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A 1:1 cocrystal of (1*R*,3*S*,4*S*,6*R*)-1,2,3,4,5,6-hexabromo-1,2,3,4,5,6-hexahydropentalene and (1*R*,2*R*,4*S*,5*S*)-1,2,3,4,5,6-hexabromo-1,2,4,5-tetrahydropentalene

Tuncer Hökelek,[a]* Duygu D. Günbaş,[b] Fatih Algı[c] and Metin Balcı[b]

[a]Department of Physics, Hacettepe University, 06800 Beytepe, Ankara, Turkey, [b]Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey, and [c]Department of Chemistry, Onsekiz Mart University, 17100 Çanakkale, Turkey

Correspondence e-mail:
merzifon@hacettepe.edu.tr

The components of the title compound, $C_8H_6Br_6$ and $C_8H_4Br_6$, are hexa- and tetrabromopentalene derivatives, which were obtained by the treatment of hexahydropentalene with a tenfold excess of bromine. The asymmetric unit consists of two half-molecules. Crystallographic centres of symmetry are located at the mid-points of the central C═C and C—C bonds. The repulsive interactions between the Br atoms may affect the molecular geometry.

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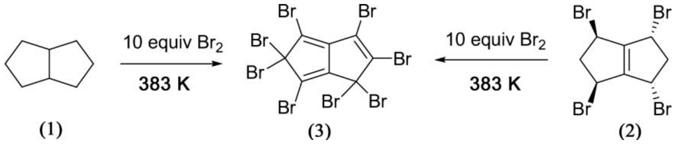
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.018 Å
R factor = 0.123
wR factor = 0.299
Data-to-parameter ratio = 18.5

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

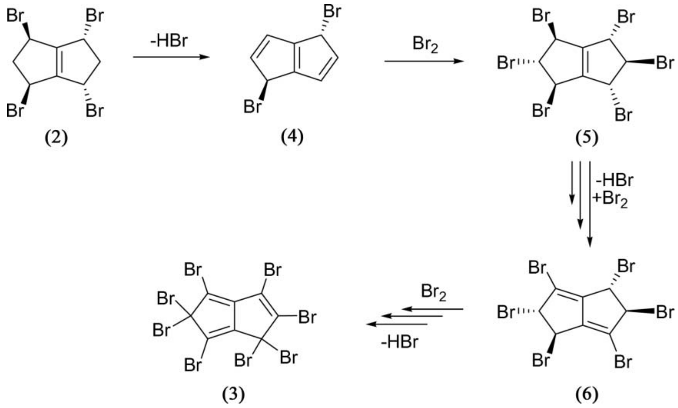
Comment

Although hydrocarbons are readily available and extremely cheap starting materials, they cannot be used in synthetic chemistry without prior activation. The activation of carbon–hydrogen bonds in aliphatic hydrocarbons is difficult to achieve and a challenging process in organic synthesis (Fokin & Schreiner, 2002; Kakiuchi & Chatani, 2003). Despite the fact that radical reactions have a bad reputation for being not particularly selective, novel halogenation methods (Crabtree & Habib, 1991; Jiang *et al.*, 2005; Barluenga *et al.*, 2005) have been changing this picture dramatically over the last decade. Our contribution to this field, exemplified by a series of high-temperature bromination reactions (Daştan & Balcı, 2005; Daştan *et al.*, 1996; Daştan *et al.*, 1994; Tutar *et al.*, 1996; Balcı *et al.*, 1992*a*,*b*; Çakmak & Balcı, 1989), has paved the way for selective functionalization of hydrocarbons (Daştan *et al.*, 1997, 1999).



Very recently, we have reported that thermal bromination of octahydropentalene (1) with four equivalents of bromine furnished tetrabromide (2) with remarkable regio- and stereospecificity (see scheme) [where the starting material (1) does not contain a double bond shared by the two rings] (Günbaş *et al.*, 2005). Furthermore, we found that treatment of both hydrocarbon (1) and tetrabromide (2) with a tenfold excess of bromine resulted in the formation of octabromide (3), and we proposed the plausible intermediacy of penta-, hexa- or heptabromides in view of the formation mechanism of the products (see second scheme).

As a proof of the assumption, we report here the structure of the cocrystal of hexabromides (1*R*,3*S*,4*S*,6*R*)-1,2,3,4,5,6-hexabromo-1,2,3,4,5,6-hexahydropentalene, (5), and (1*R*,2*R*,4*S*,5*S*)-1,2,3,4,5,6-hexabromo-1,2,4,5-tetrahydropentalene, (6).



