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3,9-Dibromo-5,7-dihydrodibenzo[c,e]-oxepine

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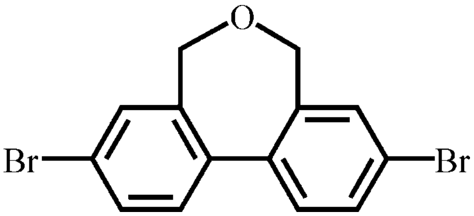
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.004 Å; R factor = 0.024; wR factor = 0.042; data-to-parameter ratio = 17.6.

The title compound, $C_{14}H_{10}Br_2O$, is a biphenyl derivative containing a $-CH_2-O-CH_2-$ bridge in the 2,2′-position. The compound displays a twisted conformation with the two benzene rings making a dihedral angle of 45.02 (5)°, while the central seven-membered ring is in a boat conformation. The molecule lies on a crystallographic twofold axis of symmetry passing through the O atom and bisecting the 1,1′ C—C bond.

Related literature

For a previous synthesis of related biphenyl molecules, see: Mislow & Glass (1961).



Experimental

Crystal data

$C_{14}H_{10}Br_2O$	V = 1235.2 (2) Å^3
M_r = 354.04	Z = 4
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
a = 16.5965 (3) Å	μ = 6.54 mm^{-1}
b = 10.2476 (6) Å	T = 291 (2) K
c = 7.2626 (14) Å	0.14 × 0.14 × 0.12 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	2468 measured reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	1371 independent reflections
T_{min} = 0.457, T_{max} = 0.498	896 reflections with $I > 2\sigma(I)$
(expected range = 0.419–0.456)	R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024	78 parameters
$wR(F^2)$ = 0.042	H-atom parameters constrained
S = 1.05	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
1371 reflections	$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BV2098).

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supplementary materials

Acta Cryst. (2008). E**64**, o1304 [**doi:10.1107/S1600536808018175**]

3,9-Dibromo-5,7-dihydrodibenzo[*c*,*e*]oxepine

H.-Q. Zhang, Bao-Li, G.-D. Yang and **Y.-G. Ma**

Comment

The dibenzo[c,e]oxepine derivatives were studied due to their optical activity as discussed in a previous article (Mislow & Glass, 1961). Introducing functional groups such as Br on the benzene ring of the dibenzo[c,e]oxepine can expand the range of their applications, such as photoluminescence, electro-luminescence devices and nonlinear optics. Herein we present the crystal structure of the title compound. In orthorhombic (space group Pbcn) crystals of 3,9-dibromo-5,7-dihydrodibenzo[c,e]oxepine, there are four molecules in the unit cell. The molecule lies on a crystallographic 2-fold axis of symmetry passing through the O and bisecting the C4-C4a bond. The compound exhibits twisted conformation between two phenyl rings with a dihedral angle of 45.02 (5)°, while central 7-member ring is in a boat conformation.

Experimental

The four-step reaction to prepare 3,9-dibromo-5,7 -dihydro dibenzo [c,e] oxepin is described as follows: (1) 2,7-Dibromophenanthrenequinone was obtained by directly brominating phenanthrenequinone in presence N-bromosuccinamide (NBS) in H_2SO_4. (2) This was followed by oxidation of 2,7-dibromophenanthrenequinone in the presence of pure oxygen and Cu(I)Cl to give 4,4-dibromodiphenic acid. (3). The reduction of 4,4-dibromodiphenic acid using $NaBH_4$ gave 4,4'-dibromo-2,2'-bis-(hydroxymethyl)-biphenyl. (4) The final production was obtained by ring closure of 4,4'-dibromo-2,2'-bis-(hydroxymethyl)-biphenyl in the presence of HBr acid. Single-crystals of X-ray diffraction quality were grown by slow evaporation of a ethanol solution.

Refinement

C-bound H atoms were geometrically positioned with C—H = 0.97 Å, $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl and C—H = 0.93 Å, $U_{iso}(H) = 1.2U_{eq}(C)$ for carbon atoms.

Figures

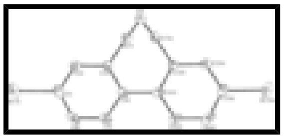


Fig. 1. The structure of the title compound, with the atom-labelling Displacement ellipsoids are drawn at the 30% probability level of arbitrary radii.

