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Key indicators

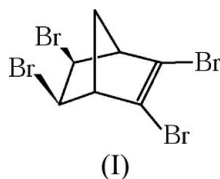
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$
 R factor = 0.048
 wR factor = 0.091
Data-to-parameter ratio = 25.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

2,3,-exo,exo-5,6-Tetrabromobicyclo[2.2.1]-hept-2-ene

The crystal structure of the title compound, $\text{C}_7\text{H}_6\text{Br}_4$, has been determined in the orthorhombic space group $Pnma$. The molecule, consisting of a six-membered ring with four Br atoms and the bridging methylene group, has a boat conformation. The molecule has crystallographic mirror (C_s) symmetry, the mirror plane passing through the atoms of the bridging methylene group.

Comment

When norbornadiene (bicyclo[3.2.1]heptadiene) is converted photochemically to the higher-energy quadricyclane, the stored energy may be released by catalytic reversal of the reaction. Since norbornadiene itself does not undergo efficient valence isomerization upon direct and/or sensitized irradiation, norbornadienes with appropriate chromophores have been synthesized and their photo-isomerization examined (Hirao *et al.*, 1984; Yoshida, 1982; Toda *et al.*, 1982). Tri- and tetrasubstituted norbornadienes have attracted considerable attention because their quadricyclanes may serve as potential solar-energy storage cells, but a convenient preparation of such norbornadienes is still not available (Harel *et al.*, 1987; Maruyama & Tamiaki, 1987; Gaussman & Hershberger, 1987; Nishino *et al.*, 1986; Fife *et al.*, 1985).



Recently, we have succeeded in the preparation of 2,3,5,6-tetrabromonorbornene by the selective bromination of norbornadiene (Tutar *et al.*, 1996; Adam *et al.*, 2002). In this study, we report the molecular and crystal structure of (I).

The molecule of (I) is shown in Fig. 1 and its geometric parameters are listed in Table 1. The X-ray study reveals that the title compound consists of a norbornene skeleton composed of two five-membered rings in envelope conformations; alternatively, it can be described as a six-membered ring with four Br atoms, two of them in *cis* positions at sp^3 C atoms, held in a boat conformation [puckering parameters: $Q = 0.983(6)\text{ \AA}$, $\theta = 90.0(4)$ and $\varphi = 60.0(4)^\circ$; Cremer & Pople, 1975] by a bridging methylene group.

The molecule contains a mirror plane which passes through atoms C4, H4A and H4B and the mid-points of the C1–C1ⁱ [1.539(7) Å] and C3–C3ⁱ bonds [symmetry code: (i) $x, \frac{1}{2} - y, z$]. The C3–C3ⁱ bond of 1.269(9) Å corresponds to a double bond involving two sp^2 C atoms.

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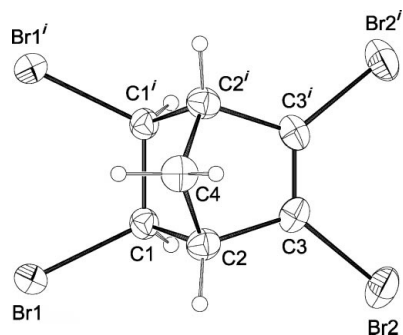


Figure 1

A view of the title compound, with the atom-numbering scheme [symmetry code (i): $x, \frac{1}{2} - y, z$]. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

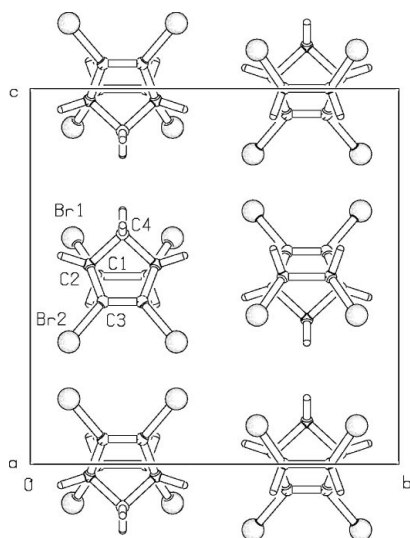


Figure 2

The molecular packing of the title compound, (I), viewed along the *a* axis.

