4,4′-Dibromo-2,2′-{[(3aS,7aS)-2,3,3a,4,-5,6,7,7a-octahydro-1H-1,3-benzimida-zole-1,3-diyl]bis(methylidene)}diphenol

Augusto Rivera,[a]* Diego Quiroga,[a] Jaime Ríos-Motta,[a] Michal Dušek[b] and Karla Fejfarová[b]

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The cyclohexane ring in the title compound, $C_{21}H_{24}Br_2N_2O_2$, adopts a chair conformation and the five-membered ring to which it is fused has a twisted envelope conformation. The asymmetric unit contains one half-molecule, which is related to the other half by a twofold rotation axis. The two N atoms of the five-membered ring are linked to the hydroxy groups by intramolecular O—H···N hydrogen bonds. In the crystal, intermolecular C—H···O and C—H···π interactions occur.

Related literature

For a related structure, see: Rivera *et al.* (2010). For uses of di-Mannich bases, see: Mitra *et al.* (2006).
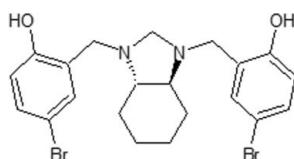
Experimental

Crystal data

$C_{21}H_{24}Br_2N_2O_2$	V = 1001.22 (5) Å^3
M_r = 496.2	Z = 2
Orthorhombic, $P2_12_12$	Cu $K\alpha$ radiation
a = 5.9645 (2) Å	μ = 5.32 mm^{-1}
b = 18.5497 (4) Å	T = 120 K
c = 9.0494 (2) Å	0.19 × 0.13 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with an Atlas detector	Diffraction, 2009) T_{min} = 0.454, T_{max} = 0.678
Absorption correction: analytical (*CrysAlis PRO*; Oxford	17493 measured reflections
	1749 independent reflections
	1739 reflections with $I > 3\sigma(I)$
	R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.015	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.049	
S = 1.21	
1749 reflections	$\Delta\rho_{max}$ = 0.11 e Å^{-3}
126 parameters	$\Delta\rho_{min}$ = −0.12 e Å^{-3}
1 restraint	Absolute structure: Flack (1983), 670 Friedel pairs
	Flack parameter: 0.008 (20)

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

*Cg*2 is the centroid of the C3–C8 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1o···N1	0.833 (19)	1.905 (18)	2.6506 (13)	148.3 (19)
C1—H1a···O1[i]	0.96	2.57	3.3351 (11)	137
C8—H8···*Cg*2[ii]	0.96	2.85	3.5407 (16)	130
C11—H11b···*Cg*2[iii]	0.96	2.86	3.728 (2)	150

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5118).

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supporting information

4,4′-Dibromo-2,2′-{[(3a*S*,7a*S*)-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3-benzimidazole-1,3-diyl]bis(methylidene)}diphenol

Augusto Rivera, Diego Quiroga, Jaime Ríos-Motta, Michal Dušek and Karla Fejfarová

S1. Comment

The title compound was obtained by reaction of racemic cyclic aminal (2*R*,7*R*,11*S*,16*S*)-1,8,10,17-tetraazapentacyclo-[8.8.1.1^{8,17}.0^{2,7}.0^{11,16}]icosane with *p*-bromophenol. The molecular structure and atom-numbering scheme for (**I**) are shown in Fig. 1. Selected angles and bond lengths are listed in Table 1. Its X-ray structure confirms the presence of intramolecular hydrogen bonds between the phenolic hydroxyl groups and nitrogen atoms [N—H, 1.903 (18) Å] that is however by 0.13 Å longer in comparison with related structure (Rivera *et al.*, 2010), whereas the N···O distance [2.6506 (14) Å] is in good agreement with the one found in related structure [2.652 (2) Å]. Similar to this related structure, the observed C—O bond length [1.353 (2) Å] is considerably shortened in relation to other Mannich bases.

In the title compound, C$_{21}$H$_{24}$Br$_2$N$_2$O$_2$, the asymmetric unit contains one-half of the molecule, which is related to the other half by a twofold rotation axis [symmetry code: - *x*, *y*, -*z*] passing through C1. The orthorhombic unit cell contains two molecules. Instead, the molecules have identical (S,S)-molecular configuration and its absolute structure was determined with a Flack parameter of 0.01 (2) (Flack, 1983).

