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(5Z,7Z,9Z)-5,10-Dibromobenzo[8]-annulene

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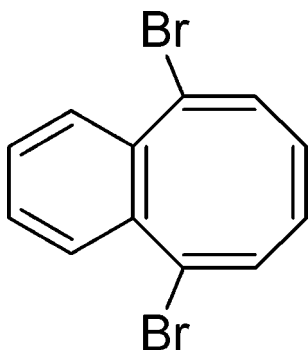
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 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.017; wR factor = 0.039; data-to-parameter ratio = 19.1.

In the structure of the title compound, $\text{C}_{12}\text{H}_8\text{Br}_2$, the two bromine substituents are oriented *exo* to the boat-shaped cyclooctatetraene at the two ring sites that are β to the ring fusion positions. The average Br—C bond distance is 1.919 (2) Å, the average distance for C=C double bonds that are Br substituted is 1.328 (2) Å, while the other two double-bond distances are 1.327 (2) and 1.398 (2) Å for the non-fused and fused bonds, respectively. Each type of ring interatomic distance is within s.u. of the average values for the four known structures, including the title compound, of benzo-fused cyclooctatetraenes that are not coordinated to a metal atom. The crystal structure features short Br \cdots Br [3.6620 (3) Å] and C \cdots H [2.834 (2) and 2.841 (2) Å] contacts.

Related literature

For general background to photochemical conversions of benzocyclooctatetraenes, see: Bender *et al.* (1982, 1986, 1988, 1991). For details of the synthesis, see: Barton *et al.* (1964). For related structures, see: Bohshar *et al.* (1984); Çelik *et al.* (2002); Jones *et al.* (1994), Kidokoro *et al.* (1983); Li *et al.* (1983). For a description of the Cambridge Structural Database, see: Allen (2002). For the PLATON suite of crystallographic software, see: Spek (2009).



Experimental

Crystal data

$\text{C}_{12}\text{H}_8\text{Br}_2$	$V = 1070.83$ (11) Å ³
$M_r = 312.00$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.5289$ (5) Å	$\mu = 7.52$ mm ⁻¹
$b = 8.3630$ (5) Å	$T = 173$ K
$c = 15.5645$ (9) Å	$0.16 \times 0.09 \times 0.08$ mm
$\beta = 105.2980$ (6)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	15053 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2008)	2426 independent reflections
$T_{\min} = 0.510$, $T_{\max} = 0.746$	2217 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$	127 parameters
$wR(F^2) = 0.039$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.49$ e Å ⁻³
2426 reflections	$\Delta\rho_{\text{min}} = -0.46$ e Å ⁻³

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT-Plus (Bruker, 2008); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXD (Sheldrick, 2008); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

This research was supported by the Natural Sciences and Engineering Research Council of Canada. The diffractometer at the University of Lethbridge X-ray Diffraction Facility was purchased with the help of NSERC and the University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5345).

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supporting information

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(5Z,7Z,9Z)-5,10-Dibromobenzo[8]annulene**Christopher O. Bender and René T. Boéré****S1. Comment**

The title compound was prepared as a starting material for synthesis of the corresponding dinitrile derivative, which was of interest in connection with studies of the photochemical conversions of benzocyclooctatetraenes (Bender *et al.*, 1982; 1986; 1988; 1991). In view of the paucity of structures that are crystallographically established for mono-benzofused cyclo-octatetraenes, we decided to undertake a crystallographic study of (I).

Only three prior structures have been reported which contain one benzo-fused cyclooctatetraene ring according to the Cambridge Structural Database (Allen, 2002; WebCSD, August 2013), excluding those with rings coordinated to metals. The parent hydrocarbon, (5Z,7Z,9Z)-benzo[8]annulene (refcode BUYYPUP), has been structurally characterized by X-ray crystallography and investigated by semi-empirical quantum mechanical methods (Li *et al.*, 1983). The only halogen-substituted example is (8-chlorobenzocyclooctatetraen-6-yl)-diphenylphosphine-oxide (refcode: CUDYUV) but this ring bears a large Ph₂P=O substituent; this structure contains two independent molecules in the asymmetric unit (Bohshar *et al.*, 1984). In dimethyl 1,4,6,9-tetramethylbenzocyclooctatetraene-5,10-dicarboxylate (refcode: LEZMAE) the two methyl ester substituents are located where the Br atoms are in (I) but this molecule also has four methyl substituents, two attached to the other ends of the same double bonds that the esters are attached to, and two in the 1 and 4 positions of the benzene rings (Jones *et al.*, 1994). Gratifyingly, all the 1,2 interatomic distances in (I) are found to lie within s.u. of the average values from these three comparison structures and (I).

