A Speculative Discussion of the Structural Details of 1-Bromo-2-iodo-benzenes

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The crystal and molecular structures of 2,4-dibromo-1-iodo-benzene (**1**) and 1,3-dibromo-2-iodo-benzene (**2**) have been determined by single crystal X-ray diffraction. The proximity of two or three large halogen substituents (Br/I) induces only minor distortions of the C-C-Br/I angles (*ca.* 2°) and the halogen atoms remain in the plane of the molecules. These undistorted structures lead to short intramolecular, sub-van-der-Waals Br–I contacts [in the range 3.465(4) to 3.530(4) Å]. The results suggest that the peripheral Br–I interactions have an attractive component which alleviates the repulsion out of steric crowding. The influence is associated with an absorption in the visible region and is possibly responsible for the enhanced reactivity of the 1,2-dihalobenzene molecules.

Key words: Bromobenzenes, Iodobenzenes, Bromo-/Iodo-Benzenes, Steric Crowding, Closed-shell Interactions

Introduction

There is great current interest in attractive interactions between closed-shell atoms [1]. This is true not only for nd^{10} species like the univalent cations of the coinage metals in general [2], and gold(I) in particular (metallophilicity, aurophilicity [3]), but also for the ns^2 and ns^2p^6 species. While the former (nd^{10}, ns^2) show significant effects only for the heaviest atoms (Z for gold: 79) where relativistic contributions are important [4, 5], pertinent phenomena are more common – and in fact have long been known – for the latter elements (ns^2p^6) even with lower atomic numbers (Z for iodine: 53) [1, 6]. The organisation of I_2 molecules in the solid state or the formation of polyiodides (from iodine molecules and iodide anions) are classical examples for this type of secondary interaction. It is known to be strong enough to co-determine molecular and supramolecular structures. Even for bromine ($Z = 35$) similar effects can still be discovered, although to a much smaller extent [6].

Poly(halo)benzenes $C_6H_xX_{6-x}$ have long been used in preparative chemistry and most of their fundamental properties are well documented [7]. Through-space interactions are expected to arise in these molecules if the halogen substituents are in neighbouring positions (1,2 or 1,2,3 *etc.*) and in particular as the number and the size of the halogen substituents is increased: Following van der Waals radii arguments, for the extreme case of the C_6X_6 series, hexa(iodo)benzene C_6I_6, significant steric repulsion could be expected which should result not only in structural distortions, but also in photophysical effects. Hexaiodobenzene indeed has a yellow-orange colour [8], and yet it has been shown to have a planar structure like all other hexahalobenzenes (X = F, Cl, Br, and I) [9]. The tilting of the iodine atoms away from the benzene plane is very small and almost within the standard deviations of the experiments. There has been agreement of the results regarding these structural characteristics in all studies based on single crystal X-ray diffraction [9], gas phase electron diffraction (except for C_6I_6) [10], vibrational [11] and photoelectron spectroscopy [12], and quantum chemical calculations [13].

In the discussion of the planar molecular geometry observed for C_6I_6 and C_6Br_6, all the authors argued that the intramolecular inter-halogen distances appeared to be surprisingly short, being well below the sum of two van der Waals radii of iodine engaged in covalent bonding [14]. Surprisingly, however, the idea that the phenomenon could also be strongly influenced by attractive instead of repulsive forces was rarely considered [13].

In the course of recent preparative studies in our laboratory [15, 16] of poly(silyl)- and poly(phosphino)-benzenes, $(H_3Si)_nC_6H_{6-n}$ and $(H_2P)_nC_6H_{6-n}$, more

