



Crystal structure of (*Z*)-*N*-benzylidene-1-phenylmethanamine oxide hydrogen peroxide monosolvate

Andrei V. Churakov,* Petr V. Prikhodchenko, Alexander G. Medvedev and Alexey A. Mikhaylov

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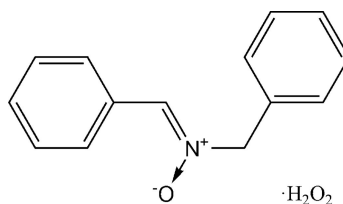
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Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii prospekt 31, Moscow 119991, Russian Federation. *Correspondence e-mail: churakov@igic.ras.ru

The title adduct, C₁₄H₁₃NO·H₂O₂, consists of (*Z*)-*N*-benzylidene-1-phenylmethanamine oxide and hydrogen peroxide molecules in a 1:1 ratio. The organic cofomer adopts a skew geometry with an inter-aryl-ring dihedral angle of 81.9 (2)°. In the crystal, the organic and peroxide molecules are linked through both peroxide O—H donor groups to oxide O-atom acceptors, giving one-dimensional chains extending along the *b* axis. Present also are weak intermolecular C—H···O hydrogen-bonding interactions.

1. Chemical context

Peroxosolvates are solid adducts that contain hydrogen peroxide molecules of crystallization in the same manner as the water in crystalline hydrates. Today, some of these are widely used as environmentally friendly bleaching compounds (Jakob *et al.*, 2012) and oxidizing agents in organic synthesis (Ahn *et al.*, 2015). Hydrogen bonding in peroxosolvates is of particular interest since it may be used for modelling of hydrogen peroxide behaviour in various significant biochemical processes (Kapustin *et al.*, 2014).



It is known that nitrones $R^1\text{-CH=N(O)-R}^2$ [R^1 , R^2 = aryl (Ar) or alkyl (Alk)] are readily available by oxidation of secondary amines using hydrogen peroxide (Goti *et al.*, 2005). We supposed that the combination of oxidizing and cocrystallizing properties of hydrogen peroxide might afford an opportunity to obtain nitron peroxosolvates in one step. We prepared the title 1:1 adduct of (*Z*)-*N*-benzylidene-1-phenylmethanamine oxide with hydrogen peroxide and the structure is reported herein.

2. Structural commentary

In the structure of the title adduct (Fig. 1), all bond lengths and angles in the organic cofomer exhibit normal values for nitron derivatives (Cambridge Structural Database, Version

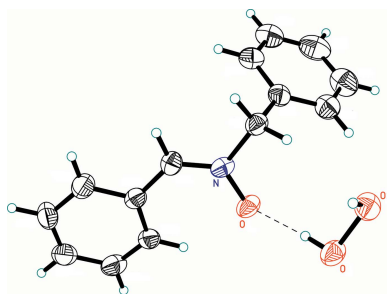


Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 \cdots O3	1.05 (5)	1.66 (5)	2.707 (5)	174 (4)
O2–H2 \cdots O3 ⁱ	1.06 (5)	1.64 (5)	2.681 (5)	166 (4)
C21–H21 \cdots O1 ⁱⁱ	0.95	2.46	3.304 (6)	148
C27–H27 \cdots O3	0.95	2.29	2.902 (6)	121
C11–H111 \cdots O1 ⁱⁱ	0.99	2.44	3.364 (7)	155
C11–H111 \cdots O2 ⁱⁱ	0.99	2.47	3.394 (7)	155
C11–H112 \cdots O2	0.99	2.52	3.407 (7)	149

Symmetry codes: (i) $x, y + 1, z$; (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.

5.38, May 2017; Groom *et al.*, 2016). The nitron fragment Ph–CH=N(O)–C is planar to within 0.128 (3) Å. It is almost perpendicular to the benzyl substituent C11–C17, with an O3–N1–C11–C12 torsion angle of 72.7 (4)°, and forms a dihedral angle between the two aryl rings of 81.9 (2)°. This is the same conformation as was previously observed in the structure of the pure cofomer (Herrera *et al.*, 2001). The organic molecule forms two hydrogen bonds, involving the negatively charged oxide atom O3, with adjacent peroxide molecules and the conformation is stabilized by an aromatic C27–H \cdots O3 hydrogen bond (Table 1). As expected, the N1–O3 \cdots O(peroxo) angles are close to trigonal [117.9 (2) and 126.2 (2)°].

