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Crystal structure of 2,2′-(ethane-1,2-diyl)bis(2,3-dihydro-1*H*-naphtho[1,2-e][1,3]oxazine): a prospective raw material for polybenzoxazines

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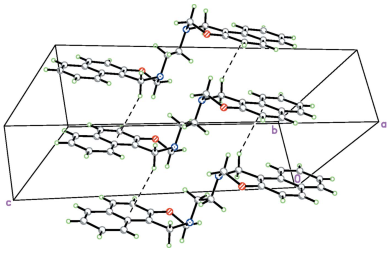
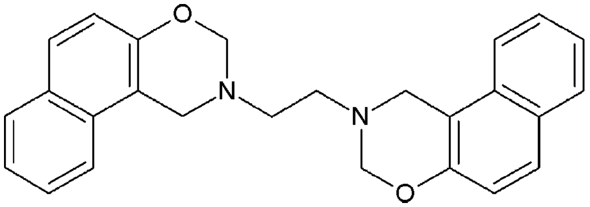
In the title compound, $C_{26}H_{24}N_2O_2$, the oxazine moiety is fused to a naphthalene ring system. The asymmetric unit consists of one half of the molecule, which lies about an inversion centre. The C atoms of the ethylene spacer group adopt an antiperiplanar arrangement. The oxazine ring adopts a half-chair conformation. In the crystal, supramolecular chains running along the *b* axis are formed *via* short C—H$\cdots\pi$ contacts. The crystal studied was a non-merohedral twin with a fractional contribution of 0.168 (2) of the minor twin component.

1. Chemical context

The oxazine moiety is well known as a building block for high-performance phenolic resins, which are of great interest in industry due to their superior mechanical and physical properties together with unusually high thermal resistance (Kiskan & Yagci, 2005). Recently, because of their high flexibility in molecular design and performance-to-cost ratio, these monomers have gained attention for the preparation of cured thermosetting resins (Song *et al.*, 2014; Yeganeh & Jangi, 2010). Benzoxazines and naphthoxazines, originally proposed by Holly & Cope (1944) and subsequently elaborated by Burke and co-workers (Burke *et al.*, 1952), are obtained by Mannich-type condensation–cyclization reactions of phenols or naphthols with formaldehyde and primary amines in a 1:2:1 ratio (Deck *et al.*, 2014). Interest in the synthesis of polybenzoxazines and polynaphthoxazines has greatly increased during the past few years as they have a great deal of molecular design flexibility compared to ordinary phenolics (Yildirim *et al.*, 2006). The title bisnapthoxazine, 2,2′-(ethane-1,2-diyl)bis(2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine), $C_{26}H_{24}N_2O_2$, was prepared by condensation of 2-naphthol with ethylenediamine and formaldehyde in a 2:1:4 molar ratio at room temperature for 15 min in methanol solution. Evaporation at room temperature afforded the title compound in 73% yield after recrystallization.





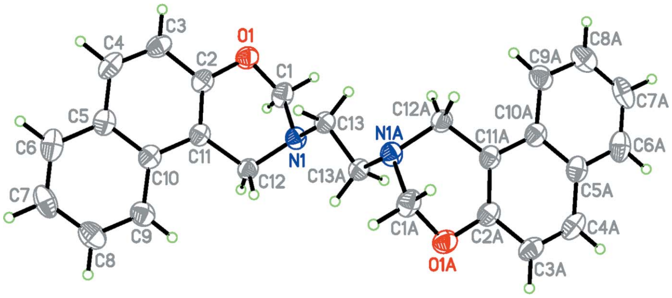


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Atoms labelled with the suffix A are generated using the symmetry operator $(1 - x, 1 - y, 1 - z)$.

