Triphenyl(3,4,5-triiodophenyl)-methane

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The crystal structure of the title compound, alternatively called 1,2,3-triiodo-5-(triphenylmethyl)benzene, $C_{25}H_{17}I_3$, is analysed in terms of $I \cdots I$ and $I \cdots \pi$ interactions and the herring-bone T motif between phenyl groups. There are two molecules in the asymmetric unit, denoted A and B. Inversion-related A molecules are connected via an $I \cdots \pi$ interaction (3.641 Å, to a C—C bond mid-point) to form an $I \cdots \pi$ dimer, and these dimers are connected through symmetry-independent B molecules via $I \cdots I$ [3.5571 (15) Å] and $I \cdots \pi$ (3.561 Å, to a C—C bond mid-point) interactions.

Comment

The Cl atom is a well known steering group in crystal engineering (Sarma & Desiraju, 1986). Halogenated derivatives of tetraphenylmethane, tetrakis(4-bromophenyl)methane (Reddy et al., 1996) and tetrakis(4-iodophenyl)methane (Anthony et

al., 1998) form diamondoid networks mediated by the halogen tetramer synthon. In the crystal structure of (4-iodophenyl)-triphenylmethane, molecules are connected via an $I \cdots \pi$ interaction [$I \cdots$(phenyl centroid) = 3.747 Å and 146.6°] to form a zigzag network (Thaimattam et al., 1998). The crystal structure of 3,4,5-triiodotoluene has an I_4 tetramer synthon (Liu et al., 1985), in which each I atom interacts with two neighbouring I atoms [$I \cdots I$ distance 3.746 (1) Å, and C—I$\cdots$I angles 92.1 (3) and 178.1 (3)°]. Such interactions, with C—I$\cdots$I—C angles close to 90 and 180°, are referred to as type II or L geometry. These dipole-induced halogen–halogen interactions (Bosch & Barnes, 2002; Jetti, Thallapally et al., 2000) have been used in crystal engineering. Against this background, we report here the crystal structure of triphenyl(3,4,5-triiodophenyl)methane, (I).
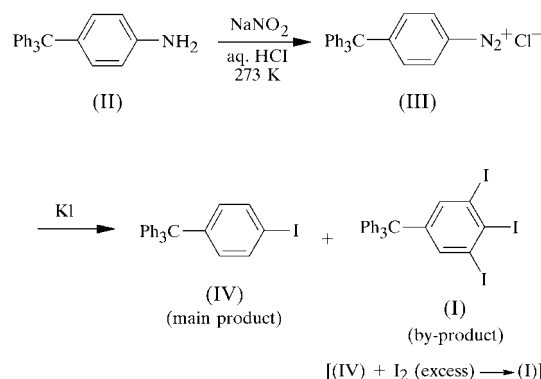
The crystal structure of the title compound involves two molecules of (I), denoted A and B, in the asymmetric unit (Fig. 1). The phenyl rings in molecules A and B adopt different conformations in the crystal when viewed down the $Csp^3 - C_I$ vector (C0—I2 and C0A—I2A); see Table 1 for torsion angles.

Inversion-related A molecules are connected via an $I2 \cdots \pi$ interaction (3.641 Å to the mid-point of the C24—C23 bond) to form an A–A dimer. The halogen–π interaction has emerged as a persistent synthon in tri- and tetrahaloaryl
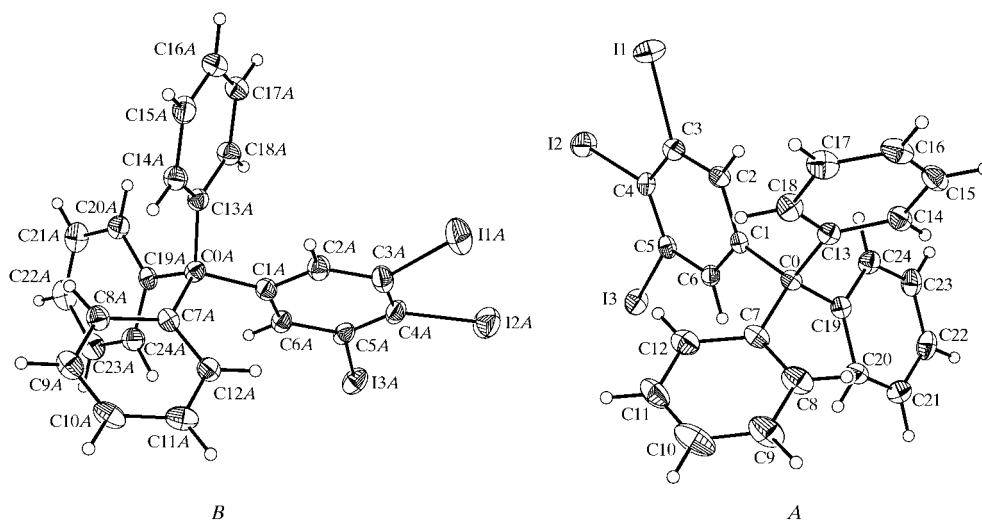