S2. Experimental

Physical Measurements

The melting point was determined with an Electrothermal apparatus, and it has not been corrected. IR spectrum was recorded as KBr pellets at 292 K on a Perkin-Elmer Paragon FT—IR instrument. NMR spectra were performed in CDCl$_3$ at room temperature on a Bruker AMX 400 Advance spectrometer.

*Preparation of 4,4′-Dibromo-2,2′-(3a*S*,7a*S*)-2,3,3a,4,5,6,7,7a-octahydro-1H-1,3- benzimidazole-1,3-diyl)bis(methylene)]diphenol) (**I**)*

A solution of (2*R*,7*R*,11*S*,16*S*)-1,8,10,17-tetraazapentacyclo[8.8.1.1^{18,17}.0^{2,7}.0^{11,16}]icosane (**3**) (276 mg, 1.00 mmol) in dioxane (3 ml) and water (4 ml), prepared beforehand following previously described procedures, was added dropwise in a dioxane solution (3 ml) containing two equivalents of *p*-bromophenol (346 mg, 2.00 mmol) in a two-necked round-bottomed flask. The mixture was refluxed for about 6 h until precipitation of a colourless solid. The resulting solid was collected by filtration, washed with cool methanol and dried under vacuum (yield 47%, m.p. = 497–499 K). Next, the crude product (100 mg, 0.202 mmol) was dissolved in 5 ml of a 4:1 mixture of chloroform: methanol. Single crystals of title compound (**I**) suitable for X-ray analysis were grown by slow evaporation of the solvent at room temperature over a period of about 2 weeks in a preferential crystallization (yield 35%). ¹H NMR (CDCl$_3$, 400 MHz): δ 1.27 (4*H*, m), 1.85 (2*H*, m), 2.05 (2*H*, m), 2.33 (2*H*, m), 3.41 (2*H*, d, J = 14.0 Hz, ArCH$_2$N), 3.51 (2*H*, s, NCH$_2$N), 4.14 (2*H*, d, J = 14.0 Hz, ArCH$_2$N), 6.69 (2*H*, d, J = 8.8 Hz), 7.06 (2*H*, s), 7.24 (2*H*, d, J = 8.8 Hz). ¹³C NMR (CDCl$_3$, 100 MHz): δ 23.9, 28.9, 55.8, 69.1, 75.7, 111.1, 118.1, 123.4, 130.6, 131.8, 156.6.

S3. Refinement

All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice H atoms attached to C atoms were nevertheless kept in ideal positions during the refinement. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as $1.2*U_{eq}$ of the parent atom.
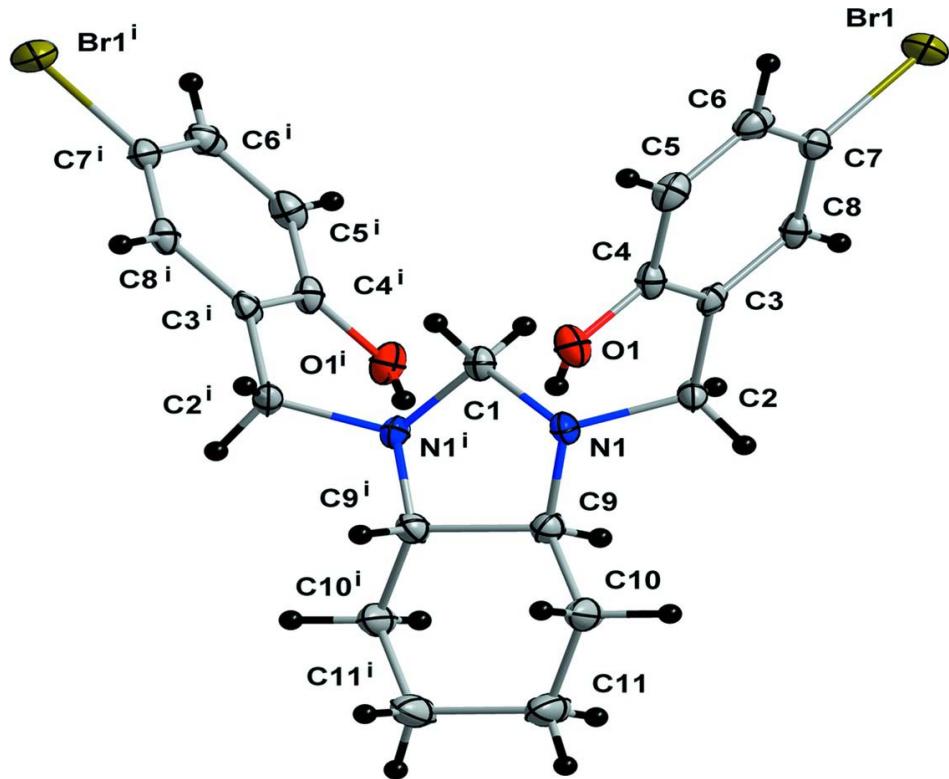
Figure 1

