IUCrData

ISSN 2414-3146

Received 8 July 2019
Accepted 11 July 2019

Edited by M. Zeller, Purdue University, USA

Keywords: crystal structure; solvate; C—I$\cdots\pi$ interactions.

CCDC reference: 1940085

Structural data: full structural data are available from iucrdata.iucr.org

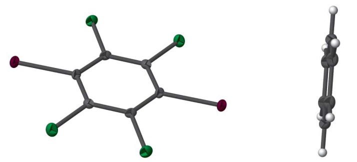
1,2,4,5-Tetrachloro-3,6-diiodobenzene benzene monosolvate

Eric Bosch*

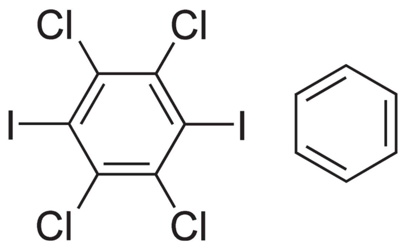
Department of Chemistry, Missouri State University, 901 South National Avenue, Springfield MO 65804 , USA. *Correspondence e-mail: ericbosch@missouristate.edu

The title compound, $C_6Cl_4I_2 \cdot C_6H_6$, crystallizes from benzene solution as cube-shaped crystals in the triclinic space group $P\overline{1}$ with $Z = 1$. The asymmetric unit of the crystal structure contains one half of each molecule. In the crystal, the benzene ring is almost orthogonal to the perhalobenzene ring and the molecules are linked by C—I$\cdots\pi$ interactions, with a close contact between the iodine atom and the benzene ring of 3.412 (1) Å.

3D view



Chemical scheme



Structure description

Halogen bonding, the attractive interaction between the electropositive σ-hole on a bonded halogen, commonly iodine, and a Lewis base, has been widely used in the supramolecular association of multi-component systems (Cavallo *et al.*, 2016). With respect to iodobenzene, it has been established that the addition of fluorine atoms to the benzene ring enhances the σ-hole on iodine resulting in stronger attractions between the components (Präsang *et al.*, 2009). Surprisingly, the application of iodoperchlorobenzenes had not been reported until we reported that the co-crystallization of 1,2,4,5-tetrachloro-3,6-diiodobenzene with 1,2-dipyridylethene resulted in a halogen-bonded co-crystal in which the alkenes were oriented such that they underwent photo-induced 2 + 2 cycloaddition (Bosch *et al.*, 2019). After preparation of 1,2,4,5-tetrachloro-3,6-diiodobenzene, recrystallization from benzene provided clear, colourless cube-shaped crystals that lost lustre and became opaque several hours after removal from the mother liquor. The crystal structure revealed that the cube-shaped crystals represented a 1:1 benzene solvate.

The asymmetric unit comprises one half of the tetrachlorodiiodobenzene and one half of the benzene molecule with a dihedral angle between the rings of 85.89 (16)°, as shown in Fig. 1. The closest contact between the tetrachlorodiiodobenzene and the benzene is between the iodine atom and C4 with a distance of 3.434 (2) Å. Indeed the C1—I1$\cdots$C4

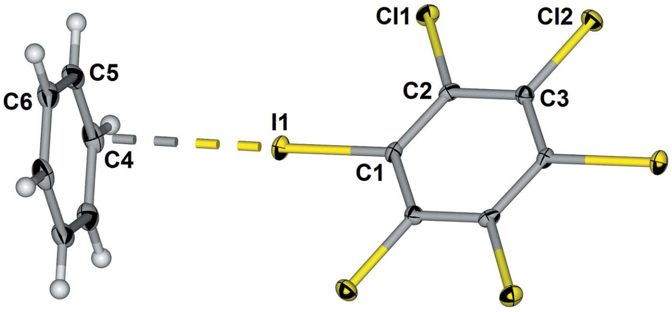


Figure 1
The asymmetric unit of the title solvate showing the atom-numbering scheme. Displacement ellipsoids of non-hydrogen atoms are drawn at the 50% level while H atoms are shown as circles of arbitrary size. The intermolecular C—I$\cdots\pi$ contact is shown as a dashed line.

bond angle is almost linear at 178.09 (6)°. This interaction is highlighted in the two Hirshfeld surface plots in Fig. 2 (Turner *et al.*, 2017). The C—I$\cdots\pi$ interactions form a stepped chain of alternating tetrachlorodiiodobenzene and benzene molecules (Fig. 3) with adjacent tetrachlorodiiodobenzene molecules slip-stacked with a centroid–centroid distance of 5.4399 (10) Å and perpendicular distance between the perhalobenzene planes of 3.6607 (7) Å (Spek, 2015).

