(1*RS*,8*SR*,9*RS*,10*RS*,11*RS*,12*RS*)-10,11-Dibromo-tetracyclo[6.4.2.0^{2,7}.0^{9,12}]tetradeca-2,4,6,13-tetraene

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The title compound, $C_{14}H_{12}Br_2$, consists of two central non-coplanar six-membered carbon rings constituting a bicyclic system, having a benzene ring fused on one side and a brominated cyclobutane ring fused on the other side at the bridging atoms of the bicyclic system. The bicyclic system has approximate D_3 symmetry and all three six-membered rings adopt boat conformations.

Comment

Benzobarrelene systems afford the possibility of several mechanistically interesting investigations. These compounds are intriguing in view of the di-π-methane rearrangement (Zimmerman, 1980; Zimmerman *et al.*, 1968), solvolytic reactivity (Barkhash, 1984; Menzek, 2000) and versatile applications (Hales *et al.*, 1995; Erden & de Meijere, 1983; Adam *et al.*, 1980; Paquette & Volz, 1976). In view of these factors, substituted benzobarrelene derivatives are important compounds that can provide information about how substituents will influence the reaction modes (Altundaş & Balcı, 1997).

(I)
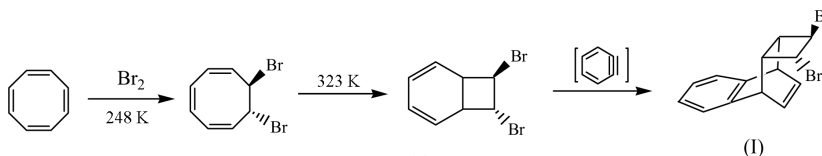
Bromination of hydrocarbons is an important process because it leads to useful intermediates for the synthesis of a large variety of bromoorganic compounds (Hileman, 1993; Chambers & James, 1979; Ruasse, 1993). These compounds have numerous industrial applications as pesticides, plastics, fire retardants and pharmaceutical chemicals.

Bromine derivatives of a compound are valuable in the synthesis of other derivatives; for example, the title compound, (I), is a starting compound for substituted benzobasketene derivatives (Aydınlı *et al.*, 2003). Compound (I) is of interest to us from the following points of view: it has a strained benzobarrelene unit, a small ring (cyclobutane) fused to a strained ring system and Br atoms, one of which is in an *endo* (*syn*) orientation.

The structures of [3.2.1]- and [2.2.2]bicyclic systems having different substituents at different positions of the bicyclic framework have been the subject of much interest in our laboratory; examples are: *exo,endo,endo*-9,9,10,11,12-penta-bromotricyclo[6.2.2.0^{2,7}]dodeca-2 (7),3,5- triene [(II); Hökelek *et al.*, 1990]; *exo,exo*-9,10,12-tribromotricyclo[6.3.1.0^{2,7}]-dodeca-2 (7),3,5,10-tetraene [(III); Hökelek *et al.*, 1991]; *exo,exo*-2,4,8-tribromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene, (IV), *endo,exo*-2,3,8-tribromo-6,7-benzobicyclo[3.2.1]octa-
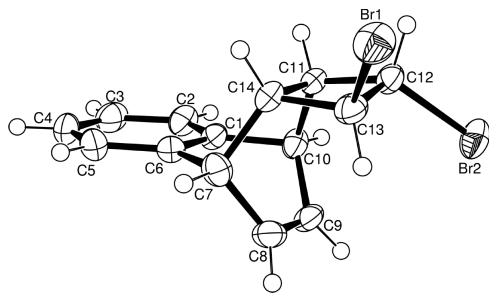
Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

3,6-diene, (V), and *exo,endo*-2,5,6-tribromo-6,7-benzotricyclo[2.2.2]octa-2,6-diene, (VI) (Balcı *et al.*, 1992); *exo,anti*-4-hydroxy-8-bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene, (VII), *exo,anti*-4,8-dibromo-2,3-benzobicyclo[3.2.1]octa-2,6-diene, (VIII), and *endo,endo*-7,8-dibromo-5,6-benzobicyclo[2.2.2]octa-2,5-ene, (IX) (Daştan *et al.*, 1994); *exo,exo*-2,3-*endo,endo*-5,6-tetrabromobicycloheptane [(X); Hökelek *et al.*, 1998]; 2,2-*exo*-3,5,6-pentabromobicycloheptane [(XI); Hökelek *et al.*, 2001]; and *exo*-(1RS,8SR,9RS,11SR)-10-chloromethyltetracyclo[6.3.2.0^{2,7}0^{9,11}]undecane-2,4,6,12-tetraene [(XII); Çoruh *et al.*, 2004].

The structure determination of the title compound, (I), was undertaken in order to confirm the formation of the brominated cyclobutane ring.