Ellipsoid plot of the title compound. Displacement ellipsoids are drawn at 50% probability level. [Symmetry codes: (i) 1-x, 1-y, z.]
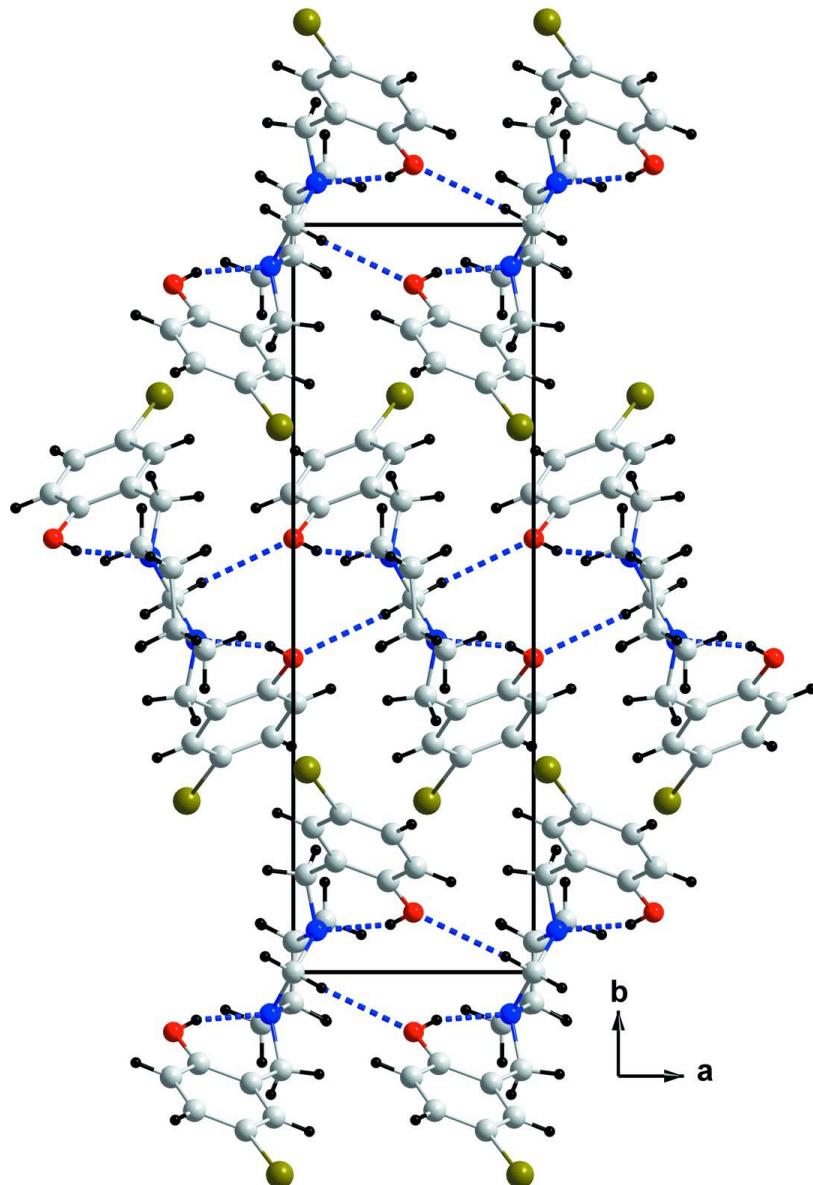
Figure 2

Hydrogen bonding of the molecules of the title compound viewed along *c*.

