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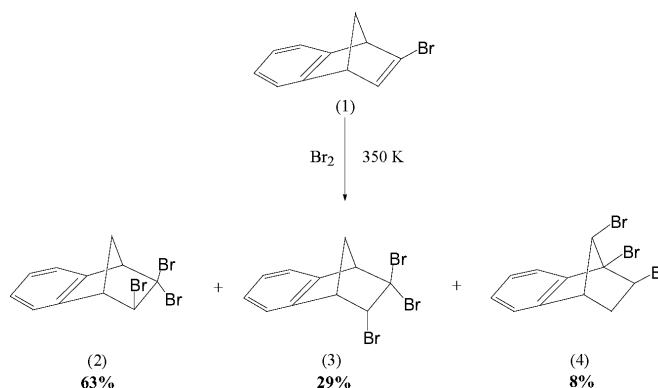
Key indicators

Single-crystal X-ray study
 $T = 297\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
 R factor = 0.033
 wR factor = 0.066
Data-to-parameter ratio = 16.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**(±)-(1*SR*,8*RS*,10*RS*)-9,9,10-Tribromo-tricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene**

The title compound, $\text{C}_{11}\text{H}_9\text{Br}_3$, consists of a norbornane skeleton, composed of two five-membered rings in envelope conformations and a six-membered ring with three Br atoms held in a boat conformation by a bridging methylene group, which constitutes a bicyclo[2.2.1]heptane system, having a benzene ring fused on one side. The repulsive interactions between the Br atoms affect the topology of the norbornane skeleton.

Comment

Addition of bromine to norbornadiene results in the products of Wagner–Meerwein rearrangement and homoallylic conjugation. Bromonorbornanes are important in the synthesis of bromonorbornadienes, which may be used for the synthesis of other substituted norbornadienes. The dangerous properties of the products formed from the bromination of norbornadiene have been pointed out by Winstein (1961). In the bromination reactions of unsaturated bicyclic systems, the reaction temperature has a dramatic influence on product distribution (Balci *et al.*, 1992*a,b*). Much interest has been focused on the halogenation of norbornadiene (Barkhash, 1984; Tutar *et al.*, 1996) and benzonorbornadiene derivatives (Barkhash, 1984; Daştan *et al.*, 1994, 2002; Horasan *et al.*, 2003), because these systems afford the possibility of several mechanistically interesting investigations. These compounds are intriguing, in view of their di- π -methane rearrangement [*viz.* a photochemical reaction of a molecular entity comprising two π systems to form an ene-(or aryl)-substituted cyclopropane; Altundaş *et al.*, 2002], solvolytic reactivity (Barkhash, 1984) and versatile properties (Cossu *et al.*, 1997; Menzek & Karakaya, 2004).



In view of this, substituted benzonorbornadiene derivatives are important compounds which can provide information on how the substituents will influence the reaction modes (Altundaş *et al.*, 2002). In addition, besides numerous indus-

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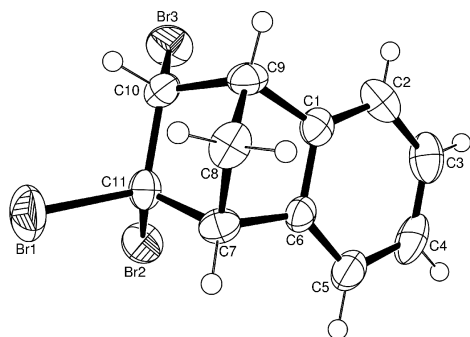


Figure 1

The molecular structure of (3), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

trial applications in the areas of pesticides, plastics, fire retardants and pharmaceutical chemicals, a bromine derivative of a compound is valuable because it is key for synthesizing other derivatives. As shown in the scheme, the title compound, (3), was prepared by published methods (Cossu *et al.*, 1997; Altundaş *et al.*, 2002), starting from 2-bromobenzonorbornadiene, (1), by high-temperature bromination. The structure determination of (3) was undertaken in order to establish the formation and identity of the tribromide.

