(1RS,2RS,3SR,4SR,9RS)-1,2,3,9-Tetrabromo-1,2,3,4-tetrahydro-1,4-methanonaphthalene

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.006 Å
R factor = 0.035
wR factor = 0.089
Data-to-parameter ratio = 16.1

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

The title compound, $C_{11}H_8Br_4$, comprises a norbornane skeleton with four Br atoms, having a benzene ring fused on one side. The structure is stabilized by weak C—H···Br intramolecular hydrogen-bonding interactions in addition to van der Waals forces.

Comment

Polymeric materials and synthetic fibres are extensively used in many areas. The demand for non-burning or flame-retardant polymers is strong in various industries. Some of these flame retardant products contain brominated organic compounds (Burleigh *et al.*, 1980). Besides industrial applications for these highly brominated compounds, such as pesticides, plastics, fire-retardants and pharmaceutical chemicals, they also play an important role as key compounds for the synthesis of other derivatives (Altundaş *et al.*, 2002; Altundaş & Balcı, 1993). In this connection, great interest has been focused on the halogenation of benzonorbornadiene (Daştan *et al.*, 1994, 2002; Altundaş *et al.*, 2000; Cristol & Nachtigall, 1967). As a continuation of our interest in this area, the structure of tetrabromide (3), which was prepared by published methods (Daştan & Balcı, 2005) starting from 2,9-dibromobenzonorbornadiene, (1), by high-temperature bromination, is reported.
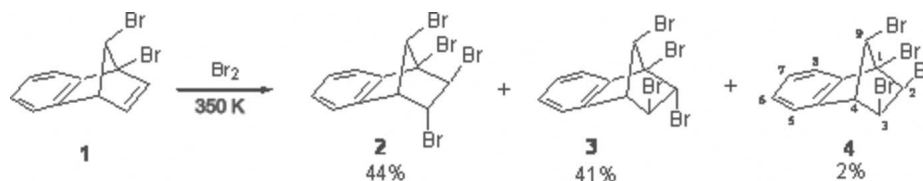
Compound (3) comprises a norbornane skeleton with four Br atoms, having a benzene ring fused on one side (Fig. 1). The average values of the Br—C bonds and the Br—C—C angles are 1.944 (3) Å and 114.7 (2)°, respectively (see Table 1). These values are within the ranges obtained for similar bonds in [1R(S),2S(R),3S(R),4S(R),9R(S)]-1,2,3,9-tetrabromo-1,2,3,4-tetrahydro-1,4-methanonaphthalene (Çelik *et al.*, 2006), which is one of a racemic pair of diastereomers with (3), and for those in similar compounds (Allen *et al.*, 1987; Çelik *et al.*, 2004; Akkurt *et al.*, 2004; Ersanlı *et al.*, 2005). The puckering parameters (Cremer & Pople, 1975) of the five-membered rings A (C1/C2/C5–C7) and B (C2–C5/C7) are Q_2 = 0.597 (4) Å and φ_2 = 70.93 (34)°, and Q_2 = 0.586 (3) Å and φ_2 = 132.31 (33)°, respectively. Ring A adopts an envelope conformation with atom C7 as the flap. However, owing to the repulsive interactions between the Br atoms in (3), ring B
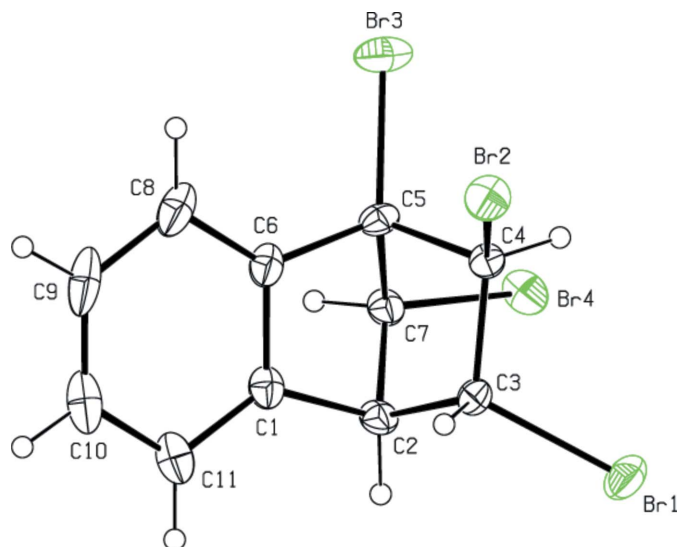
Figure 1
A view of (3), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

