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ISSN 2414-3146

1,1′-{(1*E*,1′*E*)-[Octane-1,8-diylbis(azanylylidene)]-bis(methanylylidene)}bis(naphthalen-2-ol) in the zwitterionic form

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Received 20 January 2017
Accepted 31 January 2017

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

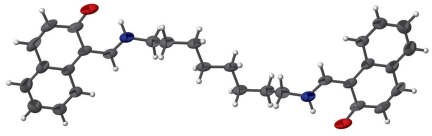
Keywords: crystal structure; zwitterion; 1,8-diaminooctane; 2-hydroxy-1-naphthaldehyde; hydrogen bonding; elemental analysis; NMR spectroscopy.

CCDC reference: 1530499

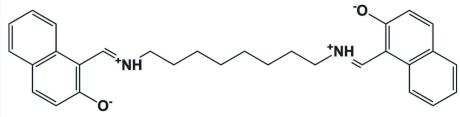
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{30}H_{32}O_2N_2$, is formed from two units of *ortho*-hydroxynaphthaldehyde bridged with 1,8-diaminooctane. In the solid state, it exists as a double zwitterion. The N atoms are protonated and the C—O$^-$ bonds lengths are 1.265 (2) Å, with intramolecular N—H···O hydrogen bonds forming *S*(6) ring motifs. The molecule has twofold rotational symmetry, with the twofold axis bisecting the central –CH_2—CH_2– bond of the bridging octane chain. In the crystal, molecules are linked by N—H···O hydrogen bonds, forming chains propagating along the [$\bar{2}$01] direction. The chains are linked *via* C—H···O hydrogen bonds, forming a supramolecular three-dimensional framework structure.

3D view



Chemical scheme



Structure description

Recently, our group has reported the crystal structures of four new Schiff bases, synthesized using literature methods by reacting primary amines and *o*-hydroxynaphthaldehyde (Merzougui *et al.*, 2016; Ouari *et al.*, 2015*a*,*b*,*c*). They crystallize as bis-zwitterionic compounds with strong intramolecular N—H···O hydrogen bonds, forming *S*(6) ring motifs. Such compounds are of interest because the azomethine C=N and C—O groups form stable transition metal complexes by coordinating through the nitrogen and oxygen atoms (Ouari *et al.*, 2010, 2015*d*).

The title compound is formed from two units of *ortho*-hydroxynaphthaldehyde bridged with 1,8-diaminooctane. The molecule has twofold rotational symmetry with the twofold axis bisecting the central –C15—C15^i– bond [symmetry code (i): $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$]. Atoms N1 and N1^i are protonated and the C1—O1 and C1^i—O1^i bond lengths are

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O1	0.93 (2)	1.87 (2)	2.602 (2)	133.6 (18)
N1—H1N···O1^{ii}	0.93 (2)	2.44 (2)	3.115 (2)	129.6 (17)
C12—H12A···O1^{iii}	0.99	2.47	3.201 (2)	131

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

1.265 (2) Å, hence the compound has crystallized as a double zwitterion with intramolecular N—H···O hydrogen bonds forming $S(6)$ ring motifs (Table 1 and Fig. 1). This is similar to the structures of the compounds mentioned above.

In the crystal, molecules are linked by N—H···O hydrogen bonds, forming chains propagating along [$\bar{2}$01] and enclosing $R_2^2(4)$ ring motifs (Table 1 and Fig. 2). The chains are linked *via* C—H···O hydrogen bonds, forming a supramolecular three-dimensional framework structure (Table 1 and Fig. 3).

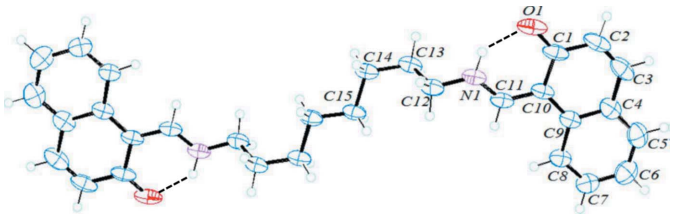


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are related to the labelled atoms by twofold rotation symmetry ($-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$). The intramolecular N—H···O hydrogen bonds are shown as dashed lines (see Table 1).

