

Crystal structure of 1,2-bis(6-bromo-3,4-dihydro-2*H*-benz[e][1,3]oxazin-3-yl)ethane: a bromine-containing bis-benzoxazine

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Received 13 October 2016

Accepted 16 October 2016

Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; benzoxazines; phenolic resins; C—H···Br and C—H···O hydrogen bonds.**CCDC reference:** 1510085**Supporting information:** this article has supporting information at journals.iucr.org/e

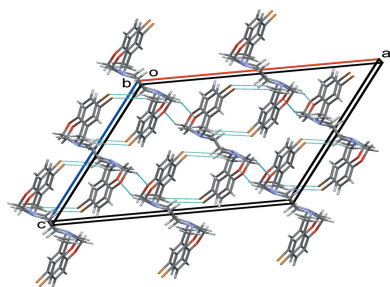
The title benzoxazine molecule, C₁₈H₁₈Br₂N₂O₂, was prepared by a Mannich-type reaction of 4-bromophenol with ethane-1,2-diamine and formaldehyde. The title compound crystallizes in the monoclinic space group *C2/c* with a centre of inversion located at the mid-point of the C—C bond of the central CH₂CH₂ spacer. The oxazinic ring adopts a half-chair conformation. The structure is compared to those of other functionalized benzoxazines synthesized in our laboratory. In the crystal, weak C—H···Br and C—H···O hydrogen bonds stack the molecules along the *b*-axis direction.

1. Chemical context

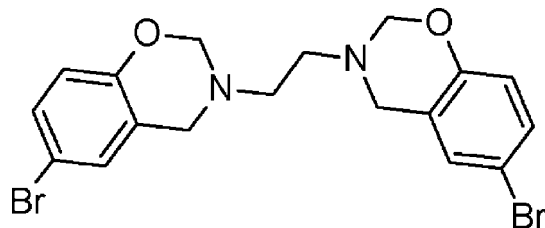
In a continuation of our work on the synthesis and characterization of bis-1,3-benzoxazines, we have studied some of the chemical properties and determined the crystal structure of the title compound. Benzoxazines form an important class of benzo-fused heterocycles with a wide spectrum of biological activities. They are also emerging as desirable phenolic resin precursors because benzoxazines can undergo ring opening without emitting volatile materials during the curing process. This leads to a final cured product with excellent properties (Pilato, 2010). Normally, the incorporation of bromine can increase the flame-retarding properties and reduce the flammability of polymers (Li, *et al.*, 2010). Recently, we have investigated the crystal structures of analogous bifunctional benzoxazines namely 3,3'-(ethane-1,2-diyl)bis(6-substituted-3,4-dihydro-2*H*-1,3-benzoxazine) (Rivera *et al.*, 2010, 2011, 2012*a,b*) that were prepared to investigate whether replacement of the substituents at the *para* position of the phenyl ring affects the electrophilic anomeric effect in the N—C—O sequence of the adjacent oxazine ring. In addition, as benzoxazine contains a tertiary nitrogen atom, the lone-pair electrons may play an important role in the interaction with guest molecules but there are no reports on the inclusion properties of polybenzoxazines (Chirachanchai *et al.*, 2011). An X-ray structural study may therefore provide a better understanding of the ability of benzoxazines to act as novel host–guest compounds. In our opinion, the title compound also has potential applications in the production of new bromine-containing phenolic resins.

2. Structural commentary

The asymmetric unit of the title compound (Fig. 1), C₁₈H₁₈Br₂N₂O₂, contains one half of the organic molecule, an



inversion centre generates the other half of the molecule (symmetry operation: $1 - x, 1 - y, 1 - z$). The six-membered oxazine heterocyclic ring adopts a half-chair conformation, with puckering parameters $Q = 0.512$ (2) Å, $\theta = 129.6$ (2)°, $\varphi = 283.6$ (3)°. This ring is analysed with respect to the plane formed by O1/C3/C4/C5, with deviations of the C2 and N1 atoms from this plane of 0.300 (6) and -0.320 (4) Å, respectively.



