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Key indicators

Single-crystal X-ray study

T = 301 K

Mean $\sigma(\text{C}-\text{C}) = 0.017 \text{ \AA}$

R factor = 0.065

wR factor = 0.149

Data-to-parameter ratio = 17.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.*endo,endo,endo*-9,9,10,11,12-Pentabromo-
tricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5-triene

The title compound, $\text{C}_{12}\text{H}_9\text{Br}_5$, involves two non-planar six-membered carbon rings constituting a bicyclic system. One of these non-planar carbon rings shares two C atoms with a benzene ring and has three Br substituents, while the second non-planar carbon ring has two Br substituents. The repulsive interaction between the neighbouring Br atoms is evidenced by the enlargement of the respective Br—C—Br and Br—C—C angles.

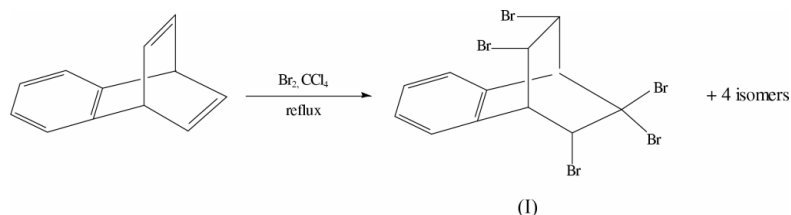
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Comment

The addition of bromine to the $\text{C}=\text{C}$ double bond is formally one of the simplest reactions of unsaturated compounds. The nature of the intermediates of the addition depends on the structure of the substrate and on the reaction medium. It has been reported that, during the bromination reaction of unsaturated bicyclic systems, the reaction temperature has a significant influence on the product distribution (Menzek *et al.*, 1997; Daştan *et al.*, 1994, 1996). In connection with our continuing interest in the synthesis of tri- and tetrasubstituted bromobenzobarrelenes (Balcı *et al.*, 1992; Hökelek *et al.*, 1990), we have studied the high-temperature bromination reaction of bromobenzobarrelene. The reaction gave a complex reaction mixture consisting of five isomeric pentabromides. In order to gain more information on the reaction mechanism and the structure of the product, an X-ray structure analysis of the title compound, (I), was carried out.



The title compound, (I), involves two non-planar six-membered carbon rings constituting a bicyclic system. One of these non-planar carbon rings shares two C atoms with a benzene ring and has three Br substituents, while the second non-planar carbon ring has two Br substituents.

As expected, the structure of the title compound (Fig. 1) has similarities with that of the pentabromotricyclo compound reported previously (Hökelek *et al.*, 1990). The five C—Br distances in the title compound range from 1.943 (12) to 1.969 (11) Å. The corresponding distances in its isomer, cited above, have values between 1.947 (5) and 1.968 (5) Å. The environment about atom C4 could be described as a distorted

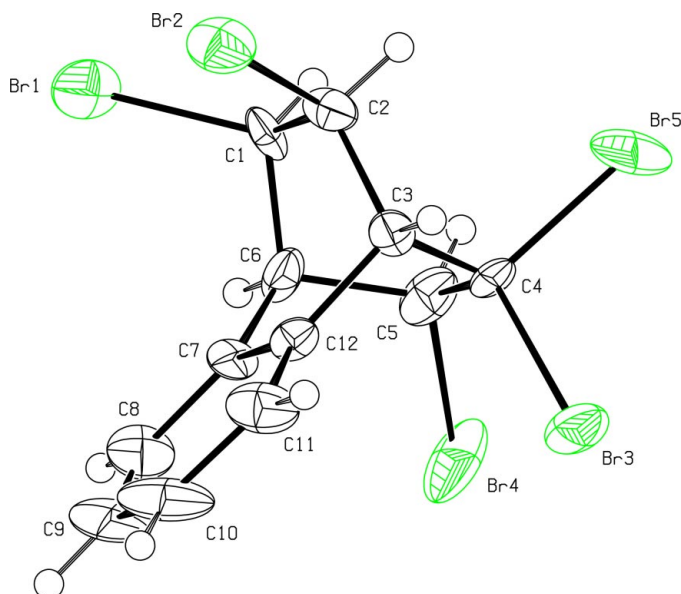


Figure 1
The title compound (*PLATON*; Spek, 2000), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

tetrahedron involving atoms C3, C5, Br3 and Br5. The C5—C4—Br3 angle, with a value of 115.0 (7)°, shows the maximum deviation from an ideal tetrahedron. That this angle is larger than the other angles about C4 and that it has the largest deviation from the conventional value of the tetrahedral angle might be explained by a repulsive interaction between Br3 and Br4. Similar repulsive forces between atoms Br1 and Br2 seem to have resulted in the angles C2—C1—Br1 [116.6 (8)°] and C1—C2—Br2 [116.9 (8)°] being larger than the other angles about C1 and C2, respectively. The moiety involving atoms C6—C12 and C3 is planar. The dihedral angles between this moiety and the planes involving atoms C6/C1/C2/C3 and C3/C4/C5/C6 are 56.74 (3) and 60.42 (4)°, respectively. The

