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COMMUNICATION

Synthesis of Tetrahalide Dianions Directed by Crystal Engineering

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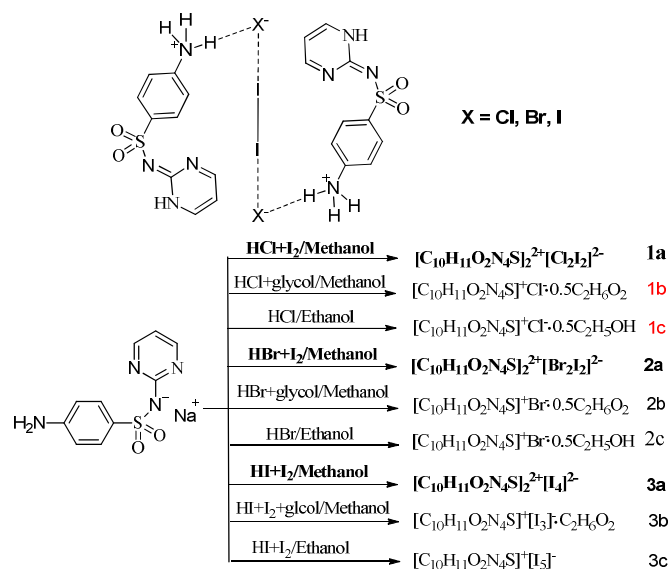
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Crystal engineering provides tools to the rational design of materials with desired structures or properties. We have exploited the analogy between hydrogen bonds and halogen bonds to trap I₂ in the channels of crystal structures, thus stabilizing 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 I₂₉³⁻, 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.



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

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 $\text{Cl}^-\cdots\text{HOC}_2\text{H}_4\text{OH}\cdots\text{Cl}^-$ and $\text{Cl}^-\cdots\text{I}^-\cdots\text{Cl}^-$ 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.

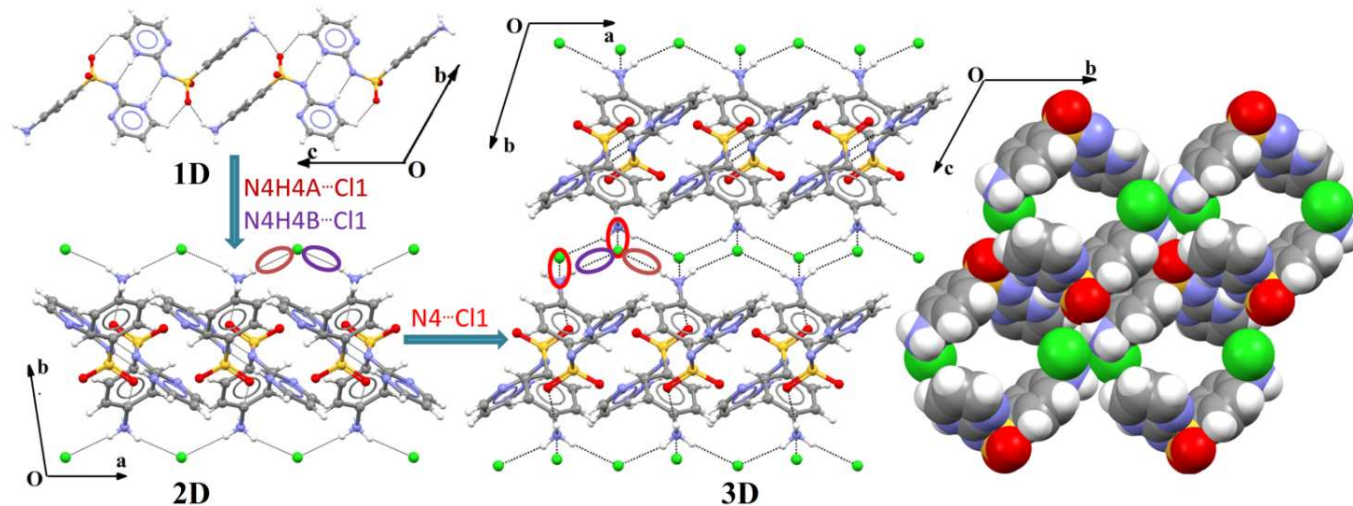


Figure 1. Stepwise analysis of secondary interactions in the scaffold for the parent compound **1b** and the tetrahalide derivatives **1a**, **2a** and **3a**; a detailed explanation of the individual interactions is given in the text. The right picture in CPK mode shows the channels with ca. 5.5 Å width.

