Supplementary data for paper: Structural isomerism in tris–tolyl halo–phosphonium and halo–arsonium tri–halides, $[(CH_3C_6H_4)_3EX][X_3]$, (E = P, As; X = Br, I).

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Weak anion–anion interactions in the structures of **1** and **2**:

The structure of **1** has no secondary I···I interactions within the sum of the van der Waals radii of two iodine atoms (3.96 Å), but does display a weak I(4)···I(1) interaction of 3.9684(18) Å from the terminal iodine atom at the other end of the $[I_3]^-$ anion to an adjacent $[(o\text{–}CH_3C_6H_4)_3PI]^+$ cation, which is at the van der Waals limit, see Fig. S1. In this way $[I_3]^-$ anions loosely bridge adjacent cations and the situation is reminiscent of the isomer (C) type of structure where both ends of the $[I_3]^-$ anion interact with $[R_3PI]^+$ cations, although the second interaction is very much weaker than the first, and the angle of the weaker interaction to the second cation is different. In the extended structure of **2**, a second $[(m\text{–}CH_3C_6H_4)_3PI]^+$ cation interacts to the terminal I(2) atom at the same end of the $[I_3]^-$ anion as the shorter interaction, i.e. approaching the isomer (B) type of structure that was observed by Cotton and Kibala for $[\{Ph_3PI\}_2I_3][I_3]$, see Fig. S2. However this distance is very long at 4.267(2) Å.

Fig. S1 I···I contacts in the extended structure of $[(o\text{–}CH_3C_6H_4)_3PI][I_3]$, **1**.

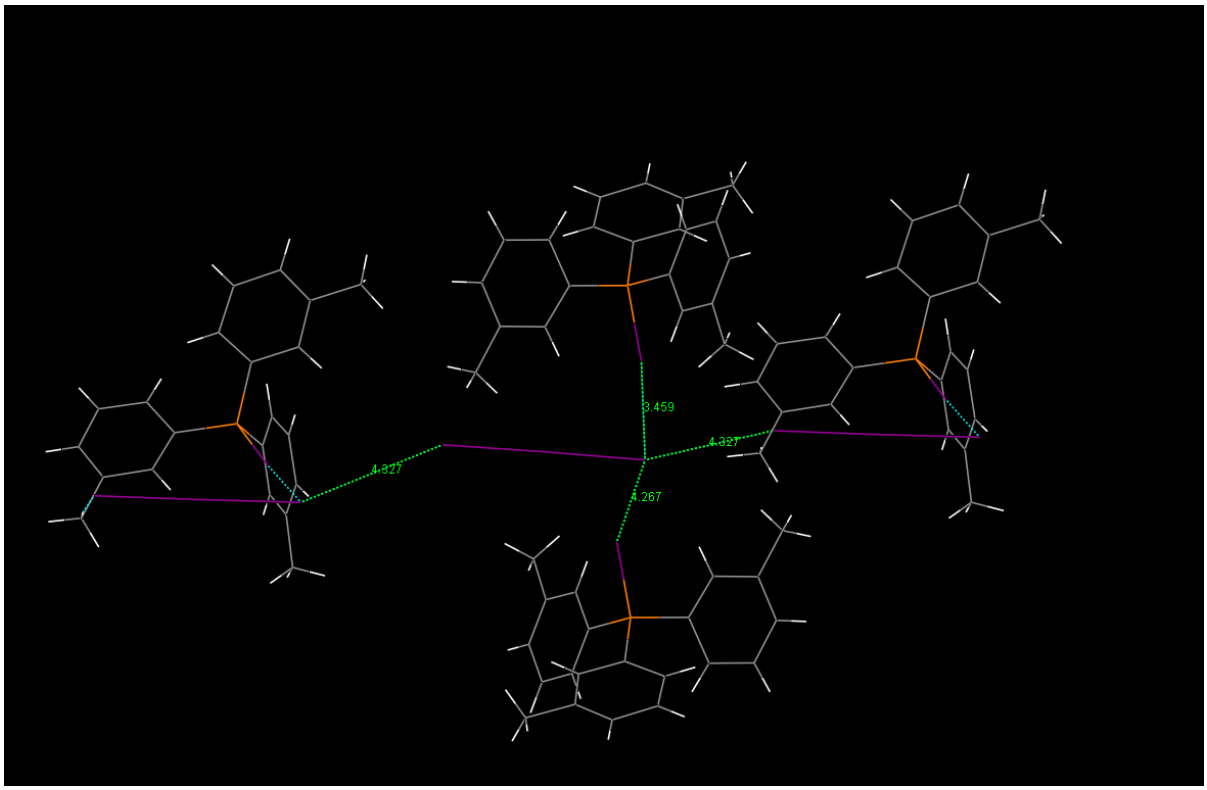

Fig. S2 I···I contacts in the extended structure of [(*m*–$CH_3C_6H_4)_3$PI][I_3], **2**.

Table of short X···H hydrogen bonds present in the structures of compounds **1** to **3** and **5**, to **12** (Table S1), and table of cation packing arrangements, and E···E separations, angles and torsions across the aryl embraces between $[Ar_3EX]^+$ cations in the extended structures of **1** to **3** and **5** to **12**.

