

Bis(methyltri-*o*-tolylphosphonium)
octaiodide

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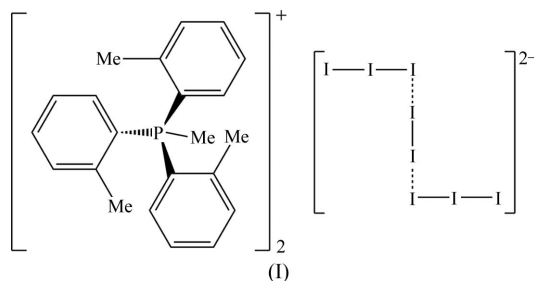
In the crystal structure of the title compound, $2C_{22}H_{24}P^+ \cdot I_8^{2-}$, the I_8^{2-} anion is located on a crystallographic inversion centre and consists of two tri-iodide anions linked by di-iodine at angles of $89.92(4)^\circ$ to form a planar 'Z'-shaped dianion. The octaiodides are linked *via* long-range interactions [$3.877(11) \text{ \AA}$] into infinite polyiodide ribbons. This is the first example of a structure containing an $[(o\text{-tolyl})_3PMe]^+$ cation, and the $C_{Me}-P-C-C_{Me}$ torsion angles of $-54.0(11)$, $-51.3(11)$ and $-48.2(11)^\circ$ indicate that the configuration is *exo*₃.

Comment

The octaiodide anion is a member of the dianionic polyiodide series $(I_{2n+2})^{2-}$, whose first three members would be expected to consist of a di-iodine combined, respectively, with two iodide anions, an iodide and tri-iodide, and two tri-iodide anions. The tetra-iodide is the most frequently encountered polyiodide in the $(I_{2n+2})^{2-}$ series and in all cases the I_4^{2-} anion is linear. No intermolecular $I \cdots I$ contacts less than 4 \AA have been observed in these compounds (Kloo & Svensson, 2003). To date no structure containing an undistorted I_6^{2-} anion has been reported. It is therefore somewhat surprising that several I_8^{2-} -containing structures are known. The first I_8^{2-} ion was determined by Havinga *et al.* (1954) in Cs_2I_8 . Generally, an I_8^{2-} ion consists of two I_3^- ions that interact with an I_2 molecule to form 'Z'-shaped $[(I_3^-)_2(I_2)]$. This geometry, which includes out-stretched ('S'-shaped) or slightly deformed forms, is the predominating geometry for all structurally characterized octaiodide ions.

In the title structure, $\{2[(o\text{-tolyl})_3PMe]^+ + I_8^{2-}\}$, (I), the I_8^{2-} anion has a 'Z' shape (Fig. 1). The bonding distances in the octaiodide indicate that it is made up of two tri-iodide anions and a di-iodine molecule (Table 1). Although the 'Z' angle is 81° in the inorganic Cs_2I_8 , the 'Z' angle of $89.92(4)^\circ$ in the current structure is the most acute seen in structures containing organic cations. In the title molecule, the I_8^{2-} 'Z' is completely flat, with the two I_3^- units configured *trans* to one another. In other words, the torsion angle defined by the angle

between the two I_3^- ions when projected down the I_2 bond is 180° , as required by the centre of inversion that relates them. This is the configuration seen in all known I_8^{2-} ions except in the salts with the tris(1,10-phenanthroline)iron(II) complex (-82.1° ; Horn *et al.*, 2001) and the dihydrogen [2.2.2]cryptand (-99.3° ; Grafe-Kavoosian *et al.*, 1998). It is interesting that the central torsion angle is either 180° or close to 90° .



