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N-[2-(4-Hydroxybenzylideneamino)-ethyl]-*N*-[2-(4-oxidobenzylideneamino)-ethyl]ammonium

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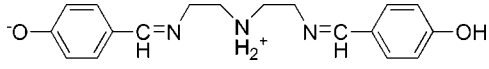
Key indicators: single-crystal X-ray study; T = 153 K; mean σ(C–C) = 0.001 Å; R factor = 0.036; wR factor = 0.112; data-to-parameter ratio = 17.0.

The title Schiff base compound, $C_{18}H_{21}N_3O_2$, was synthesized by a condensation reaction of 4-hydroxybenzaldehyde with diethylenetriamine. The crystal structure determination reveals that one of the terminal hydroxy groups is deprotonated while the imino group of the molecule is protonated; thus the compound is a zwitterion. The two terminal benzene rings are nearly parallel to one another, with a dihedral angle of 9.94 (6)°. Intermolecular O—H···O and N—H···O hydrogen bonding helps to stabilize the crystal structure.

Related literature

For general background, see: Mohamed (2006); Jiao & Liu (2005); Li *et al.* (1999); Xiao *et al.* (2006). For synthesis, see: Xiao *et al.* (2006).



Experimental

Crystal data

$C_{18}H_{21}N_3O_2$
M_r = 311.38
Orthorhombic, *Pbca*
a = 11.638 (2) Å
b = 15.667 (3) Å
c = 17.016 (3) Å
V = 3102.5 (11) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 153 (2) K
0.49 × 0.47 × 0.38 mm

Data collection

Rigaku R-AXIS SPIDER diffractometer
Absorption correction: none
28871 measured reflections
3560 independent reflections
3084 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.112
S = 1.06
3560 reflections
209 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O2^{i}	0.97	1.51	2.4846 (11)	173
N2—H2A···O1^{ii}	0.92	2.00	2.8325 (12)	149
N2—H2C···O2^{iii}	0.90	1.88	2.7075 (12)	152

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

Data collection: *RAPID-AUTO* (Rigaku, 2004); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2286).

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supplementary materials

Acta Cryst. (2007). E**63**, o3701 [**doi:10.1107/S1600536807037397**]

N-[2-(4-Hydroxybenzylideneamino)ethyl]-*N*-[2-(4-oxidobenzylideneamino)ethyl]ammonium

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Comment

Schiff bases are important organic compounds and their metal complexes had a variety of applications including biological, clinical, analytical and catalysis (Mohamed, 2006; Jiao & Liu, 2005). In particular, Schiff bases with nitrogen and oxygen atoms are important biological ligands (Li *et al.*, 1999). Some Schiff base cobalt complexes can absorb molecular oxygen, they were synthesized as functional model compounds to simulate a biological oxygen carrier (Xiao *et al.*, 1987). In our lab, the oxygenation of some cobalt complexes with Schiff bases have been investigated, and found that one molar of the complexes reacted with two molar of oxygen at room temperature (Xiao *et al.*, 2006). As part of our ongoing investigation, the title compound has been prepared and its crystal structure is reported here.

The molecule forms a U type structure (Fig. 1). The bond lengths of N1═C7 and N3═C12 (Table 1) indicate double bonds character. The C1-benzene ring is nearly parallel to the C13-benzene ring, the dihedral angle being 9.94 (6)°. The protonation of N2-imine group make the compound crystallize in a zwitterionic form. The crystal structure is stabilized by O—H···O hydrogen bonding (Table 2).

Experimental

diethylenetriamine(0.103 g, 0.001 mol) in ethyl acetate (10 ml) was dropwised to a solution of 4-hydroxybenzaldehyde (0.244 g, 0.002 mol) in ethyl acetate (20 ml) in an ice-bath, then the reaction mixture was stirred for two hours, The yellow product was isolated by filtration, washed with diethyl ether, dried and obtained 0.264 g (yield 85%) (Xiao *et al.*, 2006). Crystals suitable for single-crystal X-ray diffraction were grown from a solution of methanol by slow evaporation. Elemental analysis, found (calculated for $C_{18}H_{21}N_3O_2$): C 69.18% (69.45%), H 6.51% (6.75%), N 13.45% (13.50%).