Related benzo-fused cyclooctatrienes which have the same 5,8-dibromo substitution as found in (I) have been structurally characterized. In 5,8,10-tribromo-(8H)-benzocycloocten-7-one (refcode: BOGWAV) the cyclooctatriene ring is distorted by saturation at C8 and a ketone group at C7 (Kidokoro *et al.*, 1983), whilst 5,7,7,8,10-pentabromo-7,8-dihydrobenzocyclooctene (refcode: FABDOC) has C7 with two Br and C8 with H and Br substituents (Çelik *et al.*, 2002). The C5-Br1 and C10-Br2 distances in BOGWAV are 1.8822 (3) and 1.9309 (3) Å and in FABDOC 1.912 (7) and 1.896 (9). Thus the average C-Br bond distance in this set of three related structures is 1.910 (16) Å, with the distances in (I) found within s.u. of this value.

In the crystal structure of (I) molecules are tightly packed. There are three unique short intermolecular contacts (Figure 2), namely C2[⋯]H7ⁱ = H7[⋯]C2ⁱⁱ = 2.834 (2) Å, Br1[⋯]Br2ⁱⁱⁱ = 3.6620 (3) Å and C9[⋯]H1^{iv} = 2.841 (2) Å (symcodes employed: i, 1-x,-1/2+y,1/2-z; ii, 1-x,1/2+y,1/2-z; iii, -x,1-y,-z; iv, 1-x,-y,-z).

S2. Experimental

Samples of (I) were prepared from biphenylene via the method of Barton *et al.* (1964). Crystals were obtained from aqueous methanol (m.p. 366–368 K).

S3. Refinement

All the hydrogen atoms were located on a difference map, but for purposes of refinement are treated as riding on their attached aromatic carbon atoms with $C-H = 0.95 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$.

