—C7—H7B	110.7
C4—N3—H3	116.8 (9)	H7A—C7—H7B	108.8
O2—C4—N3	120.51 (8)	C7—C8—C8^{i}	106.57 (6)
O2—C4—C5	123.33 (9)	C7—C8—H8A	110.4
N3—C4—C5	116.06 (8)	C8^{i}—C8—H8A	110.4
C4^{i}—C5—C4	104.54 (10)	C7—C8—H8B	110.4
C4—C5—C6	112.17 (7)	C8^{i}—C8—H8B	110.4
C4—C5—H5	109.3	H8A—C8—H8B	108.6
C6—C5—H5	109.3		
C2^{i}—C1—C2—O1	89.14 (11)	C2^{i}—C1—C6—C7^{i}	−62.03 (11)
C6—C1—C2—O1	−148.42 (9)	C2—C1—C6—C7^{i}	177.76 (8)
C2^{i}—C1—C2—N3	−89.33 (10)	C2^{i}—C1—C6—C7	−177.76 (8)
C6—C1—C2—N3	33.11 (11)	C2—C1—C6—C7	62.03 (11)

O1—C2—N3—C4	−179.14 (8)	C4^{i}—C5—C6—C1	−58.65 (7)
C1—C2—N3—C4	−0.66 (13)	C4—C5—C6—C1	58.65 (7)
C2—N3—C4—O2	175.36 (9)	C4^{i}—C5—C6—C7^{i}	63.69 (12)
C2—N3—C4—C5	−1.04 (13)	C4—C5—C6—C7^{i}	−179.00 (8)
O2—C4—C5—C4^{i}	−84.18 (12)	C4^{i}—C5—C6—C7	179.00 (8)
N3—C4—C5—C4^{i}	92.10 (10)	C4—C5—C6—C7	−63.70 (12)
O2—C4—C5—C6	154.04 (9)	C1—C6—C7—C8	155.71 (9)
N3—C4—C5—C6	−29.68 (11)	C5—C6—C7—C8	−86.05 (10)
C2^{i}—C1—C6—C5	60.10 (7)	C7^{i}—C6—C7—C8	34.55 (12)
C2—C1—C6—C5	−60.11 (7)	C6—C7—C8—C8^{i}	−21.58 (8)

Symmetry code: (i) x, $-y+1/2$, z.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1^{ii}	0.855 (14)	2.021 (14)	2.8718 (11)	173.7 (13)

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

(III) 9-Methyl-9-phenyl-3,7-diazabicyclo[3.3.1]nonane-2,4,6,8-tetraone dimethylformamide monosolvate