Fig. 2. The synthesis route for the preparation of 3,9-dibromo-5,7-dihydrodibenzo[c,e]oxepine.

3,9-Dibromo-5,7-dihydrodibenzo[c,e]oxepine

Crystal data

$C_{14}H_{10}Br_2O$

$M_r = 354.04$

Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

$a = 16.5965$ (3) Å

$b = 10.2476$ (6) Å

$c = 7.2626$ (14) Å

$V = 1235.2$ (2) Å^3

$Z = 4$

$F_{000} = 688$

$D_x = 1.904$ Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 10356 reflections

θ = 2.5–54.9°

$\mu = 6.54$ mm^{-1}

$T = 291$ (2) K

Block, colorless

0.14 × 0.14 × 0.12 mm

Data collection

Rigaku R-AXIS RAPID diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 291(2)$ K

ω scans

Absorption correction: multi-scan (ABSCOR; Higashi, 1995)

$T_{min} = 0.457$, $T_{max} = 0.498$

2468 measured reflections

1371 independent reflections

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

$R_{int} = 0.014$

$\theta_{max} = 27.5°$

$\theta_{min} = 2.3°$

$h = -21\rightarrow21$

$k = -13\rightarrow12$

$l = -9\rightarrow9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.042$

$S = 1.05$

1371 reflections

78 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0103P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.28$ e Å^{-3}

$\Delta\rho_{min} = -0.46$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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}
Br1	0.677363 (15)	0.36711 (3)	0.14224 (4)	0.04966 (11)
O1	1.0000	0.0746 (2)	0.2500	0.0401 (7)
C1	0.79077 (14)	0.3698 (3)	0.1813 (3)	0.0333 (6)
C6	0.82561 (17)	0.4814 (3)	0.2538 (3)	0.0392 (7)
H6A	0.7943	0.5534	0.2846	0.047*
C3	0.91882 (13)	0.2642 (2)	0.1600 (3)	0.0251 (5)
C7	0.96934 (14)	0.1504 (2)	0.1017 (3)	0.0342 (6)
H7A	0.9373	0.0944	0.0228	0.041*
H7B	1.0143	0.1825	0.0293	0.041*
C4	0.95561 (13)	0.3761 (2)	0.2353 (3)	0.0273 (5)
C2	0.83600 (13)	0.2626 (2)	0.1339 (3)	0.0295 (6)
H2A	0.8112	0.1891	0.0845	0.035*
C5	0.90852 (16)	0.4830 (3)	0.2793 (3)	0.0361 (7)
H5A	0.9329	0.5574	0.3270	0.043*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03162 (14)	0.0648 (2)	0.05259 (17)	0.01473 (19)	−0.00240 (17)	0.0052 (2)
O1	0.0350 (15)	0.0224 (14)	0.0629 (18)	0.000	−0.0084 (15)	0.000
C1	0.0301 (13)	0.0443 (16)	0.0257 (13)	0.0091 (16)	0.0001 (11)	0.0004 (15)
C6	0.0487 (17)	0.0390 (16)	0.0299 (13)	0.0231 (19)	−0.0067 (15)	−0.0083 (12)
C3	0.0245 (13)	0.0250 (13)	0.0260 (12)	0.0011 (12)	0.0036 (13)	0.0030 (12)
C7	0.0270 (13)	0.0304 (15)	0.0452 (16)	−0.0031 (13)	0.0024 (12)	−0.0083 (12)
C4	0.0331 (13)	0.0259 (13)	0.0230 (11)	0.0045 (14)	−0.0011 (12)	0.0022 (12)
C2	0.0321 (15)	0.0282 (13)	0.0283 (12)	0.0001 (12)	0.0023 (15)	−0.0005 (12)
C5	0.0489 (18)	0.0275 (15)	0.0321 (13)	0.0069 (16)	−0.0108 (14)	−0.0061 (12)

Geometric parameters (Å, °)

Br1—C1	1.904 (2)	C3—C4	1.410 (3)
O1—C7^{i}	1.422 (3)	C3—C7	1.497 (3)
O1—C7	1.422 (3)	C7—H7A	0.9700
C1—C2	1.375 (3)	C7—H7B	0.9700
C1—C6	1.386 (3)	C4—C5	1.383 (3)
C6—C5	1.389 (3)	C4—C4^{i}	1.489 (4)
C6—H6A	0.9300	C2—H2A	0.9300

