



Synthesis of tetrahalide dianions directed by crystal engineering†

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 Cite this: *CrystEngComm*, 2015, 17, 6641

 Received 3rd July 2015,
Accepted 9th August 2015

DOI: 10.1039/c5ce01288k

www.rsc.org/crystengcomm

Crystal engineering provides tools to the rational design of materials with desired structures or properties. We have exploited the analogy between hydrogen bonds and halogen bonds to trap I₂ in the channels of crystal structures, thus stabilizing the otherwise unfavourable tetrahalides *via* charge transfer interactions.

In the context of their diffraction studies on halogen-substituted organic compounds, Sakurai *et al.*¹ classified short contacts between halogen atoms (X⋯X) in adjacent molecules into two distinct types; these categories were confirmed much later² based on CSD³ statistics and designated as type I and type II. A variety of theoretical models has been employed^{4,5} to explain the specific arrangement in crystals of dihalogen or halogenated compounds and to understand the nature of their interactions. Despite the debate concerning their nature, interhalogen contacts have been widely used in designing structures and materials.^{6–8} Recent studies showed that type I and type II halogen⋯halogen interactions do not only differ in terms of bonding. Given the electronic polarization of the halogen atoms, the type I geometry minimizes inter-repulsion and can thus be considered essentially as a kind of van der Waals force, whereas type II represents electrostatic attraction with the electrophilic region of one halogen approaching the diffuse electron density of the other.^{9,10} These type II interactions fulfil the requirements for halogen bonds (XB).¹¹

Organic as well as inorganic constituents may contribute halogen atoms to short X⋯X contacts. In particular, dihalogen molecules as donors and halide acceptors aggregate to polyhalides; among these, polyiodides are the most

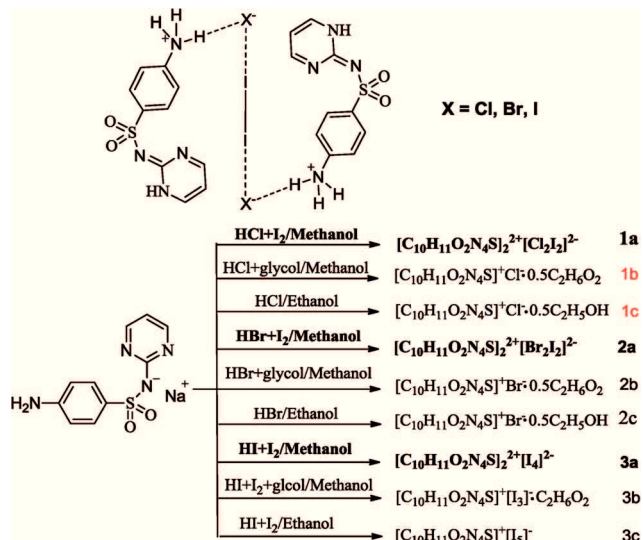
relevant compounds. Triiodide (I₃[−]), formed by addition of an iodide with an I₂, can be regarded as the strongest halogen bonded species. Due to its stability, it represents the most studied halogen bonded system. Alternatively, I₃[−] can be understood as a covalent species, not very different from I₂. With respect to synthesis, the system can be extended to tetraiodide, pentaiodide, and higher polyiodides by combining different stoichiometries of I₂ and I[−]; the resulting polyiodide anions are then stabilized by suitable cations. The most iodine-rich polyiodide documented in the literature is I₂₉^{3−}, co-templated with ferrocenium as counter-cation by Tebbe and Buchem.¹² Recently, polyiodides have received considerable attention because of their potential application as materials for solar cells.¹³ However, the rather simple tetraiodide and the isostructural tetrahalides have found less interest because of their lower stability. In a recent survey in the Cambridge Structural Database (CSD),³ 48 crystal structures containing tetrahalides have been retrieved, among which only one [Br⋯I–I⋯Br]^{2−} and two [Cl⋯I–I⋯Cl]^{2−} species were reported. Reports about rational design of tetrahalides are rare: alkylated 4,4′-bipyridines^{14a} and 1,6-bis-(trimethylammonium)hexane^{14b} have been used successfully as templates. *N*-cyclohexyl ammonium resorcinarene chloride may accommodate elemental I₂ and form [Cl⋯I–I⋯Cl]^{2−},¹⁵ but this approach cannot be extended to the analogous adducts of Cl₂ or Br₂.