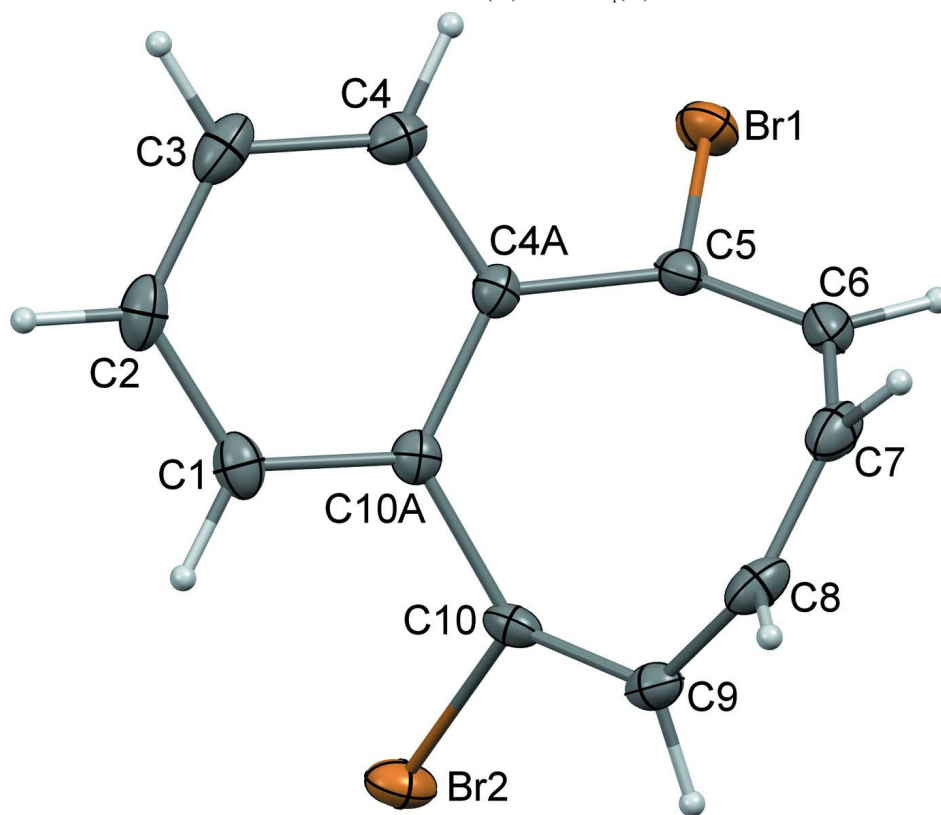
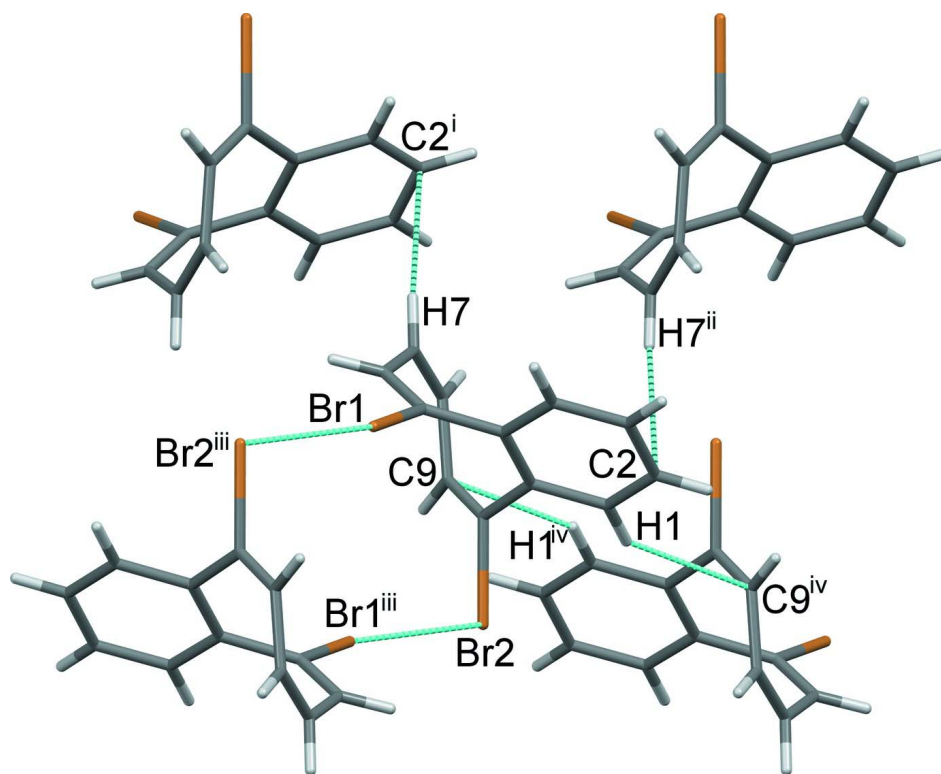


Figure 1

Molecular structure of (I) drawn with displacement ellipsoids at the 40% probability level, and also showing the atom numbering scheme.

**Figure 2**

View along the *a* axis (with *b* horizontal and *c* vertical) showing the three unique intermolecular contacts (as dashed-line tubes) that are less than the sums of the v.d. Waals' radii of the interacting atoms. (Symcodes: i, 1-*x*, -1/2+*y*, 1/2-*z*; ii, 1-*x*, 1/2+*y*, 1/2-*z*; iii, -*x*, 1-*y*, -*z*; iv, 1-*x*, -*y*, -*z*.)

(5*Z*,7*Z*,9*Z*)-5,10-Dibromobenzo[8]annulene

Crystal data

$C_{12}H_8Br_2$
 $M_r = 312.00$
 Monoclinic, $P2_1/c$
 $a = 8.5289$ (5) Å
 $b = 8.3630$ (5) Å
 $c = 15.5645$ (9) Å
 $\beta = 105.2980$ (6)°
 $V = 1070.83$ (11) Å³
 $Z = 4$
 $F(000) = 600$

$D_x = 1.935$ Mg m⁻³
 Melting point: 366 K
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9956 reflections
 $\theta = 2.5$ – 29.0 °
 $\mu = 7.52$ mm⁻¹
 $T = 173$ K
 Block, colourless
 $0.16 \times 0.09 \times 0.08$ mm

