organic papers

1,2,4,5-Tetraiodobenzene

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The title compound, $C_6H_2I_4$, has crystallographically exact C_i and approximate D_{2h} molecular symmetry. Two half-molecules comprise the asymmetric unit. The molecules are stacked along the c axis and neigbouring stacks are connected *via* weak I···I intermolecular interactions.

Comment

Analysis of the electronic structure of some iodobenzene molecules has revealed the existence of intramolecular steric repulsion and through-space interactions between vicinal iodine atoms (Cvitas *et al.*, 1977; Novak *et al.*, 2002). We show that these non-bonding interactions are also reflected in the molecular structure of 1,2,4,5-tetraiodobenzene, (I), which has vicinal iodine atoms. Comparison of the endocyclic *ipso* C—C—C angles in iodobenzene (121.2°; Merz, 2006) and in 1,3,5-triiodobenzene (122°; Margraf & Bats, 2006) with the corresponding angles in (I) clearly demonstrates that these angles in (I) are reduced. The endocyclic *ipso* angles in (I) span the range 119.2 (4)–120.7 (4)°. Although the steric repulsions in (I) are not very pronounced because each iodine has only a single vicinal iodine as its neighbour, the effect is observable. The reduction of the endocyclic angle is a consequence of the outward movement of iodine atoms as a result of steric repulsion.

(I)
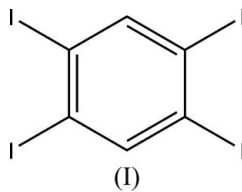
The molecules of (I) are planar and each molecule has a crystallographic centre of symmetry. The crystal packing is dominated by pairs of crystallographically distinct molecules (Fig. 1) of which there are two pairs per unit cell. The molecules are stacked along the c axis (Fig. 2). Neighbouring stacks are connected *via* weak I···I intermolecular interactions. The observed short I···I contacts between molecules from different stacks are 3.783 (5) Å and the interplanar distance between the molecules in the same stack is 3.683 (6) Å. The length of the intermolecular I···I short contacts in (I) is significantly shorter than in iodobenzene (4.093 Å) or the sum of iodine van der Waals radii (4.30 Å). Even shorter intramolecular I···I contacts (3.54 and 3.61 Å) have been observed in 1,8-diiodonaphthalene and 1,10-diiodophenanthrene (Bock *et al.*, 1998), in which I atoms are displaced out of the aromatic plane. This suggests that the

length of these contacts is unlikely to be influenced by the π–π interactions between the aromatic systems.

Experimental

The synthesis of 1,2,4,5-tetraiodobenzene was carried out according to the procedure reported previously by Novak *et al.* (2002). Single crystals were obtained by evaporation of a solution of (I) in a mixture of pyridine and ethanol.

Crystal data

$C_6H_2I_4$	$Z = 4$
$M_r = 581.68$	$D_x = 3.739$ Mg m^{-3}
Monoclinic, $P2/c$	Mo $K\alpha$ radiation
$a = 17.8144\ (8)$ Å	$\mu = 12.00$ mm^{-1}
$b = 7.4999\ (8)$ Å	$T = 223\ (2)$ K
$c = 7.9125\ (8)$ Å	Cut plate, colourless
$\beta = 102.203\ (2)°$	$0.40 \times 0.10 \times 0.08$ mm
$V = 1033.27\ (15)$ Å^3	

Data collection

Bruker SMART CCD area detector diffractometer	8332 measured reflections
φ and ω scans	3006 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	2485 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.078$
$T_{min} = 0.129$, $T_{max} = 0.381$	$\theta_{max} = 30.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rho_{max} = 1.47$ e Å^{-3}
3006 reflections	$\Delta\rho_{min} = -1.84$ e Å^{-3}
92 parameters	Extinction correction: *SHELXL97*
H-atom parameters constrained	Extinction coefficient: 0.0040 (3)

H atoms were positioned geometrically (C—H = 0.94Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. The highest peak is located 1.03 Å from atom I4 and the deepest hole 0.70 Å from atom I6.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SHELXTL* (Sheldrick, 1997*b*) and *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.
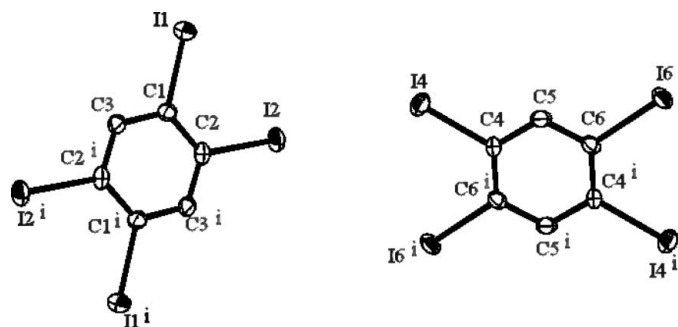
Figure 1
The molecular structure of (I), with displacement parameters drawn at the 50% probability level. H atoms have been omitted. The two crystallographically independent molecules in the unit cell are shown on the left- (*a*) and right-hand (*b*) sides of the figure. Crystallographically equivalent atoms in the two molecules are given as follows: (*a*) C1^i, C2^i, C3^i, I1^i, I2^i; symmetry code: (i) $-x$, $-y + 1$, $-z + 1$; and (*b*) C4^i, C5^i, C6^i, I3^i, I4^i; symmetry code: (i) $-x + 1$, $-y + 2$, $-z + 1$.
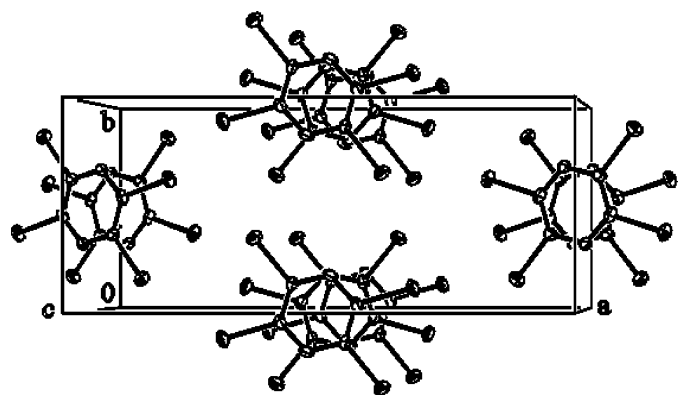

Figure 2
The packing of (I), viewed down the *c* axis. H atoms have been omitted.

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