



C—I···N short contacts as tools for the construction of the crystal packing in the crystal structure of 3,3'-(ethane-1,2-diyl)bis(6-iodo-3,4-dihydro-2H-1,3-benzoxazine)

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Received 15 March 2017

Accepted 31 March 2017

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

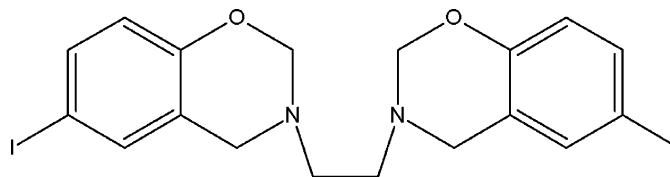
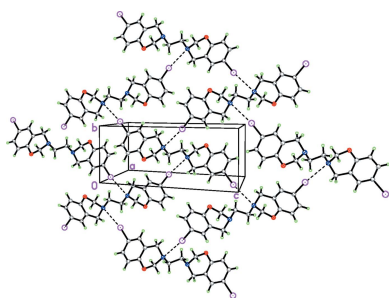
Keywords: crystal structure; short contacts; benzoxazines; phenolic resins.**CCDC reference:** 1541561**Supporting information:** this article has supporting information at journals.iucr.org/e

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The asymmetric unit of the title compound, C₁₈H₁₈I₂N₂O₂, consists of one half-molecule, completed by the application of inversion symmetry. The molecule adopts the typical structure for this class of bis-benzoxazines, characterized by an *anti* orientation of the two benzoxazine rings around the central C—C bond. The oxazinic ring adopts a half-chair conformation. In the crystal, molecules are linked by C—I···N short contacts [I···N = 3.378 (2) Å], generating layers lying parallel to the *bc* plane.

1. Chemical context

Benzoxazines have been studied for more than 70 years (Holly & Cope, 1944): they are heterocyclic compounds, which have the core structure of a benzene ring fused with an oxazine ring that can be readily synthesized by the Mannich reaction of mixing three components, either in solution or by a melt-state reaction using a combination of a phenolic derivative, formaldehyde, and a primary amine (Wattanathana *et al.*, 2014). The importance of these compounds is for the production of the corresponding polymers called poly-benzoxazines, which have been developed as a class of ring-opening phenolic resins (Ishida & Sanders, 2000). However, the usefulness of benzoxazines as precursors for a class of thermosetting phenolic resins with excellent mechanical and thermal properties was not recognized until recently (Velez-Herrera & Ishida, 2009).



As the electrophilic character of the substituents affects the stability both of the reaction intermediates and the benzoxazine ring (Hamerton *et al.*, 2006), consequently, when *p*-iodophenol, formaldehyde and ethylenediamine were allowed to react in a molar ratio of 2:4:1, the title compound (I) was formed. This article forms part of our ongoing research into improving the understanding of the structural features resulting from replacement of the halogen substituent at the

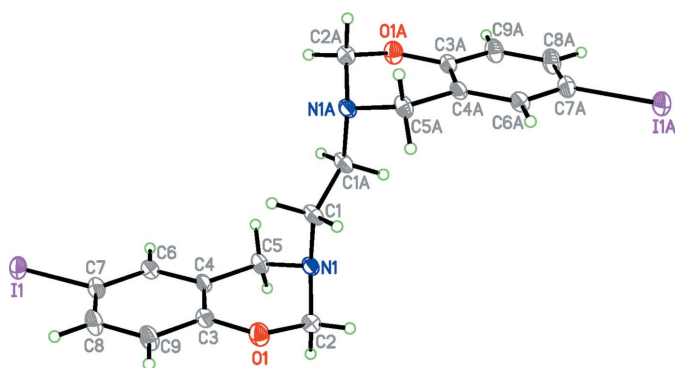


Figure 1

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

para position of the aromatic ring of bis-1,3-benzoxazines. So, an iodine functional bis-1,3-benzoxazine, namely 3,3'-(ethane-1,2-diyl)bis(6-iodo-3,4-dihydro-2H-1,3-benzoxazine) has been synthesized in high yield and purity.