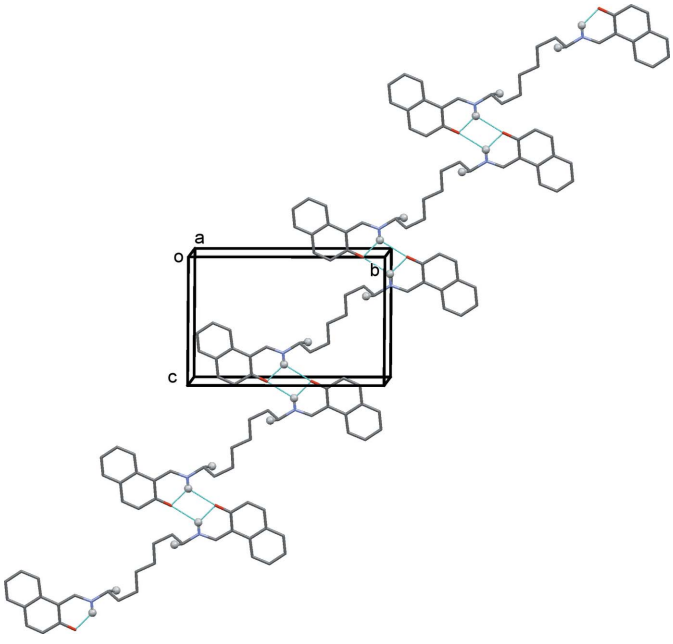


Figure 2
A partial view along the *a* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1), and for clarity, only H atoms H1N and H12A (grey balls) have been included.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{30}H_{32}N_2O_2$
M_r	452.58
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	173
a, b, c (Å)	18.0993 (12), 14.2646 (9), 9.5990 (6)
β (°)	105.345 (1)
V (Å^3)	2389.9 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.35 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2010)
T_{min}, T_{max}	0.973, 0.985
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20784, 2907, 2159
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.663
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.146, 1.13
No. of reflections	2907
No. of parameters	158
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.22

Computer programs: *APEX2* and *SAINT* (Bruker, 2010), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008).

Synthesis and crystallization

The title Schiff base was prepared by condensation between 1,8-diaminooctane (72 mg, 0.5 mmol) and 2-hydroxy-1-naphthaldehyde (172 mg, 1 mmol) in methanol (10 ml). The mixture was refluxed and stirred under a nitrogen atmosphere for 2 h. The precipitate obtained was filtered, washed with methanol and diethyl ether and dried in vacuum overnight.

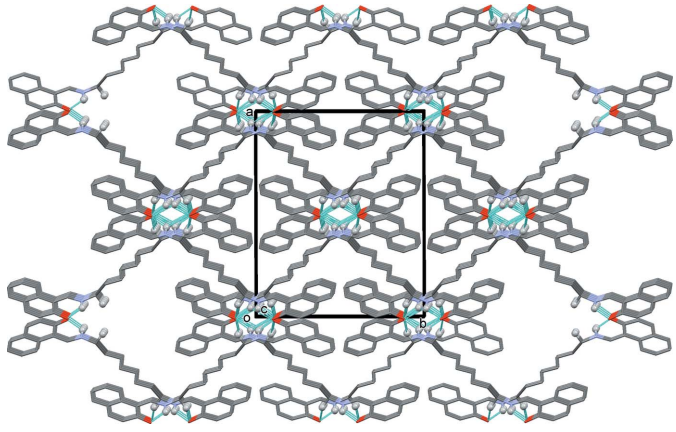


Figure 3
Crystal packing of the title compound, viewed along the *c* axis. The hydrogen bonds are shown as dashed lines (see Table 1), and for clarity, only H atoms H1N and H12A (grey balls) have been included.

Yellow single crystals of the title compound were obtained by slow evaporation of a solution in methanol (yield 71%; m.p. 438–440 K). Elemental analysis: calculated for $C_{30}H_{32}O_2N_2$: C 79.63, H 7.23, N 6.16%; found: C 79.61, H 7.13, N 6.19%.

^{1}H NMR: (DMSO-d_6, δ p.p.m.): 14.12 (C—OH), 9.07 (*s*, CH═N), 6.40–8.40 (*m*, ArH), 1.00–4.00 (*m*, aliphH); ^{13}C NMR: (DMSO-d_6, δ p.p.m.): 178.04 (C—O), 159.35 (CH═N), 100–140 (C—Ar), 23.57–55.12 (C-aliphat). The DEPT-135 spectrum shows a disappearance of resonances at 106.07, 125.46, 134.81 and 178.28 p.p.m.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

The authors gratefully acknowledge the help of Dr Jean Weiss from the CLAC laboratory at the Institut de Chimie, Université de Strasbourg, France.

