

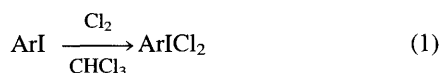
## Reduction of Intermolecular Association in the Sterically Encumbered (Dichloroiodo)arene $\text{ArICl}_2$ [ $\text{Ar} = 2,6\text{-bis}(3,5\text{-dichloro-}2,4,6\text{-trimethylphenyl})\text{benzene}$ ]

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The synthesis of the sterically encumbered (dichloroiodo)arene  $\text{ArICl}_2$  [ $\text{Ar} = 2,6\text{-bis}(3,5\text{-dichloro-}2,4,6\text{-trimethylphenyl})\text{benzene}$ ] is achieved via a novel hexachlorination reaction and an X-ray structural determination reveals a reduced intermolecular association for the hypervalent iodine species as compared to the only other crystallographically characterized (dichloroiodo)arene  $\text{PhICl}_2$  (the structure of which is re-examined in light of the present data).

Organoiodine(III) compounds continue to grow in importance as reagents in both organic and inorganic chemistry.<sup>1–5</sup> In particular,  $\text{ArIX}_2$  species ( $\text{X}_2 = \text{Cl}_2, \text{O}, \text{NR}$ ) are heavily employed for many catalysed and uncatalysed atom and group-transfer reactions.<sup>6</sup> Recently, the characteristic T-shaped geometry of aryl iodine(III) compounds has even been exploited as an architectural building block to engineer  $90^\circ$  turns in molecular structures.<sup>7</sup> The very first organoiodine(III) species, (dichloroiodo)benzene ( $\text{PhICl}_2$ ), was synthesized by Willgerodt over 100 years ago,<sup>8</sup> and since that time over two hundred representatives of this important class of compounds have been prepared.<sup>9–13</sup> The most general route is based upon the direct reaction of molecular chlorine with the aryl iodide, eqn. (1).

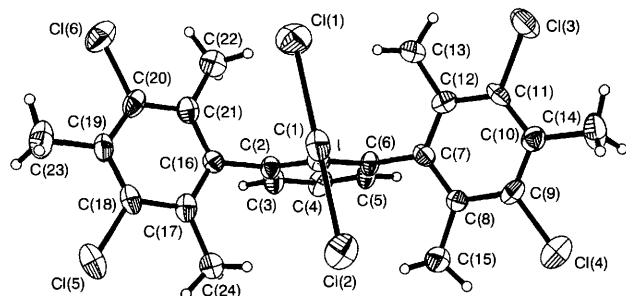


Though readily prepared, these materials are very reactive, and hence, the only structural data reported is for the parent compound  $\text{PhICl}_2$ .<sup>14†</sup>

We are currently engaged in the preparation of aryl iodine(III) species designed so that reduced aggregation states for the hypervalent iodine(III) centres may be obtained. Our strategy is based upon introduction of aryl substituents at the 2,6-positions (*ortho*) to the iodine unit to provide a protective pocket in which the electrophilic residue may reside, yet still afford accessibility to the iodine(III) centre for further reactivity. Recently, the unstable 1-(dichloroiodo)-2,4,6-tri-*tert*-butylbenzene ( $\text{ArICl}_2$ ) has been prepared.<sup>15</sup>

Reaction of 2,6-dimesitylphenyliodide **1**<sup>16</sup> with chlorine gas in  $\text{CHCl}_3$  at  $0^\circ\text{C}$  rapidly led to a yellow solution, which precipitated a yellow solid (60% yield) over a 40 min period. Recrystallization of the yellow solid from  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$  affords moisture sensitive crystals of **2**, a crystal of which was subjected to study by X-ray diffraction.‡ Indeed, a (dichloroiodo)arene had been produced, but not quite the intended target. Fig. 1 displays the ORTEP representation of the novel hexachlorinated species **2** (Scheme 1).

The geometry for the  $\lambda^3$ -iodane is the expected T-shaped, with  $\text{Cl-I-C}$  angles of  $89.4(3)$  and  $92.1(3)^\circ$ .<sup>13</sup> The  $\text{Cl-I-Cl}$  unit