4,4′-Dibromo-2,2′-{[(3a*S*,7a*S*)-2,3,3a,4,5,6,7,7a-octahydro- 1*H*-1,3-benzimidazole-1,3-diyl]bis(methylidene)}diphenol

Crystal data

$C_{21}H_{24}Br_2N_2O_2$	$F(000) = 500$
$M_r = 496.2$	$D_x = 1.646$ Mg m^{-3}
Orthorhombic, $P2_12_12$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Hall symbol: P 2 2ab	Cell parameters from 16248 reflections
$a = 5.9645$ (2) Å	$\theta = 4.8$–66.5°
$b = 18.5497$ (4) Å	$\mu = 5.32$ mm^{-1}
$c = 9.0494$ (2) Å	$T = 120$ K
$V = 1001.22$ (5) Å^3	Prism, colorless
$Z = 2$	$0.19 \times 0.13 \times 0.10$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with an Atlas detector	17493 measured reflections
	1749 independent reflections
Radiation source: X-ray tube	1739 reflections with $I > 3\sigma(I)$
Mirror monochromator	$R_{int} = 0.022$
Detector resolution: 10.3784 pixels mm^{-1}	$\theta_{max} = 66.8°$, $\theta_{min} = 4.8°$
Rotation method data acquisition using ω scans	$h = -7 \rightarrow 6$
Absorption correction: analytical	$k = -10 \rightarrow 10$
(*CrysAlis PRO*; Oxford Diffraction, 2009)	$l = -21 \rightarrow 21$
$T_{min} = 0.454$, $T_{max} = 0.678$	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.015$	
$wR(F^2) = 0.049$	Weighting scheme based on measured s.u.'s $w = 1/[\sigma^2(I) + 0.0016I^2]$
$S = 1.21$	
1749 reflections	$(\Delta/\sigma)_{max} = 0.001$
126 parameters	$\Delta\rho_{max} = 0.11$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.12$ e Å^{-3}
45 constraints	Absolute structure: Flack (1983), 670 Friedel pairs
	Absolute structure parameter: 0.008 (20)

Special details

Refinement. The refinement was carried out against all reflections. The conventional *R*-factor is always based on *F*. The goodness of fit as well as the weighted *R*-factor are based on *F* and F^2 for refinement carried out on *F* and F^2, respectively. The threshold expression is used only for calculating *R*-factors *etc*. and it is not relevant to the choice of reflections for refinement.

The program used for refinement, Jana2006, uses the weighting scheme based on the experimental expectations, see _refine_ls_weighting_details, that does not force *S* to be one. Therefore the values of *S* are usually larger than the ones from the *SHELX* program.

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Br1	0.55638 (3)	0.229059 (8)	0.146172 (18)	0.02610 (7)
O1	0.99958 (19)	0.42005 (6)	0.59844 (13)	0.0226 (3)
N1	0.59652 (10)	0.44416 (5)	0.71146 (11)	0.0163 (4)
C1	0.5	0.5	0.61175 (12)	0.0154 (6)
C2	0.5511 (3)	0.36959 (8)	0.66196 (17)	0.0165 (4)
C3	0.6757 (3)	0.35153 (7)	0.52184 (17)	0.0156 (4)
C4	0.8947 (3)	0.37777 (8)	0.49815 (18)	0.0174 (4)
C5	1.0085 (3)	0.35992 (9)	0.36866 (19)	0.0204 (4)
C6	0.9120 (3)	0.31499 (8)	0.26478 (18)	0.0205 (5)
C7	0.6975 (3)	0.28860 (8)	0.29074 (18)	0.0180 (4)
C8	0.5810 (2)	0.30615 (8)	0.41680 (17)	0.0160 (4)
C9	0.5029 (3)	0.45921 (8)	0.85825 (17)	0.0179 (4)
C10	0.6319 (3)	0.43125 (9)	0.99165 (18)	0.0268 (5)
C11	0.5129 (4)	0.45880 (10)	1.13117 (19)	0.0322 (6)
H1a	0.382527	0.479008	0.553376	0.0185*
H2a	0.39302	0.363598	0.646178	0.0198*
H2b	0.593539	0.336399	0.738387	0.0198*

