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6,6′-Dibromo-4,4′-dimethyl-3,3′-methylenebi(2*H*,4*H*-benz[e][1,3]oxazine)

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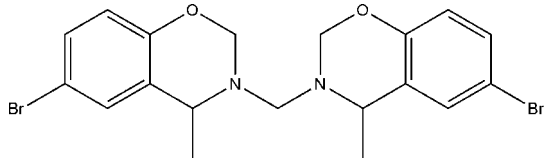
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.033; wR factor = 0.075; data-to-parameter ratio = 15.0.

In the title compound, $C_{19}H_{20}Br_2N_2O_2$, a crystallographic twofold rotation axis passes through the central C atom. The crystal structure is stabilized by weak C—H···N and intermolecular C—H···O hydrogen bonds.

Related literature

For related literature, see: Allen *et al.* (1987); Domenicano *et al.* (1975); Yang *et al.* (2005).



Experimental

Crystal data

$C_{19}H_{20}Br_2N_2O_2$
M_r = 468.19
Monoclinic, $C2/c$
a = 19.826 (4) Å
b = 11.702 (2) Å
c = 8.146 (2) Å
β = 99.92 (3)°
V = 1861.7 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.37 mm^{-1}
T = 298 (2) K
0.35 × 0.24 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.298, T_{max} = 0.459
4729 measured reflections
1722 independent reflections
1375 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.075
S = 1.08
1722 reflections
115 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.64 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···N1^{i}	0.98	2.51	2.943 (3)	107
C9—H9B···O1^{ii}	0.97	2.56	3.418 (4)	147
C9—H9A···O1^{iii}	0.97	2.56	3.418 (4)	147

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

The authors are grateful to the Science Foundation of the University of Jinan for Doctors (grant No. B0001) for financial support. X-ray data were collected at Taishan University of China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SG2184).

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supplementary materials

Acta Cryst. (2007). E**63**, o3483 [**doi:10.1107/S1600536807033089**]

6,6'-Dibromo-4,4'-dimethyl-3,3'-methylenebi(2*H*,4*H*-benz[*e*][1,3]oxazine)

G.-Y. Zhang, M. Li, W.-H. Wang and Z.-W. Qian

Comment

The title compound, (I), was prepared by reaction of racemic 2-(1-aminoethyl)-4-bromophenol, (II), with formaldehyde.

The molecule is centrosymmetric. The bond lengths observed in the two phenyl rings agree with eath other and are comparable with average values reported in the literature (Domenicano *et al.*, 1975; Allen *et al.*, 1987). The dihedral between the C1—C6 and C1a—C6a aromatic rings is 65.89 (2)°.

The molecules are linked *via* C—H···N hydrogen bonds into cyclic $R^2_2(6)$ dimers (Fig. 2). The hydrogen bonds observed in the structure are listed in Table 2.

Experimental

The title compound was prepared according to the procedure of Xiao-Feng Yang *et al.* (2005). A methanol solution (10 ml) of ammonia (0.9 mmol) and 1-(5-bromo-2-hydroxyphenyl)ethanone (0.9 mmol) wasreacted at room temperature for 24 h. After removal of the solvent, $NaBH_4$ (4.5 mmol) was added to the solution in THF/ethanol (20 ml; 1:1*v*/*v*) and stirred at 0°C until the solution became colorless. The solvent was removed under reduced pressure. Water (10 ml) was added to the residue and 1 N HCl was added dropwise until hydrogen production ceased. The mixture was neutralized with aqueous Na_2CO_3, then extracted with $CHCl_3$, and the organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. Further purification was carried out by thin-layer silica-gel chromatography (chloroform) to give colorless solid (II), yield of 90.3%. The compound (II) was reacted with formaldehyde (1.2 equivalents) in a methanol solution (10 ml). Evaporation of a methanol solution at room temperature gave crystals of (I) (m.p.675–676 K) IR (KBr): 3443 (*s*), 2974 (*m*), 1481 (*s*), 1255 (*s*), 1178 (*m*), 970 (*m*), 628 (w) cm^{-1}.