In the peroxide molecule, the O–O distance is 1.467 (4) Å. This value is close to those previously observed in the accurately determined structures of crystalline hydrogen peroxide [1.461 (3) Å; Savariault *et al.*, 1980] and urea perhydrate [1.4573 (8) Å; Fritchie & McMullan, 1981]. Partial substitutional disorder of hydrogen peroxide by water molecules (Pedersen, 1972) was not observed in the present structure since no residual peaks with an intensity of 0.14 e Å^{−3} were seen in the hydrogen peroxide molecule region (Churakov *et al.*, 2005). The H₂O₂ molecule lies on a general position and presents a skew geometry, with the H–O–O–H torsion

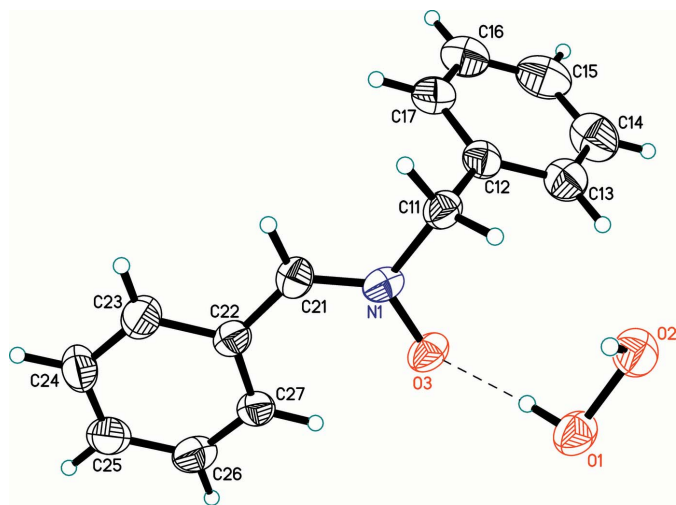


Figure 1
The asymmetric unit in the title structure. Displacement ellipsoids are shown at the 50% probability level and the hydrogen bond is drawn as a dashed line.

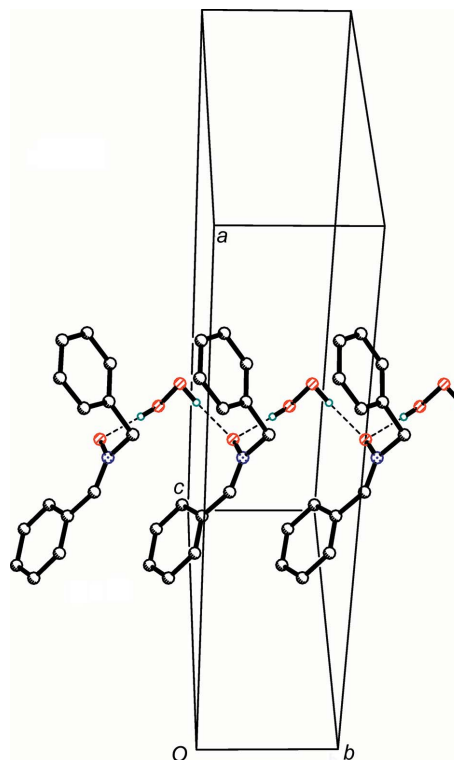


Figure 2
Hydrogen-bonded chains extending along the b axis. H atoms on C atoms have been omitted for clarity. Hydrogen bonds are drawn as dashed lines.

angle equal to 88 (4)°, and forms just two donor hydrogen bonds. It should be noted that the maximum possible number of hydrogen bonds formed by H₂O₂ is six (two donor and four acceptor; Chernyshov *et al.*, 2017).