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 Figure 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 ($-\text{SO}_2$) and donors ($-\text{NH}_3$) at both sides, which interact with the neighbours through $\text{N4}\cdots\text{H4C}^{\text{a}}\cdots\text{O1}^{\text{a}}$ and $\text{O1}^{\text{a}}\cdots\text{H4C}^{\text{a}}\cdots\text{N4}^{\text{a}}$ bonds (ref. Table S2) and thus extend the dimer to a one-dimensional chain along the crystallographic c axis (Figure 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 $-\text{NH}_3$ groups of neighbouring chains, thus acting as connectors for a 2-D motif (marked in purple and brown in Figure 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 Figure 1, center); the term "pnictogen bond" has been suggested for such contacts.¹⁹ These presumably weak $\text{N}\cdots\text{Cl}$ interactions expand the solids into the 3rd dimension. The 3-D arrangement thus obtained is further stabilized by $\pi\cdots\pi$ interactions and non-classical hydrogen bonds: neighbouring pyrimidine rings interact with a centroid \cdots 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 $\pi\cdots\pi$ interactions (centroid \cdots centroid distance 3.858 Å, lateral shift 1.076 Å); $\text{CH}\cdots\text{Cl}$ and $\text{CH}\cdots\text{O}$ 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 (Figure 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 therefore fits the channel diameter as a hydrogen bond donor very well. In a similar way, the I_2 molecule with its $\text{I}\cdots\text{I}$ distance of ca. 2.7 Å fits into the $\text{Cl}\cdots\text{Cl}$ separation across the channels, with $\text{I}\cdots\text{Cl}$ distances slightly shorter than the sum of the van-der-Waals radii, thus appropriate for a hetero-tetrahalide anion ClI_2 . Following this concept, a solution of the parent compound in methanol was offered I_2 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. The $\text{Cl}\cdots\text{I}$ 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 I_2 from crystals of **1a** at 100 °C under vacuum for 24 hours have not been successful: I_2 can only be released with degradation of the structural assembly.

Following the same strategy, the tetrahalides **2a** and **3a** have been obtained (ESI Figure S4); both are isomorphous with **1a**. Phase purity of the products was verified by X-ray powder diffraction (ESI

Figure 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 I_2 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**.

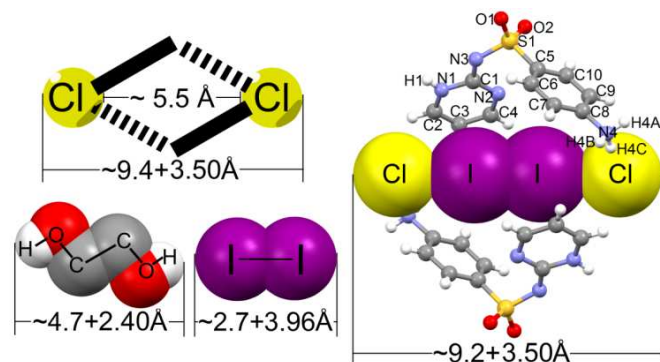


Figure 2. Left: Projection comparing the similar size requirements of ethylene glycol and a diiodine molecule; when van der Waals radii are taking into account, both match the channel diameter. Right: Representation of the I_2 guest molecule in a supramolecular ring in the crystal structure of **1a**; 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.

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 I_2 in the structures using Pauling's "bond order" versus "bond length" relationship $d_{I-I} = 2.67 - 0.85 \cdot \log n$.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 trends derived from Raman spectroscopy (ESI Figure S7): the wavenumbers for the vibration associated with the central I-I bond in the tetrahalides also decreases from $[Cl_2I_2]^{2-}$ 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 I_2 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**, respectively.¹⁶ (ESI Figure 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 $P-1$; a unit cell transformation to a non-standard setting for **3c** results in comparable lattice parameters and similar arrangement of the residues.