The C–C bond distances and angles of the aromatic rings were found to be normal. The C3–O1 bond length [1.372 (6) Å] is comparable with other previously reported C–O bond lengths for related structures [1.370 (10) and 1.388 (9) Å (Rivera *et al.*, 2012a) and 1.376 (1) Å (Rivera *et al.*, 2011)], but is found to be shorter in the *p*-chloro derivative where C–O = 1.421 (2) Å (Rivera *et al.*, 2010). Interestingly, the C2–N1 and C2–O1 distances, 1.450 (5) and 1.456 (6) Å, respectively, are significantly different from the corresponding distances in the *p*-chloro derivative [1.369 (2) and 1.529 (2) Å, respectively; Rivera *et al.*, 2010]. Indeed, the values observed here are closer to those found in the analogous compound with no *p*-substituent on the aromatic ring (1.424 and 1.463 Å, respectively; Rivera *et al.*, 2012a). This may indicate that the presence of the electron-withdrawing bromine atom does not significantly affect the adjacent oxazinic ring.

3. Supramolecular features

In the crystal, weak C5–H5B···Br1 hydrogen bonds (Table 1) lead to the formation of inversion dimers with $R_2^2(12)$ ring motifs. These combine with the inversion symmetry of the molecule to produce chains of molecules along the *c* axis. Additional weak C2–H2B···O1 hydrogen bonds link these chains, stacking molecules along the *b*-axis direction, Fig. 2.

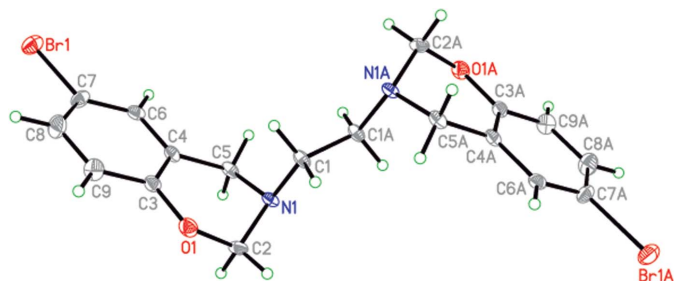


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Atoms labelled with the suffix A are generated using the symmetry operator ($1 - x, 1 - y, 1 - z$).

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C5–H5B···Br1 ⁱ	0.99	3.04	3.951 (5)	154
C2–H2B···O1 ⁱⁱ	0.99	2.64	3.506 (6)	146

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

4. Database survey

A database search yielded four comparable structures, namely 3,3'-(ethane-1,2-diyl)bis(6-methyl-3,4-dihydro-2*H*-1,3-benzoxazine) (AXAKAM; Rivera *et al.*, 2011), 3,3'-ethylenebis(3,4-dihydro-6-chloro-2*H*-1,3-benzoxazine) (NUQKAM; Rivera *et al.*, 2010), 3,3'-(ethane-1,2-diyl)bis(6-methoxy-3,4-dihydro-2*H*-1,3-benzoxazine) monohydrate (QEDDOU; Rivera *et al.*, 2012b), 3,3'-(ethane-1,2-diyl)bis(3,4-dihydro-2*H*-1,3-benzoxazine) (SAGPUN; Rivera *et al.*, 2012a). The Cl-substituted compound (NUQKAM) and the title compound are isomorphous. However, AXAKAM and SAGOUN have different space groups and in QEDDOU a solvent water molecule is included in the crystal packing.