2. Structural commentary

In general terms, the structure of the title compound (Fig. 1) is similar to those of other naphthoxazine derivatives that have been reported in that the oxazine moiety adopts a half-chair conformation (Yang *et al.*, 2007; Rivera *et al.*, 2015), with puckering parameters Q = 0.478 (3) Å, θ = 51.5 (4)°, φ = 86.6 (4)°, and the ethylene spacer group adopts an anti-periplanar arrangement as observed in 3,3′-(ethane-1,2-diyl)bis(3,4-dihydro-2*H*-1,3-benzoxazine) (Rivera *et al.*, 2012), with a N1—C13—C13$^{\rm i}$—N1$^{\rm i}$ torsion angle of 180.0° [symmetry code: (i) $1 - x, 1 - y, 1 - z$]. However, unlike the related structures, which crystallized in monoclinic space groups with one molecule in the asymmetric unit (Yang *et al.*, 2007; Rivera *et al.*, 2012, 2015), the title compound (I) crystallizes with just half a molecule in the asymmetric unit in the space group $P2_1/c$, utilizing the crystallographic inversion centre in the molecular symmetry. The other half of the molecule is generated by the symmetry operation $(1 - x, 1 - y, 1 - z)$.

Table 1
Selected short-contact geometry (Å, °).

*Cg*1 is the mid-point of the C2—C3 bond and *Cg*2 is the centroid of the C2–C4/C11/C12 ring.

C—H···C	H···C	C—H···C
C12—H12*B*···C2$^{\rm i}$	2.75	169
C12—H12*B*···C3$^{\rm i}$	2.75	142
C12–H12*B*···*Cg*1	2.654	157
C12–H12*B*···*Cg*2	3.073	155

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

The aromatic C—C bonds of naphthalene ring system have a narrow range of distances [from 1.365 (5) to 1.431 (4) Å]. The central C5—C10 bond at 1.415 (4) Å is, however, shorter by 0.014 Å than those in related structures (Yang *et al.*, 2007; Rivera *et al.*, 2015). The N1—C1 and O1—C1 bond lengths are normal and comparable to the corresponding values observed in these related structures.

3. Supramolecular features

In the crystal, the packing of the title compound is dominated by short contacts (Table 1), as indicated by a *PLATON* (Spek, 2009) analysis. These contacts result from short C12—H12*B*···C2 and C12—H12*B*···C3 separations, which at 2.75 Å are both 0.15 Å shorter than the sum of the van der Waals radii, while the C—H···*Cg*1 contact to the mid-point of the C2–-C3 bond is even shorter at approximately 2.65 Å. These contacts are also much shorter than the C—H···*Cg*2 contact to the centroid of the C2–C4/C11/C12 ring (Fig. 2). The molecules are by these short C—H···π contacts linked into chains propagating along the *b*-axis direction (Fig. 3).

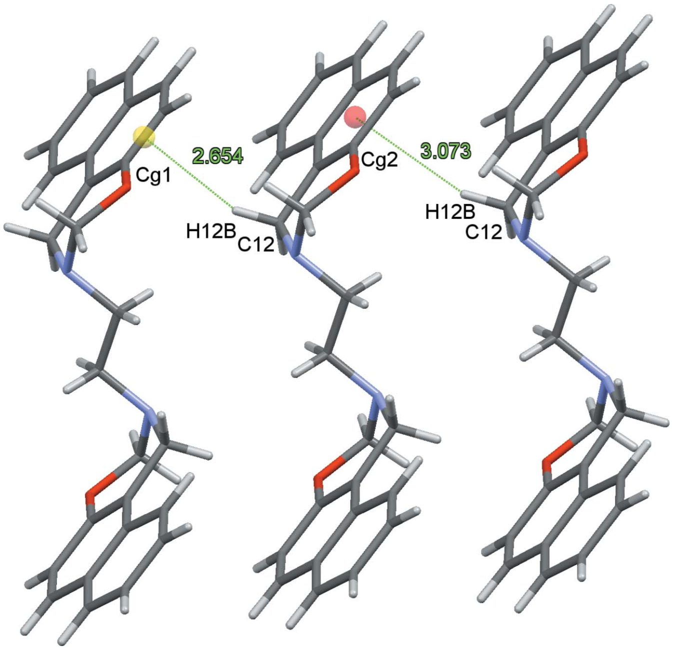


Figure 2
Possible C—H···π contacts, shown as dotted green lines, between molecules of (I). Bond mid-points and ring centroids are shown as colored spheres.

