organic compounds

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

Hai-Quan Zhang,[a]* Bao-Li,[b] Guang-Di Yang[b] and Yu-Guang Ma[b]

[a]State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, People's Republic of China, and [b]State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, People's Republic of China

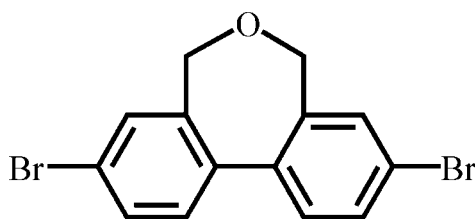Correspondence e-mail: hqzhang@ysu.edu.cn

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	$\mu = 6.54$ mm^{-1}
$b = 10.2476\ (6)$ Å	$T = 291\ (2)$ K
$c = 7.2626\ (14)$ Å	$0.14 \times 0.14 \times 0.12$ mm

Data collection

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

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*.

References

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Mislow, K. & Glass, M. (1961). *J. Am. Chem. Soc.* **83**, 2780–2781.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

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

Hai-Quan Zhang, Bao-Li, Guang-Di Yang and Yu-Guang Ma

S1. 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-di-hydro-dibenzo[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.

S2. Experimental

The four-step reaction to prepare 3,9-dibromo-5,7 -dihydro dibenzo [c,e] oxepin is described as follows: (1) 2,7-Di-bromo-phenanthrenequinone was obtained by directly brominating phenanthrenequinone in presence N-bromo-succinamide (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′-di-bromo-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.

S3. 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.
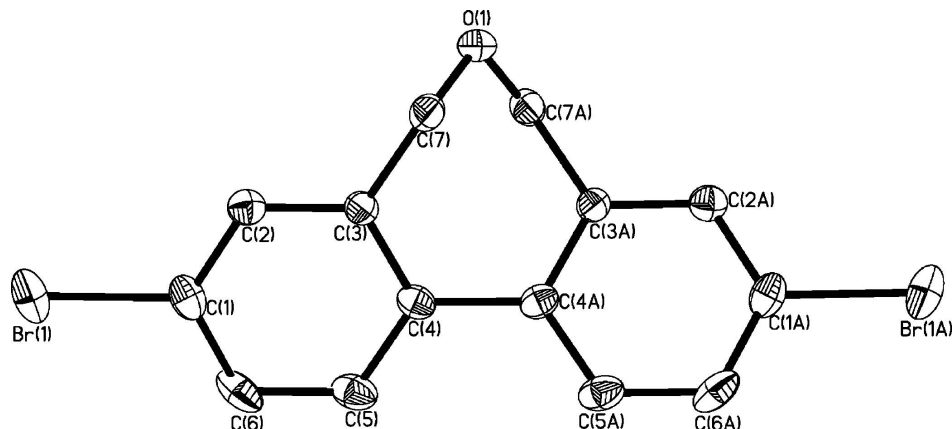
Figure 1

The structure of the title compound, with the atom-labelling Displacement ellipsoids are drawn at the 30% probability level of arbitrary radii.
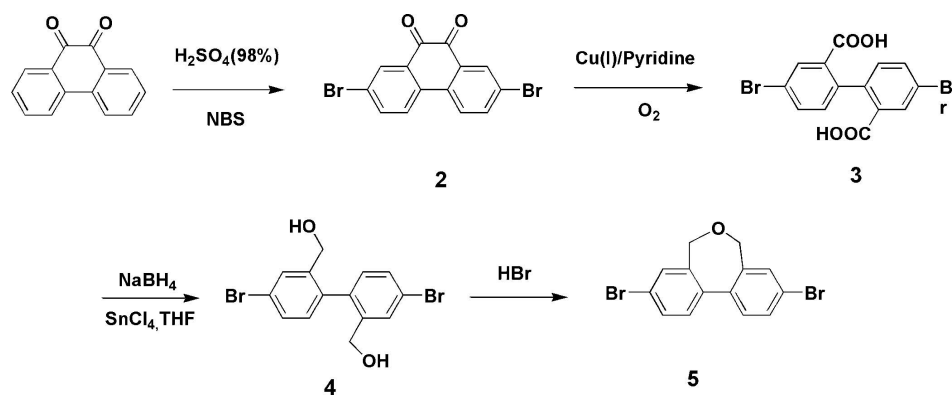
Figure 2

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

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

Crystal data

$C_{14}H_{10}Br_2O$	$F(000) = 688$
$M_r = 354.04$	$D_x = 1.904$ Mg m^{-3}
Orthorhombic, *Pbcn*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2n 2ab	Cell parameters from 10356 reflections
$a = 16.5965$ (3) Å	$\theta = 2.5$–54.9°
$b = 10.2476$ (6) Å	$\mu = 6.54$ mm^{-1}
$c = 7.2626$ (14) Å	$T = 291$ K
$V = 1235.2$ (2) Å^3	Block, colorless
$Z = 4$	$0.14 \times 0.14 \times 0.12$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
Radiation source: fine-focus sealed tube	$T_{min} = 0.457$, $T_{max} = 0.498$
Graphite monochromator	2468 measured reflections
ω scans	1371 independent reflections
	896 reflections with $I > 2\sigma(I)$

$R_{int} = 0.014$

$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$

$h = -21 \rightarrow 21$

$k = -13 \rightarrow 12$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.024$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.042$	
$S = 1.05$	H-atom parameters constrained
1371 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0103P)^2]$
78 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.28$ e Å^{-3}
	$\Delta\rho_{min} = -0.46$ e Å^{-3}

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, º)

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 code: (i) −*x*+2, *y*, −*z*+1/2.