Refinement

H atoms bonded to O and N atoms were located in a difference Fourier map and refined as riding in as-found relative positions with U_{iso}(H) = 1.5U_{eq}(O,*N*). Other H atoms were placed in calculated positions with C—H = 0.95 (aromatic) or 0.99 Å (methylene), and refined in riding mode, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

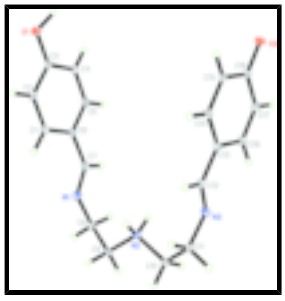


Figure 1. A view of the molecule structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
Figure 2. The packing structure of the title compound viewed down the *a* axis showing the molecular.

N-[2-(4-hydroxybenzylideneamino)ethyl]-N-[2-(4- oxidobenzylideneamino)ethyl]ammonium

Crystal data

$C_{18}H_{21}N_3O_2$	D_x = 1.333 Mg m^{-3}
M_r = 311.38	Melting point: 453 K
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 23448 reflections
a = 11.638 (2) Å	θ = 3.2–27.5º
b = 15.667 (3) Å	μ = 0.09 mm^{-1}
c = 17.016 (3) Å	*T* = 153 (2) K
V = 3102.5 (11) Å^3	Block, yellow
Z = 8	0.49 × 0.47 × 0.38 mm
F_{000} = 1328	

Data collection

Rigaku R-AXIS SPIDER diffractometer	3084 reflections with $I > 2\sigma(I)$
Radiation source: Rotating Anode	R_{int} = 0.023
Monochromator: graphite	θ_{max} = 27.5º
T = 153(2) K	θ_{min} = 3.2º
ω scans	*h* = −15→15
Absorption correction: none	*k* = −19→20
28871 measured reflections	*l* = −20→22
3560 independent reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.097P)^2 + 1.4677P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.036	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.112	$\Delta\rho_{max}$ = 0.32 e Å^{-3}

S = 1.06	$\Delta\rho_{min}$ = −0.24 e Å^{-3}
3560 reflections	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
209 parameters	Extinction coefficient: 0.0026 (6)

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.31037 (6)	0.14542 (5)	0.55715 (4)	0.02288 (18)
H1A	0.3662	0.1396	0.5148	0.034*
O2	0.94930 (6)	0.35847 (5)	0.55366 (4)	0.02240 (18)
N1	0.47454 (7)	0.12911 (5)	0.91717 (5)	0.02032 (19)
N2	0.62800 (6)	0.25607 (5)	0.98495 (5)	0.01873 (19)
H2A	0.6778	0.2263	0.9534	0.028*
H2C	0.5780	0.2862	0.9560	0.028*
N3	0.79044 (7)	0.37646 (5)	0.91501 (5)	0.02038 (19)
C1	0.35115 (9)	0.14906 (6)	0.76874 (6)	0.0209 (2)
H1B	0.3124	0.1697	0.8140	0.025*
C2	0.30268 (9)	0.16082 (6)	0.69552 (6)	0.0210 (2)
H2B	0.2309	0.1893	0.6910	0.025*
C3	0.35837 (8)	0.13108 (6)	0.62770 (5)	0.0180 (2)
C4	0.46222 (8)	0.08697 (6)	0.63589 (5)	0.0191 (2)
H4A	0.4998	0.0646	0.5908	0.023*
C5	0.51049 (9)	0.07584 (6)	0.70980 (6)	0.0193 (2)
H5A	0.5815	0.0464	0.7146	0.023*
C6	0.45656 (8)	0.10712 (6)	0.77718 (5)	0.0182 (2)
C7	0.51216 (8)	0.09588 (6)	0.85382 (6)	0.0188 (2)
H7A	0.5798	0.0620	0.8564	0.023*
C8	0.53900 (9)	0.11116 (6)	0.98880 (5)	0.0198 (2)
H8A	0.6124	0.0829	0.9751	0.024*
H8B	0.4943	0.0717	1.0224	0.024*
C9	0.56376 (8)	0.19273 (6)	1.03400 (5)	0.0183 (2)
H9A	0.4903	0.2184	1.0515	0.022*
H9B	0.6095	0.1789	1.0814	0.022*
C10	0.69938 (8)	0.31620 (6)	1.03268 (5)	0.0187 (2)
H10A	0.7717	0.2876	1.0482	0.022*