Crystal data

$C_{14}H_{12}N_2O_4{\cdot}C_3H_7NO$
M_r = 345.35
Orthorhombic, *Pbca*
a = 7.7876 (5) Å
b = 19.4656 (12) Å
c = 21.7879 (13) Å
V = 3302.8 (4) Å^3
Z = 8
F(000) = 1456
D_x = 1.389 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2856 reflections
θ = 2.3–26.0°
μ = 0.10 mm^{-1}
T = 120 K
Prism, colourless
0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART 1K CCD diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.970, T_{max} = 0.975
41691 measured reflections
5056 independent reflections
3210 reflections with $I > 2\sigma(I)$
R_{int} = 0.090
θ_{max} = 30.6°, θ_{min} = 1.9°
$h = -11 \rightarrow 11$
$k = -27 \rightarrow 27$
$l = -31 \rightarrow 30$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.124
S = 1.01
5056 reflections
235 parameters
0 restraints
Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 1.1286P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.91018 (15)	0.32972 (6)	0.24687 (5)	0.0195 (3)
O2	1.28067 (16)	0.39316 (7)	0.39546 (6)	0.0277 (3)
O3	1.05101 (18)	0.54938 (6)	0.41859 (6)	0.0284 (3)
O4	0.71389 (17)	0.48551 (6)	0.25953 (6)	0.0247 (3)
C1	0.7904 (2)	0.39619 (8)	0.33006 (7)	0.0154 (3)
H1	0.6777	0.3746	0.3193	0.019*
C2	0.9331 (2)	0.35860 (8)	0.29593 (7)	0.0156 (3)
N3	1.09219 (18)	0.36122 (7)	0.32247 (6)	0.0169 (3)
H3	1.178 (2)	0.3463 (10)	0.3014 (9)	0.020*
C4	1.1346 (2)	0.39341 (9)	0.37714 (7)	0.0176 (3)
C5	0.9888 (2)	0.42888 (8)	0.41126 (8)	0.0159 (3)
H5	1.0146	0.4280	0.4562	0.019*
C6	0.9822 (2)	0.50346 (9)	0.38999 (8)	0.0197 (4)
N7	0.89576 (19)	0.51620 (7)	0.33590 (7)	0.0196 (3)
H7	0.902 (3)	0.5588 (10)	0.3194 (9)	0.024*
C8	0.7939 (2)	0.46953 (9)	0.30509 (8)	0.0177 (3)
C9	0.8163 (2)	0.39217 (8)	0.40019 (7)	0.0157 (3)
C10	0.8217 (2)	0.31744 (8)	0.42225 (7)	0.0157 (3)
C11	0.7451 (2)	0.26429 (9)	0.38892 (8)	0.0200 (4)
H11	0.6928	0.2740	0.3505	0.024*
C12	0.7444 (2)	0.19734 (9)	0.41138 (8)	0.0229 (4)
H12	0.6912	0.1618	0.3883	0.027*
C13	0.8208 (2)	0.18232 (9)	0.46704 (8)	0.0226 (4)
H13	0.8210	0.1365	0.4821	0.027*
C14	0.8969 (2)	0.23430 (9)	0.50061 (8)	0.0218 (4)
H14	0.9496	0.2242	0.5389	0.026*
C15	0.8965 (2)	0.30139 (9)	0.47846 (8)	0.0196 (4)
H15	0.9482	0.3368	0.5021	0.024*
C16	0.6721 (2)	0.43004 (9)	0.43480 (8)	0.0205 (4)
H16A	0.6658	0.4777	0.4205	0.031*
H16B	0.6965	0.4295	0.4789	0.031*
H16C	0.5623	0.4071	0.4270	0.031*
O5	0.91561 (18)	0.64557 (7)	0.28362 (6)	0.0289 (3)
N1	0.84929 (19)	0.65410 (7)	0.18198 (7)	0.0212 (3)
C17	0.8439 (2)	0.67440 (9)	0.24001 (8)	0.0232 (4)
H17	0.7793	0.7146	0.2489	0.028*
C18	0.9381 (3)	0.59137 (10)	0.16458 (9)	0.0284 (4)
H18A	1.0181	0.5782	0.1972	0.043*
H18B	1.0020	0.5991	0.1265	0.043*

H18C	0.8541	0.5545	0.1583	0.043*
C19	0.7595 (3)	0.69190 (10)	0.13395 (9)	0.0273 (4)
H19A	0.6956	0.7301	0.1523	0.041*
H19B	0.6795	0.6611	0.1128	0.041*
H19C	0.8431	0.7099	0.1044	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0215 (6)	0.0208 (6)	0.0164 (6)	0.0008 (5)	−0.0011 (5)	−0.0023 (5)
O2	0.0151 (6)	0.0414 (8)	0.0265 (7)	−0.0016 (6)	−0.0042 (5)	−0.0007 (6)
O3	0.0373 (8)	0.0194 (7)	0.0286 (7)	−0.0081 (6)	−0.0075 (6)	−0.0011 (5)
O4	0.0294 (7)	0.0235 (7)	0.0213 (6)	0.0040 (5)	−0.0068 (5)	0.0021 (5)
C1	0.0142 (8)	0.0162 (8)	0.0160 (8)	−0.0006 (6)	−0.0027 (6)	0.0005 (6)
C2	0.0166 (8)	0.0145 (8)	0.0156 (8)	−0.0004 (6)	0.0002 (6)	0.0030 (6)
N3	0.0127 (7)	0.0211 (7)	0.0168 (7)	0.0026 (6)	0.0007 (5)	0.0004 (6)
C4	0.0176 (8)	0.0189 (8)	0.0162 (8)	−0.0033 (6)	−0.0018 (6)	0.0029 (7)
C5	0.0155 (8)	0.0174 (8)	0.0148 (8)	−0.0029 (6)	−0.0014 (6)	−0.0001 (6)
C6	0.0189 (8)	0.0194 (8)	0.0207 (9)	−0.0007 (7)	−0.0009 (7)	−0.0003 (7)
N7	0.0235 (8)	0.0153 (7)	0.0200 (7)	−0.0010 (6)	−0.0029 (6)	0.0019 (6)
C8	0.0168 (8)	0.0186 (8)	0.0177 (8)	0.0036 (6)	0.0010 (6)	−0.0019 (7)
C9	0.0140 (8)	0.0190 (8)	0.0141 (8)	−0.0015 (6)	−0.0009 (6)	−0.0009 (6)
C10	0.0140 (8)	0.0178 (8)	0.0152 (8)	−0.0023 (6)	0.0037 (6)	0.0002 (6)
C11	0.0221 (9)	0.0217 (9)	0.0162 (8)	−0.0031 (7)	−0.0002 (7)	0.0002 (7)
C12	0.0269 (9)	0.0203 (9)	0.0216 (9)	−0.0052 (7)	0.0030 (7)	−0.0032 (7)
C13	0.0255 (10)	0.0193 (9)	0.0231 (9)	0.0006 (7)	0.0050 (7)	0.0023 (7)
C14	0.0220 (9)	0.0249 (9)	0.0185 (8)	0.0002 (7)	−0.0006 (7)	0.0027 (7)
C15	0.0198 (9)	0.0208 (9)	0.0183 (8)	−0.0028 (7)	−0.0003 (7)	−0.0007 (7)
C16	0.0168 (8)	0.0246 (9)	0.0200 (8)	0.0004 (7)	0.0015 (7)	−0.0014 (7)
O5	0.0420 (8)	0.0229 (7)	0.0218 (7)	−0.0009 (6)	−0.0041 (6)	0.0037 (5)
N1	0.0230 (8)	0.0195 (7)	0.0210 (7)	0.0020 (6)	−0.0005 (6)	0.0007 (6)
C17	0.0286 (10)	0.0169 (8)	0.0240 (9)	−0.0006 (7)	0.0012 (8)	0.0011 (7)
C18	0.0328 (11)	0.0249 (10)	0.0276 (10)	0.0060 (8)	0.0064 (8)	−0.0001 (8)
C19	0.0317 (11)	0.0259 (10)	0.0244 (9)	−0.0014 (8)	−0.0075 (8)	0.0049 (8)

