

1,3-Diiodoazulene

Xue-Yi Chen,^a Jerry R. Dias,^a
Doug R. Powell,^b J. David Van
Horn^{a*} and Thomas C.
Sandreczki^a

^aDepartment of Chemistry, University of Missouri–Kansas City, 5110 Rockhill Road, Kansas City, MO 64110, USA, and ^bDepartment of Chemistry, University of Kansas, Mallott Hall, Room 6044, 1251 Wescoe Hall Drive, Lawrence, KS 66045-7582, USA

Correspondence e-mail: vanhornj@umkc.edu

Key indicators

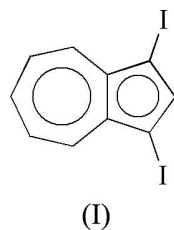
Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}–\text{C}) = 0.007$ Å
 R factor = 0.021
 wR factor = 0.055
Data-to-parameter ratio = 17.5

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-diiodoazulene, $\text{C}_{10}\text{H}_6\text{I}_2$, as expected, the molecule is planar. Also observed are short contacts between I atoms and between I and ring C atoms. The crystal structure of this compound exhibits two sets of parallel layers, nearly perpendicular to each other. The layers are formed by charge–charge interactions between some I atoms and nearby seven-membered rings of molecules in an adjacent layer. The packing is also affected by attractive dispersion forces between I atoms in adjacent layers.

Comment

Polyazulene and its derivatives are of scientific and practical interest, because they are highly conjugated aromatic hydrocarbons that can be made electrically conductive and highly paramagnetic (Wang, Lai *et al.*, 2003; Wang & Lai, 2003; Wang, Lai & Han, 2003, 2004; Wang, Xu *et al.*, 2004) Halogenated azulenes are known to be useful as monomeric building blocks for polyazulene and its derivatives (Wang & Lai, 2003). The crystal structures of aromatic halogenated azulenes, however, have not been described in the literature to date. This report on the crystal structure 1,3-diiodoazulene, (I), is a portion of our continuing work involving the preparation and analysis of electrically conductive azulene-containing polymers.



Compound (I) crystallizes in a monoclinic space group (Cc), as do some related compounds. For instance, the parent azulene (Robertson *et al.*, 1962) crystallizes in the monoclinic space group $P2_1/a$, and other variously substituted or fused azulenes (Lohr *et al.*, 1984; Wong *et al.*, 1984; Vogel *et al.*, 1984) are also found in monoclinic space groups. This is in contrast with the orthorhombic structure of the dibromoazulene presented in a separate report (Chen *et al.*, 2005).

The distance from atom I2 of one molecule to atoms C4 and C10 of neighboring molecules is about 3.45 Å (Fig. 2), indicating an interaction between the positively charged seven-membered ring and the I atom. No five-membered to seven-membered ring interactions occur, due to the large size of the I atoms. Additionally, significant attractive interactions occur between two I atoms of neighboring molecules, resulting in a short contact between them [3.83 (1) Å]. Therefore, the unit

Received 22 February 2005

Accepted 4 March 2005

Online 18 March 2005

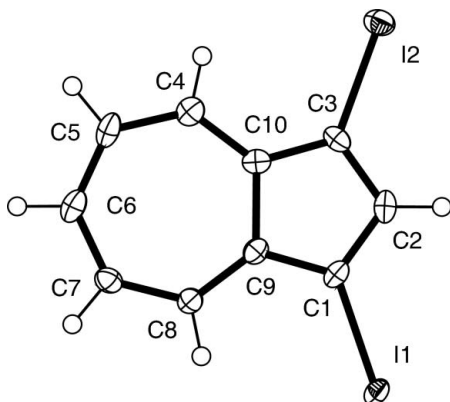


Figure 1
A perspective view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

cell volume for 1,3-diiodoazulene [984.7 (6) Å³] is only 8% larger than that of 1,3-dibromoazulene [907.4 (2) Å³; Chen *et al.*, 2005].

Experimental

Compound (I) was obtained by reacting 1.0 equivalent of azulene with 2.1 equivalents of *N*-iodosuccinimide 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 to black crystalline blocks were obtained by slow evaporation of the solvent.

Crystal data

C₁₀H₆I₂
M_r = 379.95
 Monoclinic, *C*₂
a = 7.487 (3) Å
b = 23.287 (9) Å
c = 5.675 (2) Å
 β = 95.579 (7)°
V = 984.7 (6) Å³
Z = 4

D_x = 2.563 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3884 reflections
 θ = 2.9–26.0°
 μ = 6.33 mm⁻¹
T = 100 (2) K
 Block, black
 0.25 × 0.11 × 0.06 mm

Data collection

Bruker APEX diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 T_{\min} = 0.301, T_{\max} = 0.703
 5207 measured reflections
 1903 independent reflections

1896 reflections with $I > 2\sigma(I)$
 R_{int} = 0.013
 θ_{max} = 26.0°
 h = -9 → 9
 k = -25 → 28
 l = -6 → 6

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.021
 $wR(F^2)$ = 0.055
 S = 1.01
 1903 reflections
 109 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.044P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}}$ = 0.001
 $\Delta\rho_{\text{max}}$ = 0.89 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.57 e Å⁻³
 Extinction correction: none
 Absolute structure: Flack (1983), with 935 Friedel pairs
 Flack parameter: 0.00 (4)

Table 1

Selected geometric parameters (Å, °).