H10B	0.6573	0.3316	1.0812	0.022*
C11	0.72732 (9)	0.39669 (6)	0.98682 (5)	0.0203 (2)
H11A	0.6551	0.4267	0.9731	0.024*
H11B	0.7740	0.4353	1.0199	0.024*
C12	0.75025 (8)	0.40705 (6)	0.85139 (6)	0.0188 (2)
H12A	0.6815	0.4396	0.8539	0.023*
C13	0.80451 (8)	0.39474 (6)	0.77449 (5)	0.0178 (2)
C14	0.74795 (8)	0.42303 (6)	0.70696 (5)	0.0192 (2)
H14A	0.6753	0.4503	0.7117	0.023*
C15	0.79631 (9)	0.41193 (6)	0.63302 (5)	0.0190 (2)
H15A	0.7567	0.4322	0.5879	0.023*
C16	0.90284 (9)	0.37112 (6)	0.62407 (5)	0.0176 (2)
C17	0.96003 (8)	0.34366 (6)	0.69268 (6)	0.0203 (2)
H17A	1.0329	0.3167	0.6884	0.024*
C18	0.91180 (9)	0.35543 (6)	0.76583 (6)	0.0200 (2)
H18A	0.9521	0.3365	0.8112	0.024*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0195 (4)	0.0323 (4)	0.0168 (3)	0.0039 (3)	−0.0027 (3)	0.0013 (3)
O2	0.0206 (4)	0.0307 (4)	0.0159 (3)	0.0027 (3)	0.0029 (3)	−0.0011 (3)
N1	0.0177 (4)	0.0252 (4)	0.0180 (4)	−0.0004 (3)	−0.0020 (3)	0.0003 (3)
N2	0.0175 (4)	0.0252 (4)	0.0136 (4)	−0.0030 (3)	−0.0001 (3)	−0.0005 (3)
N3	0.0179 (4)	0.0251 (4)	0.0182 (4)	−0.0013 (3)	0.0031 (3)	−0.0019 (3)
C1	0.0186 (5)	0.0251 (5)	0.0188 (5)	0.0013 (4)	0.0020 (3)	−0.0028 (4)
C2	0.0164 (5)	0.0244 (5)	0.0221 (5)	0.0033 (4)	−0.0006 (3)	−0.0014 (4)
C3	0.0171 (5)	0.0189 (4)	0.0179 (4)	−0.0029 (3)	−0.0012 (3)	0.0010 (3)
C4	0.0184 (5)	0.0215 (5)	0.0173 (4)	0.0004 (4)	0.0019 (3)	−0.0007 (3)
C5	0.0167 (5)	0.0203 (4)	0.0210 (5)	0.0022 (4)	0.0006 (3)	0.0005 (3)
C6	0.0179 (5)	0.0190 (4)	0.0178 (4)	−0.0018 (3)	−0.0007 (3)	0.0006 (3)
C7	0.0168 (5)	0.0198 (4)	0.0199 (5)	−0.0005 (3)	−0.0006 (3)	0.0012 (3)
C8	0.0185 (5)	0.0222 (5)	0.0187 (4)	0.0003 (4)	−0.0017 (3)	0.0014 (4)
C9	0.0172 (5)	0.0238 (5)	0.0139 (4)	−0.0006 (4)	0.0008 (3)	0.0016 (3)
C10	0.0165 (5)	0.0255 (5)	0.0140 (4)	−0.0014 (4)	−0.0006 (3)	−0.0028 (3)
C11	0.0190 (5)	0.0232 (5)	0.0188 (5)	−0.0004 (4)	0.0030 (3)	−0.0034 (4)
C12	0.0167 (5)	0.0189 (4)	0.0208 (5)	−0.0011 (3)	0.0022 (3)	−0.0019 (3)
C13	0.0176 (5)	0.0180 (4)	0.0178 (5)	−0.0018 (3)	0.0017 (3)	−0.0006 (3)
C14	0.0161 (5)	0.0197 (4)	0.0219 (5)	0.0013 (3)	−0.0004 (4)	−0.0006 (4)
C15	0.0188 (5)	0.0210 (4)	0.0171 (4)	−0.0002 (4)	−0.0030 (3)	0.0010 (3)
C16	0.0182 (5)	0.0183 (4)	0.0164 (4)	−0.0032 (3)	0.0011 (3)	−0.0009 (3)
C17	0.0155 (5)	0.0242 (5)	0.0211 (5)	0.0028 (4)	0.0005 (3)	0.0007 (4)
C18	0.0183 (5)	0.0242 (5)	0.0175 (4)	0.0008 (4)	−0.0011 (3)	0.0019 (3)

