3a-Bromoperhydro-2,6a-epoxy-oxireno[e][2]benzofuran

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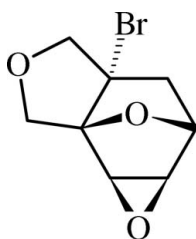Correspondence e-mail: bkosar@omu.edu.tr

In the title compound, $C_8H_9BrO_3$, the boat form of the six-membered ring is almost symmetrical with respect to the epoxy bridge. The two five-membered rings generated by the epoxy bridge of the six-membered ring adopt envelope conformations, whereas the third five-membered ring adopts a half-chair conformation. The refinement results suggest partial inversion twinning.

Related literature

For related literature, see: Büyükgüngör *et al.* (2005); Cremer & Pople (1975); Demircan *et al.* (2006); Fokas *et al.* (2003); Karaarslan *et al.* (2007); Koşar *et al.* (2006); Paulvannan & Jacobs (1999); Rogatchov *et al.* (2002); Rogers & Keay (1991); Woo & Keay (1994).

Experimental

Crystal data

$C_8H_9BrO_3$	Tetragonal, $P4_12_12$
M_r = 233.06	a = 7.9963 (8) Å
c = 25.793 (4) Å	μ = 4.95 mm^{-1}
V = 1649.2 (3) Å^3	T = 293 (2) K
Z = 8	$0.78 \times 0.65 \times 0.46$ mm
Mo $K\alpha$ radiation	

Data collection

Stoe IPDS 2 diffractometer	5824 measured reflections
Absorption correction: integration (X-RED; Stoe & Cie, 2002)	1426 independent reflections
T_{min} = 0.059, T_{max} = 0.157	1117 reflections with $I > 2\sigma(I)$
	R_{int} = 0.143

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$wR(F^2)$ = 0.110	$\Delta\rho_{min}$ = −0.29 e Å^{-3}
S = 1.02	Absolute structure: Flack (1983), with 522 Friedel pairs
1426 reflections	Flack parameter: 0.34 (3)
110 parameters	
H-atom parameters constrained	

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2437).

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supplementary materials

3a-Bromoperhydro-2,6a-epoxyoxireno[*e*][2]benzofuran

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Comment

Over the years, the intramolecular Diels–Alder reaction (IMDA) has proved to be a simple but effective step in many natural product syntheses, and the range and variety of triene systems employed is multifarious (Woo *et al.*, 1994; Rogers *et al.*, 1991). Unfortunately, examples employing furan as the dienic component (IMDAF) are less numerous due to the reluctance of the aromatic ring to undergo [4 + 2] cycloaddition. However in recent years the IMDAF has been studied extensively by several research groups (Rogatchov *et al.*, 2002; Fokas *et al.*, 2003; Paulvannan *et al.*, 1999) and consequently numerous persuasive methodologies have emerged in order to coerce the participation of the furan ring.

We have been examining systematically IMDAF cycloadditon, (Demircan *et al.*, 2006; Karaarslan *et al.*, 2007) fragmentation of furan ring following by thermal IMDAF reaction either using Lewis Acids or bases are current project. Therefore the precursor was chosen in an epoxidized form, 2 which was derived from a double bond of 1 [Scheme 1]. Here we report that this precursor, 2 shows a single-crystal specialty. Epoxidation of 1 was performed under standard condition in dichloromethane at 273 K. The solid product was purified by flash column chromatography using hexane: ethyl acetate as an eluent solvent system.

Figure 1 shows the molecular structure of the title compound. While the (O1/C1/C2/C7/C8) ring adopts a half chair conformation, tetrahydrofuran (O3/C4—C7) and bromo-attached tetrahydrofuran (O3/C7/C2/C3/C4) rings adopt envelope conformations, and the total puckering parameter Q_T values are 0.352 (7), 0.528 (7) and 0.560 (7) A°, respectively (Cremer & Pople, 1975).

