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Crystal engineering towards highly ordered polymeric structures of 1,3-dithiole-2-thione–dihalogen adducts †

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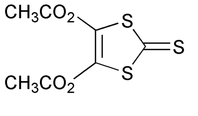
The crystal structure of an iodine monobromide adduct of dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate reveals a layered polymeric network of donor and acceptor molecules linked primarily through S···I–Br charge-transfer and hydrogen bonded interactions.

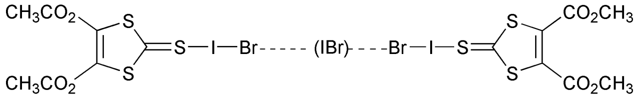
The reaction of heteroatom donor molecules with dihalogens (I_2, Br_2, Cl_2) or interhalogens (IBr, ICl) can follow a variety of pathways, the most prevalent being the formation of donor–acceptor or charge-transfer adducts containing a linear D···X–Y moiety (X = I; Y = I, Br, Cl) or insertion products containing an X–D–Y fragment (X = Y = Br, Cl).[1] Recently we have been investigating dihalogen adducts of thiocarbonyl donors based on the 1,3-dithiole-2-thione unit.[1] We are keen to explore the role that charge-transfer interactions might play in the formation of functional supramolecular assemblies. It has been postulated that these types of adduct can be used as components in molecular electronics,[2] but in order to realise this function, the materials have to conform to certain structural and electronic requirements. Consequently, the adduct has to offer some form of advantageous electroactivity, such as the ability to form stable radicals for conducting and magnetic properties, or exhibit assymetric charge-transfer for nonlinear optical applications. In the former example, the material needs to exhibit long range order in the bulk solid to achieve a magnetic state, and also an extensive network of intermolecular π-interactions for conductivity.

In view of the above, thiocarbonyl compounds containing 1,3-dithiole fragments are suitable candidates for dihalogen complexes featuring interesting electronic properties. Previous studies have shown that charge-transfer interactions can be used to link multidentate/macrocyclic donors, such as thioether crowns[3] or diazines,[4] and polymeric coordination complexes,[5] though little work has been carried out on the formation of ordered supramolecular assemblies containing relatively simple monodentate donors. We are particularly interested in the self-assembly of substituted 1,3-dithiole-2-thione species as dihalogen adducts. In this work, we have prepared the IBr adduct of dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate **1**;[6] the X-ray crystal structure of the adduct **2** reveals an array of S···I, I···Br and hydrogen bonding interactions, many of which are unprecedented for thiocarbonyl–dihalogen adducts.

Treatment of **1** with an equimolar quantity of IBr in refluxing acetonitrile resulted in the formation of a brown coloured solution. On cooling at −5 °C overnight, orange crystals of the adduct [(**1**·IBr)$_2$IBr] (**2**) were deposited (no elemental analysis data are available as **2** slowly loses IBr).



1



2

The X-ray crystal structure of **2** is shown in Fig. 1.‡ The close contact between atoms S(1) and I(1) arises from a 'charge-transfer' process from the thiocarbonyl-sulfur to the interhalogen. Thus, electron density from a lone pair of the sulfur is donated to the σ* antibonding orbital of the I–Br bond. This situation results in the formation of a weak bond [2.605(2) Å] which is significantly shorter than the sum of the van der Waals radii of the corresponding atoms (3.75 Å),[7] and a lengthened I(1)–Br(1) bond of 2.7107(11) Å [bond length of uncoordinated IBr is 2.521(4) Å].[8] The bond angle S(1)···I(1)–Br(1) between

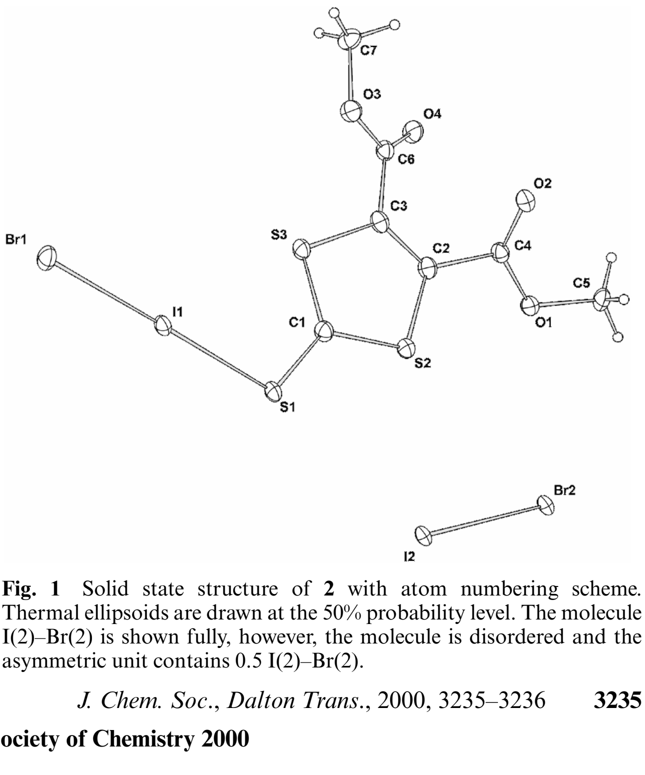


Fig. 1 Solid state structure of **2** with atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. The molecule I(2)–Br(2) is shown fully, however, the molecule is disordered and the asymmetric unit contains 0.5 I(2)–Br(2).

