Poster

Tailoring halogen bond donors for crystal engineering

S. van Terwingen[1], **F. Nie**[2], **U. Englert**[2,3]

[1]Department of Inorganic Chemistry, University of Vienna, Währinger Str. 42, 1090 Vienna, Austria, [2]Institute of Inorganic Chemistry, RWTH Aachen University, Melatener Str. 1, 52074 Aachen, Germany, [3]Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, 92 Wucheng Road, Taiyuan, Shanxi 030006, PR China

steven.van.terwingen@univie.ac.at

Halogen bonds (XB) have gained extensive interest over the last decades, especially from theoretical chemists and physicist but also from the crystal engineering community. XBs emerge from the interaction of an electron-deficient site of a (mostly heavy) halogen atom (called the XB donor) and a nucleophile, thus forming a halogen bonded adduct. The electron-poor site at the halogen has been referred to as the *σ-hole* [1], as it is located on the opposite side of the halogens bond to the organyl rest.

If a tailored XB adduct is needed, usually the Lewis basic nucleophile is altered and not the XB donor. This is due to the fact that there is a plethora of Lewis bases available for a chemist, but only a few strong XB donors are used; in particular perfluorinated halobenzenes. The fluorination increases the polarization of the bonded heavy halogen, causing the σ-hole to be more electron-deficient and, thus, forming stronger XBs. Although also non-fluorinated haloorganyls form XBs [2], the majority of encountered XB adducts in the CSD exhibits some sort of fluorinated haloorganyl. We want to expand the range of possible XB donors without compromising the strength of the σ-hole by introducing trifluoromethyl groups (CF_3) instead of direct fluorination. While a direct fluorination has a strong electron-withdrawing effect on the atom bound to the flourine, CF_3 groups are known to have a more far-reaching electron-withdrawing effect for the whole molecule [3].

We therefore re-synthesized 1,4-bis(trifluoromethyl)-2,5-diiodobenzene (BTDIB, **1**) as a prototype for our suggestion [4]. It crystallizes in the triclinic space group *P*-1 with $Z = 2$; however, there are two halfs of different BTDIB moieties situated inside the asymmetric unit, both of which have the center of gravity of their respective phenyl ring located on different centers of inversion. The crystal structure of **1** exhibits halogen bonds between the two BTDIB moieties with a distance of $d(\text{I1}\cdots\text{I2}) = 3.8082(15)$ Å and an angle of $\angle(\text{C1–I1}\cdots\text{I2}) = 165.71(17)°$ (Figure 1a). The distance is below the sum of the van der Waals radii (3.9 Å) [5], thus indicating a weak closed-shell interaction. Expanding this contact reveals a 1D chain through the crystal along [1 –1 0].

Reaction of **1** with 1,4-dimethylpyridinium iodide leads to a halogen bonded cocrystal (**2**), in which the iodide I2 acts as the halogen bond acceptor bridging two moieties of **1** at a distance of $d(\text{I1}\cdots\text{I2}) = 3.4456(5)$ Å. I2 is located on a center of inversion with Wyckoff letter 1*a*, thus forming a 1D chain of halogen bonds along [1 0 −1] (Figure 1b).

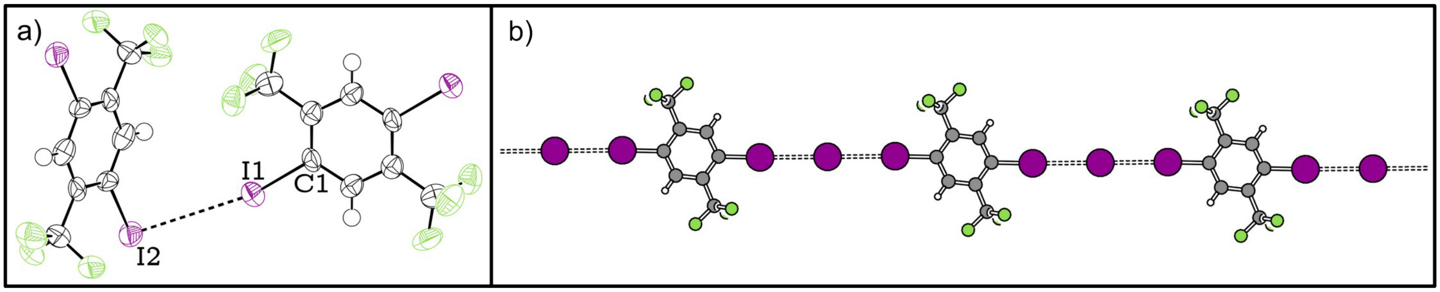

Figure 1. a) Displacement ellipsoid plot of **1** (90% probability), XB shown with a dashed line. b) Excerpt of the halogen bonded 1D chain formed by the interaction of **1** with an I^- along [1 0 –1] as found in **2**, cation omitted for clarity.

We expect these results to spark new interest in the crystal engineering community to further explore the playground of halogen bonded extended structures through not only tailoring the XB acceptor but, as shown above, the XB donor.

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