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## Structure Reports

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# 4,4'-Dimethyl-2,2'-{[2,3,3a,4,5,6,7,7a-octahydro-1*H*-benzimidazole-1,3-diyl]-bis(methylene)}diphenol

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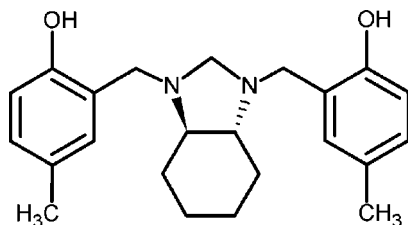
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 Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.034;  $wR$  factor = 0.090; data-to-parameter ratio = 16.8.

The asymmetric unit of the title compound,  $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_2$ , contains one half-molecule, with a twofold axis splitting the molecule in two identical halves. The structure of the racemic mixture has been reported previously [Rivera *et al.* (2009) *J. Chem. Crystallogr.* **39**, 827–830] but the enantiomer reported here crystallized in the *orthorhombic* space group  $P2_12_12$  ( $Z = 2$ ), whereas the racemate occurs in the *triclinic* space group  $P\bar{1}$  ( $Z = 2$ ). The observed molecular conformation is stabilized by two intramolecular  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds, which generate rings with graph-set motif  $S(6)$ . In the crystal, molecules are linked *via* non-classical  $\text{C}-\text{H}\cdots\text{O}$  interactions, which stack the molecules along the  $b$  axis.

## Related literature

For the structure of the original racemate, see: Rivera *et al.* (2009). For the use of 1,3-diazaheterocyclic-bridged bis(phenols) in coordination chemistry, see: Kober *et al.* (2012); Xu *et al.* (2007). For the synthesis of the precursor, (2*R*,7*R*)-1,8,10,12-tetraazatetracyclo[8.3.11<sup>8,12</sup>.0<sup>2,7</sup>]pentadecane, see: Rivera *et al.* (2012). For bond-length data, see: Allen *et al.* (1987). For graph-set analysis, see: Bernstein *et al.* (1995).



## Experimental

## Crystal data

$\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_2$   
 $M_r = 366.49$   
 Orthorhombic,  $P2_12_12$   
 $a = 18.5417$  (9) Å  
 $b = 6.0597$  (4) Å  
 $c = 8.9415$  (5) Å  
 $V = 1004.64$  (10) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.08$  mm<sup>-1</sup>  
 $T = 173$  K  
 $0.31 \times 0.27 \times 0.12$  mm

## Data collection

STOE IPDS II two-circle-diffractometer  
 Absorption correction: multi-scan (*X-AREA*; Stoe & Cie, 2001)  
 $T_{\min} = 0.976$ ,  $T_{\max} = 0.991$   
 12723 measured reflections  
 2168 independent reflections  
 2058 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.053$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.090$   
 $S = 1.04$   
 2168 reflections  
 129 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.14$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.13$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{N1}$	1.03 (4)	1.73 (4)	2.667 (2)	150 (3)
$\text{C4}-\text{H4}\cdots\text{O1}^{\text{i}}$	0.99	2.63	3.3749 (13)	133
$\text{C5}-\text{H5B}\cdots\text{O1}^{\text{ii}}$	0.99	2.63	3.522 (2)	150

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

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2012*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ5327).

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## supporting information

*Acta Cryst.* (2013). E69, o1059 [https://doi.org/10.1107/S1600536813015237]

## 4,4'-Dimethyl-2,2'-{[2,3,3a,4,5,6,7,7a-octahydro-1H-benzimidazole-1,3-diyl]bis(methylene)}diphenol

Augusto Rivera, Héctor Jairo Osorio, Mauricio Maldonado, Jaime Ríos-Motta and Michael Bolte

### S1. Comment

Chiral 1,3-diazaheterocyclic-bridged bis(phenols) form stable complexes with several metals and are of interest as ligands to metal complexes because they produce asymmetric coordination compounds (Xu *et al.*, 2007; Kober *et al.*, 2012) and therefore may be involved in enantioselective catalysis.