Each I_8^{2-} anion in the present structure associates with two adjacent anions *via* long contacts of $3.977(1) \text{ \AA}$ to form infinite polyiodide ribbons along $[100]$ (Fig. 2). Interestingly, this is the first example where the long-range interactions between I_8^{2-} ions involve both the I_3^- and I_2 moieties. In all other cases where interionic interactions occur between I_8^{2-} units, only the I_3^- ions are involved. When only one iodine in each I_3^- ion takes part in long-range interactions, a helical (Horn *et al.*, 2001) or branched (Kuhn *et al.*, 2000) chain is produced. When both terminal I_3^- iodines are employed, puckered sheets result (Grafe-Kavoosian *et al.*, 1998; Kuz'mina *et al.*, 2000). Although the number of long-range $I \cdots I$ interactions are the same in the title structure as they are in the puckered sheets, involvement of the central I_2 gives lower conformational freedom, leading to flat ribbons.

The $C_{Me}-P-C-C_{Me}$ torsion-angle values of $C22-P1-C1-C2 = -54.0(11)^\circ$, $C22-P1-C8-C9 = -51.3(11)^\circ$ and $C22-P1-C15-C16 = -48.2(11)^\circ$ confirm that the config-

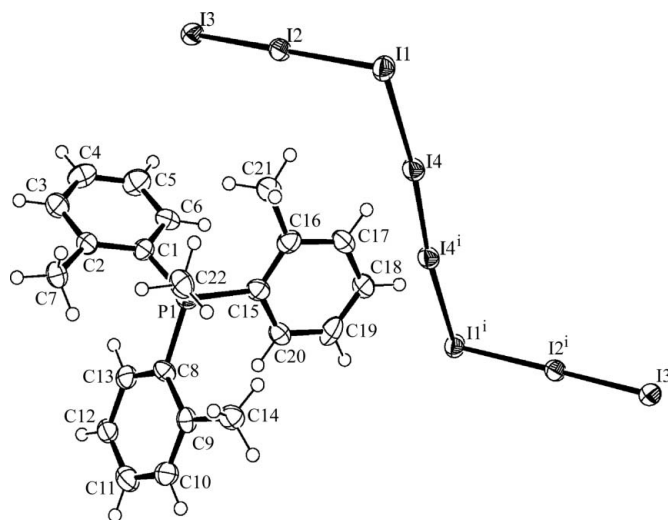


Figure 1
View of the methyltri-*o*-tolylphosphonium cation and the centrosymmetric octaiodide dianion of (I), including the atom-labelling scheme. [Symmetry code: (i) $-x + 1, -y, -z + 1$.]

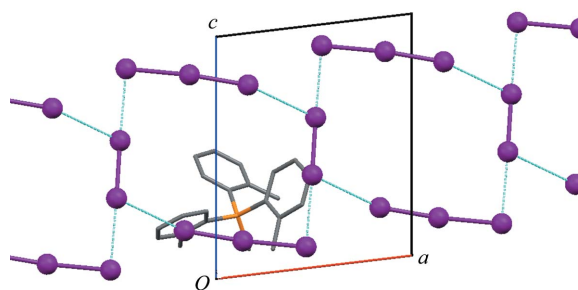
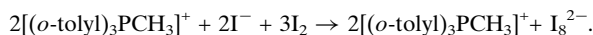


Figure 2
The octaiodide anions linked into a polyiodide ribbon viewed down the crystallographic *b* axis.

uration is *exo*₃, which is as expected for a tri-*o*-tolylphosphine moiety with a small apical substituent [cf. (*o*-tolyl)₃P=O, which is also *exo*₃ and whose corresponding torsion angles fall in the range 33.8–52.4°, with an average of 45.9°]. See Howell *et al.* (1992) for a previous example of the *exo* notation being used in tri-*o*-tolyl derivatives of P, As and Si. The larger torsion angles in the title cation reflect the slightly larger size of CH₃ relative to O and must be at the upper limit for the *exo*₃ configuration. The increased size of the apical substituent in (*o*-tolyl)₃P=S flips the structure to an *exo*₂ configuration even though, according to Pauling, CH₃ has a larger van der Waals radius than S. This is because H atoms of the *ortho*-CH₃ groups nestle between the H atoms of the apical CH₃, effectively reducing the van der Waals radius of the methyl group.