2. Structural commentary

Similar to that observed in the crystal structure of the related compounds (Rivera *et al.*, 2010, 2016a), the asymmetric unit of the title compound $C_{18}H_{18}I_2N_2O_2$, contains one-half of the formula unit; a centre of inversion is located at the mid-point of the central C1—C1($1 - x, 1 - y, 1 - z$) bond (see Fig. 1). The six-membered oxazine heterocyclic ring adopts a half-chair conformation, with puckering parameters $Q = 0.482(3) \text{ \AA}$, $\theta = 129.6(2)^\circ$, $\varphi = 283.6(3)^\circ$: with respect to the plane formed by O1/C3/C4/C5, the deviations of C2 and N1 are $0.301(3)$ and $-0.320(3) \text{ \AA}$, respectively. The observed C—O bond length [$1.376(3) \text{ \AA}$] is in a good agreement with the related *p*-fluoro and *p*-bromo structures (Rivera *et al.*,

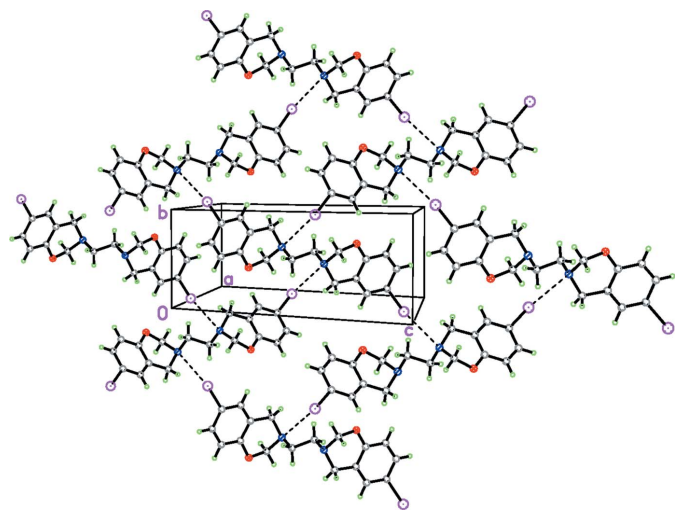


Figure 2

Crystal packing of (I), displaying C—I...N short contacts, which result in chains, forming layers propagating parallel to the *bc* plane.

Table 1

Short-contact geometry (\AA , $^\circ$).

C—I	X	C—I	I...X	C—I...X
C7—I1	N1 ⁱ	2.107(3)	3.378(2)	169.13(9)

Symmetry code: (i) $x, -y, \frac{1}{2} + z$.

2016a,b), but this value is shorter than for the *p*-chloro derivative (Rivera *et al.*, 2010). The C7—I1 bond length [$2.107(3) \text{ \AA}$] is in good agreement with the value reported for 4-iodophenol [$2.104(5) \text{ \AA}$; Merz, 2006]. The C8—C9 bond length [$1.378(4) \text{ \AA}$] is shorter than the average C—C bond length of benzene ring [$1.398(4) \text{ \AA}$]. The N1—C2 bond length [$1.435(3) \text{ \AA}$] is significantly shorter than those of N1—C5 [$1.474(3) \text{ \AA}$] and N1—C1 [$1.478(3) \text{ \AA}$], probably due to the presence of a hyperconjugative interaction between the lone-pair electrons of the nitrogen atom and the antibonding σ orbital of C—O bond ($nN \rightarrow \sigma^*_{C2-O1}$). Moreover, the C2—N1—C1 [$112.6(2)^\circ$] and C5—N1—C1 [$113.0(2)^\circ$] angles are larger than the mean value of sp^3 hybridization in ammonia (107° ; Olovsson & Templeton, 1959).