often than not the synthetic routes required metallation steps starting from the corresponding poly (halo)benzenes. Because the chlorobenzenes showed limited or erratic reactivity, the experiments had to be carried out with the polybromo-, polyiodo- or polybromo/iodo-benzenes. These compounds are known in the literature, but the information on structural details is limited. We therefore investigated two representative examples in which bromine and iodine are neighbours in different substitution patterns, *viz.* 2,4-dibromo-1-iodo- and 1,3-dibromo-2-iodo-benzene (**1**, **2**). The molecular geometries were expected to give an indication of the relative importance of attractive and repulsive effects between two different large halogen atoms (Br and I) which are held in close proximity. A literature search has shown that a 1-bromo-2-iodo-benzene molecule has been structurally characterized only in one case, where the molecule functions as a ligand to silver(I) cations [17]. In this complex the iodine atoms are the donor sites for the metal cation, which may alter the bonding situation. A 1,2,3-triiodo-benzene substitution pattern has been structurally investigated for 3,4,5-triiodotoluene [18]. Its geometrical details will be considered below, together with those of 3,4,5,6-tetraiodo-phthalic anhydride [19].

Results

The two title compounds (**1**, **2**) were obtained following published procedures and identified by their physical constants [20, 21]. Both compounds have a yellow-orange colour in solution and in the solid state.

Crystals of **1** are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. There is one independent molecule in the asymmetric unit (Fig. 1). The two C-Br distances are equal within the limit of standard deviations [C2-Br1 1.893(4), C4-Br2 1.909(3) Å], indicating that this parameter is not greatly influenced by any *ortho* or *para* effect of the iodine atom. Like the C-Br distances, the distance C1-I1 2.096(4) Å is in the usual range for bromo-/iodo-arenes and reflects the larger covalent radius of I as compared to Br [14]. The difference of 0.19 Å is exactly the difference found in the pairs HI/HBr or I_2/Br_2 [6].

The angles C2-C1-I1 and C1-C2-Br1 are widened to 122.5(3)° and 122.2(3)°, with the corresponding angles C6-C1-I1 and C3-C2-Br1 compressed to 118.4(3)° and even 116.8(3)°, respectively (Fig. 1). By contrast, the angles C3-C4-Br2 and C5-C4-Br2 are equal within the experimental limits [118.5(3) and
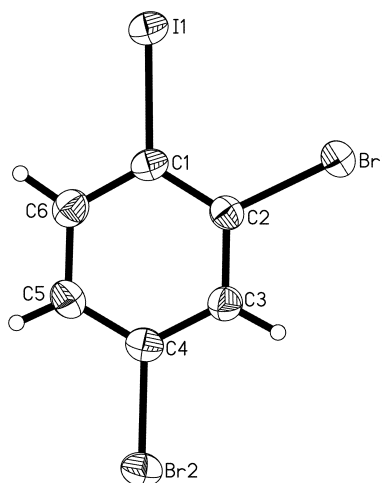

Fig. 1. Molecular structure of 2,4-dibromo-1-iodo-benzene (**1**) (ORTEP, 50% probability ellipsoids, hydrogen atoms with arbitrary radii). Selected bond lengths [Å], angles [°] and interhalogen contacts [Å]: I1-C1 2.096(4), Br1-C2 1.893(4), Br2-C4 1.909(4), C1-C2 1.393(6), C2-C3 1.393(6), C3-C4 1.389(6), C4-C5 1.368(7), C5-C6 1.397(7), C6-C1 1.383(6); I1-C1-C2 122.5(3), I1-C1-C6 118.4(3), Br1-C2-C1 122.2(3), Br1-C2-C3 116.8(3), Br2-C4-C3 118.5(3), Br2-C4-C5 119.4(3), C1-C2-C3 121.0(4), C2-C3-C4 118.1(4), C3-C4-C5 122.1(4), C4-C5-C6 118.9(4), C5-C6-C1 120.7(4); I1–Br2 3.530(4).

119.4(3)°]. Circling the ring, the endocyclic C-C-C angles show small alternations [119.1(4), 121.0(4), 118.1(4), 122.1(4), 118.9(4), 120.7(4)° for C1–C6], but taking into account the standard deviations the alternation may not be really meaningful. It appears, however, that the most electronegative substituents induce the largest C-C-C angles (Br at C2 and C4), with a corresponding compression of the neighbouring ring angles (at C3, C5). The remaining two angles (at C1, C6) are very close to the 120° standard. In agreement with this reasoning, the endohedral C-C-C angles of silyl-benzenes with electropositive -SiH_3 substituents at a ring carbon atom are generally smaller than 120° [15, 22].