Geometric parameters (Å, °)

O1—C3	1.3430 (11)	C8—C9	1.5192 (13)
O1—H1A	0.9745	C8—H8A	0.9900
O2—C16	1.3293 (11)	C8—H8B	0.9900

N1—C7	1.2747 (13)	C9—H9A	0.9900
N1—C8	1.4586 (12)	C9—H9B	0.9900
N2—C10	1.4957 (12)	C10—C11	1.5183 (14)
N2—C9	1.4968 (12)	C10—H10A	0.9900
N2—H2A	0.9170	C10—H10B	0.9900
N2—H2C	0.8972	C11—H11A	0.9900
N3—C12	1.2730 (13)	C11—H11B	0.9900
N3—C11	1.4605 (12)	C12—C13	1.4656 (13)
C1—C2	1.3801 (14)	C12—H12A	0.9500
C1—C6	1.3990 (14)	C13—C14	1.3965 (13)
C1—H1B	0.9500	C13—C18	1.4000 (14)
C2—C3	1.4031 (13)	C14—C15	1.3892 (13)
C2—H2B	0.9500	C14—H14A	0.9500
C3—C4	1.3992 (14)	C15—C16	1.4032 (14)
C4—C5	1.3883 (13)	C15—H15A	0.9500
C4—H4A	0.9500	C16—C17	1.4111 (13)
C5—C6	1.3959 (13)	C17—C18	1.3778 (13)
C5—H5A	0.9500	C17—H17A	0.9500
C6—C7	1.4666 (13)	C18—H18A	0.9500
C7—H7A	0.9500		
C3—O1—H1A	111.6	C8—C9—H9A	109.3
C7—N1—C8	116.82 (9)	N2—C9—H9B	109.3
C10—N2—C9	113.08 (7)	C8—C9—H9B	109.3
C10—N2—H2A	106.7	H9A—C9—H9B	107.9
C9—N2—H2A	107.8	N2—C10—C11	111.28 (7)
C10—N2—H2C	109.1	N2—C10—H10A	109.4
C9—N2—H2C	109.3	C11—C10—H10A	109.4
H2A—N2—H2C	110.8	N2—C10—H10B	109.4
C12—N3—C11	116.42 (9)	C11—C10—H10B	109.4
C2—C1—C6	120.91 (9)	H10A—C10—H10B	108.0
C2—C1—H1B	119.5	N3—C11—C10	110.95 (8)
C6—C1—H1B	119.5	N3—C11—H11A	109.4
C1—C2—C3	120.63 (9)	C10—C11—H11A	109.4
C1—C2—H2B	119.7	N3—C11—H11B	109.4
C3—C2—H2B	119.7	C10—C11—H11B	109.4
O1—C3—C4	122.06 (9)	H11A—C11—H11B	108.0
O1—C3—C2	119.18 (9)	N3—C12—C13	123.46 (9)
C4—C3—C2	118.75 (9)	N3—C12—H12A	118.3
C5—C4—C3	120.11 (9)	C13—C12—H12A	118.3
C5—C4—H4A	119.9	C14—C13—C18	118.25 (8)
C3—C4—H4A	119.9	C14—C13—C12	119.33 (9)
C4—C5—C6	121.20 (9)	C18—C13—C12	122.42 (9)
C4—C5—H5A	119.4	C15—C14—C13	120.97 (9)
C6—C5—H5A	119.4	C15—C14—H14A	119.5
C5—C6—C1	118.35 (9)	C13—C14—H14A	119.5
C5—C6—C7	119.34 (9)	C14—C15—C16	120.88 (9)
C1—C6—C7	122.31 (9)	C14—C15—H15A	119.6
N1—C7—C6	123.47 (9)	C16—C15—H15A	119.6
N1—C7—H7A	118.3	O2—C16—C15	121.68 (8)