3. Supramolecular features

The crystal-packing arrangement of the title compound is illustrated in Fig. 2. In contrast with related structures (Rivera *et al.*, 2016a,b, 2010), the absence of C—H...X or C—H...O interactions in the title compound is surprising. The packing of title compound is dominated by short contacts (Table 1), as indicated by a *PLATON* (Spek, 2009) analysis. Short C—I...N interactions (Table 1) are observed between neighboring molecules; it is remarkable that these short contacts present in the crystal structure of (I) has structure-directing characteristics.

4. Database survey

A search of the Cambridge Structural Database (Groom *et al.*, 2016) for short N...I contacts between an N atom bonded to three C atoms and an I atom bonded to an aromatic ring yielded 47 entries with a distance of less than 3.5 \AA . The search yielded four comparable structures, namely 3,3'-(ethane-1,2-diyl)bis(6-methyl-3,4-dihydro-2H-1,3-benzoxazine) (AXAKAM; Rivera *et al.*, 2011), 3,3'-(ethylene)bis(3,4-dihydro-6-chloro-2H-1,3-benzoxazine), (NUQKAM; Rivera *et al.*, 2010), 3,3'-(ethane-1,2-diyl)-bis(6-methoxy-3,4-dihydro-2H-1,3-benzoxazine) monohydrate (QEDDOU; Rivera *et al.*, 2012b), 3,3'-(ethane-1,2-diyl)bis(3,4-dihydro-2H-1,3-benzoxazine) (SAGPUN; Rivera *et al.*, 2012a).

5. Synthesis and crystallization

The title compound was prepared as described by Rivera *et al.* (1989). The reaction mixture was stored at room temperature for several weeks until a yellowish precipitate was formed. The

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₈ H ₁₈ I ₂ N ₂ O ₂
<i>M</i> _r	548.14
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	20.4200 (9), 5.9477 (2), 17.8414 (8)
β (°)	123.607 (3)
<i>V</i> (Å ³)	1804.69 (14)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.50
Crystal size (mm)	0.29 × 0.27 × 0.27
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}	0.395, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	39259, 2531, 2456
<i>R</i> _{int}	0.076
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.697
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.076, 1.22
No. of reflections	2531
No. of parameters	110
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.46, -1.35

Computer programs: *X-AREA* (Stoe & Cie, 2001), *SHELXS97*, *SHELXL97* and *XP* in *SHELXTL-Plus* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015).

solid was separated by filtration, washed with ethanol and crystallized from acetone solution. Yield 45.5%, m.p. 434 K.

6. Refinement details

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

JJR is grateful to COLCIENCIAS for his doctoral scholarship.

Funding information

Funding for this research was provided by: Dirección de Investigaciones, Sede Bogotá (DIB) de la Universidad Nacional de Colombia (award No. 35816).

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supporting information

Acta Cryst. (2017). E73, 664-666 [https://doi.org/10.1107/S2056989017005047]

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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: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

3,3'-(Ethane-1,2-diyl)bis(6-iodo-3,4-dihydro-2H-1,3-benzoxazine)

Crystal data

C₁₈H₁₈I₂N₂O₂

M_r = 548.14

Monoclinic, *C2/c*

a = 20.4200 (9) Å

b = 5.9477 (2) Å

c = 17.8414 (8) Å

β = 123.607 (3)°

V = 1804.69 (14) Å³

Z = 4

F(000) = 1048

D_x = 2.017 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 39259 reflections

θ = 3.3–29.9°

μ = 3.50 mm⁻¹

T = 173 K

Block, colourless

0.29 × 0.27 × 0.27 mm

Data collection

Stoe IPDS II two-circle diffractometer

Radiation source: Genix 3D IμS microfocus X-ray source

ω scans

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

T_{min} = 0.395, *T_{max}* = 1.000

39259 measured reflections

2531 independent reflections

2456 reflections with *I* > 2σ(*I*)