5. Synthesis and crystallization

An aqueous solution of formaldehyde (1.5 mL, 20 mmol) was added dropwise to a mixture of ethane-1,2-diamine (0.34 mL, 5 mmol) and 4-bromophenol (1.73 g, 10 mmol) dissolved in dioxane (10 mL). The reaction mixture was stirred for 4 h at room temperature. Single crystals were obtained from this solution by slow evaporation of the solvent.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the H atoms were located in

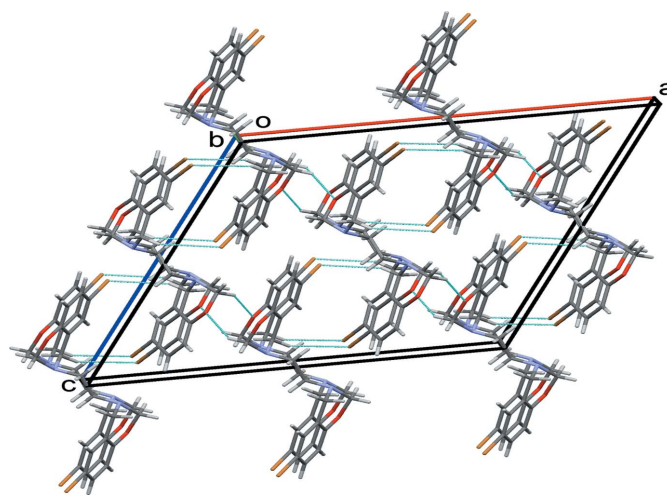


Figure 2
Packing diagram for the title compound, viewed along the *b* axis, with hydrogen bonds drawn as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₈ H ₁₈ Br ₂ N ₂ O ₂
<i>M</i> _r	454.16
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.464 (2), 5.9444 (7), 17.2225 (19)
β (°)	121.557 (7)
<i>V</i> (Å ³)	1698.0 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.79
Crystal size (mm)	0.27 × 0.26 × 0.26
Data collection	
Diffractometer	STOE IPDS II two-circle
Absorption correction	Multi-scan (<i>X-AREA</i> ; Stoe & Cie, 2001)
<i>T</i> _{min} , <i>T</i> _{max}	0.905, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	3703, 1583, 1391
<i>R</i> _{int}	0.078
(sin θ/λ) _{max} (Å ⁻¹)	0.607
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.056, 0.143, 1.07
No. of reflections	1583
No. of parameters	110
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.40, -1.92

Computer programs: *X-AREA* (Stoe & Cie, 2001), *SHELXS* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015) and *XP* in *SHELXTL-Plus* (Sheldrick, 2008).

the difference electron-density map. C-bound H atoms were fixed geometrically (C–H = 0.95 or 0.99 Å) and refined using

a riding-model approximation, with *U*_{iso}(H) set to 1.2*U*_{eq} of the parent atom.

Acknowledgements

We acknowledge the Dirección de Investigaciones, Sede Bogotá (DIB) de la Universidad Nacional de Colombia for financial support of this work (research project No. 28427). JJR is also grateful to COLCIENCIAS for his doctoral scholarship

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supporting information

Acta Cryst. (2016). E72, 1645-1647 [https://doi.org/10.1107/S2056989016016509]

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA* (Stoe & Cie, 2001); data reduction: *X-AREA* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL-2014/7* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL-2014/7* (Sheldrick, 2015).

1,2-Bis(6-bromo-3,4-dihydro-2H-benz[e][1,3]oxazin-3-yl)ethane

Crystal data

$C_{18}H_{18}Br_2N_2O_2$	$F(000) = 904$
$M_r = 454.16$	$D_x = 1.777 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 19.464 (2) \text{ \AA}$	Cell parameters from 3703 reflections
$b = 5.9444 (7) \text{ \AA}$	$\theta = 3.6\text{--}26.0^\circ$
$c = 17.2225 (19) \text{ \AA}$	$\mu = 4.79 \text{ mm}^{-1}$
$\beta = 121.557 (7)^\circ$	$T = 173 \text{ K}$
$V = 1698.0 (3) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.27 \times 0.26 \times 0.26 \text{ mm}$