With a dihedral angle Br1-C2-C1-I1 of only 0.4(5)°, the two neighbouring halogen atoms are virtually coplanar with the benzene ring, showing that the interaction of these two atoms does not lead to a mutual displacement out of the ring plane.

Crystals of **2** are also monoclinic, space group $P2_1/n$, with $Z = 4$ formula units in the unit cell and one molecule in the asymmetric unit (Fig. 2). The molecule has no crystallographically imposed symmetry. The two C-Br distances are virtually identical [1.890(4) and
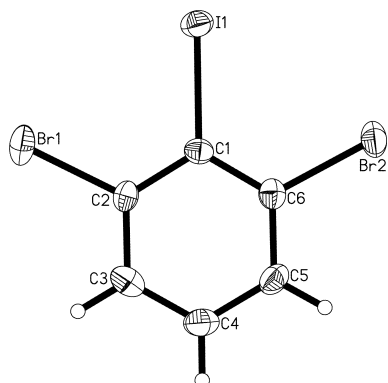
Fig. 2. Molecular structure of 1,3-dibromo-2-iodo-benzene (**2**) (ORTEP, 50% probability ellipsoids; hydrogen atoms with arbitrary radii). Selected bond lengths [Å], angles [°] and interhalogen contacts [Å]: I1-C1 2.095(4), Br1-C2 1.890(4), Br2-C6 1.891(4), C1-C2 1.406(6), C2-C3 1.393(7), C3-C4 1.385(7), C4-C5 1.387(7), C5-C6 1.394(6), C6-C1 1.391(6); I1-C1-C2 120.8(3), I1-C1-C6 121.1(3), Br1-C2-C1 122.0(3), Br1-C2-C3 117.4(3), Br2-C6-C1 121.4(3), Br2-C6-C5 117.0(3), C1-C2-C3 120.6(4), C2-C3-C4 120.2(4), C3-C4-C5 120.1(4), C4-C5-C6 119.5(4), C5-C6-C1 121.6(4). I1–Br1 3.488(4), I1–Br2 3.465(4).
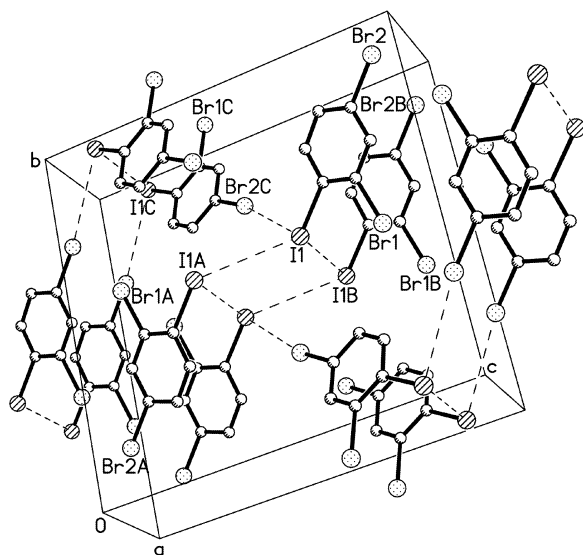

Fig. 3. Pattern of molecular packing in crystals of compound **1**. I1–I1A 3.969(4), I1–I1B 4.075(4), I1–Br2C 3.798(5) Å.