Refinement

All H atoms were positioned geometrically and treated as riding on their parent atoms, with *C*—*H*(methyl) = 0.96 Å, *C*—*H*(methylene) = 0.97 Å, C—H(methine) = 0.98 Å, C—H(aromatic) = 0.93 Å, and with U_{iso}(H) = 1.5U_{eq}(C_{methyl}) and 1.2U_{eq}($C_{aromatic}$, $C_{methylene}$, $C_{methine}$).

Figures

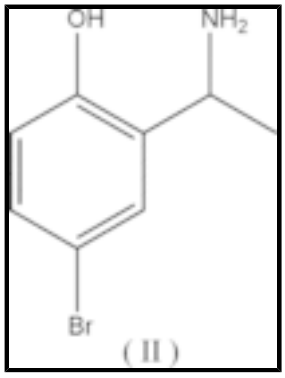

Fig. 1. Compound (II).

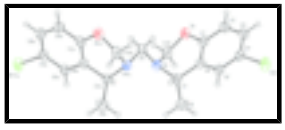

Fig. 2. The molecular structure of (I), showing the atom-labelling scheme.

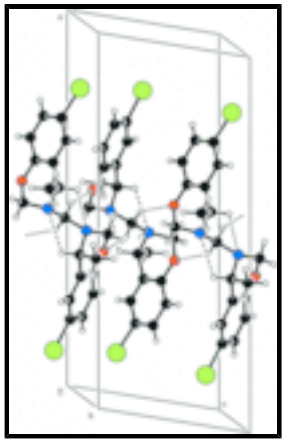

Fig. 3. A packing diagram of (I), dashed lines indicate hydrogen bonds.

6,6'-Dibromo-4,4'-dimethyl-3,3'-methylenebi(2*H*,4*H*- benz[e][1,3]oxazine)

Crystal data

$C_{19}H_{20}Br_2N_2O_2$	F_{000} = 936
M_r = 468.19	D_x = 1.670 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C2yc	Cell parameters from 1722 reflections
a = 19.826 (4) Å	θ = 2.0–25.5º
b = 11.702 (2) Å	μ = 4.37 mm^{-1}
c = 8.146 (2) Å	*T* = 298 (2) K
β = 99.92 (3)º	Block, colourless
V = 1861.7 (6) Å^3	0.35 × 0.24 × 0.18 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	1722 independent reflections
Radiation source: fine-focus sealed tube	1375 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.037$
$T = 298(2)$ K	$\theta_{max} = 25.5^{o}$
ω scans	$\theta_{min} = 2.0^{o}$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -24\rightarrow24$
$T_{min} = 0.298$, $T_{max} = 0.459$	$k = -8\rightarrow14$
4729 measured reflections	$l = -9\rightarrow9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.033$	H-atom parameters constrained
$wR(F^2) = 0.075$	$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 3.2728P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
1722 reflections	$\Delta\rho_{max} = 0.48$ e Å^{-3}
115 parameters	$\Delta\rho_{min} = -0.64$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2$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}	Occ. (<1)
C1	0.36058 (15)	0.8872 (3)	0.4372 (4)	0.0422 (7)	
C2	0.30490 (16)	0.9531 (3)	0.4563 (4)	0.0505 (8)	
H2	0.3107	1.0181	0.5230	0.061*	
C3	0.24080 (16)	0.9226 (3)	0.3766 (4)	0.0500 (8)	
H3	0.2028	0.9665	0.3881	0.060*	