In this contribution, we follow a new strategy to stabilize the ephemeral tetrahalide dianions. We recently undertook a detailed study of the properties of sulfadiazine as a neutral, cationic or anionic residue¹⁶ and as ligand in a metal complex.¹⁷ Sulfadiazine does not only represent a well-known anti-bacterial drug; rather, its geometry and charge distribution make this compound a highly suitable template for the rational design of supramolecular architectures. A stable supramolecular sulfadiazine macrocycle was able to capture ethanol or ethylene glycol by means of hydrogen bonds.¹⁶ The analogy between halogen and hydrogen bonds, both highly directional interactions, and the size match between a

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† Electronic supplementary information (ESI) available: Synthesis, single crystal X-ray crystallographic analyses, CCDC 1409609–1409615, X-ray powder diffraction results, and Raman spectroscopy. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ce01288k



Scheme 1 Construction principle of the tetrahalides, their chemical composition and relationship to the parent compound **1b**. Reaction products containing “X···I···X” moieties are highlighted in bold; compounds reported earlier indicated in red.

Cl⁻···HOC₂H₄OH···Cl⁻ and Cl⁻···I···Cl⁻ group suggested that our sulfadiazine synthon might also be a useful template for stabilizing tetrahalides. Our experiments in this context have been summarized in Scheme 1.

The sulfadiazine macrocycle¹⁶ in **1b** plays a pivotal role for the stabilization of the tetrahalides in **1a**, **2a** and **3a**; we therefore refer to **1b** as the parent compound and shortly recall its construction principles. The underlying basic interactions have been graphically represented in Fig. 1 and equally apply to the new compounds **1a**, **2a** and **3a**. In the sulfadiazinium cation, protonation occurs at a pyrimidine and at the aniline nitrogen atoms whereas the sulphonamide-N is deprotonated and formally carries a negative charge; this at first sight counterintuitive pattern is

stabilized by hydrogen bonds. The resulting symmetric sulfadiazinium pair possesses potential hydrogen bond acceptors (–SO₂) and donors (–NH₃) at both sides, which interact with the neighbours through N4–H4C···O1^a and O1···H4C^a–N4^a bonds (ref. Table S2[†]) and thus extend the dimer to a one-dimensional chain along the crystallographic *c* axis (Fig. 1, left, top). Although individual hydrogen bonds are only moderately strong, their joint effect renders the 1D chain a reliable synthon.¹⁸ Orthogonal to the extension of the hydrogen-bonded chain, Cl⁻ anions accept hydrogen bonds from two –NH₃ groups of neighbouring chains, thus acting as connectors for a 2-D motif (marked in purple and brown in Fig. 1 left, bottom). The result of our previous experimental charge density study¹⁶ suggested weak interactions between the chloride connectors and the anilinium N atoms in the adjacent layer (red circle in Fig. 1, center); the term “pnictogen bond” has been suggested for such contacts.¹⁹ These presumably weak N···Cl interactions expand the solids into the 3rd dimension. The 3-D arrangement thus obtained is further stabilized by π···π interactions and non-classical hydrogen bonds: neighbouring pyrimidine rings interact with a centroid···centroid distance of 3.693 Å and a lateral shift of 1.494 Å; the protonated anilinium groups are stabilized by hydrogen bonds, together with aromatic π···π interactions (centroid···centroid distance 3.858 Å, lateral shift 1.076 Å); CH···Cl and CH···O bonds also contribute to the molecular assembly. All of these interactions result in a robust 3D scaffold suitable for the accommodation of alternative guest molecules. A space filling representation of the framework reveals obvious channels; when van der Waals radii for X⁻ are taken into account, their open diameter amounts to ca. 5.5 Å (Fig. 1, right). Chlorides are located in the channel walls, thus acting as potential electron donors to H or halogen bond partners.

Ethylene glycol, the guest in the parent compound **1b**, features a distance of 4.9 Å between the hydroxyl H atoms and