In the bicyclo[2.2.1]heptane (norbornane) fragment of (3) (Fig. 1), the almost-perfect boat conformation of the six-membered ring (C1/C6/C7/C11/C10/C9) is evidenced by the puckering parameters (Cremer & Pople, 1975) $Q_T = 0.937$ (4) Å, $\varphi_2 = 122.2$ (2)° and $\theta_2 = 89.5$ (3)°. The boat is almost symmetrical, with a dihedral angle between the C7/C8/C9 and C1/C6/C11/C10 planes of 87.0 (3)°, and with nearly equal deviations of atoms C7 and C9 from the C1/C6/C11/C10 plane, of 0.821 (4) and 0.801 (4) Å, respectively.

Asymmetric substitution of the norbornane nucleus often produces a twist about the C7...C9 vector. This twisting can be seen in (3) from the C7–C6–C1–C9 and C7–C11–C10–C9 torsion angles of 1.2 (3) and 3.0 (4)°, respectively. The two five-membered rings have envelope conformations, with atom C8 displaced by 0.832 (5) Å from plane *A* (C7/C6/C1/C9) and by 0.905 (5) Å from plane *B* (C7/C11/C10/C9). The related puckering parameters are $q_2 = 0.552$ (5) Å and $\varphi_2 = 106.1$ (9)° for ring C1/C6–C9, and $q_2 = 0.627$ (4) Å and $\varphi_2 = -74.7$ (4)° for ring C7–C11. The dihedral angles between the planes *A*, *B* and *C* (C7–C9) are *A/B* = 66.6 (2), *A/C* = 53.0 (3) and *B/C* = 60.4 (3)°.

In the norbornane skeleton, the C–C single-bond lengths range from 1.502 (5) to 1.576 (6) Å, with a mean value of 1.539 (6) Å. Slight bond alternation is observed in the benzene ring, the distal aromatic bond C3–C4 [1.368 (7) Å] being about 0.02 Å shorter than the proximal bond C1–C6 [1.389 (5) Å]. The bond angles about the central bicyclic system deviate substantially from ideal values (Table 1), indicating the presence of significant strain in the bicyclic framework. Strain in the [2.2.1] bicyclic system is more predominant than that in the [2.2.2] bicyclooctane skeleton (Hökelek *et al.*, 1991).

There is an approximately tetrahedral environment about atom C11, but the Br1–C11–Br2 angle [106.2 (2)°] is

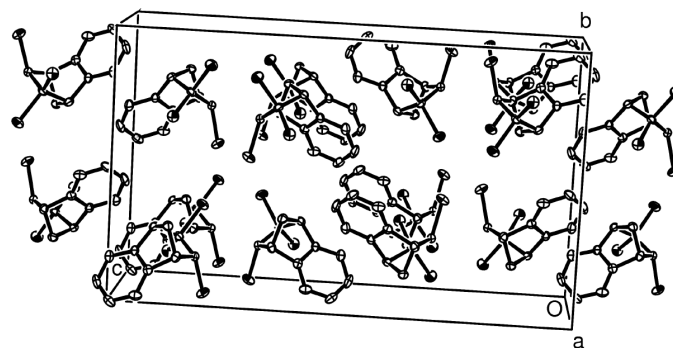


Figure 2

Packing diagram for (3). H atoms have been omitted.

smaller, and the Br2–C11–C10 [116.9 (3)°] and Br2–C11–C7 [112.7 (3)°] angles are larger, than the conventional value of the tetrahedral angle. The C11–C10–Br3 angle [117.0 (3)°] is also larger than the other angles about atom C10. This behaviour appears to be a result of a repulsive interaction between atoms Br2 and Br3. The Br–C bond lengths are nearly equal and average 1.946 (4) Å.

In the molecular packing of (3) (Fig. 2), dipole–dipole and van der Waals interactions are effective.