C4	0.23362 (15)	0.8261 (3)	0.2796 (4)	0.0441 (7)	
C5	0.28870 (15)	0.7600 (3)	0.2608 (4)	0.0417 (7)	
H5	0.2824	0.6952	0.1937	0.050*	
C6	0.35394 (14)	0.7891 (3)	0.3412 (4)	0.0382 (7)	
C7	0.41513 (14)	0.7178 (3)	0.3189 (4)	0.0411 (7)	
H7	0.4123	0.7042	0.1993	0.049*	
C8	0.41674 (18)	0.6022 (3)	0.4034 (5)	0.0614 (10)	
H8A	0.4539	0.5578	0.3756	0.092*	
H8B	0.3743	0.5631	0.3662	0.092*	
H8C	0.4230	0.6126	0.5220	0.092*	
C9	0.5000	0.8533 (4)	0.2500	0.0412 (10)	
H9A	0.4622	0.9018	0.2008	0.049*	0.50
H9B	0.5378	0.9018	0.2992	0.049*	0.50
C10	0.47610 (15)	0.8379 (3)	0.5288 (4)	0.0479 (8)	
H10A	0.5201	0.8735	0.5682	0.057*	
H10B	0.4685	0.7815	0.6110	0.057*	
Br1	0.145465 (16)	0.78480 (4)	0.16417 (5)	0.06290 (17)	
N1	0.47908 (12)	0.7813 (2)	0.3773 (3)	0.0406 (6)	
O1	0.42328 (10)	0.9242 (2)	0.5178 (3)	0.0512 (6)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0390 (16)	0.0488 (19)	0.0379 (17)	−0.0068 (14)	0.0040 (13)	−0.0015 (15)
C2	0.0505 (19)	0.0478 (19)	0.053 (2)	−0.0010 (16)	0.0093 (16)	−0.0110 (16)
C3	0.0413 (17)	0.054 (2)	0.055 (2)	0.0053 (15)	0.0099 (15)	0.0014 (17)
C4	0.0380 (16)	0.0527 (19)	0.0396 (17)	−0.0053 (14)	0.0014 (13)	0.0060 (15)
C5	0.0386 (16)	0.0472 (18)	0.0383 (17)	−0.0048 (14)	0.0035 (13)	−0.0033 (14)
C6	0.0379 (15)	0.0436 (17)	0.0330 (15)	−0.0043 (13)	0.0055 (12)	0.0012 (14)
C7	0.0360 (15)	0.0451 (18)	0.0408 (17)	−0.0030 (13)	0.0029 (13)	−0.0057 (14)
C8	0.052 (2)	0.047 (2)	0.085 (3)	−0.0017 (16)	0.0106 (18)	0.003 (2)
C9	0.037 (2)	0.045 (3)	0.040 (2)	0.000	0.0048 (18)	0.000
C10	0.0392 (16)	0.066 (2)	0.0357 (17)	−0.0054 (16)	−0.0022 (13)	−0.0020 (16)
Br1	0.03772 (19)	0.0865 (3)	0.0605 (3)	−0.00454 (18)	−0.00279 (15)	−0.0045 (2)
N1	0.0344 (12)	0.0502 (15)	0.0355 (14)	−0.0024 (11)	0.0015 (10)	−0.0022 (12)
O1	0.0392 (12)	0.0619 (15)	0.0511 (14)	−0.0078 (10)	0.0037 (10)	−0.0213 (11)

Geometric parameters (Å, °)

C1—O1	1.372 (3)	C7—C8	1.515 (4)
C1—C2	1.377 (4)	C7—H7	0.9800
C1—C6	1.383 (4)	C8—H8A	0.9600
C2—C3	1.371 (4)	C8—H8B	0.9600
C2—H2	0.9300	C8—H8C	0.9600
C3—C4	1.371 (5)	C9—N1^{i}	1.451 (4)
C3—H3	0.9300	C9—N1	1.451 (4)
C4—C5	1.368 (4)	C9—H9A	0.9700
C4—Br1	1.899 (3)	C9—H9B	0.9700