The title compound (**I**) was synthesized in a one-step reaction between the chiral macrocyclic amination (2*R*,7*R*)-1,8,10,12-tetraazatetracyclo[8.3.11<sup>8,12</sup>.0<sup>2,7</sup>]pentadecane and *p*-cresol. Single crystals of were obtained by recrystallization from CHCl<sub>3</sub> solution.

The molecular structure and atom-numbering scheme for (**I**) are shown in Fig. 1. The bond lengths and angles are within normal ranges (Allen *et al.*, 1987) and are comparable with those reported previously reported racemate (Rivera *et al.*, 2009). The space group, of the title enantiomer, *P*2<sub>1</sub>2<sub>1</sub>2, differs from that of the racemate which was triclinic, *P*-1. (Rivera *et al.*, 2009).

The crystal structure of (**I**) shows two intramolecular hydrogen bonds generating rings with graph-set motif S(6) (Bernstein *et al.*, 1995) (Table 1). In the crystal, molecules are linked *via* non-classical intermolecular C—H⋯O interactions, which stack the molecules along the *b* axis.

### S2. Experimental

The title compound was synthesized according to the published procedure (Rivera *et al.*, 2012) by reacting (2*R*,7*R*)-1,8,10,12-tetraazatetracyclo [8.3.11<sup>8,12</sup>.0<sup>2,7</sup>]pentadecane (1 mmol, [ $\alpha$ ]<sup>20</sup><sub>D</sub> -25.1, *c* = 0.6% CH<sub>2</sub>Cl<sub>2</sub>) and *p*-cresol (1 mmol). After work-up a solid was obtained by slow evaporation from chloroform at room temperature. After standing for two days, crystals suitable for X-ray diffraction were grown from a solution in CHCl<sub>3</sub> obtained in 37% yield, *m.p.* = 464 K, [ $\alpha$ ]<sup>20</sup><sub>D</sub> -54.4, *c* = 0.6 in CHCl<sub>3</sub>.

### S3. Refinement

The hydroxyl H atom was freely refined. H atoms bound to carbon were refined using a riding model with methyl C—H = 0.98 Å, aromatic C—H = 0.95 Å, secondary C—H = 0.99 Å, and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H or  $1.2U_{\text{eq}}(\text{C})$  for aromatic and secondary H.

\_reflns\_Friedel\_fraction is defined as the number of unique Friedel pairs measured divided by the number that would be possible theoretically, ignoring centric projections and systematic absences

