

1,3-Dibromoazulene

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Key indicators

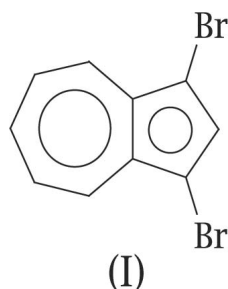
Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}–\text{C}) = 0.002$ Å
 R factor = 0.016
 wR factor = 0.046
Data-to-parameter ratio = 16.1

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

In the structure of 1,3-dibromoazulene, $\text{C}_{10}\text{H}_6\text{Br}_2$, the planar molecule sits on a crystallographic mirror plane. The Br atoms are attached to the five-membered ring adjacent to the ring fusion. Head-to-tail charge–charge interactions due to partial positive charges on ring H atoms and partial negative charges within the aromatic ring system attract adjacent 1,3-dibromoazulene molecules together. This causes them to arrange themselves in a zigzag pattern that allows close packing of the oppositely charged groups.

Comment

Polyazulene and its derivatives are of scientific and practical interest, because they are highly conjugated hydrocarbons that can be made electrically conductive and highly paramagnetic (Wang *et al.*, 2003; Wang, Lai & Han, 2004; Wang, Xu *et al.*, 2004). One important physical property of a polyazulene that can be tailored is its solubility, which requires appropriate derivatization of the azulene monomer unit. Halogenated azulenes are known to be useful as monomeric building blocks for polyazulene and its derivatives (Wang & Lai, 2003). They are also precursors for the synthesis of dumbbell-shaped alkyl-bridged diazulenyl compounds (Elwahi, 2002). The crystal structures of aromatic halogenated azulenes, however, have not been described in the literature to date. This report of the crystal structure of 1,3-dibromoazulene, (I), and a related report on 1,3-diiodoazulene (Chen *et al.*, 2005), are a portion of our continuing work involving the preparation and analysis of electrically conductive azulene-containing polymers.



Pertinent to this report is the crystal structure of the parent azulene (Robertson *et al.*, 1962), which crystallizes in the monoclinic space group $P2_1/a$. Other related structures, also having monoclinic space groups, include two variously substituted azulenes (Lohr *et al.*, 1984; Wong *et al.*, 1984) which both crystallize in the space group $P2_1/c$, and a fused bis-azulene (Vogel *et al.*, 1984) found in the space group $P2_1/n$. This is in contrast with the orthorhombic structure of the dibromoazulene presented here. The related diiodoazulene is

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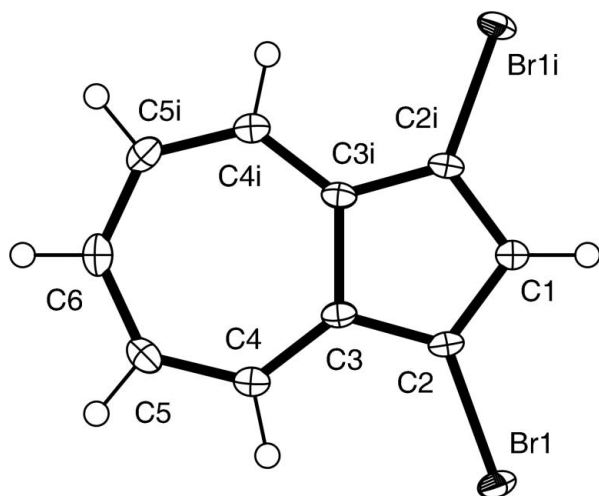


Figure 1

A perspective view of (I) with the atom-numbering scheme [symmetry code: (i) $x, -y + \frac{3}{2}, z$]. Displacement ellipsoids are drawn at the 50% probability level in all figures.

also monoclinic, but is found in the space group Cc (Chen *et al.*, 2005).

A calculation comparing the parent azulene with dibromoazulene [HF/6-31 G(d,p) level, full natural bond orbital analysis; Frisch *et al.*, 2003] indicates that the presence of the Br atoms substantially polarizes the ring current toward the five-membered ring, with significant charge on the C atoms attached to the Br atoms. The calculation also helps to explain the head-to-ring and bromine-to-ring interactions observed in the crystal structure as being of a dipolar (or charge-charge) nature. Finally, the Br atoms have very little calculated charge, which may account for the short intermolecular Br...Br distance observed in the solid state.