Geometric parameters (Å, º)

O1—C2	1.2209 (19)	C11—H11	0.9500
O2—C4	1.205 (2)	C12—C13	1.382 (3)
O3—C6	1.214 (2)	C12—H12	0.9500
O4—C8	1.213 (2)	C13—C14	1.382 (2)
C1—C2	1.524 (2)	C13—H13	0.9500
C1—C8	1.528 (2)	C14—C15	1.392 (2)
C1—C9	1.543 (2)	C14—H14	0.9500
C1—H1	1.0000	C15—H15	0.9500
C2—N3	1.368 (2)	C16—H16A	0.9800
N3—C4	1.386 (2)	C16—H16B	0.9800
N3—H3	0.861 (19)	C16—H16C	0.9800

C4—C5	1.523 (2)	O5—C17	1.237 (2)
C5—C6	1.525 (2)	N1—C17	1.325 (2)
C5—C9	1.541 (2)	N1—C18	1.454 (2)
C5—H5	1.0000	N1—C19	1.458 (2)
C6—N7	1.380 (2)	C17—H17	0.9500
N7—C8	1.380 (2)	C18—H18A	0.9800
N7—H7	0.90 (2)	C18—H18B	0.9800
C9—C10	1.533 (2)	C18—H18C	0.9800
C9—C16	1.540 (2)	C19—H19A	0.9800
C10—C15	1.392 (2)	C19—H19B	0.9800
C10—C11	1.398 (2)	C19—H19C	0.9800
C11—C12	1.392 (2)		

C2—C1—C8	105.18 (13)	C12—C11—C10	120.78 (16)
C2—C1—C9	111.30 (13)	C12—C11—H11	119.6
C8—C1—C9	113.43 (13)	C10—C11—H11	119.6
C2—C1—H1	108.9	C13—C12—C11	120.33 (17)
C8—C1—H1	108.9	C13—C12—H12	119.8
C9—C1—H1	108.9	C11—C12—H12	119.8
O1—C2—N3	121.31 (15)	C12—C13—C14	119.61 (17)
O1—C2—C1	122.78 (15)	C12—C13—H13	120.2
N3—C2—C1	115.87 (14)	C14—C13—H13	120.2
C2—N3—C4	126.58 (15)	C13—C14—C15	120.16 (17)
C2—N3—H3	117.7 (13)	C13—C14—H14	119.9
C4—N3—H3	115.2 (13)	C15—C14—H14	119.9
O2—C4—N3	120.51 (16)	C10—C15—C14	121.10 (16)
O2—C4—C5	122.95 (15)	C10—C15—H15	119.5
N3—C4—C5	116.53 (14)	C14—C15—H15	119.5
C4—C5—C6	107.97 (14)	C9—C16—H16A	109.5
C4—C5—C9	111.32 (13)	C9—C16—H16B	109.5
C6—C5—C9	111.39 (14)	H16A—C16—H16B	109.5
C4—C5—H5	108.7	C9—C16—H16C	109.5
C6—C5—H5	108.7	H16A—C16—H16C	109.5
C9—C5—H5	108.7	H16B—C16—H16C	109.5
O3—C6—N7	121.43 (16)	C17—N1—C18	120.96 (15)
O3—C6—C5	122.02 (15)	C17—N1—C19	121.26 (15)
N7—C6—C5	116.55 (15)	C18—N1—C19	117.71 (15)
C6—N7—C8	125.29 (15)	O5—C17—N1	125.66 (17)
C6—N7—H7	118.5 (13)	O5—C17—H17	117.2
C8—N7—H7	116.2 (13)	N1—C17—H17	117.2
O4—C8—N7	121.65 (16)	N1—C18—H18A	109.5
O4—C8—C1	121.45 (15)	N1—C18—H18B	109.5
N7—C8—C1	116.88 (14)	H18A—C18—H18B	109.5
C10—C9—C16	108.70 (13)	N1—C18—H18C	109.5
C10—C9—C5	111.53 (13)	H18A—C18—H18C	109.5
C16—C9—C5	109.69 (13)	H18B—C18—H18C	109.5
C10—C9—C1	111.25 (13)	N1—C19—H19A	109.5
C16—C9—C1	111.43 (13)	N1—C19—H19B	109.5