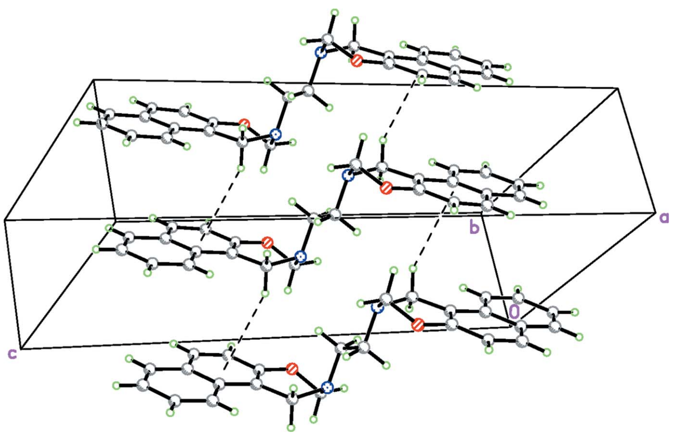


Figure 3
Crystal packing of (I), showing C—H···(C,C) short contacts that result in chains propagating along the *b*-axis direction.

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4. Database survey

The title compound is the first example of two naphthooxazine moieties linked by an ethylene bridge.

5. Synthesis and crystallization

The title compound was prepared as described by Rivera *et al.* (2006). Crystals were obtained by slow evaporation of the reaction solution at ambient temperature and were isolated from the solution before complete evaporation of the solvent mixture.

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 1.2U_{eq} of the parent atom. The crystal was a non-merohedral twin with a fractional contribution of 0.168 (2) of the minor twin component.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{26}H_{24}N_2O_2$
M_r	396.47
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	9.8658 (10), 5.0979 (4), 19.551 (2)
β (°)	96.033 (8)
V (Å^3)	977.87 (16)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.27 × 0.11 × 0.04
Data collection	
Diffractometer	Stoe IPDS II two-circle
Absorption correction	Multi-scan (*X-AREA*; Stoe & Cie, 2001)
T_{min}, T_{max}	0.443, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9335, 9335, 5706
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.130, 0.94
No. of reflections	9335
No. of parameters	137
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.53, −0.34

Computer programs: *X-AREA* (Stoe & Cie, 2001), *SHELXT* (Sheldrick, 2015*a*), *XP* in *SHELXTL-Plus* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015*b*) and *publCIF* (Westrip, 2010).

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Crystal structure of 2,2′-(ethane-1,2-diyl)bis(2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine): a prospective raw material for polybenzoxazines

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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: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2016* (Sheldrick, 2015b) and *publCIF* (Westrip, 2010).

2,2′-(Ethane-1,2-diyl)bis(2,3-dihydro-1*H*-naphtho[1,2-e][1,3]oxazine)

Crystal data

$C_{26}H_{24}N_2O_2$
$M_r = 396.47$
Monoclinic, $P2_1/c$
$a = 9.8658\ (10)$ Å
$b = 5.0979\ (4)$ Å
$c = 19.551\ (2)$ Å
$\beta = 96.033\ (8)°$
$V = 977.87\ (16)$ Å^3
$Z = 2$

$F(000) = 420$
$D_x = 1.347$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9056 reflections
$\theta = 2.8–26.4°$
$\mu = 0.09$ mm^{-1}
$T = 173$ K
Needle, colourless
0.27 × 0.11 × 0.04 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)
$T_{\min} = 0.443$, $T_{\max} = 1.000$

9335 measured reflections
9335 independent reflections
5706 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 26.4°$, $\theta_{\min} = 2.8°$
$h = -12 \rightarrow 12$
$k = -6 \rightarrow 6$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.130$
$S = 0.94$
9335 reflections
137 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.050P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}

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.