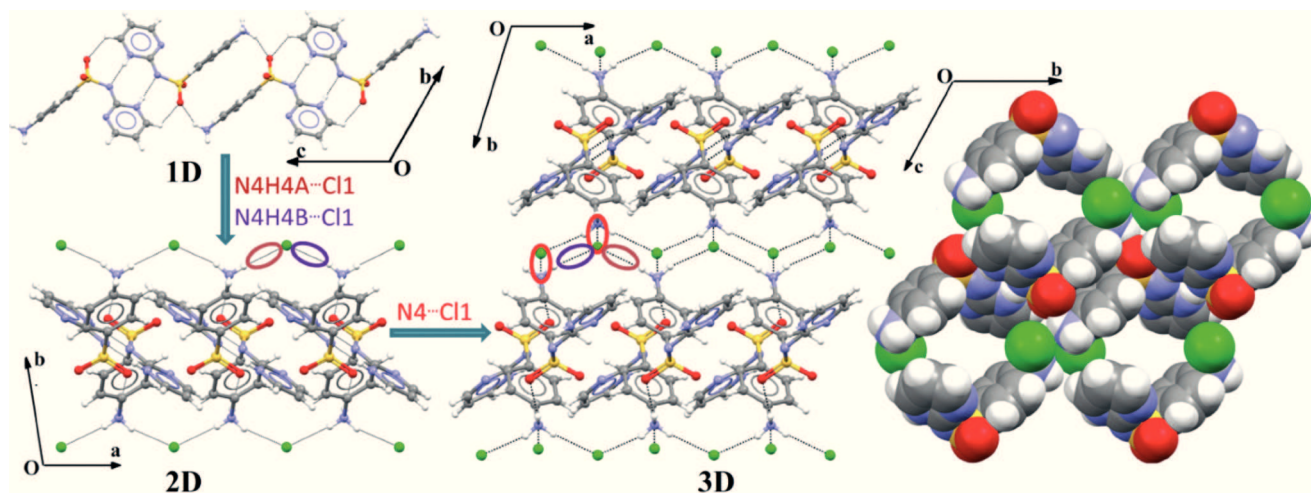


Fig. 1 Stepwise analysis of secondary interactions in the scaffold for the parent compound **1b** and the tetrahalide derivatives **1a**, **2a** and **3a**; a detailed explanation of the individual interactions is given in the text. The right picture in CPK mode shows the channels with ca. 5.5 Å width.

therefore fits the channel diameter as a hydrogen bond donor very well. In a similar way, the I₂ molecule with its I⋯I distance of *ca.* 2.7 Å fits into the Cl⋯Cl separation across the channels, with I⋯Cl distances slightly shorter than the sum of the van der Waals radii, thus appropriate for a heterotetrahalide anion Cl₂I₂²⁻ (Fig. 2). Following this concept, a solution of the parent compound in methanol was offered I₂ as an alternative guest, and indeed beautiful brown needles of **1a** were obtained in high yield.

1a crystallizes in the triclinic space group *P* $\bar{1}$ with all atoms in general positions. A crystallographic inversion center is situated at the midpoint of the I–I bond, with half of the dihalogen molecule and one molecule of sulfadiazinium hydrochloride in the asymmetric unit (Fig. 2). The Cl⋯I distance of 3.2416(6) Å with an interaction ratio R_{XB} ($R_{\text{XB}} = d_{\text{XB}} / (X_{\text{vdw}} + B_{\text{vdw}})$) of 0.87 indicates halogen bonding of moderate strength. The tetrahalide dianion is embedded in a macrocyclic supramolecule which resembles that in the parent compound; slight differences in its secondary interactions, however, stabilize the tetrahalide structure with respect to the ethylene glycol containing parent compound. The increased stability is reflected in the higher decomposition point (203–205 °C) of **1a** compared to that of the parent compound (184–186 °C). We note that our attempts to remove I₂ from crystals of **1a** at 100 °C under vacuum for 24 hours have not been successful: I₂ can only be released with degradation of the structural assembly.

Following the same strategy, the tetrahalides **2a** and **3a** have been obtained (ESI† Fig. S4); both are isomorphous with **1a**. Phase purity of the products was verified by X-ray powder diffraction (ESI† Fig. S1–S3). Rather than repeating the structure description, we here focus on the differences between these structures. Details about the secondary contacts in the three structures and in the parent compound have been documented in Table S2 (ESI†). For larger halide anions, the distances between the corresponding hydrogen bond donors interacting with the terminal atoms are elongated. Despite the fact that the halogen⋯halogen bonds between I₂ and the terminal halides also become longer as a function of the halide radius, the bond strength increases; this can approximately be represented by the decreasing value of the halogen⋯halogen interaction ratio R_{XB} . A second obvious indication for the halogen⋯halogen interaction is the central I–I bond length: the secondary interactions with the terminal halides significantly affect the bond order in the central iodine molecule. Table S2† clearly evidences the increase of the I–I distances from **2a** to **3a**.