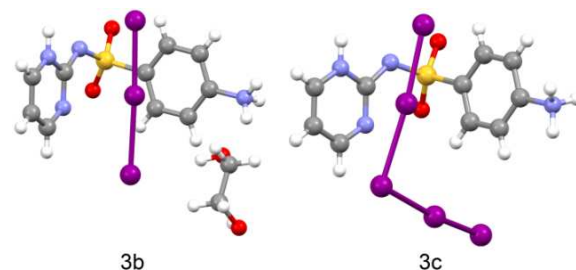


Figure 3. Structural similarity between the asymmetric units in **3b** and **3c**; an I_2 molecule in **3c** replace the ethylene glycol in **3b**.

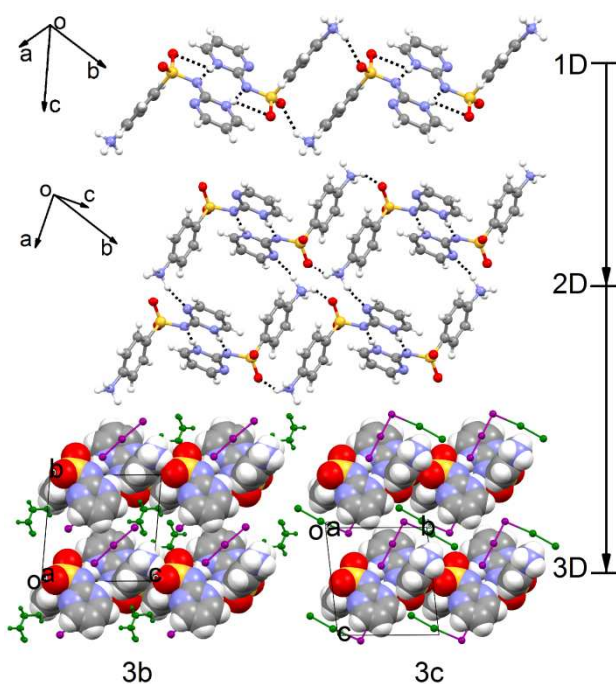


Figure 4. The construction of non-covalent frameworks in **3b** and **3c** from 1D chains via 2D sheets to 3D stacking. Guest molecules are represented as CPK models, ethylene glycol molecules in **3b** and I_2 molecules in **3c** are shown in green to highlight the structural similarity.

3b is the ethylene glycol solvate in which the positive charge of the sulfadiazinium cation is balanced by a triiodide (I_3^-) anion in the asymmetric unit (Figure 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 I_3^- anion formally aggregates to a pentaiodide I_5^- . 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 sulfadiazinium cationic dimer, and the interactions between sulfonyl-O and an anilinium H atom as well as the π ... π stacking between benzyl groups also persist, linking the dimers to 1D chains (Figure 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 NH₃ 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 Figure S6A). The I...I interactions between pentaiodide residues in **3c** are interesting. Both type I and type II halogen...halogen interactions were detected; they link the polyiodides into a double-stranded 1D polymer with macrocycles (ESI Figure 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 I₂ 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-isomorphic structures featuring I₅⁻ and I₃⁻ anions were obtained by changing the crystallization solvent.

The three compounds containing tetrahalide dianions [Cl...I...Cl]²⁻, [Br...I...Br]²⁻ and [I...I...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.

Notes and references

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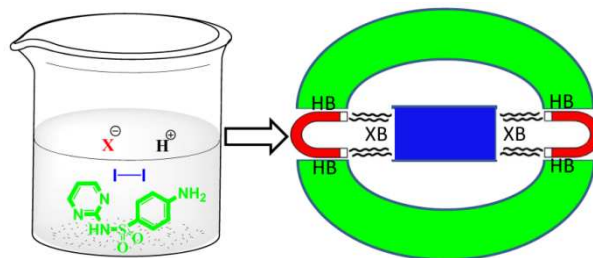
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- 5.36, November 2014; only error-free structures featuring “X-X-X-X”, “X-X-X-X” or “X-X-X-X” species without disorder were included, where “X” refers to halogen atom and the species were constrained with X...X distances of 3.6 Å, X-X...X angles of 160–180°, and number of bonded atoms.
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[X...I...X]²⁻ Stabilization by Crystal Engineering

The analogy between hydrogen bonds and halogen bonds was used to synthesize the unstable [X...I...X]²⁻ species by trapping I₂ in the channels of macrocyclic compounds.