I1—C1	2.076 (5)	C6—C7	1.374 (8)
I2—C3	2.069 (5)	C7—C8	1.403 (8)
C1—C2	1.395 (8)	C8—C9	1.381 (7)
C1—C9	1.401 (7)	C9—C10	1.501 (7)
C5—C6	1.397 (8)		
C2—C1—C9	109.9 (4)	C6—C7—C8	129.4 (5)
C9—C1—I1	124.6 (4)	C9—C8—C7	128.7 (5)
C3—C2—C1	108.8 (4)	C8—C9—C10	127.5 (5)
C10—C3—I2	125.5 (4)	C1—C9—C10	105.5 (5)
C7—C6—C5	130.0 (5)		
I1—C1—C2—C3	-177.7 (4)	I1—C1—C9—C10	177.5 (3)
C1—C2—C3—I2	177.5 (3)		

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; 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*.

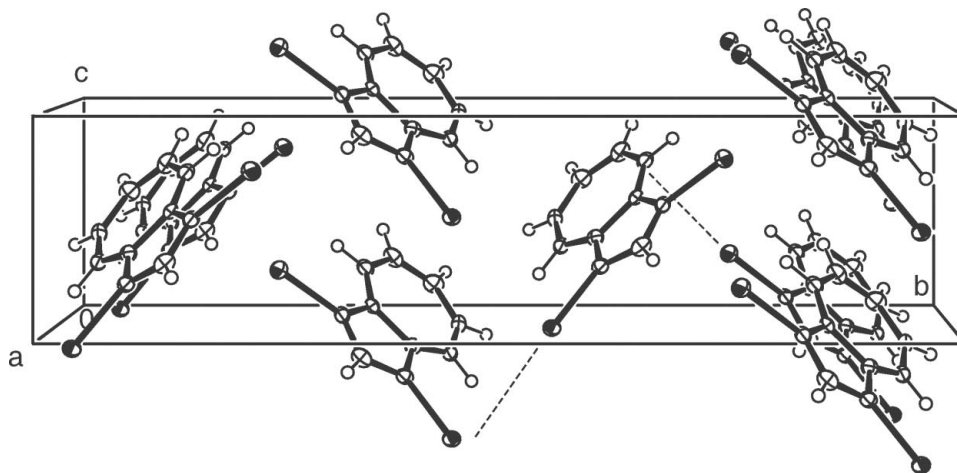


Figure 2
A view of the packing of (I), showing the interleaved parallel layers nearly perpendicular [82 (1)°] to each other. Short intermolecular contacts between I atoms [I...I 3.83 (1) Å] and between I and C atoms [I...C 3.45 (1) Å] are indicated by dashed lines.

The authors thank the National Science Foundation (grant No. CHE-0079282) and the University of Kansas for funds to acquire the diffractometer and computers used in this work.

References

- Bruker (1998). *SMART* (Version 5.625), *SAINTE* (Version 6.22) and *SHELXTL* (Version 6.12). Bruker AXS, Inc., Madison, Wisconsin, USA.
- Bruker (2002). *SADABS* (Version 2.04). Bruker AXS, Inc., Madison, Wisconsin, USA.
- Chen, X.-Y., Dias, J. R., Powell, D. R., Van Horn, J. D., Sandreczki, T. C. (2005). *Acta Cryst.* **E61**, o941–o943.
- Elwahy, A. H. M. (2002). *Tetrahedron Lett.* **43**, 711–714.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Lohr, H.-G., Engel, A., Josel, H.-P., Vogtle, F., Schuh, W. & Puff, H. (1984). *J. Org. Chem.* **49**, 1621–1627.
- Robertson, J. M., Shearer, H. M. M., Sim, G. A. & Watson, D. G. (1962). *Acta Cryst.* **15**, 1–8.
- Vogel, E., Wieland, H., Schmalstieg, L. & Lex, J. (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 717–719.
- Wang, F. & Lai, Y.-H. (2003). *Macromolecules*, **36**, 536–538.
- Wang, F., Lai, Y.-H. & Han, M.-Y. (2003). *Org. Lett.* **5**, 4791–4794.
- Wang, F., Lai, Y.-H. & Han, M.-Y. (2004). *Macromolecules*, **37**, 3222–3230.
- Wang, F., Lai, Y.-H., Kocherginsky, N. M. & Koteski, Y. Y. (2003). *Org. Lett.* **5**, 995–998.
- Wang, W., Xu, J., Lai, Y.-H. & Wang, F. (2004). *Macromolecules*, **37**, 3546–3553.
- Wong, H. N. C., So, K. P. & Mak, T. C. W. (1984). *Z. Kristallogr.* **169**, 117–125.