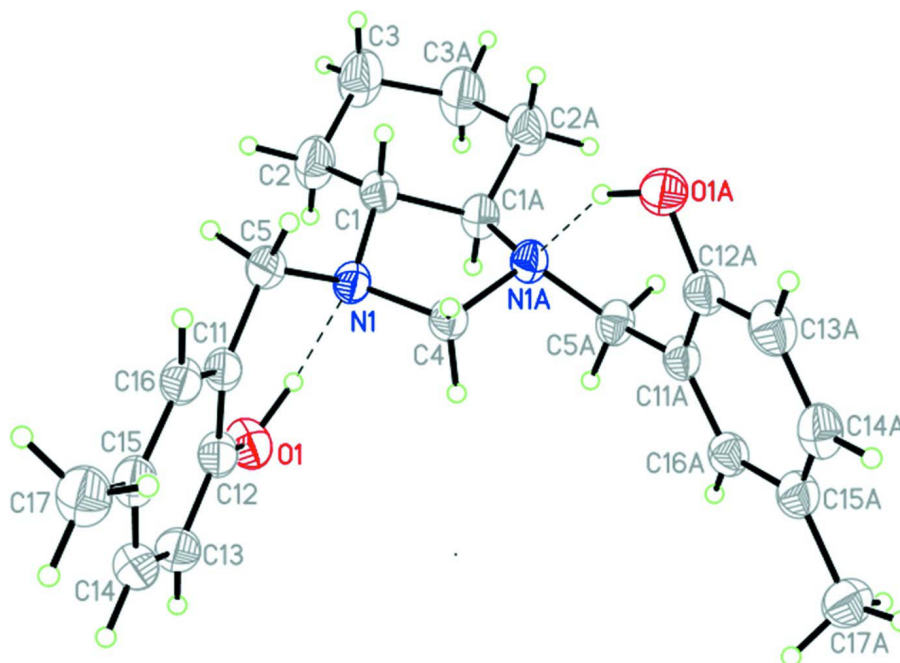


Figure 1

A perspective view of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres with arbitrary radii. Intramolecular hydrogen bonds are drawn as dashed lines.

#### 4,4'-Dimethyl-2,2'-[2,3,3a,4,5,6,7,7a-octahydro-1H-benzimidazole-1,3-diyl]bis(methylene)diphenol

##### Crystal data

$C_{23}H_{30}N_2O_2$

$M_r = 366.49$

Orthorhombic,  $P2_12_12$

$a = 18.5417(9) \text{ \AA}$

$b = 6.0597(4) \text{ \AA}$

$c = 8.9415(5) \text{ \AA}$

$V = 1004.64(10) \text{ \AA}^3$

$Z = 2$

$F(000) = 396$

$D_x = 1.212 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 16515 reflections

$\theta = 2.2\text{--}27.5^\circ$

$\mu = 0.08 \text{ mm}^{-1}$

$T = 173 \text{ K}$

Plate, colourless

$0.31 \times 0.27 \times 0.12 \text{ mm}$

##### Data collection

STOE IPDS II two-circle-diffractometer

Radiation source: Genix 3D  $I\mu$ S microfocus X-ray source

$\omega$  scans

Absorption correction: multi-scan (*X-Area*; Stoe & Cie, 2001)

$T_{\min} = 0.976$ ,  $T_{\max} = 0.991$

12723 measured reflections

2168 independent reflections

2058 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 26.9^\circ$ ,  $\theta_{\min} = 2.2^\circ$

$h = -23 \rightarrow 23$

$k = -7 \rightarrow 7$

$l = -11 \rightarrow 11$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.090$

$S = 1.04$

2168 reflections

129 parameters

0 restraints

Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.1419P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL*,  
 $Fc^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.075 (11)