exhibits a conformation twisted about the C5—C7 bond. Plane *C* (C1/C2/C5/C6/C8–C11) has maximum deviations at C1, C2 and C9 of 0.020 (4), −0.017 (4) and −0.016 (5) Å, respectively. The dihedral angle between planes *D* (C2/C5/C7) and *C* is 56.64 (19)°, and that between planes *E* (C2–C5) [maximum deviation from planarity of 0.077 (4) Å for C2] and *C* is 68.69 (13)°, while that between planes *D* and *E* is 54.76 (22)° (Nardelli, 1999).

The crystal structure of (3) is stabilized by weak C—H···Br intramolecular hydrogen-bonding interactions in addition to van der Waals forces (Table 2).

Table 1
Selected geometric parameters (Å, °).

Br1—C3	1.964 (3)	Br3—C5	1.917 (3)
Br2—C4	1.946 (3)	Br4—C7	1.949 (3)
Br1—C3—C2	114.23 (19)	Br3—C5—C6	116.8 (2)
Br1—C3—C4	112.8 (2)	Br3—C5—C7	116.2 (2)
Br2—C4—C3	112.9 (2)	Br4—C7—C2	116.8 (2)
Br2—C4—C5	113.08 (19)	Br4—C7—C5	115.5 (3)
Br3—C5—C4	113.6 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···Br4	0.98	2.79	3.199 (3)	106

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 and 0.98 Å for aromatic and methine H atoms, respectively, and with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *COLLECT* (Bruker, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

Experimental

To a magnetically stirred solution of (1) (2.0 g, 6.67 mmol) (Daştan & Balcı, 2005) in refluxing CCl$_4$ (20 ml) was added dropwise a hot solution of bromine (1.52 g, 9.50 mmol) in CCl$_4$ (3 ml) over a period of 5 min. The resulting reaction mixture was heated for 1 min at reflux temperature. The solvent was evaporated, the residue was crystallized from CH$_2$Cl$_2$–*n*-pentane (1:2) and pure tetrabromide (3) was obtained (700 mg). After separation of the majority of (3), the residue was chromatographed on silica gel (100 g) using *n*-hexane as eluant. The first fraction was a mixture of tetrabromides (2) and (3). The solution was allowed to stand for 2 h in a refrigerator and the resulting crystals were identified as tetrabromide (2). After separation of the crystals, the residue was analysed by NMR. Tetrabromide (2) (Daştan & Balcı, 2005): 600 mg, crystals, 750 mg mixture, total 44% yield. Tetrabromide (3) (Daştan & Balcı, 2005): 700 mg, crystals, 555 mg mixture, total 41% yield. The second fraction (from a silica-gel column) was identified as tetrabromide (4) (Daştan & Balcı, 2005) (61 mg, 2% yield; m.p. 446–447 K). Spectroscopic analysis for (3): ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.51–7.24 (*m*, 4H, H-aryl), 5.12 (*d*, $J_{2,3}$ = 4.2 Hz, 1H, H2), 4.37 (*t*, $J_{4,9} = J_{3,9}$ = 1.9 Hz, 1H, H9), 3.80 (*m*, 2H, H3 and H4). Analysis calculated for C$_{11}$H$_8$Br$_4$: C 28.73, H 1.75%; found: C 28.34, H 1.66%. Crystals of (3) suitable for X-ray analysis were obtained by slow evaporation of a CH$_2$Cl$_2$–*n*-pentane (1:3) solution at room temperature.

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