Refinement. Refined as a 2-component twin

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
N1	0.3328 (2)	0.3467 (5)	0.51587 (12)	0.0291 (6)
O1	0.14340 (19)	0.6404 (5)	0.52587 (10)	0.0346 (5)
C1	0.1935 (3)	0.4104 (7)	0.49256 (16)	0.0351 (8)
H1A	0.135064	0.258586	0.501152	0.042*
H1B	0.185528	0.440900	0.442290	0.042*
C2	0.1675 (3)	0.6281 (6)	0.59661 (15)	0.0302 (7)
C3	0.0926 (3)	0.8089 (6)	0.63272 (17)	0.0350 (8)
H3	0.029986	0.925542	0.608217	0.042*
C4	0.1107 (3)	0.8150 (7)	0.70288 (17)	0.0370 (8)
H4	0.061911	0.939265	0.726968	0.044*
C5	0.2015 (3)	0.6382 (7)	0.74028 (15)	0.0319 (7)
C6	0.2182 (3)	0.6366 (7)	0.81341 (16)	0.0397 (8)
H6	0.169242	0.759116	0.837964	0.048*
C7	0.3039 (3)	0.4611 (7)	0.84895 (16)	0.0419 (9)
H7	0.313599	0.460117	0.897805	0.050*
C8	0.3771 (3)	0.2834 (7)	0.81263 (17)	0.0421 (9)
H8	0.436829	0.162438	0.837424	0.051*
C9	0.3648 (3)	0.2792 (7)	0.74225 (15)	0.0355 (8)
H9	0.415732	0.155997	0.718946	0.043*
C10	0.2761 (3)	0.4585 (6)	0.70373 (15)	0.0295 (7)
C11	0.2593 (3)	0.4567 (6)	0.63016 (15)	0.0276 (7)
C12	0.3413 (3)	0.2746 (6)	0.58900 (14)	0.0288 (7)
H12A	0.437938	0.278593	0.608671	0.035*
H12B	0.307562	0.092959	0.593092	0.035*
C13	0.4289 (2)	0.5552 (6)	0.50126 (15)	0.0290 (7)
H13A	0.430945	0.691415	0.537435	0.035*
H13B	0.397638	0.638414	0.456628	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0234 (11)	0.0348 (16)	0.0294 (13)	−0.0034 (11)	0.0031 (9)	0.0008 (11)
O1	0.0264 (10)	0.0434 (14)	0.0335 (12)	0.0053 (9)	0.0002 (8)	0.0001 (10)
C1	0.0240 (14)	0.047 (2)	0.0339 (16)	−0.0011 (13)	0.0013 (12)	−0.0078 (15)
C2	0.0194 (13)	0.0348 (18)	0.0365 (17)	−0.0036 (13)	0.0034 (12)	−0.0013 (14)
C3	0.0233 (13)	0.035 (2)	0.047 (2)	0.0023 (13)	0.0047 (13)	−0.0013 (15)
C4	0.0284 (14)	0.033 (2)	0.051 (2)	−0.0017 (13)	0.0120 (14)	−0.0119 (15)
C5	0.0270 (14)	0.0336 (18)	0.0358 (18)	−0.0090 (13)	0.0070 (12)	−0.0041 (14)

C6	0.0412 (17)	0.040 (2)	0.0398 (19)	−0.0157 (16)	0.0151 (14)	−0.0116 (16)
C7	0.0501 (19)	0.048 (2)	0.0286 (17)	−0.0210 (17)	0.0061 (14)	0.0037 (15)
C8	0.0444 (17)	0.043 (2)	0.038 (2)	−0.0089 (16)	−0.0002 (15)	0.0075 (16)
C9	0.0355 (15)	0.034 (2)	0.0377 (19)	−0.0048 (14)	0.0057 (13)	0.0047 (15)
C10	0.0244 (13)	0.0273 (17)	0.0374 (17)	−0.0071 (12)	0.0067 (12)	−0.0008 (13)
C11	0.0232 (12)	0.0280 (17)	0.0322 (16)	−0.0049 (12)	0.0058 (11)	−0.0010 (13)
C12	0.0266 (13)	0.0287 (17)	0.0319 (16)	0.0005 (12)	0.0067 (12)	0.0002 (13)
C13	0.0250 (13)	0.0322 (18)	0.0302 (15)	0.0019 (12)	0.0047 (12)	0.0014 (14)

Geometric parameters (Å, º)