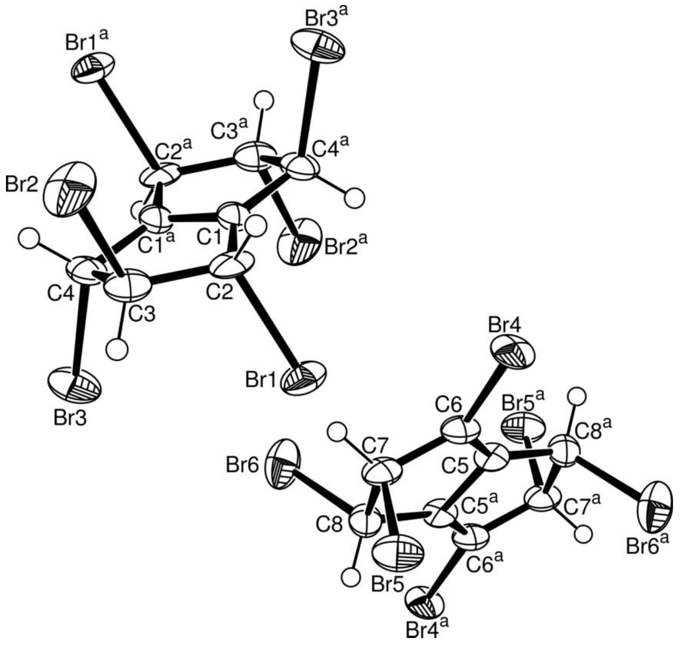


Figure 1

An *ORTEP-3* (Farrugia, 1997) drawing of the title structure, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. For the left-hand molecule, the 'a' superscripts denote the symmetry position $(1 - x, -y, -z)$ and, for the right-hand molecule, $(-x, 1 - y, 1 - z)$.

The asymmetric unit of the title structure consists of one half-molecule of (5) and one half-molecule of (6) (Fig. 1). Crystallographic centres of symmetry are located at the mid-points of the central $C1=C1^{i}$ and $C5-C5^{ii}$ bonds [symmetry codes: (i) $1 - x, -y, -z$; (ii) $-x, 1 - y, 1 - z$].

Rings *A* ($C1^{i}$/C1–C4) and *B* ($C5^{ii}$/C5–C8) are each nearly planar, with maximum deviations of 0.1010 (3) Å (C3) and 0.0581 (2) Å (C8) from the least-squares planes. They form a dihedral angle of 60.2 (5)°. Ring *A* has a local pseudo-mirror plane running through C3 and the midpoint of the $C1=C1^{i}$ bond, while ring *B* does not (Table 1). The Br atoms are displaced on opposite sides of the ring planes as follows: Br1 −1.899 (6), Br2 1.971 (7), Br3 −1.932 (6) (for ring *A*) and Br4 0.021 (7), Br5 −1.843 (5), Br6 1.895 (7) Å (for ring *B*).

The C—C—C bond angles are in the ranges 102.9 (10)–113.7 (13) (for ring *A*) and 103.3 (9)–111.1 (11)° (for ring *B*), with mean values of 107.46 (11) and 107.78 (11)°, respectively. The C—C—Br angles are in the ranges 107.1 (8)–111.0 (8) and 107.4 (8)–125.7 (10)°, for rings *A* and *B*, respectively. The angles C5—C6—Br4 and C7—C6—Br4 are much larger than the other C—C—Br angles (Table 1).

The C—Br bonds are in the ranges 1.972 (12)–1.994 (11) and 1.874 (12)–1.993 (12) Å for the two molecules (Table 1). The C—C single bonds are in the ranges 1.443 (16)–1.532 (18) and 1.464 (18)–1.520 (15) Å, with mean values of 1.494 (16) and 1.467 (17) Å for rings *A* and *B*, respectively.

The repulsive interactions between the Br atoms may affect the molecular structure. Dipole–dipole and van der Waals interactions are effective in the molecular packing (Fig. 2).

Experimental

Bromine (80 mmol, 5 ml) was added dropwise to octahydropentalene (1) (1.0 g, 8 mmol) at 383 K over a period of 3 h with stirring. The resulting solution was stirred at the same temperature for an additional 15 min. After cooling to room temperature, the mixture including unreacted hydrocarbon was treated with CH_2Cl_2 (30 ml) and the solvent was removed by rotary evaporation. Hexane (20 ml) was then added and the mixture was allowed to stand overnight at room temperature to give the octabromide, (3), which was recrystallized from *n*-hexane–CH_2Cl_2 (1:1) (yield 1.6 g, 48%, m.p. 485 K), along with trace amounts of hexabromides, (5), (yield 5 mg, 1%, m.p. 469 K) and (6). The major product is the octabromide (3). The products (5) and (6) are the minor products and formed as intermediates by the formation of octabromide (3) (see second scheme).