3. Supramolecular features

In the title crystal, the organic and peroxide molecules are linked into hydrogen-bonded chains extending along the b axis through charge-supported moderate HOOH \cdots O[−]N hydrogen bonds, with O \cdots O separations of 2.707 (5) and 2.681 (5) Å (Table 1 and Fig. 2). Similar chains formed by N -oxide and H₂O₂ molecules were previously observed in the structure of risperidone N -oxide hydrogen peroxide methanol solvate (Ravikumar *et al.*, 2005). In the present one-dimensional structure, minor weak non-aromatic C–H \cdots O(peroxide) hydrogen-bonding interactions are also present.

4. Database survey

The Cambridge Structural Database (Groom *et al.*, 2016) contains data for nine peroxosolvates of N - and P -oxides with one or two $R_3X^+ \rightarrow O^-$ functional groups ($X = N, P$; $R = \text{Alk}, \text{Ar}$). It is of interest that all of these were obtained by oxidation of the corresponding amines (phosphines) using hydrogen peroxide, followed by immediate crystallization from the reaction mixtures. Analysis of the crystal packing for these compounds reveals three main supramolecular motifs

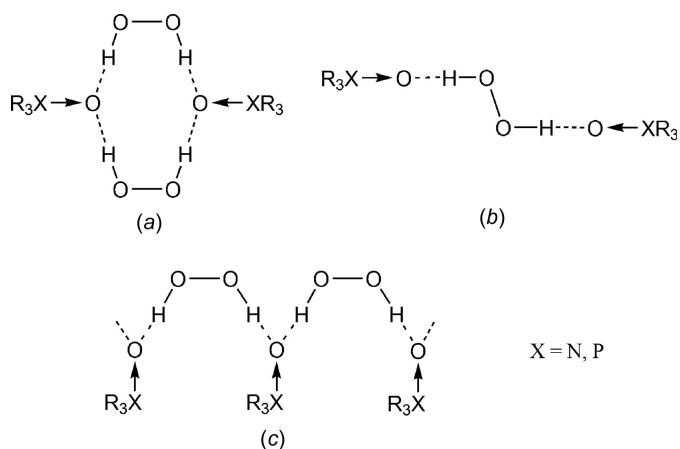


Figure 3
Hydrogen-bonded motifs in the structures of *N*- and *P*-oxides.

(Fig. 3*a–c*). Compounds BAFGOH (Ahn *et al.*, 2015), BAFJUQ (Ahn *et al.*, 2015), VANVOX (Hilliard *et al.*, 2012) and XETSUK (Čermák *et al.*, 2001) belong to type *a* [$R_4^2(10)$]; compounds EKULUR (Chandrasekaran *et al.*, 2002), TPPOPH (Thierbach *et al.*, 1980) and UKEFEV (Sevcik *et al.*, 2003) represent type *b* [$D_2^2(6)$]. Finally, the title compound and DATHIQ (Ravikumar *et al.*, 2005) are of type *c* [$C_2^1(5)$]. The relative simplicity of these motifs is caused by the absence of active H atoms in cofomers of the aforementioned compounds. The special case is the three-dimensional structure of triethylenediamine *N,N'*-dioxide triperoxosolvate (FURFIH; Kay Hon & Mak, 1987).

5. Synthesis and crystallization

Needle-shaped crystals of the title compound crystallized spontaneously from a saturated solution of dibenzylamine in 50% hydrogen peroxide after holding for 3 d at room temperature. **Caution!** Handling procedures for concentrated hydrogen peroxide (danger of explosion) are described in detail by Wolanov *et al.* (2010).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Peroxide H atoms were found from a difference electron-density map and refined with individual isotropic displacement parameters and restrained O–H distances. All other H atoms were placed in calculated positions, with C–H = 0.95 (aromatic) or 0.99 Å (methylene), and treated as riding atoms, with relative isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Acknowledgements

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Table 2
Experimental details.