The title compound, (I), contains two central non-coplanar six-membered carbon rings constituting a bicyclic system, which has a benzene C1–C6 ring (*A*) on one side and a brominated cyclobutane ring fused on the other side at the bridging atoms of the bicyclic system (Fig. 1). One of the Br atoms is in a *syn* orientation. As can be seen from the torsion angles (Table 1) and the puckering parameters (Cremer & Pople, 1975), the bicyclic system has approximate D_3 symmetry.

In the bicyclic fragment, all three six-membered rings adopt boat conformations: $Q_T = 0.79$ (2) Å, $\varphi_2 = -1.88$ (15) and $\theta_2 = 89.19$ (15)° for the C7–C14 ring; $Q_T = 0.767$ (2) Å, $\varphi_2 = -58.85$ (14) and $\theta_2 = 90.11$ (12)° for the C1/C6–C10 ring; $Q_T = 0.884$ (2) Å, $\varphi_2 = 118.31$ (13) and $\theta_2 = 91.33$ (13)° for the C1/C6/C7/C14/C11/C10 ring.

Bond angles about the central bicyclic system deviate substantially from ideal values. The external angles C2—C1—C10 [126.6 (3)°] and C5—C6—C7 [126.6 (2)°] are larger than the internal angles C12—C11—C10 [122.2 (3)°] and C13—C14—C7 [116.7 (3)°] [average 119.5°]. The tetrahedral angles also exhibit significant distortion: C6—C7—C14 [104.4 (3)°] and C1—C10—C11 [103.3 (2)°] [average 103.9°], and C6—C7—C8 [106.1 (3)°], C14—C7—C8 [107.1 (3)°], C1—C10—C9 [106.6 (3)°] and C11—C10—C9 [108.6 (3)°] [average 107.1°]. The average values of the corresponding external and tetrahedral angles in the similar [2.2.2]bicyclic systems are 126.1, 107.1 and 107.9° in (II), 126.6, 108.5 and 105.6° in (VI), 126.5, 107.1 and 106.5° in (IX), and 126.9, 103.2 and 107.8° in (XII), respectively. The angles C7—C8—9 [115.1 (3)°] and C10—
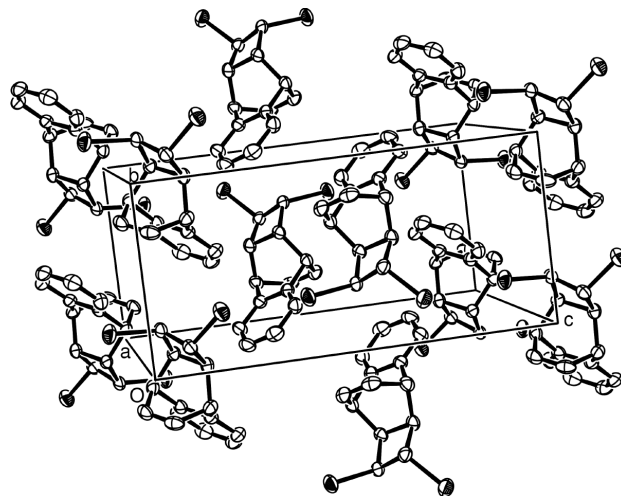
Figure 2
Packing diagram, viewed approximately down the *a* axis. H atoms have been omitted.

C9—C8 [115.2 (3)°] about the double bond have an average value of 115.2°. These results indicate the presence of significant strain in the bicyclic framework. The degree of the strain is manifest most obviously in the deviations from ideality of the bond angles in the bicyclic ring system. However, the strain in the [3.2.1]bicyclic system is more predominant than in the [2.2.2]bicyclooctane skeleton (Hökelek *et al.*, 1991).

The dihedral angles between planes *A*, *B* (C1/C6/C7/C10), *C* (C7–C10), *D* (C7,C10,C11,C14) and *E* (C11–C14) are as follows: *A*/*B* = 0.76 (7), *B*/*C* = 57.34 (8), *B*/*D* = 64.58 (9), *C*/*D* = 58.08 (10) and *D*/*E* = 59.30 (11)°.

As can be seen from the packing diagram (Fig. 2), the molecules are aligned approximately parallel to the *b* axis and stacked parallel to the (101) plane. Dipole–dipole and van der Waals interactions are effective in the packing of molecules in the crystal structure.

Experimental

A solution of anthranilic acid (11.45 g, 83.6 mmol) in acetone (50 ml) was added, over a period of 3 h, to a refluxing solution of *trans*-7,8-dibromobicyclo[4.2.0]octa-2,4-diene (5.52 g, 20.9 mmol) and isopentyl nitrite (9.78 g, 89.6 mmol) in dichloromethane (100 ml). The mixture was then refluxed for an additional 1 h and evaporated to give a black residue of tarry appearance. The residue was subjected to column chromatography (silica gel, 50 g), eluting with *n*-hexane (yield 2.84 g, 40%), and crystallized from dichloromethane–*n*-hexane (1:3).