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.41870 (7)	0.5018 (2)	0.60166 (17)	0.0414 (3)
H1	0.4384 (19)	0.376 (6)	0.668 (4)	0.097 (11)*
N1	0.44460 (7)	0.0979 (2)	0.70721 (16)	0.0303 (3)
C1	0.45928 (9)	0.0063 (3)	0.85614 (19)	0.0340 (4)
H1A	0.4393	-0.1468	0.8611	0.041*
C2	0.43253 (11)	0.1352 (4)	0.9905 (2)	0.0477 (5)
H2A	0.3792	0.1414	0.9901	0.057*
H2B	0.4513	0.2880	0.9873	0.057*
C3	0.45917 (12)	0.0182 (5)	1.1318 (2)	0.0596 (7)
H3A	0.4458	0.1074	1.2204	0.071*
H3B	0.4347	-0.1264	1.1405	0.071*
C4	0.5000	0.0000	0.6072 (3)	0.0305 (5)
H4	0.5217	0.1150	0.5427	0.037*
C5	0.36990 (9)	0.0576 (3)	0.6571 (2)	0.0332 (4)
H5A	0.3362	0.1007	0.7378	0.040*
H5B	0.3634	-0.1021	0.6380	0.040*
C11	0.35166 (9)	0.1843 (3)	0.5173 (2)	0.0301 (4)
C12	0.37743 (9)	0.3996 (3)	0.4958 (2)	0.0330 (4)
C13	0.35991 (10)	0.5134 (3)	0.3660 (2)	0.0389 (4)
H13	0.3788	0.6571	0.3496	0.047*
C14	0.31501 (10)	0.4180 (4)	0.2604 (2)	0.0389 (4)
H14	0.3032	0.4983	0.1724	0.047*
C15	0.28681 (10)	0.2075 (3)	0.2801 (2)	0.0359 (4)
C16	0.30625 (9)	0.0935 (3)	0.4097 (2)	0.0320 (4)
H16	0.2878	-0.0511	0.4249	0.038*
C17	0.23790 (11)	0.1007 (4)	0.1658 (2)	0.0452 (5)
H17A	0.2278	0.2060	0.0852	0.068*
H17B	0.1926	0.0571	0.2138	0.068*
H17C	0.2617	-0.0300	0.1241	0.068*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0387 (7)	0.0295 (6)	0.0559 (8)	-0.0030 (6)	-0.0083 (6)	-0.0022 (7)
N1	0.0243 (7)	0.0345 (7)	0.0319 (7)	0.0019 (6)	0.0008 (5)	0.0008 (6)
C1	0.0298 (9)	0.0385 (8)	0.0337 (9)	0.0043 (7)	0.0003 (6)	0.0036 (8)
C2	0.0383 (10)	0.0677 (14)	0.0371 (10)	0.0140 (10)	0.0033 (9)	-0.0034 (10)
C3	0.0501 (13)	0.0951 (19)	0.0335 (10)	0.0207 (13)	0.0048 (9)	0.0018 (12)
C4	0.0262 (10)	0.0315 (11)	0.0339 (11)	0.0007 (9)	0.000	0.000
C5	0.0251 (8)	0.0346 (8)	0.0398 (9)	-0.0014 (7)	-0.0005 (7)	0.0043 (7)
C11	0.0238 (7)	0.0296 (8)	0.0369 (9)	0.0024 (6)	0.0013 (7)	0.0006 (7)
C12	0.0274 (8)	0.0301 (8)	0.0414 (9)	0.0012 (7)	0.0003 (7)	-0.0015 (8)
C13	0.0371 (9)	0.0316 (8)	0.0482 (10)	0.0008 (7)	0.0058 (8)	0.0062 (8)
C14	0.0377 (9)	0.0410 (10)	0.0380 (9)	0.0077 (8)	0.0028 (8)	0.0062 (8)
C15	0.0305 (8)	0.0409 (10)	0.0363 (9)	0.0048 (7)	0.0014 (8)	-0.0021 (8)
C16	0.0270 (8)	0.0303 (8)	0.0388 (9)	0.0001 (7)	0.0020 (7)	-0.0013 (7)
C17	0.0427 (10)	0.0546 (11)	0.0384 (10)	0.0024 (9)	-0.0037 (8)	-0.0041 (10)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C12	1.365 (2)	C5—C11	1.505 (2)
O1—H1	1.03 (4)	C5—H5A	0.9900
N1—C1	1.468 (2)	C5—H5B	0.9900
N1—C5	1.476 (2)	C11—C16	1.392 (3)
N1—C4	1.485 (2)	C11—C12	1.403 (2)
C1—C1 <sup>i</sup>	1.512 (3)	C12—C13	1.389 (3)
C1—C2	1.516 (3)	C13—C14	1.386 (3)
C1—H1A	1.0000	C13—H13	0.9500
C2—C3	1.531 (3)	C14—C15	1.390 (3)
C2—H2A	0.9900	C14—H14	0.9500
C2—H2B	0.9900	C15—C16	1.396 (3)
C3—C3 <sup>i</sup>	1.530 (4)	C15—C17	1.512 (3)
C3—H3A	0.9900	C16—H16	0.9500
C3—H3B	0.9900	C17—H17A	0.9800
C4—N1 <sup>i</sup>	1.485 (2)	C17—H17B	0.9800
C4—H4	0.9900	C17—H17C	0.9800
C12—O1—H1	105 (2)	N1—C5—H5B	109.2
C1—N1—C5	112.75 (14)	C11—C5—H5B	109.2
C1—N1—C4	105.47 (13)	H5A—C5—H5B	107.9
C5—N1—C4	113.58 (14)	C16—C11—C12	118.61 (17)
N1—C1—C1 <sup>i</sup>	101.79 (11)	C16—C11—C5	120.55 (15)
N1—C1—C2	117.60 (15)	C12—C11—C5	120.78 (16)
C1 <sup>i</sup> —C1—C2	110.66 (14)	O1—C12—C13	119.01 (16)
N1—C1—H1A	108.8	O1—C12—C11	121.19 (17)
C1 <sup>i</sup> —C1—H1A	108.8	C13—C12—C11	119.79 (17)
C2—C1—H1A	108.8	C14—C13—C12	120.22 (17)
C1—C2—C3	108.07 (17)	C14—C13—H13	119.9