C5—C6	1.388 (4)	C10—N1	1.410 (4)
C5—H5	0.9300	C10—O1	1.447 (4)
C6—C7	1.509 (4)	C10—H10A	0.9700
C7—N1	1.476 (4)	C10—H10B	0.9700
O1—C1—C2	116.6 (3)	C8—C7—H7	107.5
O1—C1—C6	121.5 (3)	C7—C8—H8A	109.5
C2—C1—C6	121.9 (3)	C7—C8—H8B	109.5
C3—C2—C1	119.7 (3)	H8A—C8—H8B	109.5
C3—C2—H2	120.1	C7—C8—H8C	109.5
C1—C2—H2	120.1	H8A—C8—H8C	109.5
C4—C3—C2	118.9 (3)	H8B—C8—H8C	109.5
C4—C3—H3	120.5	N1^{i}—C9—N1	109.1 (3)
C2—C3—H3	120.5	N1^{i}—C9—H9A	109.9
C5—C4—C3	121.6 (3)	N1—C9—H9A	109.9
C5—C4—Br1	119.0 (2)	N1^{i}—C9—H9B	109.9
C3—C4—Br1	119.3 (2)	N1—C9—H9B	109.9
C4—C5—C6	120.3 (3)	H9A—C9—H9B	108.3
C4—C5—H5	119.8	N1—C10—O1	114.3 (2)
C6—C5—H5	119.8	N1—C10—H10A	108.7
C1—C6—C5	117.5 (3)	O1—C10—H10A	108.7
C1—C6—C7	121.8 (3)	N1—C10—H10B	108.7
C5—C6—C7	120.7 (3)	O1—C10—H10B	108.7
N1—C7—C6	110.3 (2)	H10A—C10—H10B	107.6
N1—C7—C8	110.7 (2)	C10—N1—C9	114.4 (3)
C6—C7—C8	113.2 (3)	C10—N1—C7	110.8 (2)
N1—C7—H7	107.5	C9—N1—C7	113.4 (2)
C6—C7—H7	107.5	C1—O1—C10	113.3 (2)
O1—C1—C2—C3	178.7 (3)	C5—C6—C7—N1	164.6 (3)
C6—C1—C2—C3	−1.0 (5)	C1—C6—C7—C8	111.4 (3)
C1—C2—C3—C4	0.3 (5)	C5—C6—C7—C8	−70.8 (4)
C2—C3—C4—C5	0.0 (5)	O1—C10—N1—C9	66.8 (3)
C2—C3—C4—Br1	−178.5 (3)	O1—C10—N1—C7	−63.0 (3)
C3—C4—C5—C6	0.4 (5)	N1^{i}—C9—N1—C10	163.0 (2)
Br1—C4—C5—C6	178.9 (2)	N1^{i}—C9—N1—C7	−68.6 (2)
O1—C1—C6—C5	−178.3 (3)	C6—C7—N1—C10	42.8 (3)
C2—C1—C6—C5	1.4 (5)	C8—C7—N1—C10	−83.2 (3)
O1—C1—C6—C7	−0.4 (5)	C6—C7—N1—C9	−87.5 (3)
C2—C1—C6—C7	179.3 (3)	C8—C7—N1—C9	146.5 (3)
C4—C5—C6—C1	−1.0 (5)	C2—C1—O1—C10	164.8 (3)
C4—C5—C6—C7	−179.0 (3)	C6—C1—O1—C10	−15.5 (4)
C1—C6—C7—N1	−13.2 (4)	N1—C10—O1—C1	48.1 (4)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···N1^{i}	0.98	2.51	2.943 (3)	107