C3—C2	1.388 (3)	C5—H5A	0.9300
C7^{i}—O1—C7	113.8 (2)	O1—C7—H7B	108.7
C2—C1—C6	121.8 (2)	C3—C7—H7B	108.7
C2—C1—Br1	119.40 (19)	H7A—C7—H7B	107.6
C6—C1—Br1	118.8 (2)	C5—C4—C3	119.3 (2)
C1—C6—C5	118.3 (2)	C5—C4—C4^{i}	121.75 (17)
C1—C6—H6A	120.9	C3—C4—C4^{i}	118.96 (16)
C5—C6—H6A	120.9	C1—C2—C3	119.8 (2)
C2—C3—C4	119.5 (2)	C1—C2—H2A	120.1
C2—C3—C7	120.5 (2)	C3—C2—H2A	120.1
C4—C3—C7	120.0 (2)	C4—C5—C6	121.4 (3)
O1—C7—C3	114.29 (19)	C4—C5—H5A	119.3
O1—C7—H7A	108.7	C6—C5—H5A	119.3
C3—C7—H7A	108.7		

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

Fig. 1

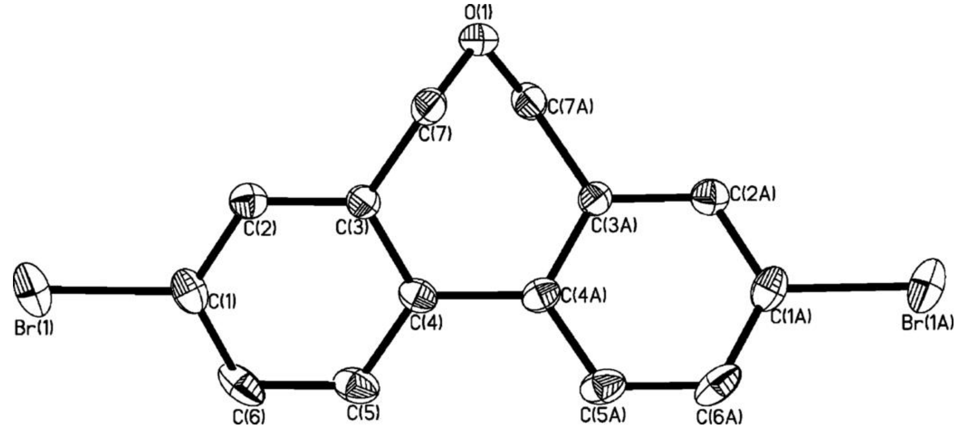
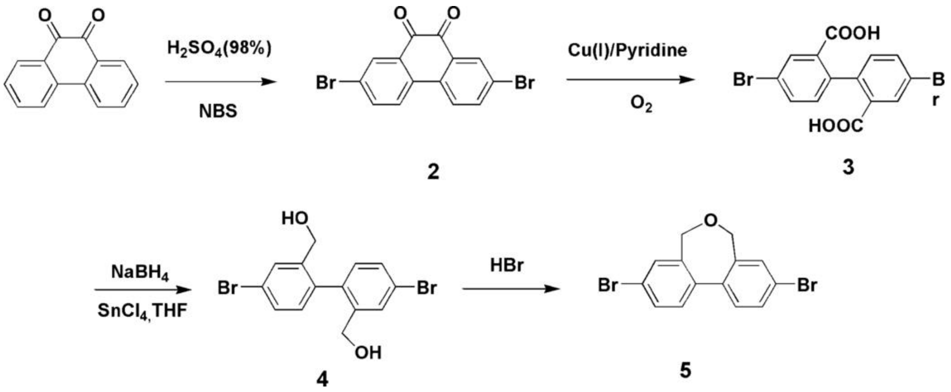


Fig. 2


O
O
H_2SO_4(98%)
NBS
Br
Br
2
Cu(I)/Pyridine
O_2
COOH
HOOC
Br
B
r
3
$NaBH_4$
$SnCl_4$,THF
HO
OH
Br
Br
4
HBr
O
Br
Br
5