Figure 1
A view of the two symmetry-independent molecules, A and B, in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radii. Molecules A and B have different conformations in terms of their rotation about the C0—C1 (C0A—C1A) bond.

organic compounds

inclusion host structures (Jetti *et al.*, 2001; Rahman *et al.*, 2002, 2003).

The I···π *A*–*A* dimers in (I) are connected to symmetry-independent *B* molecules *via* an I2*A*···I3 interaction [I2*A*···I3 = 3.5571 (15) Å, C4*A*—I2*A*···I3 = 166.21 (20)° and C5—I3···I2*A* = 90.95 (17)°] and an I3···π interaction (3.561 Å to the mid-point of the C10*A*—C11*A* bond) (Fig. 2), such that atom I3 acts as both an acceptor and a donor group.

We note that the I···π interaction is shorter to the C—C bond mid-point than to the phenyl ring centroid. Furthermore, the approach geometry is such that the polar δ^+ region along the C—X bond points towards the δ^- π cloud of the phenyl ring (Jetti *et al.*, 2001). This is identical to the polarization-induced type II halogen–halogen geometry discussed by Bosch & Barnes (2002) and Jetti, Thallapally *et al.* (2000). Thus, I···π and I···I type II interactions exhibit a similar approach geometry because both of these interactions are electrostatic in nature.

Inversion-related *B* molecules in (I) do not have any significant close contacts between them.

We are currently carrying out a statistical study of halogen–π interactions in the Cambridge Structural Database (Allen, 2002) to analyse the approach of the halogen atom to the C—C bond mid-point or the phenyl ring centroid. One brief conclusion is that the heavier halogens (Br or I) prefer the

bond mid-point approach, in agreement with our observations in (I).

The triphenylmethyl groups in (I) engage in intermolecular edge-to-face and vertex-to-face herring-bone T motifs (Jetti, Xue *et al.*, 2000) through C—H···π interactions in the range 2.78–2.85 Å.

Experimental

Triphenyl(3,4,5-triiodophenyl)methane, (I), was obtained as a by-product in the preparation of aryl iodide (IV) (Jetti, Xue *et al.*, 2000) from arylamine (II) by diazotization and iodination (see scheme). While the exact mechanism for iodination at the *meta*-phenyl positions is not clear, we believe that the initially formed *para*-iodophenyl compound, (IV), undergoes electrophilic substitution with I_2 (formed by the oxidation of KI with $NaNO_2$) during the heating phase of the reaction, affording the triiodo compound, (I). 4-(Triphenylmethyl)-aniline, (II) (3.0 g, 9 mmol), was dissolved in concentrated HCl (9 ml) and H_2O (9 ml), and the mixture was cooled in ice. $NaNO_2$ (2.5 g, 36 mmol) was dissolved in H_2O (9 ml) and cooled to 273 K. This $NaNO_2$ solution was then added in small portions to the cooled anilinium–HCl solution and shaken well. A solution of KI (5.5 g, 33 mmol) in water (6 ml) was added slowly to the diazonium salt solution. The mixture was allowed to stand for a few hours at room temperature and was then heated on a boiling water bath until gas evolution ceased (*ca* 15 h). The reaction mixture was cooled to room temperature and neutralized with 10% aqueous NaOH. The precipitated solid was filtered off and the major compound was characterized as (4-iodophenyl)triphenylmethane, (IV) (m.p. 505 K). The minor component of the reaction product, (I), was separated by column chromatography (m.p. 483 K).