Synthesis and crystallization

1,2,4,5-Tetrachloro-3,6-diiodobenzene was prepared by the reaction of 1,2,4,5-tetrachlorobenzene with iodine and sodium metaperiodate in concentrated sulfuric acid. Cube-shaped crystals of the title solvate were obtained on recrystallization from benzene solution. Crystallization from mesitylene, chloroform or dichloromethane yielded block-shaped crystals with structures similar to that previously reported (Reddy *et al.*, 2006).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

We thank the Missouri State University Provost Incentive Fund that funded the purchase of the X-ray diffractometer.

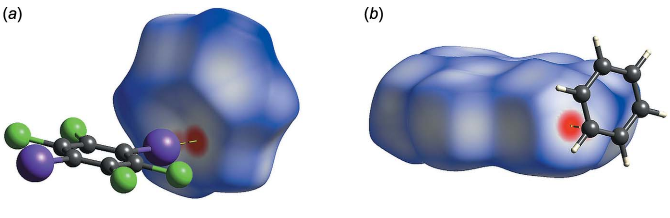


Figure 2
Two views of the Hirshfeld surface of the title solvate highlighting the short contact between I1 and C4 with the halobenzene shown as a ball and stick model in (*a*) and the benzene ring shown as a ball and stick model in (*b*).

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_6Cl_4I_2{\cdot}C_6H_6$
M_r	545.77
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	5.4399 (4), 6.3599 (4), 11.0232 (8)
α, β, γ (°)	96.702 (1), 92.728 (1), 98.599 (1)
V (Å^3)	373.69 (5)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.90
Crystal size (mm)	0.39 × 0.12 × 0.05
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
$T_{\min}$, $T_{\max}$	0.611, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4913, 1668, 1634
R_{int}	0.018
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.644
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.013, 0.032, 1.09
No. of reflections	1668
No. of parameters	82
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.46, −0.39

Computer programs: *SMART* and *SAINT* (Bruker, 2014), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *X-SEED* (Barbour, 2001).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.

Bosch, E., Kruse, S. J., Krueger, H. R. Jr & Groeneman, R. H. (2019). *Cryst. Growth Des.* **19**, 3092–3096.

Bruker (2014). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cavallo, G., Metrangolo, P., Milani, R., Pilati, T., Priimagi, A., Resnati, G. & Terraneo, G. (2016). *Chem. Rev.* **116**, 2478–2601.

Präsang, C., Whitwood, A. C. & Bruce, D. W. (2009). *Cryst. Growth Des.* **9**, 5319–5326.

Reddy, C. M., Kirchner, M. T., Gundakaram, R. C., Padmanabhan, K. A. & Desiraju, G. R. (2006). *Chem. Eur. J.* **12**, 2222–2234.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2015). *Acta Cryst.* C**71**, 9–18.

Turner, M. J., Mckinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. The University of Western Australia.

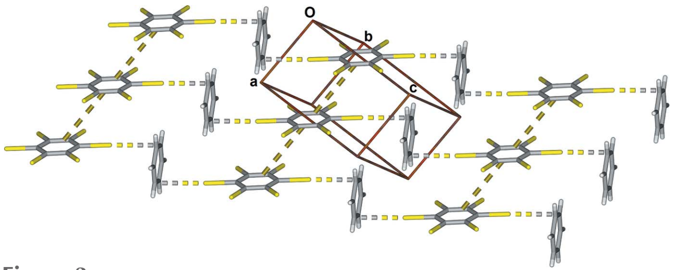


Figure 3
Partial view of the crystal structure of the title solvate showing the stepped chain formed by the C—I$\cdots\pi$ interactions and also showing the offset π-stacking of the 1,4-diiodotetrachlorobenzene molecules.

full crystallographic data

IUCrData (2019). **4**, x190993 [https://doi.org/10.1107/S2414314619009933]