C1—C2—H2A	110.1	C12—C13—H13	119.9
C3—C2—H2A	110.1	C13—C14—C15	121.48 (18)
C1—C2—H2B	110.1	C13—C14—H14	119.3
C3—C2—H2B	110.1	C15—C14—H14	119.3
H2A—C2—H2B	108.4	C14—C15—C16	117.54 (18)
C3 <sup>i</sup> —C3—C2	112.71 (18)	C14—C15—C17	122.16 (19)
C3 <sup>i</sup> —C3—H3A	109.0	C16—C15—C17	120.28 (18)
C2—C3—H3A	109.0	C11—C16—C15	122.30 (17)
C3 <sup>i</sup> —C3—H3B	109.0	C11—C16—H16	118.8
C2—C3—H3B	109.0	C15—C16—H16	118.8
H3A—C3—H3B	107.8	C15—C17—H17A	109.5
N1 <sup>i</sup> —C4—N1	106.00 (19)	C15—C17—H17B	109.5
N1 <sup>i</sup> —C4—H4	110.5	H17A—C17—H17B	109.5
N1—C4—H4	110.5	C15—C17—H17C	109.5
N1—C5—C11	112.24 (14)	H17A—C17—H17C	109.5
N1—C5—H5A	109.2	H17B—C17—H17C	109.5
C11—C5—H5A	109.2		
C5—N1—C1—C1 <sup>i</sup>	160.26 (17)	C16—C11—C12—O1	176.16 (15)
C4—N1—C1—C1 <sup>i</sup>	35.78 (19)	C5—C11—C12—O1	-1.1 (2)
C5—N1—C1—C2	-78.7 (2)	C16—C11—C12—C13	-2.7 (2)
C4—N1—C1—C2	156.83 (15)	C5—C11—C12—C13	180.00 (15)
N1—C1—C2—C3	-175.55 (19)	O1—C12—C13—C14	-176.61 (17)
C1 <sup>i</sup> —C1—C2—C3	-59.2 (2)	C11—C12—C13—C14	2.3 (3)
C1—C2—C3—C3 <sup>i</sup>	53.8 (3)	C12—C13—C14—C15	-0.4 (3)
C1—N1—C4—N1 <sup>i</sup>	-14.09 (8)	C13—C14—C15—C16	-0.9 (3)
C5—N1—C4—N1 <sup>i</sup>	-138.05 (15)	C13—C14—C15—C17	-179.83 (18)
C1—N1—C5—C11	170.22 (14)	C12—C11—C16—C15	1.4 (3)
C4—N1—C5—C11	-69.88 (17)	C5—C11—C16—C15	178.62 (16)
N1—C5—C11—C16	144.70 (16)	C14—C15—C16—C11	0.5 (3)
N1—C5—C11—C12	-38.1 (2)	C17—C15—C16—C11	179.38 (17)

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

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ N1	1.03 (4)	1.73 (4)	2.667 (2)	150 (3)
C4—H4 $\cdots$ O1 <sup>ii</sup>	0.99	2.63	3.3749 (13)	133
C5—H5B $\cdots$ O1 <sup>iii</sup>	0.99	2.63	3.522 (2)	150

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