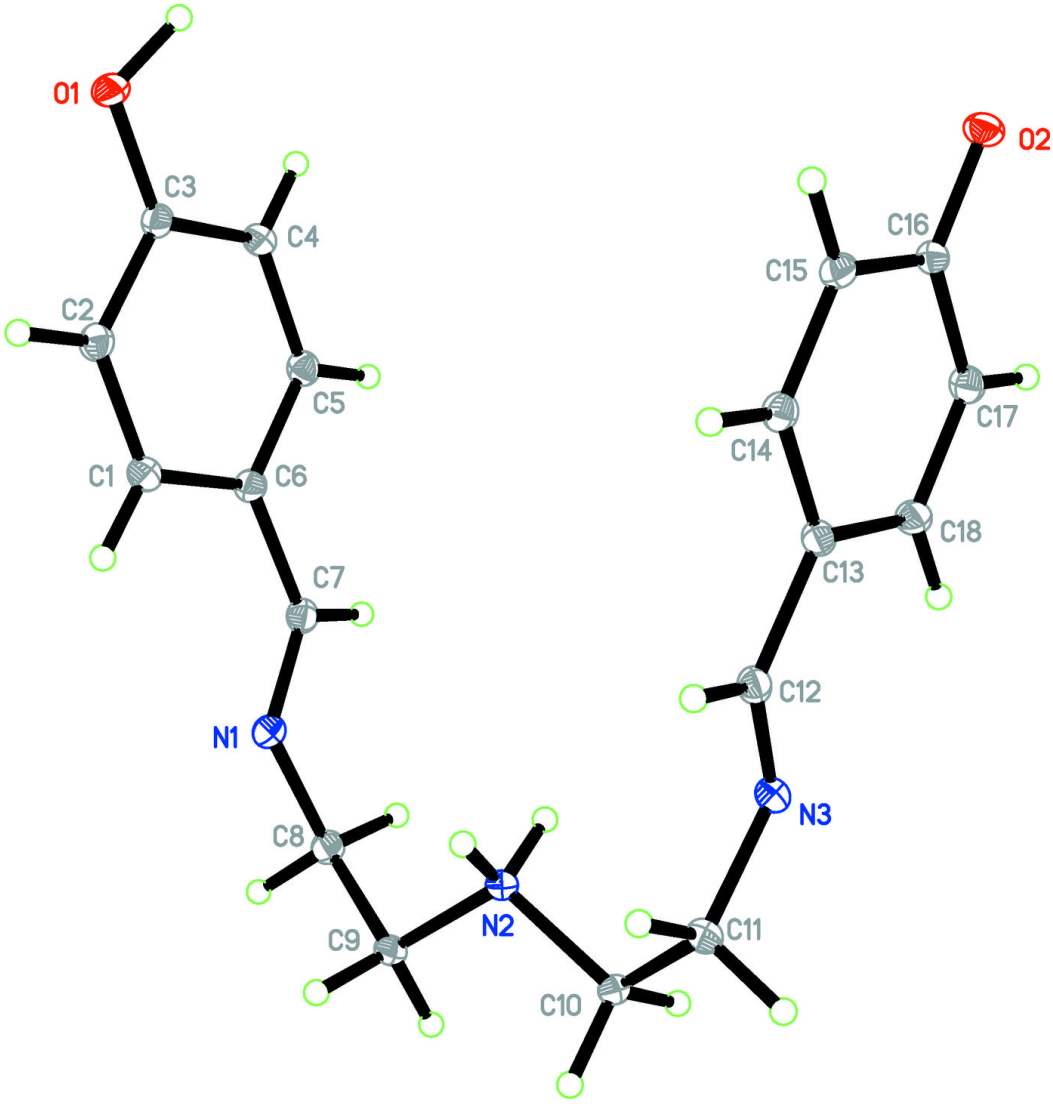
C6—C7—H7A	118.3	O2—C16—C17	120.56 (9)
N1—C8—C9	111.00 (8)	C15—C16—C17	117.76 (8)
N1—C8—H8A	109.4	C18—C17—C16	120.96 (9)
C9—C8—H8A	109.4	C18—C17—H17A	119.5
N1—C8—H8B	109.4	C16—C17—H17A	119.5
C9—C8—H8B	109.4	C17—C18—C13	121.15 (9)
H8A—C8—H8B	108.0	C17—C18—H18A	119.4
N2—C9—C8	111.72 (7)	C13—C18—H18A	119.4
N2—C9—H9A	109.3		
C6—C1—C2—C3	−0.18 (16)	C9—N2—C10—C11	−159.33 (8)
C1—C2—C3—O1	−178.33 (9)	C12—N3—C11—C10	127.76 (9)
C1—C2—C3—C4	1.95 (15)	N2—C10—C11—N3	−59.52 (10)
O1—C3—C4—C5	178.05 (9)	C11—N3—C12—C13	178.42 (8)
C2—C3—C4—C5	−2.24 (14)	N3—C12—C13—C14	173.33 (9)
C3—C4—C5—C6	0.78 (15)	N3—C12—C13—C18	−6.70 (15)
C4—C5—C6—C1	0.99 (14)	C18—C13—C14—C15	0.49 (14)
C4—C5—C6—C7	−178.39 (9)	C12—C13—C14—C15	−179.54 (9)