Data collection

Bruker APEXII CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube, Bruker
 D8
 Graphite monochromator
 Detector resolution: 66.06 pixels mm⁻¹
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2008)

$T_{\min} = 0.510$, $T_{\max} = 0.746$
 15053 measured reflections
 2426 independent reflections
 2217 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\max} = 27.4$ °, $\theta_{\min} = 2.5$ °
 $h = -11 \rightarrow 11$
 $k = -10 \rightarrow 10$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.039$
 $S = 1.04$
 2426 reflections
 127 parameters
 0 restraints
 Primary atom site location: dual

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0171P)^2 + 0.5892P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$

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. Structure first solved in $P2_1$; used the *PLATON* "Addsym" tool to find the true space group and refinement continued in $P2_1/c$ (Spek, 2009).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.00196 (2)	0.47441 (2)	0.12658 (2)	0.02901 (6)
Br2	0.33582 (2)	0.24542 (2)	-0.10638 (2)	0.02977 (6)
C1	0.2640 (2)	-0.0177 (2)	0.03420 (12)	0.0251 (4)
H1	0.3169	-0.0572	-0.0081	0.030*
C2	0.1703 (2)	-0.1200 (2)	0.06965 (13)	0.0289 (4)
H2	0.1598	-0.2291	0.0522	0.035*
C3	0.0918 (2)	-0.0629 (2)	0.13055 (12)	0.0287 (4)
H3	0.0285	-0.1332	0.1557	0.034*
C4	0.1056 (2)	0.0963 (2)	0.15478 (11)	0.0240 (4)
H4	0.0496	0.1351	0.1958	0.029*
C4A	0.20053 (19)	0.2013 (2)	0.11986 (10)	0.0187 (3)
C5	0.2100 (2)	0.3709 (2)	0.14745 (11)	0.0210 (3)
C6	0.3398 (2)	0.4538 (2)	0.19030 (12)	0.0264 (4)
H6	0.3235	0.5615	0.2054	0.032*
C7	0.5062 (2)	0.3917 (2)	0.21606 (12)	0.0282 (4)
H7	0.5615	0.3944	0.2776	0.034*
C8	0.5866 (2)	0.3322 (2)	0.16108 (12)	0.0270 (4)
H8	0.6935	0.2938	0.1867	0.032*
C9	0.5240 (2)	0.3205 (2)	0.06401 (12)	0.0239 (4)
H9	0.5851	0.3714	0.0289	0.029*
C10	0.3892 (2)	0.2449 (2)	0.02106 (11)	0.0206 (3)
C10A	0.28235 (19)	0.1430 (2)	0.05945 (11)	0.0187 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02787 (10)	0.02768 (10)	0.03510 (11)	0.00464 (7)	0.01468 (8)	-0.00192 (8)

Br2	0.02890 (10)	0.04284 (12)	0.01930 (9)	0.00265 (8)	0.00940 (7)	0.00122 (7)
C1	0.0269 (9)	0.0217 (9)	0.0237 (9)	0.0048 (7)	0.0016 (7)	-0.0011 (7)
C2	0.0294 (9)	0.0177 (9)	0.0326 (10)	-0.0018 (7)	-0.0041 (8)	0.0015 (8)
C3	0.0240 (9)	0.0264 (10)	0.0308 (10)	-0.0070 (7)	-0.0016 (7)	0.0094 (8)
C4	0.0202 (8)	0.0286 (9)	0.0229 (8)	-0.0020 (7)	0.0052 (7)	0.0032 (7)
C4A	0.0173 (7)	0.0198 (8)	0.0170 (8)	-0.0005 (6)	0.0012 (6)	0.0014 (6)
C5	0.0233 (8)	0.0227 (9)	0.0193 (8)	0.0011 (7)	0.0098 (6)	0.0007 (7)
C6	0.0338 (10)	0.0236 (9)	0.0233 (9)	-0.0048 (8)	0.0101 (7)	-0.0057 (7)
C7	0.0277 (9)	0.0325 (10)	0.0214 (9)	-0.0114 (8)	0.0015 (7)	0.0010 (8)
C8	0.0200 (8)	0.0298 (10)	0.0287 (9)	-0.0054 (7)	0.0019 (7)	0.0055 (8)
C9	0.0223 (8)	0.0252 (9)	0.0269 (9)	0.0008 (7)	0.0111 (7)	0.0039 (7)
C10	0.0227 (8)	0.0228 (9)	0.0178 (8)	0.0063 (7)	0.0081 (6)	0.0011 (6)
C10A	0.0171 (7)	0.0192 (8)	0.0174 (8)	0.0009 (6)	0.0006 (6)	0.0019 (6)