Funding information

Funding for this research was provided by: Ministère de l'Enseignement Supérieur et de la Recherche Scientifique.

References

Bruker (2010). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Merzougui, M., Ouari, K. & Weiss, J. (2016). *J. Mol. Struct.* **1120**, 239–244.

Ouari, K., Bendia, S., Merzougui, M. & Bailly, C. (2015*b*). *Acta Cryst.* E**71**, o51–o52.

Ouari, K., Bendia, S., Weiss, J. & Bailly, C. (2015*d*). *Spectrochim. Acta Part A*, **135**, 624–631.

Ouari, K., Merzougui, M., Bendia, S. & Bailly, C. (2015*a*). *Acta Cryst.* E**71**, o351–o352.

Ouari, K., Merzougui, M. & Karmazin, L. (2015*c*). *Acta Cryst.* E**71**, 1010–1012.

Ouari, K., Ourari, A. & Weiss, J. (2010). *J. Chem. Crystallogr.* **40**, 831–836.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

full crystallographic data

IUCrData (2017). **2**, x170169 [https://doi.org/10.1107/S2414314617001699]

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Crystal data

$C_{30}H_{32}N_2O_2$
M_r = 452.58
Monoclinic, $C2/c$
Hall symbol: -C 2yc
a = 18.0993 (12) Å
b = 14.2646 (9) Å
c = 9.5990 (6) Å
β = 105.345 (1)°
V = 2389.9 (3) Å^3
Z = 4
$F(000)$ = 968
D_x = 1.258 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6936 reflections
θ = 2.3–28.0°
μ = 0.08 mm^{-1}
T = 173 K
Prism, yellow
0.35 × 0.25 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2010)
T_{min} = 0.973, T_{max} = 0.985
20784 measured reflections
2907 independent reflections
2159 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 28.1°, θ_{min} = 1.8°
h = −22→23
k = −18→14
l = −12→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.146
S = 1.13
2907 reflections
158 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 2.0625P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
C1	0.03219 (9)	1.19048 (15)	0.05578 (16)	0.0474 (5)
C2	0.01367 (10)	1.27725 (17)	−0.02317 (18)	0.0576 (6)
H2	−0.0178	1.2756	−0.1196	0.069*
C3	0.03949 (10)	1.35977 (17)	0.0356 (2)	0.0595 (6)
H3	0.0264	1.4148	−0.0214	0.071*
C4	0.08643 (9)	1.36885 (14)	0.18190 (19)	0.0488 (4)
C5	0.10920 (11)	1.45675 (16)	0.2428 (2)	0.0610 (5)
H5	0.0944	1.5117	0.1863	0.073*
C6	0.15275 (11)	1.46479 (16)	0.3835 (3)	0.0628 (6)
H6	0.1677	1.5248	0.4242	0.075*
C7	0.17461 (10)	1.38405 (14)	0.4656 (2)	0.0524 (5)
H7	0.2045	1.3893	0.5628	0.063*
C8	0.15364 (9)	1.29760 (13)	0.40838 (17)	0.0441 (4)
H8	0.1696	1.2436	0.4665	0.053*
C9	0.10847 (8)	1.28615 (13)	0.26391 (16)	0.0401 (4)
C10	0.08336 (8)	1.19633 (13)	0.19953 (15)	0.0397 (4)
C11	0.10777 (8)	1.11267 (13)	0.27413 (16)	0.0413 (4)
H11	0.1414	1.1180	0.3684	0.050*
C12	0.11699 (10)	0.94316 (14)	0.30608 (17)	0.0478 (4)
H12A	0.0730	0.9030	0.3101	0.057*