N1—C1	1.439 (3)	C6—C7	1.369 (5)
N1—C13	1.472 (4)	C6—H6	0.9500
N1—C12	1.470 (4)	C7—C8	1.398 (5)
O1—C2	1.380 (4)	C7—H7	0.9500
O1—C1	1.453 (4)	C8—C9	1.369 (4)
C1—H1A	0.9900	C8—H8	0.9500
C1—H1B	0.9900	C9—C10	1.425 (4)
C2—C11	1.375 (4)	C9—H9	0.9500
C2—C3	1.415 (4)	C10—C11	1.431 (4)
C3—C4	1.365 (5)	C11—C12	1.517 (4)
C3—H3	0.9500	C12—H12A	0.9900
C4—C5	1.418 (4)	C12—H12B	0.9900
C4—H4	0.9500	C13—C13^{i}	1.518 (5)
C5—C10	1.415 (4)	C13—H13A	0.9900
C5—C6	1.422 (4)	C13—H13B	0.9900
C1—N1—C13	112.9 (2)	C6—C7—H7	120.3
C1—N1—C12	108.6 (2)	C8—C7—H7	120.3
C13—N1—C12	113.4 (2)	C9—C8—C7	121.7 (3)
C2—O1—C1	112.5 (2)	C9—C8—H8	119.2
N1—C1—O1	113.5 (2)	C7—C8—H8	119.2
N1—C1—H1A	108.9	C8—C9—C10	120.4 (3)
O1—C1—H1A	108.9	C8—C9—H9	119.8
N1—C1—H1B	108.9	C10—C9—H9	119.8
O1—C1—H1B	108.9	C5—C10—C9	118.1 (3)
H1A—C1—H1B	107.7	C5—C10—C11	120.0 (3)
C11—C2—O1	122.9 (3)	C9—C10—C11	121.8 (3)
C11—C2—C3	121.9 (3)	C2—C11—C10	118.5 (3)
O1—C2—C3	115.2 (3)	C2—C11—C12	119.8 (3)
C4—C3—C2	119.7 (3)	C10—C11—C12	121.7 (3)
C4—C3—H3	120.1	N1—C12—C11	112.6 (2)
C2—C3—H3	120.1	N1—C12—H12A	109.1
C3—C4—C5	120.8 (3)	C11—C12—H12A	109.1
C3—C4—H4	119.6	N1—C12—H12B	109.1
C5—C4—H4	119.6	C11—C12—H12B	109.1
C10—C5—C4	119.0 (3)	H12A—C12—H12B	107.8
C10—C5—C6	119.5 (3)	N1—C13—C13^{i}	110.8 (3)

C4—C5—C6	121.5 (3)	N1—C13—H13A	109.5
C7—C6—C5	120.9 (3)	C13$^{\text{i}}$—C13—H13A	109.5
C7—C6—H6	119.5	N1—C13—H13B	109.5
C5—C6—H6	119.5	C13$^{\text{i}}$—C13—H13B	109.5
C6—C7—C8	119.4 (3)	H13A—C13—H13B	108.1

C13—N1—C1—O1	−62.2 (3)	C6—C5—C10—C11	179.5 (3)
C12—N1—C1—O1	64.5 (3)	C8—C9—C10—C5	−0.3 (4)
C2—O1—C1—N1	−50.6 (3)	C8—C9—C10—C11	−179.0 (3)
C1—O1—C2—C11	16.5 (4)	O1—C2—C11—C10	−179.6 (3)
C1—O1—C2—C3	−164.7 (2)	C3—C2—C11—C10	1.6 (4)
C11—C2—C3—C4	−0.2 (5)	O1—C2—C11—C12	1.3 (4)
O1—C2—C3—C4	−179.0 (3)	C3—C2—C11—C12	−177.5 (3)
C2—C3—C4—C5	−1.5 (5)	C5—C10—C11—C2	−1.4 (4)
C3—C4—C5—C10	1.6 (4)	C9—C10—C11—C2	177.2 (3)
C3—C4—C5—C6	−178.0 (3)	C5—C10—C11—C12	177.6 (3)
C10—C5—C6—C7	−1.0 (5)	C9—C10—C11—C12	−3.7 (4)
C4—C5—C6—C7	178.6 (3)	C1—N1—C12—C11	−43.2 (3)
C5—C6—C7—C8	0.8 (5)	C13—N1—C12—C11	83.2 (3)
C6—C7—C8—C9	−0.3 (5)	C2—C11—C12—N1	12.7 (4)
C7—C8—C9—C10	0.1 (5)	C10—C11—C12—N1	−166.3 (3)
C4—C5—C10—C9	−178.8 (3)	C1—N1—C13—C13$^{\text{i}}$	−156.7 (3)
C6—C5—C10—C9	0.8 (4)	C12—N1—C13—C13$^{\text{i}}$	79.2 (4)
C4—C5—C10—C11	−0.1 (4)		

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