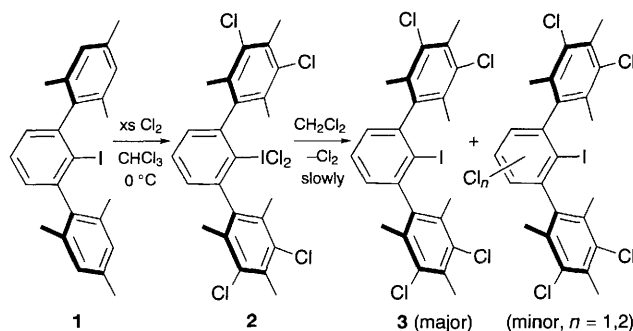


**Fig. 1** ORTEP diagram of  $\text{ArICl}_2$  [ $\text{Ar} = 2,6\text{-bis}(3,5\text{-dichloro-}2,4,6\text{-trimethylphenyl})\text{benzene}$ ] **2**. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{I-C}(1)$  2.125(11),  $\text{I-C}(1)$  2.49(4),  $\text{I-C}(2)$  2.469(4),  $\text{Cl}(1)\text{-I-C}(2)$  178.36(13),  $\text{Cl}(1)\text{-I-C}(1)$  92.1(3),  $\text{Cl}(2)\text{-I-C}(1)$  89.4(3). Selected torsion angles ( $^\circ$ ):  $\text{Cl}(1)\text{-I-C}(1)\text{-C}(2)$   $-80.3(9)$ ,  $\text{Cl}(2)\text{-I-C}(1)\text{-C}(6)$  101.9(9),  $\text{Cl}(2)\text{-I-C}(1)\text{-C}(2)$  99.2(9),  $\text{Cl}(2)\text{-I-C}(1)\text{-C}(2)$   $-78.6(9)$ .

is linear [ $178.3(1)^\circ$ ] and the  $\text{I-Cl}$  distances of 2.469(4) and 2.491(4)  $\text{\AA}$  for **2** are slightly longer than the corresponding distance in  $\text{PhICl}_2$  [2.45(2)  $\text{\AA}$ ]. Values for the carbon-iodine bond distances in both compounds are 2.127(13) and 2.00(5)  $\text{\AA}$ , respectively. A longer carbon-iodine distance for **2** is consistent with increased steric repulsions between the  $\text{ICl}_2$  unit and the dichloromesityl groups. The two chlorine atoms in **2** have little effect on the carbon-iodine bond length, for the corresponding mean  $\text{I-C}$  bond length in 2,6-bis(3,5-dichloro-2,4,6-trimethylphenyl)iodobenzene **3** is 2.109  $\text{\AA}$  (two molecules in asymmetric unit).<sup>17</sup>

The  $\text{Cl-I-Cl}$  vector in **2** is tilted with respect to the plane of the central phenyl ring yielding an average torsion angle of  $79^\circ$ , which is significantly more tilted compared with  $\text{PhICl}_2$  (torsion angle =  $86^\circ$ ). The less precise nature of the structure of  $\text{PhICl}_2$  and the secondary  $\text{Cl}\cdots\text{I}$  interactions might account for a torsion angle deviating from the idealized  $90^\circ$  value, but the sterically encumbered environment of **2** would predict less, not more, departure from  $90^\circ$ . Similar deviations have been noted in structural determinations of  $\text{PhI}(\text{O}_2\text{CR})_2$  [ $\text{R} = \text{Me}$  ( $75^\circ$ ) and  $\text{R} = \text{CH}_2\text{Cl}$  ( $79.2^\circ$ )], though the interpretation of these effects is obscured by intramolecular or intermolecular  $\text{I}\cdots\text{O}$  contacts. Such effects are absent in the structure of  $\text{ArI}(\text{OAc})_2$  (**4**,  $\text{Ar} = 2,4,6\text{-tri-}t\text{-butylbenzene}$ ), where the extreme steric environment precludes significant deviation from  $90^\circ$  [ $87.3(5)\text{--}89.8(5)^\circ$  for three crystallographically independent molecules].<sup>15</sup> A recent computational study of  $\text{PhICl}_2$  and  $\text{PhIF}_2$  has indicated the optimal torsion angle to be  $90^\circ$  based on electronic considerations.<sup>18</sup>

Analysis of the packing diagram of compound **2** (Fig. 2) reveals a dimeric association of the  $\text{ArICl}_2$  entities with intermolecular  $\text{Cl}\cdots\text{I}$  interactions occurring in the crystalline state. The intermolecular  $\text{Cl}\cdots\text{I}$  distance of 3.816  $\text{\AA}$  is longer than that for  $\text{PhICl}_2$  (3.40  $\text{\AA}$ ), and considerably longer than the  $\text{I-Cl}$  distances for the centrosymmetric dimer  $[\text{Ph}_2\text{ICl}]_2$  (mean  $d_{\text{ICl}} = 3.085$   $\text{\AA}$ ).<sup>19</sup> The packing of **2** also reveals the  $\text{I}_2\text{Cl}_4$  plane is sandwiched above and below by two dichloromesityl groups, whilst the two remaining dichloromesityl groups are engaged in  $\pi$ -stacking with neighbouring molecules. Interestingly, the dichloromesityl groups that sandwich the  $\text{I}_2\text{Cl}_4$  unit are aligned in such a manner to place these rings parallel to the  $\text{Cl-I-Cl}$  vector [angle between central phenyl ring and outer phenyl ring =  $78.2(4)^\circ$ ], while the other dichloromesityl groups are