Crystal data

$C_{14}H_{12}Br_2$	$D_x = 1.880$ Mg m^{-3}
$M_r = 340.06$	Mo *K*α radiation
Monoclinic, $P2_1/c$	Cell parameters from 3489
$a = 11.7056$ (9) Å	reflections
$b = 6.9920$ (5) Å	$\theta = 2.3–26.0°$
$c = 14.6897$ (11) Å	$\mu = 6.71$ mm^{-1}
$\beta = 92.052$ (1)°	$T = 293$ (2) K
$V = 1201.52$ (15) Å^3	Prism, colourless
$Z = 4$	$0.35 \times 0.19 \times 0.17$ mm

Data collection

Nonius KappaCCD diffractometer	1916 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.048$
Absorption correction: multi-scan	$\theta_{max} = 28.0°$
($SADABS$; Sheldrick, 1996)	$h = -11 \rightarrow 15$
$T_{min} = 0.236$, $T_{max} = 0.319$	$k = -9 \rightarrow 9$
6990 measured reflections	$l = -19 \rightarrow 17$
2758 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0408P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.082$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.91$	$\Delta\rho_{max} = 0.70$ e Å^{-3}
2758 reflections	$\Delta\rho_{min} = -0.67$ e Å^{-3}
146 parameters	Extinction correction: $SHELXL$97
H-atom parameters constrained	Extinction coefficient: 0.0176 (7)

Table 1
Selected geometric parameters (Å, °).

Br1—C13	1.952 (3)	C6—C5	1.388 (4)
Br2—C12	1.954 (3)	C6—C7	1.518 (5)
C8—C9	1.310 (5)	C13—C14	1.550 (4)
C8—C7	1.514 (5)	C14—C11	1.545 (4)
C9—C10	1.504 (5)	C14—C7	1.550 (4)
C12—C13	1.515 (5)	C10—C11	1.561 (4)
C12—C11	1.534 (4)	C2—C3	1.392 (5)
C1—C2	1.371 (5)	C5—C4	1.395 (5)
C1—C6	1.392 (5)	C4—C3	1.373 (5)
C1—C10	1.531 (4)		
C9—C8—C7	115.1 (3)	C11—C14—C13	88.9 (2)
C8—C9—C10	115.2 (3)	C7—C14—C13	116.7 (3)
C13—C12—C11	90.6 (2)	C8—C7—C6	106.1 (3)
C13—C12—Br2	116.3 (2)	C8—C7—C14	107.1 (3)
C11—C12—Br2	119.7 (2)	C6—C7—C14	104.4 (3)
C2—C1—C6	120.8 (3)	C9—C10—C1	106.6 (3)
C2—C1—C10	126.6 (3)	C9—C10—C11	108.6 (3)
C6—C1—C10	112.6 (3)	C1—C10—C11	103.3 (2)
C5—C6—C1	119.7 (3)	C1—C2—C3	119.5 (3)
C5—C6—C7	126.6 (3)	C6—C5—C4	119.2 (3)
C1—C6—C7	113.8 (3)	C3—C4—C5	120.5 (3)
C12—C13—C14	89.7 (3)	C12—C11—C14	89.2 (2)
C12—C13—Br1	115.6 (2)	C12—C11—C10	122.2 (3)
C14—C13—Br1	117.0 (2)	C14—C11—C10	108.9 (3)
C11—C14—C7	110.4 (3)	C4—C3—C2	120.2 (3)
C7—C8—C9—C10	−1.4 (4)	C8—C9—C10—C1	−52.9 (4)
C10—C1—C6—C7	−0.6 (4)	C8—C9—C10—C11	57.8 (4)
C9—C8—C7—C6	54.6 (4)	C6—C1—C10—C9	53.0 (4)
C9—C8—C7—C14	−56.5 (4)	C6—C1—C10—C11	−61.4 (3)
C1—C6—C7—C8	−52.1 (4)	C7—C14—C11—C10	−3.5 (3)
C1—C6—C7—C14	60.9 (4)	C9—C10—C11—C14	−51.6 (3)
C11—C14—C7—C8	56.1 (3)	C1—C10—C11—C14	61.3 (3)
C11—C14—C7—C6	−56.1 (3)		

H atoms were positioned geometrically at distances of Csp^2—H = 0.93 Å and Csp^3—H = 0.98 Å, and refined using a riding model. The U_{iso}(H) values were constrained to be $1.2U_{eq}$ of the carrier atom.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); 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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