Experimental

Equimolar quantities of methyl iodide and tri-*o*-tolylphosphine were reacted in dry dichloromethane at room temperature. The containers were stoppered and further precautions to protect the sample from the atmosphere were deemed unnecessary. Anhydrous dichloromethane (25 ml) was added to a dry Rotaflo tube. To this solution was added (*o*-CH₃C₆H₄)₃P (1.005 g, 3.30 mmol) which dissolved rapidly. Iodomethane (0.60 ml, 9.91 mol) was added slowly over a period of several minutes. After 5 min, a white solid gradually formed and the reaction was left to stir for a further 24 h. The solid was then isolated using standard Schlenk techniques and dried *in vacuo* for 2 h to yield 1.394 g of a solid (94.6% yield). Analysis calculated for C₂₂H₂₄I₄P: C 59.2, H 5.4, I 28.5%; found: C 59.1, H 5.3, I 28.1%. For recrystallization, the compound was dissolved in CH₂Cl₂. Iodine was added to the solution, which was dissolved in dichloromethane in a 2:1 molar ratio. The solution was allowed to stand for 4 d to allow dark-red crystals to form by slow evaporation:



Crystal data

2C ₂₂ H ₂₄ P ⁺ ·I ₈ ²⁻	$\gamma = 73.073 (1)^\circ$
$M_r = 1653.96$	$V = 1288.83 (6) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 9.6680 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 12.3567 (3) \text{ \AA}$	$\mu = 4.90 \text{ mm}^{-1}$
$c = 12.8186 (4) \text{ \AA}$	$T = 100 \text{ K}$
$\alpha = 62.364 (1)^\circ$	$0.15 \times 0.1 \times 0.1 \text{ mm}$
$\beta = 76.410 (1)^\circ$	

Data collection

Nonius KappaCCD diffractometer	4776 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	4776 independent reflections
$T_{\min} = 0.527$, $T_{\max} = 0.640$	3762 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.069$	247 parameters
$wR(F^2) = 0.183$	H-atom parameters constrained
$S = 1.15$	$\Delta\rho_{\max} = 4.65 \text{ e \AA}^{-3}$
4776 reflections	$\Delta\rho_{\min} = -2.84 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1–P1	1.800 (12)	I1–I2	3.0162 (11)
C8–P1	1.806 (11)	I2–I3	2.8511 (11)
C15–P1	1.825 (12)	I4–I4 ⁱ	2.7663 (17)
C22–P1	1.808 (13)		
I3–I2–I1	174.42 (4)	C1–P1–C15	109.4 (5)
C1–P1–C22	109.8 (6)	C22–P1–C15	109.8 (6)
C1–P1–C8	108.7 (5)	C8–P1–C15	108.7 (5)
C22–P1–C8	110.4 (5)		

Symmetry code: (i) $-x + 1, -y, -z + 1$.

H atoms were constrained to chemically reasonable positions, with C–H bond lengths set at 0.95 Å for phenyl and at 0.98 Å for methyl groups. $U_{\text{iso}}(\text{H})$ values were set at 1.2 times the U_{eq} values of the attached C atoms in phenyl rings and at 1.5 times the U_{eq} values for methyl H atoms. The largest peaks remaining in the difference map have electron densities of 4.7 and 3.6 e Å⁻³. They are arranged linearly on either side of I4 at distances of 2.924 and 2.964 Å, forming an I₃⁻ shape. No credible twin model was found, and no indication of spot splitting could be seen in the X-ray images. It was therefore concluded that the best explanation for the residual electron density was a minor secondary phase that had intergrown with the primary structure.

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: WinGX (Farrugia, 1999) and publCIF (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3253). Services for accessing these data are described at the back of the journal.

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