R_{int} = 0.076

θ_{max} = 29.7°, θ_{min} = 3.6°

h = -28→28

k = -7→8

l = -24→24

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.030

wR(*F*²) = 0.076

S = 1.22

2531 reflections

110 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0378*P*)² + 4.0804*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.002

Δρ_{max} = 1.46 e Å⁻³

Δρ_{min} = -1.35 e Å⁻³

Extinction correction: SHELXL2016
 (Sheldrick, 2015),
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0034 (2)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.60686 (2)	−0.05887 (3)	0.93105 (2)	0.02375 (9)
O1	0.68205 (12)	0.6146 (3)	0.71878 (13)	0.0231 (4)
N1	0.60465 (12)	0.4020 (4)	0.58050 (14)	0.0174 (4)
C1	0.53347 (15)	0.5410 (4)	0.54603 (16)	0.0207 (5)
H1A	0.545662	0.699539	0.541455	0.025*
H1B	0.516975	0.534394	0.588747	0.025*
C2	0.67584 (15)	0.5254 (5)	0.63881 (17)	0.0214 (5)
H2A	0.678708	0.651795	0.604633	0.026*
H2B	0.721287	0.425521	0.657944	0.026*
C3	0.66459 (15)	0.4585 (4)	0.76215 (17)	0.0187 (4)
C4	0.62686 (14)	0.2547 (4)	0.72243 (15)	0.0171 (4)
C5	0.60538 (15)	0.1994 (4)	0.62851 (16)	0.0199 (4)
H5A	0.643793	0.090235	0.632478	0.024*
H5B	0.552776	0.128136	0.594033	0.024*
C6	0.61047 (15)	0.1080 (4)	0.77133 (16)	0.0191 (4)
H6	0.585192	−0.031336	0.745502	0.023*
C7	0.63083 (15)	0.1641 (5)	0.85739 (16)	0.0208 (5)
C8	0.66757 (17)	0.3687 (5)	0.89574 (17)	0.0250 (5)
H8	0.681043	0.407706	0.954297	0.030*
C9	0.68424 (17)	0.5143 (5)	0.84831 (17)	0.0236 (5)
H9	0.709313	0.653654	0.874439	0.028*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.02726 (12)	0.02815 (12)	0.01965 (12)	0.00072 (6)	0.01537 (9)	0.00344 (6)
O1	0.0281 (9)	0.0214 (8)	0.0185 (8)	−0.0058 (7)	0.0121 (7)	−0.0023 (7)
N1	0.0167 (9)	0.0205 (9)	0.0129 (8)	0.0030 (7)	0.0069 (7)	0.0024 (7)
C1	0.0207 (11)	0.0228 (11)	0.0130 (10)	0.0046 (9)	0.0060 (9)	0.0010 (8)
C2	0.0188 (10)	0.0271 (12)	0.0168 (10)	−0.0008 (9)	0.0089 (9)	0.0013 (9)
C3	0.0185 (10)	0.0207 (11)	0.0150 (10)	0.0001 (8)	0.0081 (9)	0.0021 (8)
C4	0.0166 (9)	0.0219 (10)	0.0109 (9)	0.0022 (8)	0.0064 (8)	0.0017 (8)
C5	0.0248 (11)	0.0198 (10)	0.0133 (9)	0.0014 (9)	0.0093 (9)	−0.0005 (8)
C6	0.0196 (10)	0.0197 (10)	0.0154 (10)	0.0005 (8)	0.0081 (8)	0.0009 (8)
C7	0.0235 (11)	0.0227 (11)	0.0163 (10)	0.0011 (9)	0.0110 (9)	0.0030 (9)

C8	0.0338 (13)	0.0266 (13)	0.0156 (10)	-0.0017 (11)	0.0144 (10)	-0.0019 (9)
C9	0.0311 (13)	0.0224 (11)	0.0151 (10)	-0.0037 (10)	0.0114 (10)	-0.0032 (9)