Crystal data	$\text{C}_{14}\text{H}_{13}\text{NO}\cdot\text{H}_2\text{O}_2$
Chemical formula	245.27
M_r	Monoclinic, $P2_1/c$
Crystal system, space group	150
Temperature (K)	21.802 (15), 4.597 (3), 12.742 (9)
a, b, c (Å)	97.598 (11)
β (°)	1265.8 (16)
V (Å ³)	4
Z	Mo $K\alpha$
Radiation type	0.09
μ (mm ⁻¹)	0.40 × 0.04 × 0.04
Crystal size (mm)	
Data collection	
Diffractometer	Bruker SMART APEXII area-detector
Absorption correction	Multi-scan (SADABS; Bruker, 2008)
$T_{\text{min}}, T_{\text{max}}$	0.965, 0.996
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7458, 2227, 1113
R_{int}	0.108
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.077, 0.218, 1.05
No. of reflections	2227
No. of parameters	172
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.27, -0.26

Computer programs: APEX2 (Bruker, 2008), SAINT (Bruker, 2008), SHELXS97 (Sheldrick, 2008), SHELXL97 (Sheldrick, 2008), SHELXTL (Sheldrick, 2008).

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE* (Bruker, 2008); 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: *SHELXTL* (Sheldrick, 2008).

(Z)-N-Benzylidene-1-phenylmethanamine oxide hydrogen peroxide monosolvate

Crystal data

$C_{14}H_{13}NO \cdot H_2O_2$

$M_r = 245.27$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 21.802$ (15) Å

$b = 4.597$ (3) Å

$c = 12.742$ (9) Å

$\beta = 97.598$ (11)°

$V = 1265.8$ (16) Å³

$Z = 4$

$F(000) = 520$

$D_x = 1.287$ Mg m⁻³

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

Cell parameters from 737 reflections

$\theta = 3.2$ – 21.9 °

$\mu = 0.09$ mm⁻¹

$T = 150$ K

Needle, colourless

$0.40 \times 0.04 \times 0.04$ mm

Data collection

Bruker SMART APEXII area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2008)

$T_{\min} = 0.965$, $T_{\max} = 0.996$

7458 measured reflections

2227 independent reflections

1113 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.108$

$\theta_{\max} = 25.1$ °, $\theta_{\min} = 1.9$ °

$h = -25 \rightarrow 25$

$k = -5 \rightarrow 5$

$l = -15 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.077$

$wR(F^2) = 0.218$

$S = 1.05$

2227 reflections

172 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$

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

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

$$\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.034 (6)

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. 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 $F^2 > 2\text{sigma}(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.23321 (15)	0.7522 (7)	1.0077 (3)	0.0427 (9)
O2	0.28942 (16)	0.9116 (7)	0.9911 (3)	0.0442 (10)
O3	0.22608 (15)	0.3093 (6)	0.8666 (2)	0.0377 (9)
N1	0.23366 (18)	0.3713 (7)	0.7676 (3)	0.0319 (10)
C11	0.2883 (2)	0.5529 (9)	0.7569 (4)	0.0342 (12)
H112	0.2894	0.7210	0.8057	0.041*
H111	0.2855	0.6284	0.6836	0.041*
C12	0.3463 (2)	0.3775 (9)	0.7821 (4)	0.0344 (12)
C13	0.3802 (2)	0.3866 (10)	0.8826 (4)	0.0438 (13)
H13	0.3672	0.5083	0.9356	0.053*
C14	0.4332 (2)	0.2183 (12)	0.9054 (5)	0.0573 (16)
H14	0.4563	0.2229	0.9741	0.069*
C15	0.4521 (3)	0.0431 (12)	0.8270 (5)	0.0592 (17)
H15	0.4888	-0.0694	0.8422	0.071*
C16	0.4190 (2)	0.0295 (12)	0.7281 (5)	0.0521 (15)
H16	0.4317	-0.0952	0.6756	0.063*
C17	0.3671 (2)	0.1997 (10)	0.7062 (4)	0.0423 (13)
H17	0.3447	0.1954	0.6370	0.051*
C21	0.1988 (2)	0.2713 (9)	0.6851 (4)	0.0334 (11)
H21	0.2083	0.3366	0.6184	0.040*
C22	0.1470 (2)	0.0714 (9)	0.6825 (4)	0.0330 (12)
C23	0.1155 (2)	0.0141 (11)	0.5825 (4)	0.0432 (13)
H23	0.1280	0.1064	0.5221	0.052*
C24	0.0658 (2)	-0.1774 (11)	0.5704 (4)	0.0480 (14)
H24	0.0438	-0.2129	0.5022	0.058*
C25	0.0486 (2)	-0.3157 (11)	0.6579 (4)	0.0479 (14)
H25	0.0149	-0.4481	0.6499	0.057*
C26	0.0800 (2)	-0.2629 (11)	0.7565 (4)	0.0443 (14)
H26	0.0681	-0.3606	0.8164	0.053*
C27	0.1284 (2)	-0.0708 (9)	0.7696 (4)	0.0356 (12)
H27	0.1495	-0.0341	0.8384	0.043*
H1	0.232 (2)	0.588 (9)	0.950 (4)	0.060 (15)*