Data collection

STOE IPDS II two-circle diffractometer	3703 measured reflections
Radiation source: Genix 3D $I\mu S$ microfocus X-ray source	1583 independent reflections
ω scans	1391 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (X-Area; Stoe & Cie, 2001)	$R_{\text{int}} = 0.078$
$T_{\text{min}} = 0.905$, $T_{\text{max}} = 1.000$	$\theta_{\text{max}} = 25.6^\circ$, $\theta_{\text{min}} = 3.6^\circ$
	$h = -20 \rightarrow 23$
	$k = -7 \rightarrow 7$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.099P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.143$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 1.40 \text{ e \AA}^{-3}$
1583 reflections	$\Delta\rho_{\text{min}} = -1.92 \text{ e \AA}^{-3}$
110 parameters	Extinction correction: <i>SHELXL-2014/7</i>
0 restraints	(Sheldrick 2015),
Hydrogen site location: inferred from neighbouring sites	$Fc^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.0037 (8)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.60406 (3)	-0.02845 (9)	0.93353 (3)	0.0226 (3)
O1	0.67962 (18)	0.6369 (6)	0.7231 (2)	0.0176 (7)
N1	0.6072 (2)	0.4166 (7)	0.5842 (2)	0.0130 (8)
C1	0.5323 (2)	0.5473 (7)	0.5467 (3)	0.0141 (10)
H1A	0.5430	0.7067	0.5401	0.017*
H1B	0.5124	0.5406	0.5891	0.017*
C2	0.6783 (3)	0.5494 (8)	0.6434 (3)	0.0155 (10)
H2A	0.6811	0.6770	0.6082	0.019*
H2B	0.7268	0.4552	0.6639	0.019*
C3	0.6620 (3)	0.4788 (8)	0.7681 (3)	0.0141 (9)
C4	0.6259 (2)	0.2721 (8)	0.7288 (3)	0.0142 (9)
C5	0.6091 (2)	0.2158 (8)	0.6343 (3)	0.0140 (9)
H5A	0.6513	0.1123	0.6400	0.017*
H5B	0.5566	0.1372	0.5995	0.017*
C6	0.6083 (2)	0.1218 (8)	0.7781 (3)	0.0147 (9)
H6	0.5841	-0.0193	0.7526	0.018*
C7	0.6265 (3)	0.1804 (8)	0.8655 (3)	0.0164 (9)
C8	0.6619 (3)	0.3870 (9)	0.9044 (3)	0.0223 (10)
H8	0.6741	0.4248	0.9639	0.027*
C9	0.6787 (3)	0.5348 (8)	0.8552 (3)	0.0192 (11)
H9	0.7021	0.6768	0.8807	0.023*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0261 (4)	0.0229 (4)	0.0255 (4)	0.00128 (17)	0.0181 (3)	0.00527 (19)
O1	0.0161 (15)	0.0160 (18)	0.0166 (15)	-0.0043 (12)	0.0058 (13)	-0.0018 (13)
N1	0.0078 (16)	0.0135 (19)	0.0148 (17)	0.0005 (13)	0.0039 (14)	0.0003 (15)
C1	0.010 (2)	0.013 (2)	0.014 (2)	0.0037 (16)	0.0029 (19)	-0.0009 (18)
C2	0.012 (2)	0.016 (2)	0.019 (2)	-0.0051 (16)	0.0081 (18)	-0.0034 (18)
C3	0.0114 (19)	0.014 (2)	0.014 (2)	0.0000 (15)	0.0047 (17)	0.0021 (17)
C4	0.0093 (18)	0.015 (2)	0.014 (2)	0.0023 (16)	0.0030 (15)	0.0016 (17)
C5	0.0105 (19)	0.012 (2)	0.016 (2)	0.0009 (15)	0.0039 (16)	-0.0021 (17)
C6	0.0098 (18)	0.015 (2)	0.018 (2)	0.0015 (15)	0.0062 (16)	0.0022 (18)
C7	0.020 (2)	0.014 (2)	0.020 (2)	0.0032 (16)	0.0137 (18)	0.0057 (18)
C8	0.028 (2)	0.023 (3)	0.017 (2)	-0.001 (2)	0.0126 (19)	-0.0036 (19)
C9	0.023 (2)	0.015 (2)	0.019 (2)	-0.0003 (17)	0.011 (2)	-0.0020 (18)

Geometric parameters (Å, °)