1.891(4) Å] and equal to those in **1**. The same is true for the C-I distance of 2.095(4) Å. As might be expected, the angles C1-C6-Br2 and C1-C2-Br1 are large at 121.4(3) and 122.0(3)°, with the angles C5-C6-Br2 and C3-C2-Br1 compressed to 117.0(3) and 117.4(3)°, respectively. The variations of the endocyclic C-C-angles are smaller than for **1** and not really outside
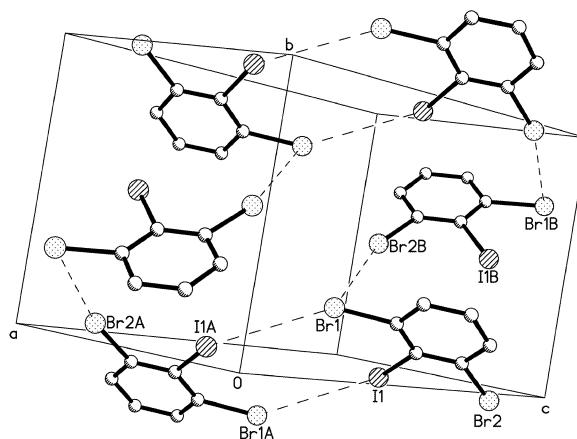

Fig. 4. Pattern of molecular packing in crystals of compound **2**. I1–Br1A 3.926(4), Br1–Br2B 3.633(5) Å.

the standard limits, but the largest values are found for the atoms C2 and C6 bearing the electronegative bromine substituents. The two dihedral angles Br-C-C-I are small at 1.5(5)° and −2.2(5)° indicating only minor deviations of the substituents (to opposite sides) from the benzene plane.

The most interesting aspect of the two structures concerns the *intra*molecular Br–I contacts, which are 3.465(4) and 3.488(4) Å in **2** and 3.530(4) Å in **1**. It is tempting to refer to the most simple mixed bromine/iodine compound, crystalline iodine bromide IBr, as a standard, where *inter*molecular I–Br contacts were found to be 3.24 and 3.39 Å, as compared to the short *intra*molecular distance (*i.e.* the I-Br bond length) of 2.52 Å [23]. However, the special nature of the I-Br bond may not offer suitable reference values, and the shortest *inter*molecular contacts in the crystal structures of **1** and **2** should better serve this purpose.

*Inter*molecular *mixed* I–Br contacts are found in the crystals of **2** [I1–Br2A 3.798 Å], complemented by long I–I contacts of 3.969(4) and 4.075(5) Å (Fig. 3). In crystals of **1** the shortest intermolecular contact is the *homo*atomic Br1–Br2A distance of 3.633(5) Å, complemented by a long I1–Br1A contact of 3.926(4) Å (Fig. 4).

For comparison, in hexaiodobenzene the *intra*molecular I–I contacts are 3.50 Å (average), with the *inter*molecular contacts I–I only slightly longer at 3.77 Å. Similarly, in 3,4,5-triiodotoluene the corresponding contacts are 3.613(1) (*intra*) and 3.746(1) Å (*inter*). These sets of data show that both the *intra*- and *inter*molecular contacts can be much shorter than sug-

gested by tabulated van der Waals radii ($2 \times 2.15 =$ 4.30 [14a], $2 \times 1.98 = 3.96$ [14b], $2 \times 2.20 = 4.40$ Å [14c] for iodine; $2 \times 1.95 = 3.90$ [14a], $2 \times 1.85 = 3.70$ [14b], $2 \times 2.00 = 4.00$ Å [14c] for bromine). It is important to note that the short *intra*molecular contacts are realized in **1** and **2** or in 3,4,5-triiodotoluene without significant structural consequences (halogen out-of-the-plane displacement, benzene ring puckering *etc.*). It should also be remembered that benzene rings bearing six really large substituents like trimethylsilyl -$SiMe_3$ undergo severe puckering as demonstrated for $[C_6(SiMe_3)_6]$ (which also is deeply coloured) [24]. Even $[C_6(SiH_3)_6]$, with much smaller silyl substituents, still exhibits alternating positioning of the -SiH_3 groups above and below the benzene plane [15f, 15g].

In another reference compound, 3,4,5,6-tetraiodophthalic anhydride, the average *intra*molecular contact between the four neighbouring iodine atoms is 3.545(1) Å, not much longer than in C_6I_6 [average 3.50 Å], but shorter than in 3,4,5-triiodo-toluene [3.613(1) Å]. Clearly, in this case only two of four iodine atoms have the opportunity to undergo a small lateral displacement, as compared to two out of three in the 3,4,5-$I_3C_6H_2Me$ case, but there is also an influence of the fused five-membered anhydride ring and its oxo substituents [19].