For closely related compounds, see Koşar *et al.* (2006), Büyükgüngör *et al.* (2005).

Experimental

To a solution of *meta*-chloroperbenzoic acid (*m*-CPBA) (0.54 mg, 3.15 mmol), which had previously been purified and re-crystallized from dry diethyl ether, in dichloromethane (10 ml), cooled to 273 K, was added dropwise a solution of 7a-bromo-1,6,7,7a-tetrahydro-3a,6-epoxy-2-benzofuran (3.15 mmol) in dichloromethane (10 ml) over a period of 3 min. The reaction mixture was stirred at room temperature for 4 h and then diluted with cold 4% sodium bicarbonate solution (4 ml). The organic layer was separated, washed with water (20 ml) and concentrated *in vacuo*. The residue was subjected to flash column chromatography. As white crystal (0.48 g, 65%). m.p: 345–346 K, t.l.c., (Hexane: Ethyl acetate (8:2)): Rf: 0.35.

Refinement

All H atoms were positioned geometrically and refined using a riding model with C—H = 0.96 and 0.97 Å, and U_{iso} = 1.5 U_{eq}(C). The crystal turned out to be a racemic twin with a ratio of twin components of 0.52 (4)/0.48 (4).
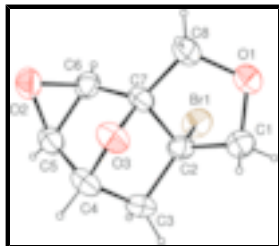
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Figures

Fig. 1. The molecular structure of the title compound, with atom labels and 30% probability displacement ellipsoids for non-H atoms.

3a-Bromoperhydro-2,6a-epoxyoxireno[e][2]benzofuran

Crystal data

$C_8H_9BrO_3$	$Z = 8$
$M_r = 233.06$	$F_{000} = 928$
Tetragonal, $P4_12_12$	$D_x = 1.877$ Mg m^{-3}
Hall symbol: P 4abw 2nw	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.9963$ (8) Å	Cell parameters from 8780 reflections
$b = 7.9963$ (8) Å	$\theta = 2.6–25.0º$
$c = 25.793$ (4) Å	$\mu = 4.95$ mm^{-1}
$\alpha = 90º$	$T = 293$ (2) K
$\beta = 90º$	Block, colourless
$\gamma = 90º$	$0.78 \times 0.65 \times 0.46$ mm
$V = 1649.2$ (3) Å^3	

Data collection

Stoe IPDS 2 diffractometer	1426 independent reflections
Radiation source: fine-focus sealed tube	1117 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.143$
Detector resolution: 6.67 pixels mm^{-1}	$\theta_{max} = 24.9º$
$T = 293(2)$ K	$\theta_{min} = 2.7º$
ω scans	$h = -9 \rightarrow 9$
Absorption correction: integration (X-RED; Stoe & Cie, 2002)	$k = -9 \rightarrow 8$
$T_{min} = 0.059$, $T_{max} = 0.157$	$l = -19 \rightarrow 30$
5824 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2]$