**Scheme 1**

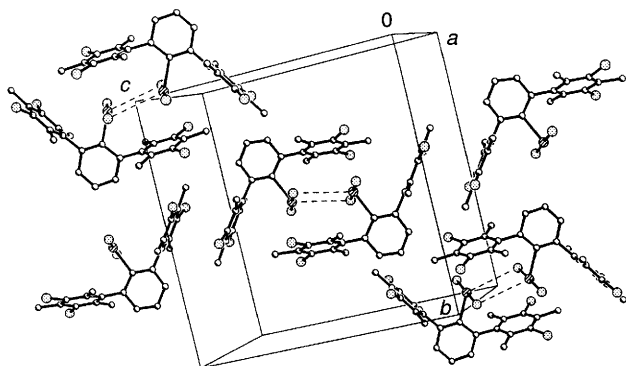
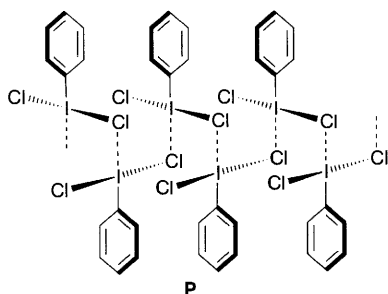


Fig. 2 Packing diagram illustrating intermolecular I...Cl interactions between molecules of **2**



essentially orthogonal to the central phenyl ring [interplanar angle =  $89.4(4)^\circ$ ].

Association of molecules of  $\text{PhICl}_2$  is described as involving pairs of molecules.<sup>20</sup> Since a reduced association number would be expected for the more sterically encumbered **2**, we re-examined the structure of  $\text{PhICl}_2$  using published data. Interestingly, the true nature of  $\text{PhICl}_2$  in the solid state is not dimeric, but polymeric **P**. Alternating  $\text{PhICl}_2$  units contain phenyl rings oriented perpendicular to one another, forming zig-zag non-interacting polymer chains. Much effort has gone into the structure elucidation of iodosylbenzene,  $[\text{PhIO}]_n$ , with the result of a polymeric structure being consistent with all available evidence.<sup>21–24</sup> The structure of  $\text{PhICl}_2$  can thus be related to that of  $[\text{PhIO}]_n$  by loss of terminal chloride and replacement of bridging chloride for oxide.

Compound **2**, although somewhat thermally stable in the solid state, undergoes facile decomposition in  $\text{CH}_2\text{Cl}_2$  solution, even at reduced temperatures, to afford predominantly **3** (Scheme 1). Compound **3** is structurally similar to **1** and **2** with flanking aryl groups nearly orthogonal to the iodine containing phenyl ring.<sup>§17</sup> MS analysis of the microcrystalline product obtained from solutions of **2** revealed measurable quantities of the mono- (~15%) and di- (~5%) chlorinated derivatives of **3** present, mirroring reactivity reported for  $\text{PhICl}_2$ , albeit at lower temperatures.

The flanking aryl groups of **2** thus serve to reduced the aggregation of the (dichloroiodo)arene and also to increase the lability of the chlorine atoms.

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## Footnotes

† The structure of *para*-chloro(dichloroiodo)benzene is mentioned in D. A. Bekoe and R. Hulme, *Nature*, 1956, **177**, 1230, but no bond distances or angles were given.

‡ *Crystal data* for **2**,  $\text{C}_{24}\text{H}_{21}\text{Cl}_6\text{I}$ ,  $M = 649.0$ , monoclinic,  $P2(1)/n$ ,  $a = 9.080(4)$ ,  $b = 17.042(2)$ ,  $c = 16.698(2)$ ,  $\beta = 100.35(2)$ ,  $V = 2541.8(12)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.696$   $\text{g cm}^{-3}$ ,  $\mu = 1.902$   $\text{mm}^{-1}$ , absorption correction ( $\psi$ ) were applied. Data were collected on a Siemens P4 diffractometer (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$ ,  $\theta$ - $2\theta$  mode,  $\theta$  range =  $2.39$  to  $22.5$ ) at 298 K. Solution and refinement (full-matrix least squares analysis on  $F^2$ ) was performed using SHELXTL PLUS, PC Version 5.1 $\beta$ . All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in idealized locations and refined riding on attached carbon atoms with common isotropic displacement parameters equal to  $0.08$   $\text{\AA}^2$ , resulting in final discrepancy values of  $R1 = 6.90\%$  and  $wR2 = 12.7\%$ , and  $\text{GOF} = 1.16$  for 3314 unique observed data and 281 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Torsion angles for compound **3** range from  $71.8(3)$  to  $81.1(4)^\circ$ .

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