H12B	0.1446	0.9600	0.4064	0.057*
C13	0.17022 (10)	0.88827 (14)	0.23865 (17)	0.0481 (4)
H13A	0.2175	0.9251	0.2467	0.058*
H13B	0.1452	0.8790	0.1347	0.058*
C14	0.19159 (10)	0.79304 (14)	0.30986 (17)	0.0493 (5)
H14A	0.2201	0.7571	0.2526	0.059*
H14B	0.1439	0.7581	0.3070	0.059*
C15	0.24003 (9)	0.79781 (13)	0.46606 (16)	0.0461 (4)
H15A	0.2880	0.8321	0.4694	0.055*
H15B	0.2118	0.8337	0.5237	0.055*
N1	0.08863 (8)	1.02829 (11)	0.22613 (15)	0.0460 (4)
O1	0.00462 (7)	1.11356 (11)	−0.00035 (12)	0.0605 (4)
H1N	0.0548 (13)	1.0243 (15)	0.135 (2)	0.067 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0272 (7)	0.0888 (14)	0.0267 (7)	0.0027 (8)	0.0080 (6)	−0.0046 (8)
C2	0.0343 (9)	0.1043 (17)	0.0311 (8)	0.0120 (10)	0.0034 (6)	0.0074 (10)
C3	0.0359 (9)	0.0938 (16)	0.0482 (10)	0.0212 (10)	0.0101 (8)	0.0201 (11)
C4	0.0300 (8)	0.0695 (13)	0.0489 (9)	0.0141 (8)	0.0141 (7)	0.0069 (9)
C5	0.0461 (10)	0.0653 (13)	0.0736 (13)	0.0165 (9)	0.0192 (10)	0.0100 (11)
C6	0.0490 (11)	0.0615 (13)	0.0805 (15)	0.0027 (9)	0.0217 (10)	−0.0120 (11)
C7	0.0392 (9)	0.0656 (12)	0.0516 (10)	−0.0006 (8)	0.0108 (8)	−0.0106 (9)
C8	0.0345 (8)	0.0605 (11)	0.0371 (8)	0.0010 (7)	0.0090 (6)	−0.0031 (7)
C9	0.0237 (7)	0.0641 (11)	0.0347 (7)	0.0066 (7)	0.0112 (6)	−0.0004 (7)
C10	0.0242 (7)	0.0693 (11)	0.0264 (7)	0.0028 (7)	0.0081 (5)	−0.0024 (7)
C11	0.0288 (7)	0.0689 (11)	0.0266 (7)	−0.0028 (7)	0.0080 (6)	−0.0065 (7)
C12	0.0483 (10)	0.0646 (12)	0.0320 (8)	−0.0091 (8)	0.0132 (7)	−0.0030 (7)
C13	0.0437 (9)	0.0713 (12)	0.0291 (7)	−0.0052 (8)	0.0092 (7)	0.0001 (8)
C14	0.0439 (9)	0.0703 (13)	0.0301 (8)	−0.0067 (8)	0.0035 (7)	−0.0045 (8)
C15	0.0367 (8)	0.0679 (12)	0.0308 (8)	−0.0134 (8)	0.0036 (6)	−0.0035 (7)
N1	0.0397 (7)	0.0694 (10)	0.0281 (6)	−0.0057 (7)	0.0076 (5)	−0.0049 (7)
O1	0.0425 (7)	0.1048 (12)	0.0307 (6)	−0.0068 (7)	0.0037 (5)	−0.0135 (7)

Geometric parameters (Å, º)

C1—O1	1.265 (2)	C10—C11	1.402 (2)
C1—C2	1.444 (3)	C11—N1	1.303 (2)
C1—C10	1.446 (2)	C11—H11	0.9500
C2—C3	1.335 (3)	C12—N1	1.455 (2)
C2—H2	0.9500	C12—C13	1.513 (2)
C3—C4	1.442 (3)	C12—H12A	0.9900
C3—H3	0.9500	C12—H12B	0.9900
C4—C5	1.399 (3)	C13—C14	1.524 (3)
C4—C9	1.416 (2)	C13—H13A	0.9900
C5—C6	1.377 (3)	C13—H13B	0.9900
C5—H5	0.9500	C14—C15	1.525 (2)
C6—C7	1.392 (3)	C14—H14A	0.9900
C6—H6	0.9500	C14—H14B	0.9900
C7—C8	1.363 (3)	C15—C15^{i}	1.514 (4)
C7—H7	0.9500	C15—H15A	0.9900
C8—C9	1.421 (2)	C15—H15B	0.9900
C8—H8	0.9500	N1—H1N	0.93 (2)
C9—C10	1.443 (2)		
O1—C1—C2	120.62 (15)	N1—C11—C10	126.00 (14)
O1—C1—C10	122.48 (18)	N1—C11—H11	117.0
C2—C1—C10	116.90 (18)	C10—C11—H11	117.0
C3—C2—C1	121.84 (16)	N1—C12—C13	112.44 (13)
C3—C2—H2	119.1	N1—C12—H12A	109.1
C1—C2—H2	119.1	C13—C12—H12A	109.1