Geometric parameters (Å, °)

I1—C7	2.107 (3)	C3—C4	1.400 (3)
O1—C3	1.376 (3)	C4—C6	1.399 (3)
O1—C2	1.460 (3)	C4—C5	1.515 (3)
N1—C2	1.435 (3)	C5—H5A	0.9900
N1—C5	1.474 (3)	C5—H5B	0.9900
N1—C1	1.478 (3)	C6—C7	1.391 (3)
C1—C1 ⁱ	1.523 (5)	C6—H6	0.9500
C1—H1A	0.9900	C7—C8	1.394 (4)
C1—H1B	0.9900	C8—C9	1.378 (4)
C2—H2A	0.9900	C8—H8	0.9500
C2—H2B	0.9900	C9—H9	0.9500
C3—C9	1.397 (4)		
I1...N1 ⁱⁱ	3.378 (2)		
C3—O1—C2	113.3 (2)	C6—C4—C5	122.1 (2)
C2—N1—C5	108.45 (19)	C3—C4—C5	119.3 (2)
C2—N1—C1	112.6 (2)	N1—C5—C4	111.6 (2)
C5—N1—C1	113.0 (2)	N1—C5—H5A	109.3
N1—C1—C1 ⁱ	111.0 (3)	C4—C5—H5A	109.3
N1—C1—H1A	109.4	N1—C5—H5B	109.3
C1 ⁱ —C1—H1A	109.4	C4—C5—H5B	109.3
N1—C1—H1B	109.4	H5A—C5—H5B	108.0
C1 ⁱ —C1—H1B	109.4	C7—C6—C4	120.7 (2)
H1A—C1—H1B	108.0	C7—C6—H6	119.7
N1—C2—O1	113.5 (2)	C4—C6—H6	119.7
N1—C2—H2A	108.9	C6—C7—C8	120.1 (2)
O1—C2—H2A	108.9	C6—C7—I1	120.46 (19)
N1—C2—H2B	108.9	C8—C7—I1	119.41 (18)
O1—C2—H2B	108.9	C9—C8—C7	119.7 (2)
H2A—C2—H2B	107.7	C9—C8—H8	120.2
O1—C3—C9	116.9 (2)	C7—C8—H8	120.2
O1—C3—C4	122.7 (2)	C8—C9—C3	120.5 (3)
C9—C3—C4	120.3 (2)	C8—C9—H9	119.7
C6—C4—C3	118.6 (2)	C3—C9—H9	119.7
C2—N1—C1—C1 ⁱ	150.8 (3)	C1—N1—C5—C4	-77.2 (2)
C5—N1—C1—C1 ⁱ	-85.9 (3)	C6—C4—C5—N1	161.7 (2)
C5—N1—C2—O1	-65.2 (3)	C3—C4—C5—N1	-18.6 (3)
C1—N1—C2—O1	60.5 (3)	C3—C4—C6—C7	0.4 (4)
C3—O1—C2—N1	47.5 (3)	C5—C4—C6—C7	-179.9 (2)
C2—O1—C3—C9	167.3 (2)	C4—C6—C7—C8	0.3 (4)
C2—O1—C3—C4	-14.5 (3)	C4—C6—C7—I1	-179.47 (18)

O1—C3—C4—C6	-179.0 (2)	C6—C7—C8—C9	-0.6 (4)
C9—C3—C4—C6	-0.9 (4)	I1—C7—C8—C9	179.2 (2)
O1—C3—C4—C5	1.2 (4)	C7—C8—C9—C3	0.1 (4)
C9—C3—C4—C5	179.3 (2)	O1—C3—C9—C8	178.9 (3)
C2—N1—C5—C4	48.3 (3)	C4—C3—C9—C8	0.7 (4)

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