Br1—C7	1.909 (5)	C3—C4	1.402 (6)
O1—C3	1.372 (6)	C4—C6	1.393 (7)
O1—C2	1.455 (6)	C4—C5	1.519 (6)
N1—C2	1.450 (5)	C5—H5A	0.9900
N1—C5	1.462 (6)	C5—H5B	0.9900
N1—C1	1.470 (5)	C6—C7	1.397 (7)
C1—C1 ⁱ	1.538 (8)	C6—H6	0.9500
C1—H1A	0.9900	C7—C8	1.396 (7)
C1—H1B	0.9900	C8—C9	1.373 (8)
C2—H2A	0.9900	C8—H8	0.9500
C2—H2B	0.9900	C9—H9	0.9500
C3—C9	1.398 (7)		
C3—O1—C2	113.7 (4)	C6—C4—C5	121.9 (4)
C2—N1—C5	108.0 (3)	C3—C4—C5	118.9 (4)
C2—N1—C1	112.6 (4)	N1—C5—C4	112.2 (4)
C5—N1—C1	113.8 (3)	N1—C5—H5A	109.2
N1—C1—C1 ⁱ	110.2 (4)	C4—C5—H5A	109.2
N1—C1—H1A	109.6	N1—C5—H5B	109.2
C1 ⁱ —C1—H1A	109.6	C4—C5—H5B	109.2
N1—C1—H1B	109.6	H5A—C5—H5B	107.9
C1 ⁱ —C1—H1B	109.6	C4—C6—C7	119.5 (4)
H1A—C1—H1B	108.1	C4—C6—H6	120.3
N1—C2—O1	113.4 (4)	C7—C6—H6	120.3
N1—C2—H2A	108.9	C8—C7—C6	121.3 (4)
O1—C2—H2A	108.9	C8—C7—Br1	119.4 (4)
N1—C2—H2B	108.9	C6—C7—Br1	119.2 (4)
O1—C2—H2B	108.9	C9—C8—C7	118.9 (4)
H2A—C2—H2B	107.7	C9—C8—H8	120.5
O1—C3—C9	117.2 (4)	C7—C8—H8	120.5
O1—C3—C4	122.5 (4)	C8—C9—C3	120.8 (5)
C9—C3—C4	120.3 (5)	C8—C9—H9	119.6
C6—C4—C3	119.2 (4)	C3—C9—H9	119.6
C2—N1—C1—C1 ⁱ	151.1 (5)	C1—N1—C5—C4	-77.1 (4)
C5—N1—C1—C1 ⁱ	-85.6 (6)	C6—C4—C5—N1	161.5 (4)
C5—N1—C2—O1	-64.9 (5)	C3—C4—C5—N1	-20.1 (5)
C1—N1—C2—O1	61.6 (5)	C3—C4—C6—C7	0.3 (6)
C3—O1—C2—N1	47.8 (5)	C5—C4—C6—C7	178.7 (4)
C2—O1—C3—C9	166.5 (4)	C4—C6—C7—C8	0.1 (7)
C2—O1—C3—C4	-15.8 (5)	C4—C6—C7—Br1	-178.8 (3)
O1—C3—C4—C6	-178.7 (4)	C6—C7—C8—C9	0.2 (7)
C9—C3—C4—C6	-1.1 (6)	Br1—C7—C8—C9	179.2 (4)
O1—C3—C4—C5	2.9 (6)	C7—C8—C9—C3	-1.0 (7)

C9—C3—C4—C5	-179.5 (4)	O1—C3—C9—C8	179.2 (4)
C2—N1—C5—C4	48.7 (5)	C4—C3—C9—C8	1.4 (7)

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

Hydrogen-bond geometry (\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>
C5—H5B \cdots Br1 ⁱⁱ	0.99	3.04	3.951 (5)	154
C2—H2B \cdots O1 ⁱⁱⁱ	0.99	2.64	3.506 (6)	146

Symmetry codes: (ii) $-x+1, y, -z+3/2$; (iii) $-x+3/2, y-1/2, -z+3/2$.