Deplano *et al.* proposed an empirical criterion to distinguish molecular polyiodides from the adducts of the fundamental iodine species based on the bond order n of the I₂ in the structures using Pauling's "bond order" versus "bond length" relationship $d_{\text{I-I}} = 2.67 - 0.85 \times \log n$.²⁰ Species with I–I bond order $n < 0.6$ can be considered as discrete polyiodide entities. According to this estimation, the bond order for the central I–I bond decreases from 0.88 in **1a** via 0.83 in **2a** to 0.77 in **3a**. This distance-based estimation matches the

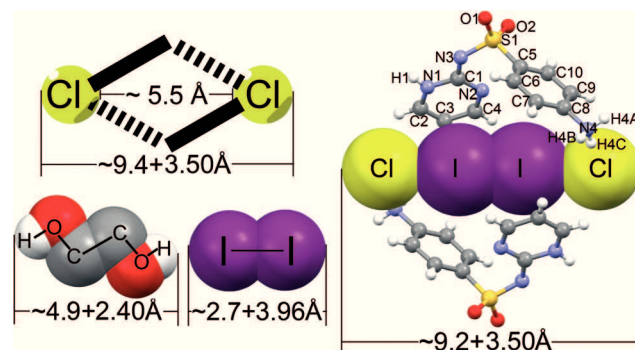


Fig. 2 Left: Projection comparing the similar size requirements of ethylene glycol and a diiodine molecule; when van der Waals radii are taken into account, both match the channel diameter. Right: Representation of the I₂ guest molecule in a supramolecular ring in the crystal structure of **1a**; the situation is very similar for **2a** and **3a**. The atom labelling corresponds to that in the reported structure,¹⁶ hydrogen atoms attached to carbon are not labelled.

trends derived from Raman spectroscopy (ESI† Fig. S7): the wavenumbers for the vibration associated with the central I–I bond in the tetrahalides also decreases from [Cl₂I₂]²⁻ in **1a** via **2a** to the tetraiodide in **3a**, thus indicating increasing interaction between the central and the peripheral halogen atoms. When the strict Deplano criterion is applied, one may therefore doubt the tetrahalides character of the anions and rather describe them as adducts of two terminal halides to a central I₂ molecule. In the present contribution, we rather adopt the more tolerant distance criterion proposed by Svensson and Kloo¹³ who accept I⋯I contact distances up to 3.4 Å for polyiodides. According to this concept, **3a** should be considered as a tetraiodide rather than an adduct.

To complete the systematics with respect to crystal engineering, we also prepared the corresponding solvates of the sulfadiazine bromides **2b** (with ethylene glycol) and **2c** (with ethanol). They are isomorphous with the analogous chlorides **1b** and **1c**, respectively¹⁶ (ESI† Fig. S5). Under the same reaction conditions used for the preparation of the chlorides and bromides, however, the reaction with hydroiodic acid yielded the entirely different compounds **3b** (with ethylene glycol) and **3c** (with ethanol).

The structures of **3b** and **3c** are closely related: both compounds crystallize in the triclinic space group *P* $\bar{1}$; a unit cell transformation to a non-standard setting for **3c** results in comparable lattice parameters and similar arrangement of the residues.

3b is the ethylene glycol solvate in which the positive charge of the sulfadiazinium cation is balanced by a triiodide (I₃⁻) anion in the asymmetric unit (Fig. 3, left), whereas in **3c**, the solvent site is not occupied by ethylene glycol but rather by an additional iodine molecule which in contact with an I₃⁻ anion formally aggregates to a pentaiodide I₅⁻. Although **3b** and **3c** differ from the other compounds with respect to the conformation of the sulfadiazinium cations, similar secondary interactions exist in all solids: intermolecular hydrogen bonds between the pyrimidine amide groups lead to

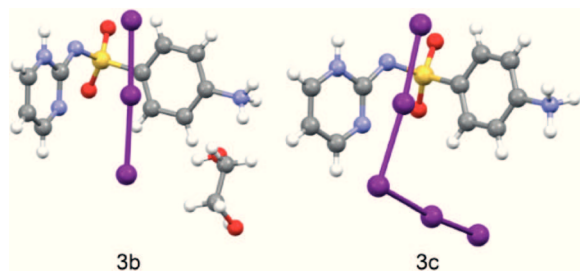


Fig. 3 Structural similarity between the asymmetric units in **3b** and **3c**; an I_2 molecule in **3c** replace the ethylene glycol in **3b**.