H5	1.155662	0.379087	0.351434	0.0245*
H6	0.991627	0.302257	0.176355	0.0245*
H8	0.433442	0.286947	0.43234	0.0192*
H9	0.362416	0.434666	0.870296	0.0214*
H10a	0.782412	0.449589	0.989185	0.0322*
H10b	0.63082	0.3795	0.991145	0.0322*
H11a	0.5957	0.444143	1.217041	0.0386*
H11b	0.367722	0.43676	1.138666	0.0386*
H1o	0.904 (3)	0.4361 (12)	0.657 (2)	0.0272*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03375 (13)	0.02617 (12)	0.01839 (12)	−0.00261 (7)	−0.00326 (7)	−0.00361 (7)
O1	0.0184 (6)	0.0183 (5)	0.0312 (7)	−0.0015 (4)	−0.0002 (5)	−0.0041 (5)
N1	0.0203 (7)	0.0104 (6)	0.0182 (7)	0.0013 (5)	0.0010 (5)	−0.0010 (5)
C1	0.0145 (10)	0.0119 (9)	0.0197 (10)	0.0006 (7)	0	0
C2	0.0189 (7)	0.0107 (7)	0.0199 (7)	−0.0017 (5)	0.0040 (7)	−0.0010 (6)
C3	0.0185 (7)	0.0095 (6)	0.0188 (7)	0.0034 (6)	0.0013 (6)	0.0036 (6)
C4	0.0176 (7)	0.0110 (7)	0.0236 (8)	0.0019 (5)	−0.0012 (6)	0.0012 (6)
C5	0.0174 (7)	0.0167 (7)	0.0271 (8)	0.0016 (6)	0.0032 (6)	0.0049 (7)
C6	0.0229 (9)	0.0184 (7)	0.0201 (8)	0.0063 (6)	0.0029 (6)	0.0046 (6)
C7	0.0243 (8)	0.0134 (6)	0.0165 (8)	0.0034 (6)	−0.0013 (6)	0.0005 (6)
C8	0.0143 (7)	0.0119 (7)	0.0220 (8)	0.0018 (5)	−0.0021 (6)	0.0023 (6)
C9	0.0215 (8)	0.0153 (8)	0.0169 (7)	0.0023 (5)	0.0009 (6)	0.0022 (6)
C10	0.0437 (10)	0.0176 (7)	0.0191 (8)	0.0094 (6)	−0.0006 (8)	0.0008 (7)
C11	0.0521 (12)	0.0251 (10)	0.0193 (8)	0.0110 (8)	0.0014 (9)	0.0042 (7)

Geometric parameters (Å, º)

Br1—C7	1.9080 (16)	C5—H5	0.96
O1—C4	1.353 (2)	C6—C7	1.390 (2)
O1—H1o	0.84 (2)	C6—H6	0.96
N1—C1	1.4895 (12)	C7—C8	1.375 (2)
N1—C2	1.4789 (18)	C8—H8	0.96
N1—C9	1.4677 (18)	C9—C9^i	1.514 (2)
C1—H1a	0.96	C9—C10	1.523 (2)
C1—H1a^i	0.96	C9—H9	0.96
C2—C3	1.507 (2)	C10—C11	1.536 (3)
C2—H2a	0.96	C10—H10a	0.96
C2—H2b	0.96	C10—H10b	0.96
C3—C4	1.410 (2)	C11—C11^i	1.536 (3)
C3—C8	1.390 (2)	C11—H11a	0.96
C4—C5	1.394 (2)	C11—H11b	0.96
C5—C6	1.382 (2)		
C4—O1—H1o	108.6 (14)	C5—C6—H6	120.6356
C1—N1—C2	113.34 (9)	C7—C6—H6	120.636