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† Electronic supplementary information (ESI) available: colour versions of the packing diagram of **2** viewed along the *b* axis with and without H-bonds. See http://www.rsc.org/suppdata/dt/b0/b005570k/

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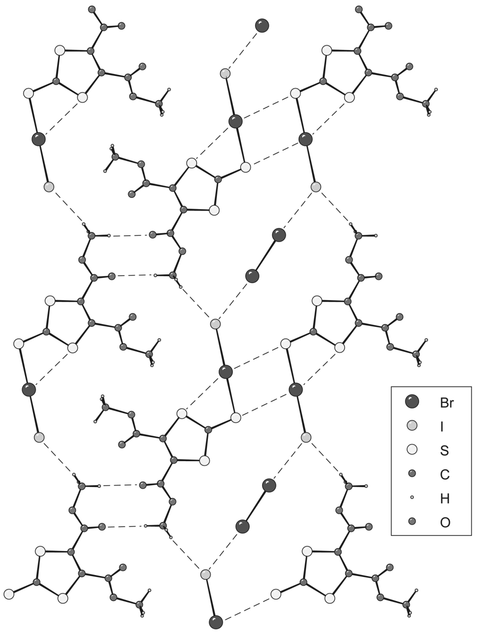

Fig. 2 Packing diagram of **2** viewed along the *b* axis showing intermolecular S···I, halogen–halogen close contacts and H-bonds.

the two components is 178.01(7)° giving a linear conformation. A further significant intramolecular interaction is seen between the heterocyclic sulfur S(3) and I(1) [3.361(3) Å]; thus, the donor effectively chelates the iodine monobromide, resulting in a four-membered ring involving the S(1)···I(1)···S(3)–C(1) atoms.

A further half molecule of IBr is included in the asymmetric unit, with a 50% probability of iodine or bromine [Fig. 1 shows the complete I(2)–Br(2) molecule]. This molecule is independent of any interactions from the heterocycle and effectively acts as a bridge between two adjacent **1**·IBr units; the I–Br bond in the bridging iodine monobromide molecule is elongated [$d_{\mathrm{I(2)–Br(2)}}$ = 2.7173(13) Å]. The distances between the terminal bromine atoms of the **1**·IBr moieties of **2** and the bridging IBr molecule, Br(1)···I(2)/Br(2), are 3.3614(13) Å. The bond angles I(2)–Br(2)···Br(1) and I(1)–Br(1)···Br(2) are 175.21 and 130.14°, respectively.

The supramolecular structure of **2** is illustrated in Fig. 2.§ The structure contains perfectly eclipsed stacks of the donor and interhalogen acceptor and the interatomic distance between identical atoms in each layer is 5.816 Å. The S(1)–I(1) unit of the complex forms dimers through weak intermolecular bonds (3.669 Å) between S(1)–I(1′) and S(1′)–I(1), forming a four-membered ring between the adducts. In conjunction with the interactions between the dihalogen molecules, this feature gives rise to polymer chains within each sheet of the structure, which can be seen in Fig. 2.

The role of the diester functionality in the solid is also identified in Fig. 2, which includes further interactions through hydrogen bonding. A second set of dimers is formed between the methyl protons of one ester group and the carbonyl oxygen in the equivalent functional group of an adjacent molecule [H(5a)···O(2) = 2.427 Å]. Through a similar interaction, the second ester functionality serves to link adjacent molecules within the same stack, giving rise to a second polymer chain rather than forming dimers [H(7b)···O(4) = 2.430 Å, not shown in Fig. 2]. Finally, a third hydrogen bond between H(5b) and Br(1) (2.8183 Å) provides an additional interstack interaction. Overall, the hydrogen bonding network serves as a cross-linker to the linear polymer chain, resulting in a very rigid three-dimensional self-assembled superstructure.

The low frequency Raman spectrum of **2** contains two bands, a strong, broad, band at 186 cm^{-1}, together with a slightly weaker one at 147 cm^{-1}. These two bands can be attributed to the antisymmetric and symmetric stretching vibrations of the S–I–Br components of **2** respectively. Given the similarity in the bond lengths between the chelated and the bridging IBr molecules in **2**, it seems likely that the band at 186 cm^{-1} also has a contribution from the bridging IBr molecules.

In summary, we have presented the X-ray crystal structure of a new 1,3-dithiole-2-thione–IBr adduct (**2**) and identified two key points: (i) the precedence for occluding a free molecule of IBr, which could interact with suitable strong donors analogous to **1**, thereby providing open shell species *via* a formal charge-transfer process; (ii) a highly ordered array of supramolecular interactions which is desirable for magnetic and/or conducting properties in the bulk solid. In the pursuit of electroactive thiocarbonyl-dihalogen adducts for molecular electronics applications, the major challenge now is to design stronger thiocarbonyl electron donors than **1**, whilst retaining a highly ordered structure through suitable supramolecular functionalities.

Notes and references

‡ Crystal data for **2**. $C_7H_6BrIO_4S_3 \cdot 0.5IBr$, $M = 560.51$, triclinic, $a = 5.8163(3)$, $b = 8.7676(4)$, $c = 14.8481(9)$ Å, $\alpha = 77.310(2)$, $\beta = 83.073(2)$, $\gamma = 84.686(2)°$, $V = 731.58(7)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$, $Z = 2$, $\mu = 7.765$ mm^{-1}, 5844 reflections measured, 2518 unique ($R_{\mathrm{int}} = 0.0645$) which were used in all calculations. CCDC reference number 186/2163. See http://www.rsc.org/suppdata/dt/b0/b005570k/ for crystallographic files in .cif format.

§ The molecule I(2)–Br(2) is disordered around the inversion centre such that opposing orientations are statistically distributed throughout the crystal.

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