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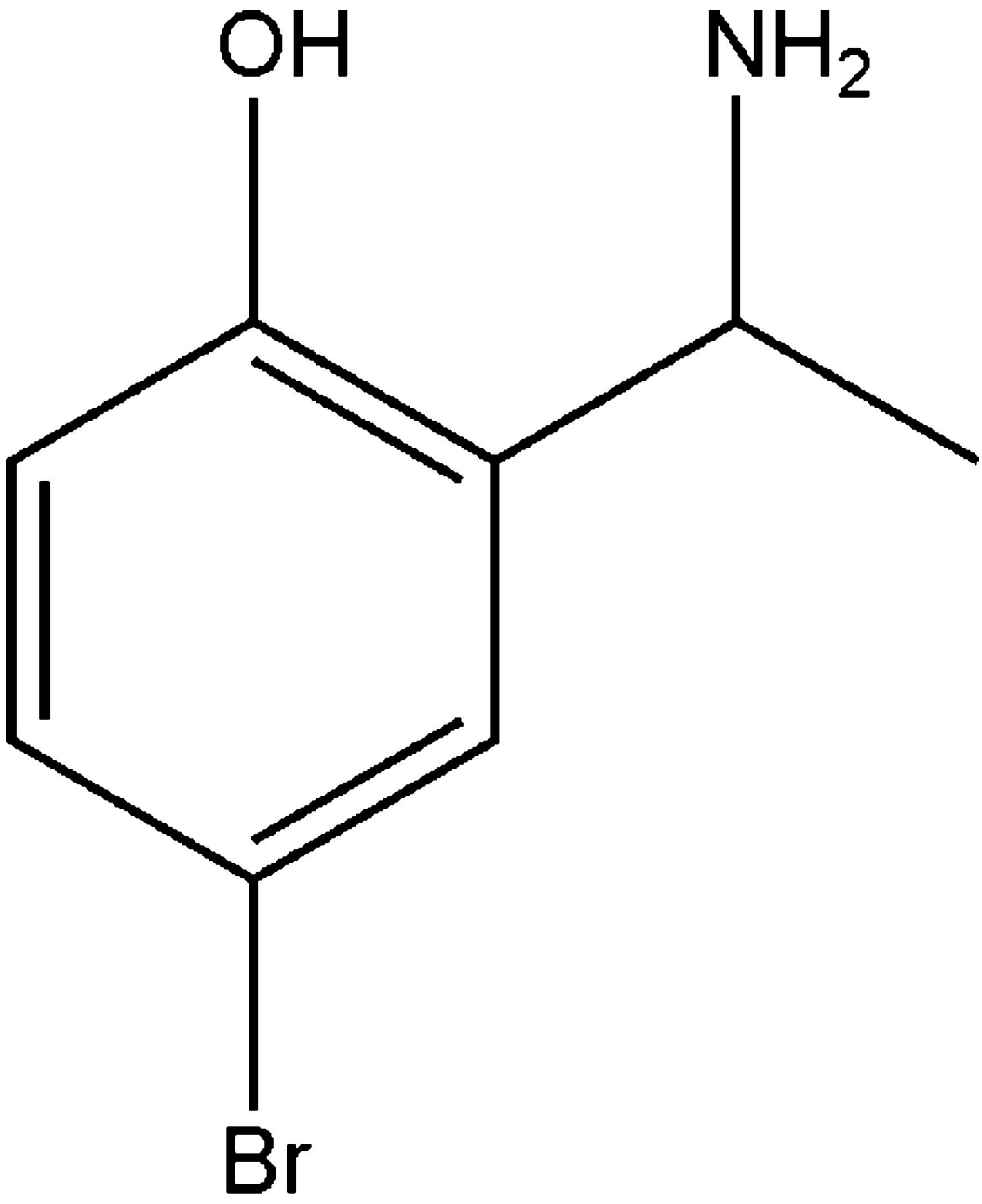
Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2; (ii) −*x*+1, −*y*+2, −*z*+1; (iii) *x*, −*y*+2, *z*−1/2.

Fig. 1



(II)

Fig. 2

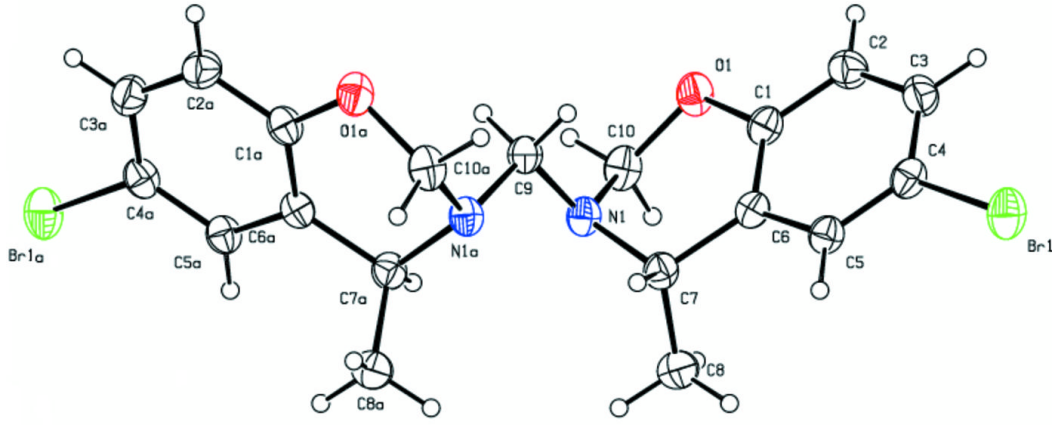

C2a
C3a
O1a
C1a
C10a
C9
C10
O1
C1
C2
C3
C4
C4a
Br1a
C6a
C5a
N1a
N1
C6
C5
Br1
C7a
C7
C8a
C8

Fig. 3