Crystal data

$C_{25}H_{17}I_3$	Mo $K\alpha$ radiation
$M_r = 698.09$	Cell parameters from 6227
Triclinic, $P\bar{1}$	reflections
$a = 11.567$ (4) Å	$\theta = 2.5$–28.2°
$b = 12.833$ (4) Å	$\mu = 4.21$ mm^{-1}
$c = 17.572$ (6) Å	$T = 203$ (2) K
$\alpha = 108.031$ (6)°	Plate, colourless
$\beta = 95.774$ (6)°	$0.56 \times 0.32 \times 0.19$ mm
$\gamma = 111.805$ (6)°	
$V = 2233.0$ (13) Å^3	
$Z = 4$	
$D_x = 2.076$ Mg m^{-3}	

Data collection

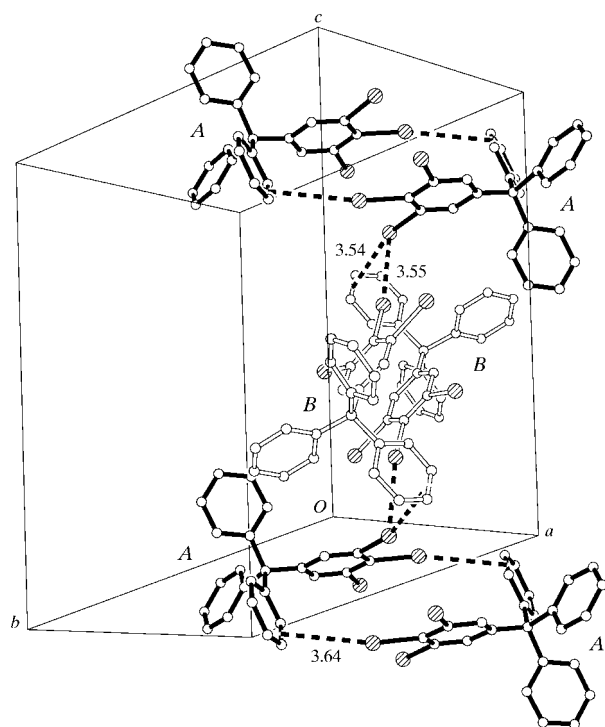|	
Bruker SMART CCD area-detector diffractometer	10 771 independent reflections
	8116 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.036$
Absorption correction: empirical (*SADABS*; Blessing, 1995)	$\theta_{max} = 28.4°$
	$h = -15 \rightarrow 15$
$T_{min} = 0.212$, $T_{max} = 0.450$	$k = -17 \rightarrow 17$
27 474 measured reflections	$l = -23 \rightarrow 22$

Figure 2
A packing diagram for (I), showing the I···π interactions between inversion-related molecules (*A*–*A*) in the halogen–π dimer synthon. The *A*–*A* dimers are connected through an inversion-related pair of *B* molecules *via* I···π and I···I (type II) interactions (*A*–*B*). H atoms bonded to C atoms have been omitted for clarity. Covalent bonds in *A* and *B* molecules are shaded differently. Intermolecular interactions are given in Å.

Table 1
Selected geometric parameters (°).

C4*A*—I2*A*—I3	166.2 (2)	C5—I3—I2*A*	90.95 (17)
C2—C1—C0—C7	109.6 (7)	C2*A*—C1*A*—C0*A*—C7*A*	−80.5 (8)
C2—C1—C0—C19	−127.5 (7)	C2*A*—C1*A*—C0*A*—C19*A*	162.0 (6)
C2—C1—C0—C13	−6.3 (9)	C2*A*—C1*A*—C0*A*—C13*A*	40.3 (8)
C6—C1—C0—C19	52.8 (7)	C6*A*—C1*A*—C0*A*—C19*A*	−15.9 (10)
C6—C1—C0—C13	174.0 (6)	C6*A*—C1*A*—C0*A*—C13*A*	−137.6 (7)
C6—C1—C0—C7	−70.1 (7)	C6*A*—C1*A*—C0*A*—C7*A*	101.6 (8)

Table 2
Geometry of short contacts (Å).

| I2A···I3 | 3.5571 (15) | C23ii···I2 | 3.649 (8) |
| C10A^i···I3 | 3.574 (8) | | |

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1061P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.059$	$+ 8.9076P]$
$wR(F^2) = 0.184$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
10 771 reflections	$\Delta\rho_{max} = 3.74$ e Å^{-3}
505 parameters	$\Delta\rho_{min} = -2.97$ e Å^{-3}
H-atom parameters constrained	

H atoms were included using a riding model, with a fixed C—H distance of 0.94 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. It was not possible to obtain better quality crystals and thus better R values and a more appropriate weighting scheme. The residual electron density is less than 1 e Å^{-3} at distances of more than 1 Å from the I-atom positions.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1609). Services for accessing these data are described at the back of the journal.

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