Experimental

Compound (3) was prepared according to the literature method (Cossu *et al.*, 1997; Altundaş *et al.*, 2002). Compound (1) (200 mg, 0.90 mmol) was dissolved in CCl₄ (80 ml) in a 100 ml two-necked flask, which was equipped with a reflux condenser and an inlet glass tube touching the bottom of the reaction flask. The inlet glass tube was connected to a 2 ml round-bottomed flask, which contained bromine (160 mg, 1.0 mmol). Bromine vapour was obtained by heating the flask to 373 K and was transferred directly to the refluxing solution of (1) in CCl₄ at 350 K in 2 min while stirring magnetically. After stirring at the reaction temperature for 2 min, the solvent was removed under reduced pressure. The oily residue was subjected to column chromatography (silica gel, 90 g), eluting with hexane. The products, (2) (yield 217 mg, 63%), (3) (100 mg, 29%, m.p. 357–358 K) and (4) (28 mg, 8%) were isolated. Recrystallization of compound (3) from ether–hexane (1:3) gave colourless crystals.

Crystal data

C₁₁H₉Br₃
M_r = 380.91
 Orthorhombic, *Pbca*
a = 7.4853 (17) Å
b = 13.449 (3) Å
c = 22.653 (5) Å
V = 2280.5 (9) Å³
Z = 8
D_x = 2.219 Mg m⁻³

Mo Kα radiation
 Cell parameters from 2676 reflections
 $\theta = 3\text{--}25^\circ$
 $\mu = 10.57\text{ mm}^{-1}$
T = 297 (2) K
 Prism, colourless
 0.40 × 0.28 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2690 independent reflections
φ and ω scans	1562 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	$R_{\text{int}} = 0.077$
$T_{\text{min}} = 0.039$, $T_{\text{max}} = 0.225$	$\theta_{\text{max}} = 28.0^\circ$
12 253 measured reflections	$h = -9 \rightarrow 9$
	$k = -17 \rightarrow 17$
	$l = -29 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.066$
 $S = 0.82$
 2690 reflections
 163 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0251P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.0001$
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.62 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none

Table 1

Selected geometric parameters (\AA , $^\circ$).

Br1—C11	1.970 (4)	C6—C7	1.502 (5)
Br2—C11	1.934 (4)	C7—C8	1.550 (6)
Br3—C10	1.935 (4)	C7—C11	1.552 (6)
C1—C6	1.389 (5)	C8—C9	1.524 (6)
C1—C9	1.521 (6)	C9—C10	1.546 (6)
C3—C4	1.368 (7)	C10—C11	1.576 (6)
C2—C1—C9	133.6 (4)	C8—C9—C10	99.2 (4)
C6—C1—C9	106.2 (4)	C9—C10—C11	102.5 (3)
C5—C6—C7	131.8 (4)	C9—C10—Br3	113.5 (3)
C1—C6—C7	107.2 (4)	C11—C10—Br3	117.0 (3)
C6—C7—C8	100.0 (3)	C7—C11—C10	102.9 (3)
C6—C7—C11	107.3 (3)	C7—C11—Br2	112.7 (3)
C8—C7—C11	99.5 (3)	C10—C11—Br2	116.9 (3)
C9—C8—C7	94.6 (3)	C7—C11—Br1	108.9 (3)
C1—C9—C8	100.7 (4)	C10—C11—Br1	109.2 (3)
C1—C9—C10	108.6 (4)	Br2—C11—Br1	106.16 (19)
C6—C1—C9—C8	32.8 (4)	C1—C6—C7—C11	69.4 (4)
C6—C1—C9—C10	-70.9 (4)	C1—C9—C8—C7	-50.7 (4)
C9—C1—C6—C7	1.2 (4)	C8—C9—C10—C11	-39.5 (4)
C1—C6—C7—C8	-34.0 (4)	C7—C11—C10—C9	3.0 (4)

H atoms were located from difference syntheses and refined isotropically. The refined C—H distances are in the range 0.83 (3)–0.98 (4) \AA .

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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