C5—C9—C1	104.20 (13)	H19A—C19—H19B	109.5
C15—C10—C11	118.01 (15)	N1—C19—H19C	109.5
C15—C10—C9	120.04 (14)	H19A—C19—H19C	109.5
C11—C10—C9	121.86 (14)	H19B—C19—H19C	109.5

C8—C1—C2—O1	−88.55 (18)	C4—C5—C9—C16	−179.36 (13)
C9—C1—C2—O1	148.23 (15)	C6—C5—C9—C16	−58.79 (18)
C8—C1—C2—N3	89.02 (16)	C4—C5—C9—C1	−59.96 (16)
C9—C1—C2—N3	−34.20 (19)	C6—C5—C9—C1	60.61 (16)
O1—C2—N3—C4	178.71 (15)	C2—C1—C9—C10	−58.45 (17)
C1—C2—N3—C4	1.1 (2)	C8—C1—C9—C10	−176.82 (13)
C2—N3—C4—O2	−178.77 (16)	C2—C1—C9—C16	−179.93 (13)
C2—N3—C4—C5	0.6 (2)	C8—C1—C9—C16	61.69 (18)
O2—C4—C5—C6	87.7 (2)	C2—C1—C9—C5	61.86 (16)
N3—C4—C5—C6	−91.58 (17)	C8—C1—C9—C5	−56.52 (17)
O2—C4—C5—C9	−149.71 (16)	C16—C9—C10—C15	−77.40 (18)
N3—C4—C5—C9	31.0 (2)	C5—C9—C10—C15	43.7 (2)
C4—C5—C6—O3	−96.53 (19)	C1—C9—C10—C15	159.54 (15)
C9—C5—C6—O3	140.95 (17)	C16—C9—C10—C11	99.18 (17)
C4—C5—C6—N7	82.61 (18)	C5—C9—C10—C11	−139.75 (16)
C9—C5—C6—N7	−39.9 (2)	C1—C9—C10—C11	−23.9 (2)
O3—C6—N7—C8	−170.25 (17)	C15—C10—C11—C12	−0.2 (2)
C5—C6—N7—C8	10.6 (2)	C9—C10—C11—C12	−176.84 (16)
C6—N7—C8—O4	175.77 (16)	C10—C11—C12—C13	−0.4 (3)
C6—N7—C8—C1	−5.8 (2)	C11—C12—C13—C14	0.5 (3)
C2—C1—C8—O4	87.35 (18)	C12—C13—C14—C15	0.0 (3)
C9—C1—C8—O4	−150.80 (15)	C11—C10—C15—C14	0.7 (2)
C2—C1—C8—N7	−91.04 (16)	C9—C10—C15—C14	177.42 (15)
C9—C1—C8—N7	30.8 (2)	C13—C14—C15—C10	−0.6 (3)
C4—C5—C9—C10	60.15 (17)	C18—N1—C17—O5	3.0 (3)
C6—C5—C9—C10	−179.28 (13)	C19—N1—C17—O5	179.89 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1^{i}	0.861 (19)	2.12 (2)	2.9650 (19)	168.3 (18)
N7—H7···O5	0.90 (2)	1.86 (2)	2.7682 (19)	178.6 (18)

Symmetry code: (i) x+1/2, y, −z+1/2.