Compound	Short X···H hydrogen bonds / Å [a]
$[(o\text{-}CH_3C_6H_4)_3PI][I_3]$ **1**	I(2)···H(9): 3.16
$[(m\text{-}CH_3C_6H_4)_3PI][I_3]$ **2**	None shorter than the sum of the van der Waals radii
$[\{(p\text{-}CH_3C_6H_4)_3PI\}_2I_3][I_3]$ **3**	I(2)···H(7A): 3.16; I(5)···H(17): 3.17
$[\{(p\text{-}CH_3C_6H_4)_3AsI\}_2I_3][I_3]$ **5**	I(2)···H(14B): 3.18
$[\{Ph_3AsI\}_2I_3][I_3]$ **6**	I(6)···H(18): 3.06
$[(o\text{-}CH_3C_6H_4)_3PBr][Br_3]$ **7**	Br(2)···H(6): 2.93; Br(4)···H(18): 3.00
$[\{(m\text{-}CH_3C_6H_4)_3PBr\}_2Br_3][Br_3]$ **8**	Br(2)···H(26): 2.97; Br(2)···H(13): 3.05; Br(5)···H(28C): 3.03; Br(6)···H(19): 2.94; Br(6)···H(30): 2.92; Br(6)···H(34): 3.00; Br(8)···H(28B): 2.99; Br(8)···H(41): 2.89
$[\{(p\text{-}CH_3C_6H_4)_3PBr\}_2Br_3][Br_3]$ **9**	Br(3)···H(16): 2.95; Br(4)···H(19): 2.90
$[(o\text{-}CH_3C_6H_4)_3AsBr][Br_3]$ **10**	Br(2)···H(6): 2.90; Br(4)···H(11): 3.05
$[(p\text{-}CH_3C_6H_4)_3AsBr][Br_3]$ **11**	Br(2)···H(20): 2.86; Br(2)···H(21C): 2.99; Br(3)···H(12): 3.01; Br(3)···H(26): 2.95; Br(4)···H(13): 2.99; Br(4)···H(27): 2.94; Br(6)···H(23): 3.00; Br(6)···H(30): 2.88; Br(7)···H(5): 3.02; Br(7)···H(24): 2.95; Br(8)···H(41): 2.95; Br(8)···H(42C): 3.01
$[Ph_3AsBr][Br_3]$ **12**	Br(3)···H(6): 2.95; Br(4)···H(9): 2.98

[a] Sum of the van der Waals radii of iodine and hydrogen is 3.18 Å, sum of the van der Waals radii of bromine and hydrogen is 3.05 Å.

Table S1 Details of non classical I···H and Br···H hydrogen bonding in the structures of **1** to **3** and **5** to **12**.

Compound	Packing arrangement of cations	Isomer type	E···E separation (Å)	E···E···E angle / °	X– E···E–X torsion angle across embrace / °
[(*o*-$CH_3C_6H_4)_3$PI][I_3] **1**	side–to–side, anti–parallel, one (OFF), one (MF), forms a chain with square motif	A	7.417	131.87	167.29
[(*m*-$CH_3C_6H_4)_3$PI][I_3] **2**	side–to–side, anti–parallel, one (OFF), one (EF), forms a chain with square motif	A	6.494	138.19	153.84
[{(*p*-$CH_3C_6H_4)_3$PI}$_2I_3$][I_3] **3**	side–to–side, anti–parallel, single (OFF) embrace, forms a chain with square motif	C	6.418	158.20	–142.55
[{(*p*-$CH_3C_6H_4)_3$AsI}$_2I_3$][I_3] **5**	side–to–side, anti–parallel, single (OFF) embrace, forms a chain with square motif	C	6.422	158.47	–142.09
[{Ph_3AsI}$_2I_3$][I_3] **6**	side–to–side, parallel, single (OFF) embrace, forms chains	B	6.328	152.81	–9.62
[(*o*-$CH_3C_6H_4)_3$PBr][Br_3] **7**	side–to–side, anti–parallel, one (OFF), one (MF), forms a chain with square motif	A	7.361	132.62	167.23
[{(*m*-$CH_3C_6H_4)_3$PBr}$_2Br_3$][Br_3] **8** (two independent molecules)	side–to–side, parallel, single (OFF) embrace, forms chains of alternating P(1) and P(2) cations – separations slightly different on each side.	C	6.935, 7.072	155.52 twice	139.79 / 135.78
[{(*p*-$CH_3C_6H_4)_3$PBr}$_2Br_3$][Br_3] **9**	side–to–side, anti–parallel, single (OFF) embrace, forms a chain with square motif	C	6.578	156.15	145.25
[(*o*-$CH_3C_6H_4)_3$AsBr][Br_3] **10**	side–to–side, anti–parallel, one (OFF), one (MF), forms a chain with square motif	A	7.389	133.18	167.96
[(*p*-$CH_3C_6H_4)_3$AsBr][Br_3] **11**	side–to–side, anti–parallel, one (OFF), one (EF), chain of As(1) cations with square motif	A	5.790	157.61	–168.04
(two independent molecules)	side–to–side, anti–parallel, one (OFF), one (EF), chain of As(2) cations with square motif		5.716	167.22	175.71
[Ph_3AsBr][Br_3] **12**	side–to–side, anti–parallel, one (OFF), one (EF), forms a chain with square motif	A	5.751	141.81	–168.53

Table S2 Comparison of cation packing arrangements and E···E separations, angles and torsions across the aryl embraces between $[Ar_3EX]^+$ cations in the extended structures of **1** to **3** and **5** to **12**. Key: (EF): edge–to–face aryl embrace, (OFF): offset face–to–face embrace, (MF): methyl–to–face embrace.