H2 0.268 (2) 1.058 (10) 0.933 (4) 0.057 (15)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.054 (2)	0.0379 (19)	0.038 (2)	-0.0100 (17)	0.0135 (17)	-0.0039 (15)
O2	0.050 (2)	0.0394 (19)	0.044 (2)	-0.0075 (17)	0.0069 (18)	-0.0001 (16)
O3	0.052 (2)	0.0361 (17)	0.026 (2)	-0.0051 (15)	0.0106 (16)	0.0026 (14)
N1	0.041 (2)	0.027 (2)	0.029 (2)	0.0001 (18)	0.012 (2)	-0.0011 (17)
C11	0.041 (3)	0.033 (2)	0.029 (3)	-0.005 (2)	0.008 (2)	-0.001 (2)
C12	0.038 (3)	0.030 (2)	0.036 (3)	-0.007 (2)	0.006 (2)	0.004 (2)
C13	0.043 (3)	0.045 (3)	0.044 (4)	0.000 (3)	0.005 (3)	0.005 (2)
C14	0.047 (3)	0.064 (4)	0.058 (4)	0.003 (3)	-0.002 (3)	0.019 (3)
C15	0.052 (4)	0.048 (3)	0.080 (5)	0.004 (3)	0.020 (4)	0.016 (3)
C16	0.044 (3)	0.054 (3)	0.060 (4)	0.004 (3)	0.014 (3)	0.006 (3)
C17	0.042 (3)	0.043 (3)	0.043 (3)	-0.002 (3)	0.012 (3)	0.004 (2)
C21	0.038 (3)	0.031 (2)	0.031 (3)	0.004 (2)	0.001 (2)	0.001 (2)
C22	0.035 (3)	0.034 (2)	0.030 (3)	0.004 (2)	0.007 (2)	0.000 (2)
C23	0.046 (3)	0.047 (3)	0.035 (3)	0.000 (3)	0.004 (3)	-0.003 (2)
C24	0.039 (3)	0.056 (3)	0.046 (4)	-0.005 (3)	-0.005 (3)	-0.007 (3)
C25	0.042 (3)	0.051 (3)	0.053 (4)	-0.008 (3)	0.016 (3)	-0.013 (3)
C26	0.051 (3)	0.042 (3)	0.043 (3)	-0.002 (3)	0.017 (3)	-0.005 (2)
C27	0.033 (3)	0.038 (3)	0.037 (3)	-0.001 (2)	0.009 (2)	-0.004 (2)

Geometric parameters (Å, °)

O1—O2	1.467 (4)	C16—C17	1.375 (7)
O1—H1	1.05 (4)	C16—H16	0.9500
O2—H2	1.06 (4)	C17—H17	0.9500
O3—N1	1.325 (4)	C21—C22	1.454 (6)
N1—C21	1.297 (6)	C21—H21	0.9500
N1—C11	1.475 (6)	C22—C23	1.390 (6)
C11—C12	1.498 (6)	C22—C27	1.393 (6)
C11—H112	0.9900	C23—C24	1.388 (7)
C11—H111	0.9900	C23—H23	0.9500
C12—C17	1.388 (6)	C24—C25	1.378 (7)
C12—C13	1.392 (7)	C24—H24	0.9500
C13—C14	1.388 (7)	C25—C26	1.371 (7)
C13—H13	0.9500	C25—H25	0.9500
C14—C15	1.389 (8)	C26—C27	1.368 (7)
C14—H14	0.9500	C26—H26	0.9500
C15—C16	1.368 (8)	C27—H27	0.9500
C15—H15	0.9500		
O2—O1—H1	102 (3)	C17—C16—H16	120.6
O1—O2—H2	97 (3)	C16—C17—C12	122.0 (5)
C21—N1—O3	124.2 (4)	C16—C17—H17	119.0
C21—N1—C11	121.3 (4)	C12—C17—H17	119.0