where $P = (F_o{}^2 + 2F_c{}^2)/3$

$wR(F^2) = 0.110$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.42$ e Å^{-3}
1426 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}
110 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 522 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.34 (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 $F^2 > 2sigma(F^2)$ 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}
C1	0.6184 (11)	−0.2846 (8)	0.3165 (3)	0.070 (2)
H1A	0.7033	−0.3242	0.3403	0.084*
H1B	0.5265	−0.3638	0.3162	0.084*
C2	0.5583 (8)	−0.1138 (7)	0.3317 (2)	0.0528 (15)
C3	0.5627 (7)	−0.0588 (8)	0.3896 (2)	0.0568 (16)
H3A	0.4592	−0.0055	0.4001	0.068*
H3B	0.5866	−0.1519	0.4125	0.068*
C4	0.7069 (8)	0.0648 (9)	0.3875 (3)	0.0639 (19)
H4	0.7611	0.0845	0.4210	0.077*
C5	0.6421 (9)	0.2222 (9)	0.3614 (3)	0.0602 (16)
H5	0.5544	0.2908	0.3773	0.072*
C6	0.6362 (8)	0.1761 (8)	0.3068 (2)	0.0570 (16)
H6	0.5440	0.2119	0.2844	0.068*
C7	0.6960 (7)	−0.0041 (8)	0.3073 (2)	0.0516 (15)
C8	0.7576 (10)	−0.1007 (9)	0.2614 (3)	0.071 (2)
H8A	0.7220	−0.0478	0.2294	0.085*
H8B	0.8787	−0.1071	0.2616	0.085*
O1	0.6858 (7)	−0.2648 (6)	0.26597 (18)	0.0793 (15)
O2	0.7611 (6)	0.2926 (6)	0.3246 (2)	0.0738 (14)
O3	0.8157 (5)	−0.0030 (6)	0.34874 (18)	0.0660 (13)
Br1	0.34058 (9)	−0.07413 (11)	0.29948 (3)	0.0739 (3)

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Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.092 (6)	0.059 (4)	0.058 (4)	0.005 (4)	−0.003 (4)	0.007 (3)
C2	0.055 (3)	0.057 (3)	0.047 (3)	0.006 (4)	−0.005 (3)	0.007 (3)
C3	0.057 (4)	0.074 (4)	0.039 (3)	0.014 (4)	0.003 (3)	0.005 (3)
C4	0.062 (4)	0.086 (5)	0.044 (4)	0.001 (4)	−0.003 (3)	−0.016 (4)
C5	0.060 (4)	0.065 (4)	0.055 (4)	−0.003 (4)	0.001 (3)	−0.014 (3)
C6	0.054 (4)	0.058 (4)	0.060 (4)	−0.010 (3)	−0.001 (3)	0.005 (3)
C7	0.053 (3)	0.060 (4)	0.042 (3)	0.000 (3)	0.003 (3)	−0.009 (3)
C8	0.086 (5)	0.069 (4)	0.058 (4)	−0.004 (5)	0.015 (4)	−0.016 (4)
O1	0.106 (4)	0.067 (3)	0.065 (3)	−0.003 (3)	0.022 (3)	−0.014 (3)
O2	0.075 (3)	0.070 (3)	0.076 (3)	−0.022 (3)	0.011 (3)	−0.017 (3)
O3	0.052 (2)	0.089 (3)	0.057 (3)	0.010 (3)	−0.002 (2)	−0.013 (2)
Br1	0.0620 (4)	0.0834 (6)	0.0764 (5)	−0.0113 (4)	−0.0173 (4)	0.0136 (4)

Geometric parameters (Å, °)

C1—O1	1.418 (8)	C4—H4	0.9800
C1—C2	1.501 (9)	C5—C6	1.458 (9)
C1—H1A	0.9700	C5—O2	1.459 (9)
C1—H1B	0.9700	C5—H5	0.9800
C2—C7	1.542 (9)	C6—O2	1.441 (8)
C2—C3	1.556 (8)	C6—C7	1.518 (9)
C2—Br1	1.956 (6)	C6—H6	0.9800
C3—C4	1.519 (8)	C7—O3	1.435 (7)
C3—H3A	0.9700	C7—C8	1.498 (9)
C3—H3B	0.9700	C8—O1	1.437 (9)
C4—O3	1.431 (7)	C8—H8A	0.9700
C4—C5	1.518 (10)	C8—H8B	0.9700
O1—C1—C2	105.1 (5)	O2—C5—C4	112.7 (6)
O1—C1—H1A	110.7	C6—C5—H5	121.6
C2—C1—H1A	110.7	O2—C5—H5	121.6
O1—C1—H1B	110.7	C4—C5—H5	121.6
C2—C1—H1B	110.7	O2—C6—C5	60.4 (4)
H1A—C1—H1B	108.8	O2—C6—C7	113.1 (5)
C1—C2—C7	100.5 (5)	C5—C6—C7	102.8 (5)
C1—C2—C3	120.1 (5)	O2—C6—H6	121.4
C7—C2—C3	102.4 (5)	C5—C6—H6	121.4
C1—C2—Br1	108.7 (5)	C7—C6—H6	121.4
C7—C2—Br1	111.7 (4)	O3—C7—C8	111.9 (6)
C3—C2—Br1	112.5 (4)	O3—C7—C6	102.2 (5)
C4—C3—C2	99.6 (5)	C8—C7—C6	125.9 (6)
C4—C3—H3A	111.9	O3—C7—C2	100.1 (5)
C2—C3—H3A	111.9	C8—C7—C2	105.3 (5)
C4—C3—H3B	111.9	C6—C7—C2	108.6 (5)
C2—C3—H3B	111.9	O1—C8—C7	105.9 (6)