Crystal data

$C_8H_6Br_6 \cdot C_8H_4Br_6$
$M_r = 1161.04$
Triclinic, $P\bar{1}$
$a = 8.258$ (2) Å
$b = 8.483$ (2) Å
$c = 10.850$ (5) Å
$\alpha = 72.274$ (3)°
$\beta = 71.128$ (3)°
$\gamma = 69.733$ (2)°
$V = 658.6$ (4) Å^3
$Z = 1$
$D_x = 2.927$ Mg m^{-3}
Cu $K\alpha$ radiation
$\mu = 21.72$ mm^{-1}
$T = 298$ (2) K
Block, colourless
0.15 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non–profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.109$, $T_{max} = 0.113$
2495 measured reflections
2364 independent reflections
2314 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 69.0°$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.123$
$wR(F^2) = 0.299$
$S = 1.36$
2364 reflections
128 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 5.38$ e Å^{-3}
$\Delta\rho_{min} = -2.98$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0054 (10)

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Table 1
Selected geometric parameters (Å, °).

Br1—C2	1.980 (11)	C3—C2	1.532 (18)
Br2—C3	1.972 (12)	C3—C4	1.502 (16)
Br3—C4	1.994 (11)	C4—C1^{i}	1.500 (15)
Br4—C6	1.874 (12)	C5—C5^{ii}	1.41 (2)
Br5—C7	1.987 (12)	C5—C8^{ii}	1.474 (16)
Br6—C8	1.993 (12)	C6—C5	1.349 (16)
C1—C1^{i}	1.37 (2)	C6—C7	1.464 (18)
C1—C2	1.443 (16)	C8—C5^{ii}	1.474 (16)
C1—C4^{i}	1.500 (15)	C8—C7	1.520 (15)
C1^{i}—C1—C2	113.7 (13)	C6—C5—C5^{ii}	109.6 (14)
C1^{i}—C1—C4^{i}	109.4 (12)	C6—C5—C8^{ii}	140.2 (10)
C2—C1—C4^{i}	136.9 (10)	C5^{ii}—C5—C8^{ii}	109.9 (11)
C1—C2—C3	102.9 (10)	C5—C6—C7	111.1 (11)
C1—C2—Br1	108.2 (8)	C5—C6—Br4	125.7 (10)
C3—C2—Br1	111.0 (8)	C7—C6—Br4	123.0 (9)
C4—C3—C2	107.6 (10)	C6—C7—C8	105.0 (10)
C4—C3—Br2	107.1 (8)	C6—C7—Br5	108.9 (9)
C2—C3—Br2	107.6 (7)	C8—C7—Br5	108.7 (8)
C1^{i}—C4—C3	103.7 (9)	C5^{ii}—C8—C7	103.3 (9)
C1^{i}—C4—Br3	108.1 (7)	C5^{ii}—C8—Br6	107.4 (8)
C3—C4—Br3	109.4 (8)	C7—C8—Br6	108.0 (8)
C1^{i}—C1—C2—C3	−10.0 (15)	C7—C6—C5—C5^{ii}	2.1 (17)
C4—C3—C2—C1	15.9 (11)	C5—C6—C7—C8	−7.6 (14)
C2—C3—C4—C1^{i}	−15.9 (12)	C5^{ii}—C8—C7—C6	9.7 (13)

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x, -y+1, -z+1$.

The highest peak and deepest hole in the final difference electron-density map were located 1.21 and 1.23 Å, respectively, from atoms Br1 and Br3. H atoms were positioned geometrically, with C—H = 0.98 Å, and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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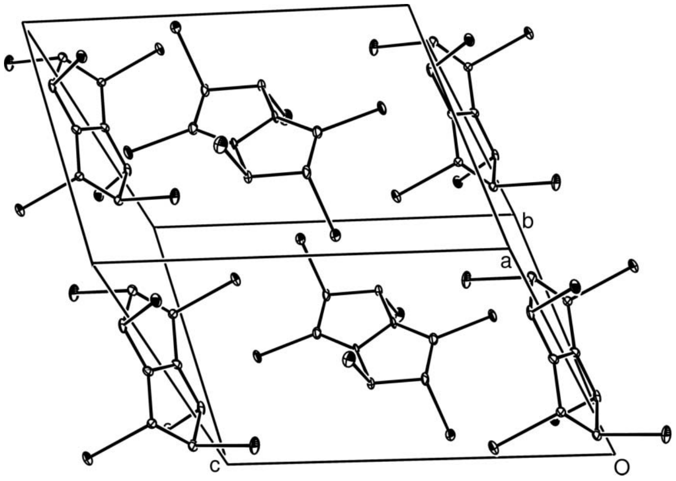

Figure 2
A packing diagram. H atoms have been omitted.

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