Returning to the title compounds with their mixed bromine/iodine substitution, the observed molecular geometries thus suggest that the C-Br and C-I bonds involving the neighbouring halogen atoms are not under significant strain, but are readily accommodated. Obviously, at an *intra*molecular I–Br distance of *ca.* 3.50 Å (**1**, **2**), the repulsive contributions are largely compensated by attractive forces between the two formally closed-shell atoms. Without this compensation, significant distortions would have to be expected to reach equilibrium distances like those which are observed for the *inter*molecular contacts (*ca.* 3.80 Å in **1**). Only the latter are in good agreement with tabulated values: $1.85(Br) + 1.98(I) = 3.83$ Å [14b]. The *inter*molecular Br–Br contact in the crystals of compound **2** [3.633(4)] Å is close to the calculated value (3.79 Å [14b]) and happens to be exactly the same as the *intra*molecular Br–Br contact observed between the two "decks" on decabromoruthenocene [3.61 Å], for which the eclipsed conformation can be ascribed to Br–Br *attraction* [25]. The I–I contacts in the crystal of **2** [3.969(3), 4.075(3) Å] are again in agreement with tabulated data ($2 \times 1.98 = 3.96$ Å [14b]).

Table 1. Crystal data, data collection and structure refinement of compounds **1** and **2**.

	1	**2**
Empirical formula	$C_6H_3Br_2I$	$C_6H_3Br_2I$
M	361.80	361.80
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	7.6727(2)	4.0751(1)
b/Å	8.3511(2)	14.1701(3)
c/Å	13.0183(4)	14.0851(4)
β/°	105.2073(11)	90.3980(9)
V/Å^3	804.94(4)	813.32(4)
ρ_{calc}/g cm^{-3}	2.985	2.955
Z	4	4
$F(000)$	648	648
(Mo-K$_\alpha$) (cm^{-1})	138.15	136.73
T/K	143	143
Refls. measured	25734	13348
Refls. unique	1869	1825
	$[R_{int} = 0.055]$	$[R_{int} = 0.049]$
Refined parameters	82	94
$R1[I \geq 2\sigma(I)]$	0.0356	0.0287
$wR2^a$	0.0968	0.0697
Weighting scheme	$a = 0.0015$	$a = 0.0503$
	$b = 2.4104$	$b = 1.8270$
σ_{fin}(max/min)/eÅ^{-3}	1.833 / −1.844	0.589 / −0.713

Following the above argument, it is even tempting to speculate that in 1-bromo-2-iodo-substituted benzene molecules the bromine atoms activate the neighbouring iodine atoms for substitution reactions by this interaction, how weak it may ever be. In previous preparative studies it was noted that *e.g.* silylation and phosphination of arenes with a 1,2,4,5-tetrabromo substitution pattern lead only to the 1,4-disilylated/-diphosphinated products. Even under more forcing conditions the 2,5-positions remained unaffected and no complete substitution could be accomplished [15]. No other explanation has been offered to date for these observations.

Experimental Section

Preparations

Compounds **1** and **2** were synthesized following literature procedures. The analytical data of the samples were in good agreement with published values [21, 22].

Determination of the crystal structures

Specimens of suitable quality and size of 2,4-dibromo-1-iodo-benzene (**1**) and 1,3-dibromo-2-iodo-benzene (**2**) were mounted on the ends of quartz fibers in inert perfluoropolyalkylether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-

monochromated Mo-K$_\alpha$ radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97). The displacements were treated anisotropically for all non-hydrogen atoms. The hydrogen atoms were calculated in ideal positions and allowed to ride on their parent atoms with fixed isotropic contributions for those bound to 1,3-dibromo-2-iodo-benzene (**2**). The hydrogen atoms bound to 2,4-dibromo-1-iodo-benzene (**1**) were located and refined with isotropic displacement parameters. Absorption corrections for both structures were carried out using DELABS, as part of the PLATON suite of programs. Further informations on crystal data, data collection and structure refinement are summarized in Table 1.

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