Geometric parameters (Å, °)

Br1—C5	1.9234 (17)	C4A—C5	1.478 (2)
Br2—C10	1.9145 (17)	C5—C6	1.327 (2)
C1—C2	1.382 (3)	C6—C7	1.465 (3)
C1—C10A	1.397 (2)	C6—H6	0.9500
C1—H1	0.9500	C7—C8	1.326 (3)
C2—C3	1.381 (3)	C7—H7	0.9500
C2—H2	0.9500	C8—C9	1.467 (3)
C3—C4	1.380 (3)	C8—H8	0.9500
C3—H3	0.9500	C9—C10	1.327 (2)
C4—C4A	1.398 (2)	C9—H9	0.9500
C4—H4	0.9500	C10—C10A	1.484 (2)
C4A—C10A	1.398 (2)		
C2—C1—C10A	121.12 (17)	C5—C6—C7	124.91 (17)
C2—C1—H1	119.4	C5—C6—H6	117.5
C10A—C1—H1	119.4	C7—C6—H6	117.5
C3—C2—C1	119.75 (17)	C8—C7—C6	125.79 (16)
C3—C2—H2	120.1	C8—C7—H7	117.1
C1—C2—H2	120.1	C6—C7—H7	117.1
C4—C3—C2	119.95 (17)	C7—C8—C9	125.45 (17)
C4—C3—H3	120.0	C7—C8—H8	117.3
C2—C3—H3	120.0	C9—C8—H8	117.3
C3—C4—C4A	121.04 (17)	C10—C9—C8	125.57 (16)
C3—C4—H4	119.5	C10—C9—H9	117.2
C4A—C4—H4	119.5	C8—C9—H9	117.2
C10A—C4A—C4	119.05 (16)	C9—C10—C10A	127.81 (16)
C10A—C4A—C5	122.07 (15)	C9—C10—Br2	117.29 (13)
C4—C4A—C5	118.88 (15)	C10A—C10—Br2	114.52 (12)
C6—C5—C4A	128.45 (16)	C1—C10A—C4A	119.06 (16)
C6—C5—Br1	117.39 (13)	C1—C10A—C10	118.30 (15)
C4A—C5—Br1	113.91 (12)	C4A—C10A—C10	122.64 (15)

C10A—C1—C2—C3	0.6 (3)	C7—C8—C9—C10	-57.1 (3)
C1—C2—C3—C4	0.9 (3)	C8—C9—C10—C10A	-6.8 (3)
C2—C3—C4—C4A	-1.2 (3)	C8—C9—C10—Br2	-179.26 (14)
C3—C4—C4A—C10A	0.0 (2)	C2—C1—C10A—C4A	-1.7 (2)
C3—C4—C4A—C5	179.50 (16)	C2—C1—C10A—C10	177.97 (15)
C10A—C4A—C5—C6	-62.3 (2)	C4—C4A—C10A—C1	1.4 (2)
C4—C4A—C5—C6	118.2 (2)	C5—C4A—C10A—C1	-178.05 (15)
C10A—C4A—C5—Br1	123.72 (14)	C4—C4A—C10A—C10	-178.29 (15)
C4—C4A—C5—Br1	-55.72 (18)	C5—C4A—C10A—C10	2.3 (2)
C4A—C5—C6—C7	2.9 (3)	C9—C10—C10A—C1	-118.0 (2)
Br1—C5—C6—C7	176.62 (14)	Br2—C10—C10A—C1	54.57 (18)
C5—C6—C7—C8	58.2 (3)	C9—C10—C10A—C4A	61.7 (2)
C6—C7—C8—C9	1.3 (3)	Br2—C10—C10A—C4A	-125.75 (14)
