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5,7,7,8,10-Pentabromo-7,8-dihydrobenzocyclooctene

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.014 Å
R factor = 0.043
wR factor = 0.107
Data-to-parameter ratio = 18.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{12}H_7Br_5$, the eight-membered ring adopts a boat conformation. The repulsive interactions between the Br atoms affect the conformation of the molecule.

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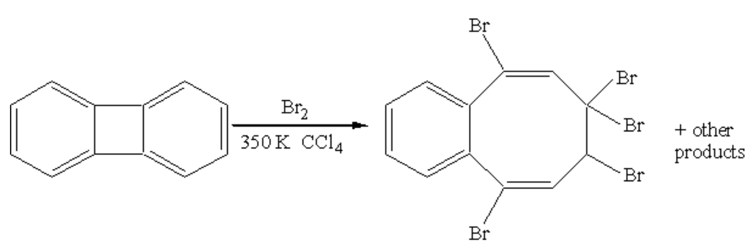
Comment

As a result of its physical and chemical properties and partial antiaromaticity, biphenylene has received a great deal of attention. As expected, biphenylene has been shown to have some specific reactivity. For example, it has been brominated in the presence of pyridine to give a monobromobiphenylene (substitution product) in a yield of 49%, and in the absence of a catalyst to give benzo[8]annulene derivatives (ring-opening products) as the main product. However, bromination of biphenylene is tedious and unsatisfactory. The nature of the intermediates and the reaction mechanisms are complicated, and some suggested structures are questionable (Cava & Mitchen, 1965; Barton, 1969). Furthermore, it has been observed that biphenylene generally shows low reactivity with bromine at room temperature, where substantial amounts of unreacted biphenylene are recovered (Barton *et al.*, 1964; Kidokoro *et al.*, 1982).



(I)

A survey of the literature on eight-membered rings and ones fused to aromatic molecules shows that these rings are some of the most difficult to prepare, owing to their high steric energy and transannular effects (Imai *et al.*, 1999). Eight-membered cyclic compounds are found widely in nature, and many biologically active cyclooctanoid natural products (Petasis & Patane, 1992) and synthetic compounds have been studied. Therefore, an X-ray crystal structure determination of (I) was undertaken to elucidate its molecular conformation.

Fig. 1 shows the conformation and molecular structure of compound (I) with the atomic numbering scheme. In the eight-membered ring, C7—C8 and C11—C12 are double bonds of length 1.32 (1) and 1.30 (1) Å, respectively. The bond lengths and angles in (I) are in accordance with conventional values, except for the C9—C10 bond length [1.42 (1) Å], which