C2—C1—C6—C5	−1.29 (15)	C13—C14—C15—C16	0.70 (15)
C2—C1—C6—C7	178.07 (9)	C14—C15—C16—O2	178.66 (9)
C8—N1—C7—C6	179.39 (8)	C14—C15—C16—C17	−1.43 (14)
C5—C6—C7—N1	173.30 (9)	O2—C16—C17—C18	−179.09 (9)
C1—C6—C7—N1	−6.06 (15)	C15—C16—C17—C18	1.00 (14)
C7—N1—C8—C9	130.85 (9)	C16—C17—C18—C13	0.18 (15)
C10—N2—C9—C8	−153.53 (8)	C14—C13—C18—C17	−0.93 (14)
N1—C8—C9—N2	−57.22 (10)	C12—C13—C18—C17	179.10 (9)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1A···O2^{i}	0.97	1.51	2.4846 (11)	173
N2—H2A···O1^{ii}	0.92	2.00	2.8325 (12)	149
N2—H2C···O2^{iii}	0.90	1.88	2.7075 (12)	152

Symmetry codes: (i) *x*−1/2, −*y*+1/2, −*z*+1; (ii) *x*+1/2, *y*, −*z*+3/2; (iii) *x*−1/2, *y*, −*z*+3/2.

Fig. 1


O1
C3
C4
C2
C5
C1
C6
C7
N1
C8
C9
N2
C10
C11
N3
C12
C13
C14
C15
C16
O2
C17
C18