C1—N1—C9	105.60 (9)	Br1—C7—C6	119.62 (12)
C2—N1—C9	112.48 (10)	Br1—C7—C8	118.88 (12)
N1—C1—N1ⁱ	105.43 (9)	C6—C7—C8	121.48 (15)
N1—C1—H1a	109.4713	C3—C8—C7	120.37 (14)
N1—C1—H1aⁱ	109.4712	C3—C8—H8	119.8142
N1ⁱ—C1—H1a	109.4712	C7—C8—H8	119.8142
N1ⁱ—C1—H1aⁱ	109.4713	N1—C9—C9ⁱ	101.48 (12)
H1a—C1—H1aⁱ	113.2317	N1—C9—C10	117.42 (13)
N1—C2—C3	111.86 (12)	N1—C9—H9	110.1556
N1—C2—H2a	109.4713	C9ⁱ—C9—C10	110.62 (13)
N1—C2—H2b	109.4715	C9ⁱ—C9—H9	117.0073
C3—C2—H2a	109.471	C10—C9—H9	100.9265
C3—C2—H2b	109.4709	C9—C10—C11	107.74 (15)
H2a—C2—H2b	106.9725	C9—C10—H10a	109.471
C2—C3—C4	120.52 (13)	C9—C10—H10b	109.4714
C2—C3—C8	120.64 (14)	C11—C10—H10a	109.4709
C4—C3—C8	118.78 (14)	C11—C10—H10b	109.4716
O1—C4—C3	121.76 (14)	H10a—C10—H10b	111.1472
O1—C4—C5	118.47 (13)	C10—C11—C11ⁱ	112.17 (15)
C3—C4—C5	119.78 (14)	C10—C11—H11a	109.4713
C4—C5—C6	120.83 (14)	C10—C11—H11b	109.4711
C4—C5—H5	119.5819	C11ⁱ—C11—H11a	109.4712
C6—C5—H5	119.5833	C11ⁱ—C11—H11b	109.4713
C5—C6—C7	118.73 (15)	H11a—C11—H11b	106.632
C2—N1—C1—N1ⁱ	138.00 (9)	O1—C4—C5—C6	177.87 (15)
C9—N1—C1—N1ⁱ	14.44 (9)	C3—C4—C5—C6	−1.9 (2)
C1—N1—C2—C3	68.53 (14)	C4—C5—C6—C7	0.9 (2)
C9—N1—C2—C3	−171.77 (12)	C5—C6—C7—Br1	177.93 (12)
C1—N1—C9—C10	−157.29 (11)	C5—C6—C7—C8	−0.1 (2)
C1—N1—C9—C9ⁱ	−36.62 (13)	Br1—C7—C8—C3	−177.66 (11)
C2—N1—C9—C10	78.61 (16)	C6—C7—C8—C3	0.4 (2)
C2—N1—C9—C9ⁱ	−160.72 (12)	N1—C9—C10—C11	175.39 (13)
N1—C2—C3—C4	37.37 (19)	C9ⁱ—C9—C10—C11	59.64 (18)
N1—C2—C3—C8	−145.54 (13)	N1—C9—C9ⁱ—N1ⁱ	45.12 (14)
C2—C3—C4—O1	−0.5 (2)	N1—C9—C9ⁱ—C10ⁱ	170.46 (12)
C2—C3—C4—C5	179.31 (14)	C10—C9—C9ⁱ—N1ⁱ	170.46 (12)
C8—C3—C4—O1	−177.62 (14)	C10—C9—C9ⁱ—C10ⁱ	−64.21 (18)
C8—C3—C4—C5	2.2 (2)	C9—C10—C11—C11ⁱ	−55.1 (2)
C2—C3—C8—C7	−178.55 (14)	C10—C11—C11ⁱ—C10ⁱ	54.8 (2)
C4—C3—C8—C7	−1.4 (2)		

Symmetry code: (i) −x+1, −y+1, z.

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of the C3–C8 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*o*···N1	0.833 (19)	1.905 (18)	2.6506 (13)	148.3 (19)

C1—H1*a*···O1^{ii}	0.96	2.57	3.3351 (11)	137
C8—H8···*Cg*2^{iii}	0.96	2.85	3.5407 (16)	130
C11—H11*b*···*Cg*2^{iv}	0.96	2.86	3.728 (2)	150

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