In the crystal structure of (I), individual molecules lie on a crystallographic mirror plane that passes through atoms C1 and C6, bisecting the fused five- and seven-membered rings. The rings are planar, but stack in an offset herring-bone pattern that apparently maximizes the dipolar interactions between molecules in the same stack. The distance between atom C6 of one molecule and atoms C3 and C3' of the ring fusion bond of a neighboring molecule in the same stack is about 2.76 Å (Fig. 2), indicating a strong interaction between the positively charged seven-membered ring and the negatively charged five-membered ring. The only significant close contacts between adjacent stacks are intermolecular Br...Br interactions [3.549 (2) Å].

Experimental

Compound (I) was obtained by reacting 1.0 equivalent of azulene with 2.1 equivalents of *N*-bromosuccinimide in dichloromethane at room temperature overnight (Elwahi, 2002). The solvent was then removed under vacuum below 273 K. Purification was accomplished by column chromatography, using neutral alumina as substrate and hexanes as eluent. Dark-blue blocks were obtained by slow evaporation of the solvent.

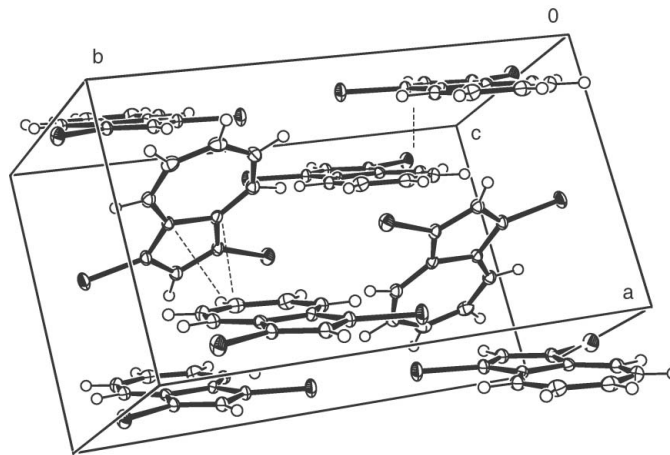


Figure 2

A view of the packing of (I), showing the zigzag stack of the dibromo-substituted azulene molecules. Charge-charge interactions of parallel [3.24 (1) Å] and herringbone [3.36 (1) Å] geometry are indicated by dashed lines.

Crystal data

$C_{10}H_6Br_2$
 $M_r = 285.97$
 Orthorhombic, $Pnma$
 $a = 8.3575$ (14) Å
 $b = 15.114$ (2) Å
 $c = 7.1840$ (12) Å
 $V = 907.4$ (2) Å³
 $Z = 4$
 $D_x = 2.093$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 4195 reflections
 $\theta = 2.7$ – 26.0°
 $\mu = 8.87$ mm⁻¹
 $T = 100$ (2) K
 Block, blue
 $0.28 \times 0.20 \times 0.20$ mm

Data collection

Bruker APEX diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{min} = 0.120$, $T_{max} = 0.170$
 7311 measured reflections
 931 independent reflections

870 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$
 $\theta_{max} = 26.0^\circ$
 $h = -10 \rightarrow 10$
 $k = -18 \rightarrow 18$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.016$
 $wR(F^2) = 0.046$
 $S = 0.96$
 931 reflections
 58 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.6P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.48$ e Å⁻³
 $\Delta\rho_{min} = -0.36$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Br1—C2	1.879 (2)	C3—C3 ⁱ	1.499 (2)
C1—C2	1.399 (2)	C4—C5	1.392 (2)
C2—C3	1.396 (2)	C5—C6	1.395 (2)
C3—C4	1.386 (2)		
C2 ⁱ —C1—C2	107.0 (2)	C4—C3—C3 ⁱ	127.6 (1)
C3—C2—C1	110.9 (2)		
Br1—C2—C3—C3 ⁱ	−179.4 (1)		

Symmetry codes: (i) $x, -y + \frac{3}{2}, z$.

All H atoms were included in calculated positions using a riding model, with C—H = 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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