C2—C3—C4	122.73 (19)	N1—C12—H12B	109.1
C2—C3—H3	118.6	C13—C12—H12B	109.1
C4—C3—H3	118.6	H12A—C12—H12B	107.8
C5—C4—C9	120.40 (17)	C12—C13—C14	112.59 (14)
C5—C4—C3	121.34 (19)	C12—C13—H13A	109.1
C9—C4—C3	118.25 (19)	C14—C13—H13A	109.1
C6—C5—C4	120.9 (2)	C12—C13—H13B	109.1
C6—C5—H5	119.5	C14—C13—H13B	109.1
C4—C5—H5	119.5	H13A—C13—H13B	107.8
C5—C6—C7	119.3 (2)	C13—C14—C15	114.38 (15)
C5—C6—H6	120.3	C13—C14—H14A	108.7
C7—C6—H6	120.3	C15—C14—H14A	108.7
C8—C7—C6	120.89 (18)	C13—C14—H14B	108.7
C8—C7—H7	119.6	C15—C14—H14B	108.7
C6—C7—H7	119.6	H14A—C14—H14B	107.6
C7—C8—C9	121.64 (17)	C15^{i}—C15—C14	113.11 (18)
C7—C8—H8	119.2	C15^{i}—C15—H15A	109.0
C9—C8—H8	119.2	C14—C15—H15A	109.0
C4—C9—C8	116.85 (17)	C15^{i}—C15—H15B	109.0
C4—C9—C10	119.43 (15)	C14—C15—H15B	109.0
C8—C9—C10	123.70 (16)	H15A—C15—H15B	107.8
C11—C10—C9	121.09 (13)	C11—N1—C12	124.11 (14)
C11—C10—C1	118.29 (16)	C11—N1—H1N	116.0 (13)
C9—C10—C1	120.63 (16)	C12—N1—H1N	119.9 (13)
O1—C1—C2—C3	177.27 (16)	C4—C9—C10—C11	176.09 (13)
C10—C1—C2—C3	−3.0 (2)	C8—C9—C10—C11	−5.2 (2)
C1—C2—C3—C4	−1.0 (3)	C4—C9—C10—C1	−3.9 (2)
C2—C3—C4—C5	−176.55 (17)	C8—C9—C10—C1	174.82 (13)
C2—C3—C4—C9	2.7 (3)	O1—C1—C10—C11	5.2 (2)
C9—C4—C5—C6	−0.6 (3)	C2—C1—C10—C11	−174.52 (14)
C3—C4—C5—C6	178.70 (17)	O1—C1—C10—C9	−174.87 (14)
C4—C5—C6—C7	0.3 (3)	C2—C1—C10—C9	5.5 (2)
C5—C6—C7—C8	0.2 (3)	C9—C10—C11—N1	−179.99 (14)
C6—C7—C8—C9	−0.4 (3)	C1—C10—C11—N1	0.0 (2)
C5—C4—C9—C8	0.3 (2)	N1—C12—C13—C14	−172.37 (14)
C3—C4—C9—C8	−179.00 (14)	C12—C13—C14—C15	−66.4 (2)
C5—C4—C9—C10	179.08 (15)	C13—C14—C15—C15^{i}	179.72 (17)
C3—C4—C9—C10	−0.2 (2)	C10—C11—N1—C12	178.34 (14)
C7—C8—C9—C4	0.2 (2)	C13—C12—N1—C11	−111.09 (17)
C7—C8—C9—C10	−178.53 (15)		

Symmetry code: (i) −*x*+1/2, −*y*+3/2, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.93 (2)	1.87 (2)	2.602 (2)	133.6 (18)

N1—H1*N*···O1^{ii}	0.93 (2)	2.44 (2)	3.115 (2)	129.6 (17)
C12—H12*A*···O1^{iii}	0.99	2.47	3.201 (2)	131

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