1,2,4,5-Tetrachloro-3,6-diiodobenzene benzene monosolvate

Eric Bosch

1,2,4,5-Tetrachloro-3,6-diiodobenzene benzene monosolvate

Crystal data

$C_6Cl_4I_2{\cdot}C_6H_6$
$M_r = 545.77$
Triclinic, $P\overline{1}$
$a = 5.4399\ (4)$ Å
$b = 6.3599\ (4)$ Å
$c = 11.0232\ (8)$ Å
$\alpha = 96.702\ (1)°$
$\beta = 92.728\ (1)°$
$\gamma = 98.599\ (1)°$
$V = 373.69\ (5)$ Å^3
$Z = 1$
$F(000) = 252$
$D_x = 2.425$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4302 reflections
$\theta = 3.3–27.3°$
$\mu = 4.90$ mm^{-1}
$T = 100$ K
Cut cube, colourless
0.39 × 0.12 × 0.05 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3660 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
$T_{\min} = 0.611$, $T_{\max} = 1.000$
4913 measured reflections
1668 independent reflections
1634 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 27.3°$, $\theta_{\min} = 1.9°$
$h = -7 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.013$
$wR(F^2) = 0.032$
$S = 1.09$
1668 reflections
82 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0129P)^2 + 0.2107P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.63204 (2)	0.24241 (2)	0.70975 (2)	0.01586 (5)
Cl1	0.70962 (8)	0.35540 (7)	0.42245 (4)	0.01743 (9)
C1	0.8497 (3)	0.0970 (3)	0.58350 (15)	0.0125 (3)
Cl2	1.04287 (8)	0.14760 (7)	0.24148 (4)	0.01843 (9)
C2	0.8716 (3)	0.1608 (3)	0.46708 (16)	0.0130 (3)
C3	1.0207 (3)	0.0648 (3)	0.38431 (16)	0.0127 (3)
C4	0.2926 (4)	0.4936 (3)	0.92088 (17)	0.0220 (4)
H4	0.150280	0.488464	0.866558	0.026*
C5	0.4738 (4)	0.6732 (3)	0.93667 (18)	0.0216 (4)
H5	0.455940	0.791629	0.893655	0.026*
C6	0.6826 (4)	0.6801 (3)	1.01573 (18)	0.0217 (4)
H6	0.808105	0.803023	1.026540	0.026*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01473 (7)	0.01688 (7)	0.01605 (7)	0.00549 (4)	0.00276 (4)	−0.00209 (4)
Cl1	0.0194 (2)	0.01586 (19)	0.0194 (2)	0.00981 (16)	0.00007 (16)	0.00377 (15)
C1	0.0112 (7)	0.0113 (7)	0.0143 (8)	0.0021 (6)	0.0016 (6)	−0.0017 (6)
Cl2	0.0233 (2)	0.0205 (2)	0.0141 (2)	0.00780 (16)	0.00371 (16)	0.00617 (16)
C2	0.0122 (7)	0.0100 (7)	0.0170 (8)	0.0031 (6)	−0.0016 (6)	0.0017 (6)
C3	0.0129 (8)	0.0132 (8)	0.0117 (7)	0.0014 (6)	−0.0004 (6)	0.0013 (6)
C4	0.0160 (8)	0.0363 (11)	0.0149 (8)	0.0092 (8)	0.0013 (7)	0.0019 (7)
C5	0.0240 (9)	0.0251 (9)	0.0182 (9)	0.0086 (8)	0.0063 (7)	0.0052 (7)
C6	0.0192 (9)	0.0257 (10)	0.0191 (9)	0.0015 (7)	0.0050 (7)	−0.0008 (7)

Geometric parameters (Å, º)

I1—C1	2.0922 (17)	C4—C5	1.381 (3)
Cl1—C2	1.7254 (17)	C4—C6^{ii}	1.394 (3)
C1—C2	1.396 (2)	C4—H4	0.9500
C1—C3^{i}	1.400 (2)	C5—C6	1.390 (3)
Cl2—C3	1.7215 (17)	C5—H5	0.9500
C2—C3	1.397 (2)	C6—H6	0.9500
C2—C1—C3^{i}	118.86 (15)	C5—C4—C6^{ii}	120.31 (18)
C2—C1—I1	121.01 (12)	C5—C4—H4	119.8
C3^{i}—C1—I1	120.13 (12)	C6^{ii}—C4—H4	119.8
C1—C2—C3	120.44 (15)	C4—C5—C6	119.78 (18)
C1—C2—Cl1	120.37 (13)	C4—C5—H5	120.1
C3—C2—Cl1	119.17 (13)	C6—C5—H5	120.1
C2—C3—C1^{i}	120.70 (16)	C5—C6—C4^{ii}	119.90 (19)
C2—C3—Cl2	119.10 (13)	C5—C6—H6	120.0
C1^{i}—C3—Cl2	120.21 (13)	C4^{ii}—C6—H6	120.0

Symmetry codes: (i) $-x+2, -y, -z+1$; (ii) $-x+1, -y+1, -z+2$.