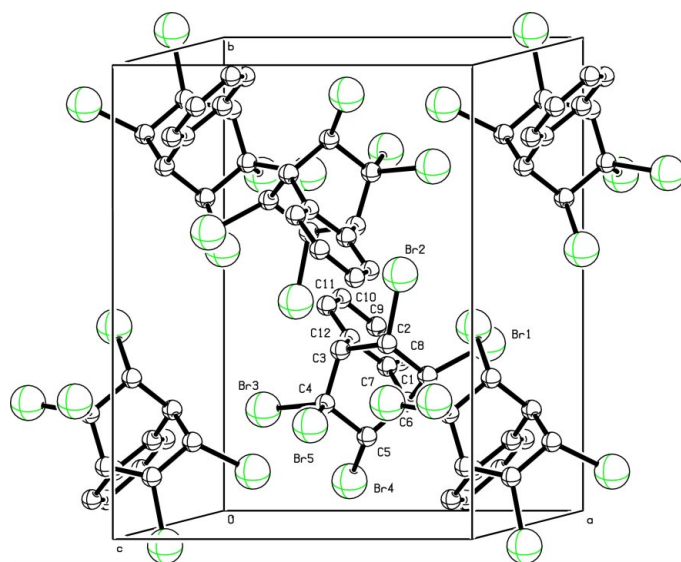


Figure 2
A view of the unit cell (*PLATON*; Spek, 2000). H atoms have been omitted for clarity.

shortest intermolecular contact is observed between Br3 and Br5 of neighbouring molecules at 3.570 (11) Å; this is just less than the sum of the van der Waals radii for Br atoms (Fig. 2).

Experimental

2-Bromobenzobarrelene (1165 mg, 5 ml) was dissolved in 40 ml of CCl₄ in a 100 ml flask which was equipped with a reflux condenser. The solution was heated, while being stirred magnetically, until carbon tetrachloride started to reflux. To the refluxing solution was added a hot solution (338–343 K) of bromine (1650 mg, 10.3 mmol) in 10 ml of CCl₄, in one portion. The resulting mixture was heated for 15 min at reflux temperature. After being cooled to room temperature the solvent was evaporated. The oily residue was chromatographed on silica gel (140 g), eluting with *n*-hexane. The title compound was isolated as the last fraction in a yield of 7%.

Crystal data

C ₁₂ H ₉ Br ₅	$D_x = 2.553 \text{ Mg m}^{-3}$
$M_r = 552.74$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 9.8779 (12) \text{ \AA}$	$\theta = 2.4\text{--}26.0^\circ$
$b = 13.0945 (13) \text{ \AA}$	$\mu = 13.95 \text{ mm}^{-1}$
$c = 11.5305 (11) \text{ \AA}$	$T = 301 (2) \text{ K}$
$\beta = 105.354 (7)^\circ$	Prism, colourless
$V = 1438.2 (3) \text{ \AA}^3$	$0.25 \times 0.20 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.071$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 26.0^\circ$
Absorption correction: ψ scan (Fair, 1990)	$h = -12 \rightarrow 11$
$T_{\text{min}} = 0.047$, $T_{\text{max}} = 0.123$	$k = 0 \rightarrow 16$
2897 measured reflections	$l = 0 \rightarrow 14$
2761 independent reflections	3 standard reflections
1585 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 1.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1154P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.149$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.93$	$\Delta\rho_{\text{max}} = 2.25 \text{ e \AA}^{-3}$
2761 reflections	$\Delta\rho_{\text{min}} = -1.07 \text{ e \AA}^{-3}$
155 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0020 (6)

Table 1

Selected geometric parameters (Å, °).

C1—Br1	1.948 (11)	C5—Br4	1.943 (12)
C2—Br2	1.948 (11)	C4—Br5	1.969 (11)
C4—Br3	1.947 (10)		
C2—C1—Br1	116.6 (8)	C6—C5—Br4	108.9 (8)
C3—C2—Br2	107.6 (7)	C4—C5—Br4	116.2 (8)
C1—C2—Br2	116.9 (8)	C3—C4—Br5	111.6 (7)
C3—C4—Br3	108.0 (7)	C5—C4—Br5	107.6 (8)
C5—C4—Br3	115.0 (7)		

H atoms bonded to C atoms were placed geometrically. All H atoms were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Some residual electron density was observed around the Br atoms at distances less than 1 Å.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993); cell refinement: *SHELXL97* (Sheldrick, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97*; molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL97*.

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