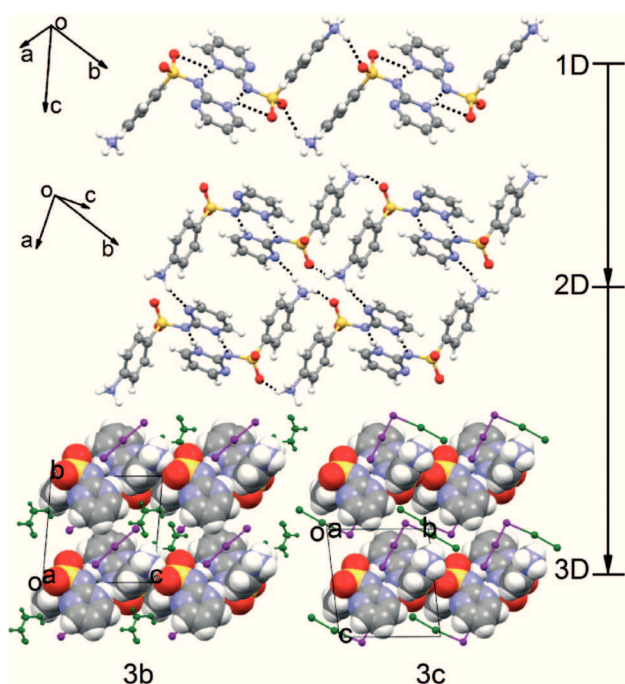


Fig. 4 The construction of non-covalent frameworks in **3b** and **3c** from 1D chains via 2D sheets to 3D stacking. Most molecules are represented as CPK models, ethylene glycol molecules in **3b** and I_2 molecules in **3c** are shown in green to highlight the structural similarity.

sulfadiazinium cationic dimer, and the interactions between sulfonyl-*O* and an anilinium H atom as well as the $\pi \cdots \pi$ stacking between benzyl groups also persist, linking the dimers to 1D chains (Fig. 4, top). The chains in **3b/3c** and those in the remaining compounds use different sulfonyl oxygen atoms as hydrogen bond acceptors. Without the small halide anions, a H atom of the anilinium group in the cation serves as hydrogen bond donor to the neighboring sulfadiazine chain in [101] direction. The third NH_3 proton interacts with the guest ethylene glycol in **3b** and with the pentaiodide in **3c**. The ethylene glycol in **3b** adopts a gauche conformation, acting as hydrogen bond acceptor towards the cationic framework and as hydrogen bond donor with respect to triiodide (ESI† Fig. S6A). The $I \cdots I$ interactions between pentaiodide residues in **3c** are interesting. Both type I and type II halogen \cdots halogen interactions were detected; they

link the polyiodides into a double-stranded 1D polymer with macrocycles (ESI† Fig. S6B).

Conclusions

Crystal engineering aims at the rational construction of new materials with certain target features. We herein apply these concepts to tetrahalides: due to charge repulsion in these relatively small dianions, their direct synthesis is difficult and only well-designed approaches are promising. In this contribution we offer a systematic access to tetrahalides by combining the structural features of an established solid and the basic concepts of crystal engineering. Exploiting the analogy between hydrogen and halogen bonds, we have been able to encapsulate I_2 molecules in the channels of a robust framework stabilized by secondary interactions. The interaction ratios R_{XB} in the resulting structures allow an alternative interpretation as adducts, but their physical properties rather suggest to consider them tetrahalides: strong polarization in the iodine results in tight binding of the central halogen molecule – it may not be removed under vacuum at 100 °C. As often observed when secondary interactions are involved, our strategy is quite sensitive to changes in the reaction conditions. Two hardly predictable pseudo-isomorphous structures featuring I_5^- and I_3^- anions were obtained by changing the crystallization solvent.

The three compounds containing tetrahalide dianions $[Cl \cdots I \cdots Cl]^{2-}$, $[Br \cdots I \cdots Br]^{2-}$ and $[I \cdots I \cdots I]^{2-}$ are isostructural, thus facilitating their systematic comparison. In our future work we will address electron distribution and bonding in these challenging many-electron systems by a combination of theoretical calculations and experimental charge density; the latter will be based on high resolution diffraction.

Acknowledgements

Financial support for F. P. from China Scholarship Council and Academy of Finland (K. R. grant no. 265328 and 263256) is kindly acknowledged.

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