O3—N1—C11	114.4 (4)	N1—C21—C22	127.8 (4)
N1—C11—C12	110.1 (3)	N1—C21—H21	116.1
N1—C11—H112	109.6	C22—C21—H21	116.1
C12—C11—H112	109.6	C23—C22—C27	118.8 (4)
N1—C11—H111	109.6	C23—C22—C21	115.4 (4)
C12—C11—H111	109.6	C27—C22—C21	125.8 (5)
H112—C11—H111	108.1	C24—C23—C22	120.3 (5)
C17—C12—C13	118.4 (5)	C24—C23—H23	119.8
C17—C12—C11	120.8 (5)	C22—C23—H23	119.8
C13—C12—C11	120.9 (4)	C25—C24—C23	119.6 (5)
C14—C13—C12	120.2 (5)	C25—C24—H24	120.2
C14—C13—H13	119.9	C23—C24—H24	120.2
C12—C13—H13	119.9	C26—C25—C24	120.2 (5)
C13—C14—C15	119.3 (6)	C26—C25—H25	119.9
C13—C14—H14	120.3	C24—C25—H25	119.9
C15—C14—H14	120.3	C27—C26—C25	120.6 (5)
C16—C15—C14	121.3 (6)	C27—C26—H26	119.7
C16—C15—H15	119.4	C25—C26—H26	119.7
C14—C15—H15	119.4	C26—C27—C22	120.4 (5)
C15—C16—C17	118.8 (5)	C26—C27—H27	119.8
C15—C16—H16	120.6	C22—C27—H27	119.8
C21—N1—C11—C12	-103.9 (5)	C11—N1—C21—C22	174.4 (4)
O3—N1—C11—C12	72.7 (4)	N1—C21—C22—C23	176.4 (4)
N1—C11—C12—C17	82.7 (5)	N1—C21—C22—C27	-6.0 (7)
N1—C11—C12—C13	-96.6 (5)	C27—C22—C23—C24	1.2 (7)
C17—C12—C13—C14	-0.7 (7)	C21—C22—C23—C24	179.0 (4)
C11—C12—C13—C14	178.7 (4)	C22—C23—C24—C25	-1.4 (7)
C12—C13—C14—C15	0.5 (7)	C23—C24—C25—C26	0.5 (7)
C13—C14—C15—C16	-1.1 (8)	C24—C25—C26—C27	0.6 (7)
C14—C15—C16—C17	1.8 (8)	C25—C26—C27—C22	-0.8 (7)
C15—C16—C17—C12	-2.0 (7)	C23—C22—C27—C26	-0.1 (7)
C13—C12—C17—C16	1.4 (7)	C21—C22—C27—C26	-177.6 (4)
C11—C12—C17—C16	-178.0 (4)	H1—O1—O2—H2	88 (4)
O3—N1—C21—C22	-1.8 (7)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O3	1.05 (5)	1.66 (5)	2.707 (5)	174 (4)
O2—H2 \cdots O3 ⁱ	1.06 (5)	1.64 (5)	2.681 (5)	166 (4)
C21—H21 \cdots O1 ⁱⁱ	0.95	2.46	3.304 (6)	148
C27—H27 \cdots O3	0.95	2.29	2.902 (6)	121
C11—H111 \cdots O1 ⁱⁱ	0.99	2.44	3.364 (7)	155
C11—H111 \cdots O2 ⁱⁱ	0.99	2.47	3.394 (7)	155
C11—H112 \cdots O2	0.99	2.52	3.407 (7)	149

Symmetry codes: (i) $x, y+1, z$; (ii) $x, -y+3/2, z-1/2$.