H3A—C3—H3B	109.6	O1—C8—H8A	110.5
O3—C4—C5	102.3 (6)	C7—C8—H8A	110.5
O3—C4—C3	103.9 (5)	O1—C8—H8B	110.5
C5—C4—C3	107.2 (5)	C7—C8—H8B	110.5
O3—C4—H4	114.1	H8A—C8—H8B	108.7
C5—C4—H4	114.1	C1—O1—C8	109.2 (5)
C3—C4—H4	114.1	C6—O2—C5	60.4 (4)
C6—C5—O2	59.2 (4)	C4—O3—C7	96.7 (4)
C6—C5—C4	103.3 (6)		
O1—C1—C2—C7	−37.0 (7)	C1—C2—C7—O3	−87.4 (5)
O1—C1—C2—C3	−148.2 (6)	C3—C2—C7—O3	36.9 (6)
O1—C1—C2—Br1	80.3 (6)	Br1—C2—C7—O3	157.5 (4)
C1—C2—C3—C4	107.5 (7)	C1—C2—C7—C8	28.8 (7)
C7—C2—C3—C4	−2.6 (6)	C3—C2—C7—C8	153.1 (6)
Br1—C2—C3—C4	−122.6 (5)	Br1—C2—C7—C8	−86.3 (6)
C2—C3—C4—O3	−33.0 (6)	C1—C2—C7—C6	166.0 (5)
C2—C3—C4—C5	74.8 (6)	C3—C2—C7—C6	−69.7 (6)
O3—C4—C5—C6	32.7 (6)	Br1—C2—C7—C6	50.9 (6)
C3—C4—C5—C6	−76.2 (6)	O3—C7—C8—O1	97.0 (7)
O3—C4—C5—O2	−29.1 (7)	C6—C7—C8—O1	−138.2 (6)
C3—C4—C5—O2	−138.1 (5)	C2—C7—C8—O1	−10.8 (8)
C4—C5—C6—O2	−108.7 (6)	C2—C1—O1—C8	32.6 (8)
O2—C5—C6—C7	109.5 (5)	C7—C8—O1—C1	−13.2 (8)
C4—C5—C6—C7	0.8 (6)	C7—C6—O2—C5	−91.9 (6)
O2—C6—C7—O3	29.0 (6)	C4—C5—O2—C6	92.3 (6)
C5—C6—C7—O3	−34.1 (6)	C5—C4—O3—C7	−53.5 (6)
O2—C6—C7—C8	−99.9 (7)	C3—C4—O3—C7	58.0 (6)
C5—C6—C7—C8	−162.9 (6)	C8—C7—O3—C4	−168.7 (6)
O2—C6—C7—C2	134.1 (5)	C6—C7—O3—C4	54.1 (5)
C5—C6—C7—C2	71.1 (6)	C2—C7—O3—C4	−57.6 (5)

Fig. 1