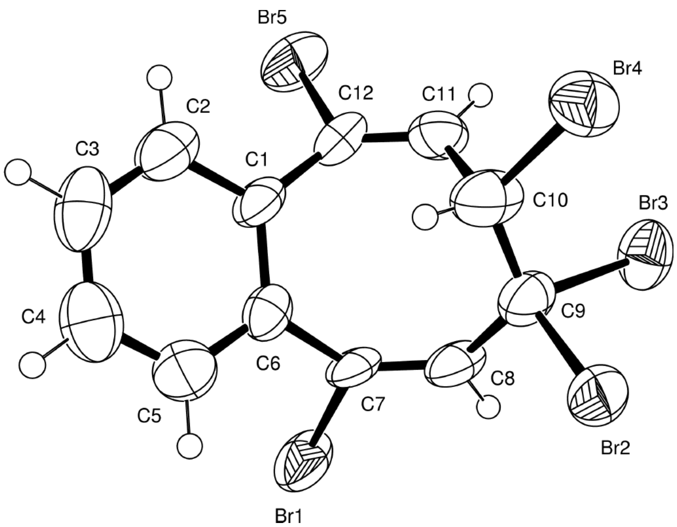


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

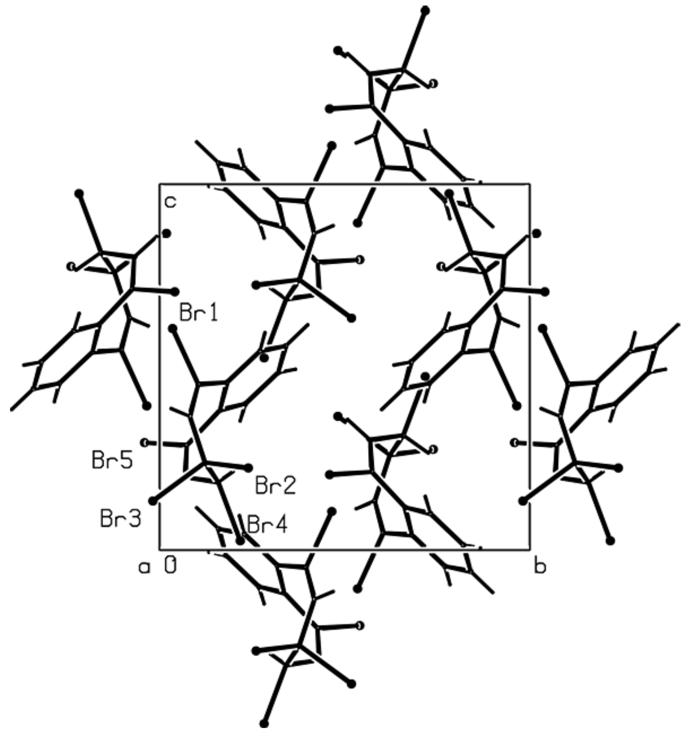


Figure 3
A view of the packing of the title compound.

is slightly shortened compared with a typical Csp^3—Csp^3 bond.

The Br—C—C bond angles are between 103.2 (7) and 119.3 (7)°, with an average value of 112.6 (7)°, compared with 115.1 (6)° in *exo,exo*-9,10,12-tribromotricyclo[6.3.1.02,7]-dodeca-2(7),3,5,10-tetraene (Hökelek *et al.*, 1991) and 113.9 (7)° in *exo,exo*-2,3-*endo,endo*-5,6-tetrabromobicycloheptane (Hökelek *et al.*, 1998).

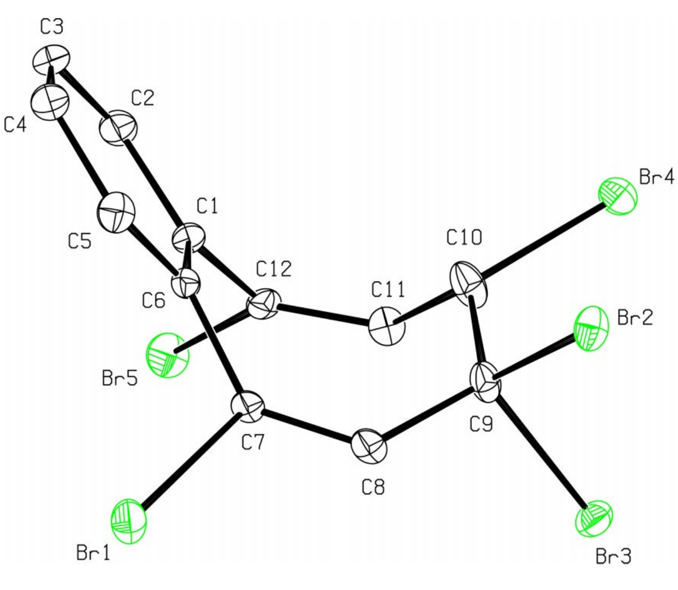


Figure 2
The eight-membered ring of the title compound adopts a boat-like conformation.

As shown in Fig. 2, least-squares-planes calculations indicate that the eight-membered ring is folded to form a boat-like conformation [the deviations of atoms C1, C6, C9 and C10 are 0.791 (9), 0.887 (8), 0.610 (9) and 1.081 (11) Å, respectively, from the mean plane through atoms C7, C8, C11 and C12]. The total puckering amplitude Q_T is 1.241 (1) Å (Cremer & Pople, 1975).

There are no unusual short contacts between the molecules, and the crystal structure is stabilized by van der Waals interactions. The molecules are stacked on top of one another along the *a* axis (Fig. 3).

Experimental

Biphenylene (0.5 g, 6.57 mmol) was dissolved in CCl_4 (40 ml) in a flask (100 ml) which was equipped with a reflux condenser. The solution was heated with magnetic stirring until CCl_4 started to reflux. To the refluxing solution, in the dark, bromine (1.59 g, 10 mmol) was added dropwise over 20 min. The reaction progress was monitored by thin-layer chromatography (TLC) or ^{1}H NMR. The starting material was completely converted to products in 3 h. After cooling to room temperature, the solvent was evaporated, providing 2.0 g of crude material. TLC was carried out on Merck silica F254 0.255 mm plates, and spots were visualized, where appropriate, by UV fluorescence at 254 nm. Classic column chromatography was performed using Merck 60 (70–230 Mesh) silica. Melting points were determined on a Thomas–Hoover capillary melting points apparatus. Solvents were concentrated at reduced pressure. IR spectra were recorded on a Perkin–Elmer 980 instrument. Mass spectra were recorded on a VG Zab Spec GC-MS spectrometer under electron-impact (EI) and chemical ionization conditions. NMR spectra were recorded on a Bruker AC 200 L instrument at 200 MHz for ^{1}H and at 50 MHz for ^{13}C NMR.