The geometry of (I) is consistent with that reported for other norbornenes. The Br—C bond distances are nearly equal to each other, the average value being 1.910 (6) Å. The Br—C—C bond angles are within the range 110.0 (4)–127.1 (5)°, [average values for related compounds are 111.2 (3)° (Hökelek *et al.*, 1990), 115.1 (6)° (Hökelek *et al.*, 1991), 113.9 (7)° (Hökelek *et al.*, 1998) and 112.6 (7)° (Hökelek *et al.*, 2001)]. The C2—C4—C2ⁱ angle [91.3 (6)°] is very different from the tetrahedral value. In the literature, corresponding angles are reported to be 101.0 (9)° (Büyükgüngör, 1989), 93.3 (8)° (Hökelek *et al.*, 1998), 94.3 (7)° (Akkurt *et al.*, 2000) and 95.9 (9)° (Hökelek *et al.*, 2001).

Experimental

To a solution of 2,2,3,5,6-pentabromonorbornane (1.5 g, 3.05 mmol) in dry and freshly distilled tetrahydrofuran (50 ml) was added potassium *tert*-butoxide solution (0.85 g, 7.63 mmol) in dry and freshly distilled tetrahydrofuran (30 ml). The resulting reaction mixture was magnetically stirred for 12 h at room temperature. The reaction progress was monitored by thin-layer chromatography. When the reaction was complete, the reaction mixture was diluted with water (100 ml) and diethyl ether (100 ml). The organic layer was

washed with water (4 × 50 ml), and dried over MgSO₄. After evaporation of the solvent, the residue was passed through a short silica-gel (15 g) column and eluted with hexane. Recrystallization from CH₂Cl₂–hexane afforded 2,3,5,6-tetrabromo-bicyclo[2.2.1]hept-2-ene, (I), in 90% yield: m.p. 419–419.5 K. ¹H NMR (CDCl₃, 250 MHz): δ 2.25 p.p.m. (*dt*, H₇, *B* side of *AB* system, *J*_{7*ab*} = 12 Hz, *J*_{7₂} = *J*_{2₃} = 4 Hz), 2.4 p.p.m. (*dt*, *B* side of *AB* system), 3.25 p.p.m. (*t*, H₁, H₄), 4.2 (*d*, H₅ and H₆); ¹³C NMR (CDCl₃, 62 MHz): δ 127.8 (C₂, C₃), 61.5 (C₁, C₄), 50.6 (C₅, C₆), 43.5 (C₇).

Crystal data

C₇H₆Br₄
M_r = 409.72
 Orthorhombic, *Pnma*
a = 6.681 (5) Å
b = 12.040 (5) Å
c = 12.326 (5) Å
V = 991.5 (9) Å³
Z = 4
D_x = 2.745 Mg m⁻³

Mo Kα radiation
 Cell parameters from 1296 reflections
 θ = 2.4–29.5°
 μ = 16.17 mm⁻¹
T = 293 K
 Prism, colorless
 0.30 × 0.13 × 0.10 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: refined from Δ*F* (cubic fit to sinθ/λ, 24 parameters; Parkin *et al.*, 1995)
*T*_{min} = 0.057, *T*_{max} = 0.198
 16 499 measured reflections

1330 independent reflections
 813 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.153
 θ_{max} = 29.5°
h = −9 → 9
k = −16 → 16
l = −16 → 16

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.048
wR (*F*²) = 0.092
S = 1.01
 1330 reflections
 53 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + 0.4407P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.83 e Å⁻³
 Δρ_{min} = −0.60 e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0015 (3)

Table 1

Selected geometric parameters (Å, °).

Br1—C1	1.958 (5)	C2—C3	1.535 (9)
Br2—C3	1.862 (6)	C2—C4	1.528 (9)
C1—C2	1.534 (8)	C3—C3 ⁱ	1.269 (9)
C1—C1 ⁱ	1.539 (7)		
Br1—C1—C2	110.0 (4)	C3—C2—C4	101.3 (5)
Br1—C1—C1 ⁱ	116.0 (3)	Br2—C3—C2	125.2 (4)
C1 ⁱ —C1—C2	102.1 (4)	Br2—C3—C3 ⁱ	127.1 (5)
C1—C2—C3	104.8 (5)	C2—C4—C2 ⁱ	91.3 (6)
C1—C2—C4	102.5 (5)		
Br1—C1—C2—C3	168.1 (4)	C1—C2—C3—Br2	−101.2 (5)
Br1—C1—C2—C4	−86.6 (5)	C4—C2—C3—Br2	152.6 (5)
Br1—C1—C1 ⁱ —C2 ⁱ	119.6 (4)	Br2—C3—C3 ⁱ —C2 ⁱ	172.9 (4)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

All H atoms were positioned geometrically at distances of 0.98 (CH) and 0.97 Å (CH₂) and refined using a riding model. The *U*_{iso}(H) values were set to 1.2*U*_{eq}(C) of the carrier atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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