The product mixture obtained (2.0 g) was chromatographed on silica gel, eluting with hexane. 5,7,7,8,10-Pentabromo-7,8-dihydrobenzocyclooctene, (I), was isolated as the second component (110 mg, 2% yield); colorless crystals, m.p. 393–394 K (dichloromethane/petroleum ether, 1:3). Compound (I): IR (max, KBr/cm^{-1}): 3040, 2980, 1630, 1610, 1480, 1430, 1330, 1250, 1190, 950, 950, 900, 870, 860, 760. ^{1}H NMR (200 MHz, $CDCl_3$): 7.60 (*m*, 1H, arom.), 7.45 (*m*, 3H, arom.) 7.45 (*s*, 1H, H1), 6.65 (*d*, *J* 9.03, 1H, H4), 4.66 (*d*, 1H, H3); ^{13}C NMR (50 MHz, $CDCl_3$): 137.33 (*d*), 133.64 (*d*), 136.56 (*d*), 133.96 (*s*), 130.67 (*d*) 130.16 (*d*), 130.02 (*d*), 128.73 (*d*), 121.60 (*s*), 118.61 (*s*), 58.43 (*d*), 64.65 (*d*); MS (*m/z*, EI): 57/549/551/553/555, (*M*+, 3), 467/469/471/473/475 (*M*+, −Br, 80), 387/389/393 (*M*+, −2Br, 5), 309/311/313 (*M*+ −3Br, 41), 230/232 (*M*+, −4Br, 100), 150 (*M*+, −5Br, 60); found: C 26.93, H 1.21; $C_{12}H_7Br_5$ requires C 26.17, H 1.28%.

Crystal data

$C_{12}H_7Br_5$	D_x = 2.488 Mg m^{-3}
M_r = 550.73	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
a = 11.727 (5) Å	θ = 2.6–26.3°
b = 11.250 (5) Å	μ = 13.64 mm^{-1}
c = 12.104 (5) Å	T = 293 (2) K
β = 112.957 (5)°	Prism, colorless
V = 1470.4 (11) Å^3	0.40 × 0.20 × 0.12 mm
Z = 4	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	R_{int} = 0.057
Non-profiled ω scans	θ_{max} = 25.6°
Absorption correction: refined from ΔF (*SHELXA*; Sheldrick, 1998)	$h = -13 \rightarrow 14$
T_{min} = 0.047, T_{max} = 0.195	$k = 0 \rightarrow 13$
2899 measured reflections	$l = -14 \rightarrow 0$
2766 independent reflections	3 standard reflections frequency: 120 min intensity decay: 4%
1358 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.043	$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.107	$(\Delta/\sigma)_{max}$ < 0.001
S = 0.97	$\Delta\rho_{max}$ = 0.69 e Å^{-3}
2766 reflections	$\Delta\rho_{min}$ = −0.72 e Å^{-3}
154 parameters	

Table 1
Selected geometric parameters (Å, °).

C6—C7	1.488 (11)	C10—C11	1.496 (12)
C8—C7	1.323 (11)	C10—Br4	1.911 (9)
C8—C9	1.482 (12)	C1—C2	1.398 (12)
C9—C10	1.422 (13)	C1—C12	1.477 (12)
C9—Br2	1.963 (9)	C12—C11	1.298 (11)
C9—Br3	2.057 (10)	C12—Br5	1.896 (8)
C7—Br1	1.912 (8)		
C1—C6—C7	121.8 (8)	C9—C10—C11	113.7 (8)
C7—C8—C9	130.7 (9)	C6—C1—C12	122.1 (8)
C10—C9—C8	118.0 (8)	C11—C12—C1	125.5 (8)
C8—C7—C6	131.8 (8)	C12—C11—C10	121.9 (9)
C7—C8—C9—C10	−24.1 (16)	C7—C6—C1—C12	−6.0 (13)
C9—C8—C7—C6	−2.4 (18)	C6—C1—C12—C11	−57.1 (13)
C1—C6—C7—C8	60.5 (14)	C1—C12—C11—C10	−0.9 (15)
C8—C9—C10—C11	−51.5 (13)	C9—C10—C11—C12	94.2 (12)

H atoms were placed geometrically and refined using the usual riding model.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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