Review

Fluorinated elements of Group 15 as pnictogen bond donor sites

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ABSTRACT

The presence of fluorine atom(s) in a molecule makes the σ-hole potentials of surrounding atoms more positive and thus increases their tendencies to interact attractively with nucleophiles. This review shows that in the crystal structures of fluorinated derivatives of the Group 15 atoms, close contacts between Group 15 atoms and negative sites (e.g. lone pair possessing atoms and anions) are quite common. These close contacts are taken as indications of attractive interactions. The collection of single crystal X-ray structures analysed in this paper demonstrates that the ability of fluorinated atoms of Group 15 to work as electrophilic sites, namely to function as pnictogen bond donors, is fairly general. The directionalities and separations of these pninctogen bonds are convincing experimental evidences that linking a fluorine to a pnictogen atom increases its electrophilicity to the point that pnictogen bonding formation may become a determinant of the lattice structures in crystalline solids. Pnictogen bonding formation may become an heuristic principle for predicting some of the short contacts that are present in the crystal structures of compounds containing fluorinated atoms of Group 15, particularly when polyfluorinated. Pnictogen derivatives containing other moieties may also work as effective electrophilic sites and a convenient design of the used tectons may allow pnictogen bond to become a general and reliable tool in crystal engineering.

1. Introduction

In-depth understanding of weak bonds, commonly called interactions, is instrumental in the control of a wide variety of properties of organic and inorganic derivatives in the solid, liquid and gas phases [1,2]. The particular attention given in the last decade to supramolecular chemistry and nanotechnologies has increased the interest in intermolecular interactions since they mediate recognition and self-assembly processes and thereby affect phenomena as diverse as the binding of drugs to the target enzyme [3,4], the functional properties of molecular [5,6] and polymeric [7] materials, and chemical reactivity in stoichiometric and catalytic processes under homogeneous [8–10] and heterogeneous [11,12] conditions.

Hydrogen bonding, by far the most important and frequently occurring interaction, continues to receive attention in both its fundamental and applied aspects [13]. This is true as well for other less common types of interactions, e.g., π–π [14,15], cation-π [16,17], anion-π [18,19], and aurophilic [20,21].

New vistas in the area of weak bonding were opened by the recognition that the anisotropic electronic distribution of a covalently-bonded atom often determines how the atom participates in attractive noncovalent interactions. In 1992–1994 [22–24], analyses of molecular electrostatic potentials elucidated the basis for the formation of stable adducts between covalently-bonded halogen atoms and negative sites, such as Lewis bases. Such adducts had long been known experimentally [25–27] but were poorly understood from the theoretical point of view.

It is now well-established 28 that covalently-bonded halogen atoms, both univalent and hypervalent [29], have regions of lower electronic density on their outer sides, on the extensions of the covalent bonds in which they are involved. These regions, labelled σ-holes [30], often have positive electrostatic potentials associated with them and thus can interact attractively with negative sites, e.g. lone pairs, π-electrons and anions. The term "halogen bond" (XB) [31,32] is used to designate the resulting weak bonds, which have been found to be important in fields as different as material sciences and biopharmacology [33].

Regions of higher electronic density are found on the lateral sides of covalently-bonded halogen atoms. These give rise to negative electrostatic potentials through which the halogens can interact attractively with positive sites, e.g. electron-poor hydrogens, positive σ-hole potentials, and metal cations [34,35].

Anisotropic electronic density around a bonded atom and regions of lower density (σ-holes) opposite to covalent bonds are not limited to halogen atoms (Group 17 elements) [36,37], but occur also for hydrogen [28,38] and for atoms of Group 18 [39,40], 16 [41,42], 15 [43,44], and 14 [45–47]. Any atom having a positive σ-hole potential is electrophilic and can interact attractively with negative sites; the results

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C1–Se···N1: 166.33°
C2–Se···N2: 170.40°
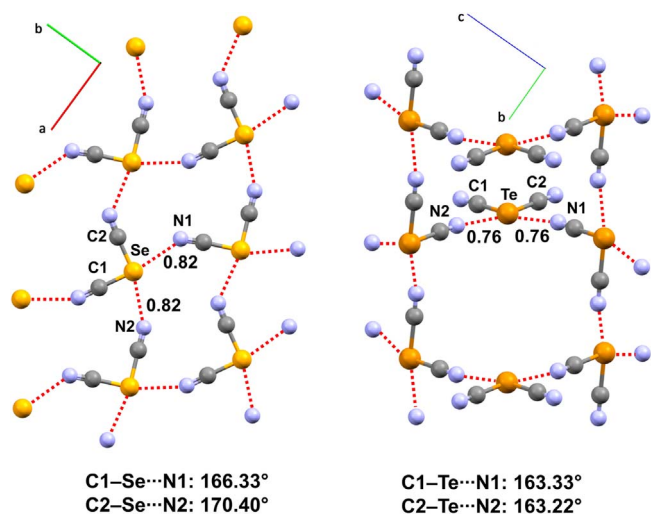
C1–Te···N1: 163.33°
C2–Te···N2: 163.22°

Fig. 1. Ball and stick representation (Mercury 3.9) of the two dimensional network that CBs (red dotted lines) form in the crystal of selenium dicyanide (left) and tellurium dicyanide (right). Color code: Grey, carbon; light blue, nitrogen; light ocher, selenium; dark ocher, tellurium. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

are sometimes called aerogen bond (AB), chalcogen bond (CB), pnictogen bond (PB), and tetrel bond (TB) when elements of Group 18, 16, 15, and 14, respectively, are involved. All of these bondings are subsets of σ-hole bonding. The more polarizable is a covalently-bonded atom and the more electron-attracting are the nearby residues, the more positive (or less negative) are likely to be its σ-hole potential(s), usually enabling for the formation of stronger interactions and shorter separations [28]. Due to the relatively focused nature of positive σ-hole potentials [28] these bonds tend to be quite directional. In an interaction R–A···B, where A is the atom with the positive σ-hole potential and B is the negative site, the angle R–A···B is generally between 155° and 180°. The largest number of σ-holes that an atom can have, and through which it may interact, is usually equal to the number of its covalent bonds.

The crystal structures of $Se(CN)_2$ and $Te(CN)_2$ nicely exemplify some of the general trends discussed above. They consist of two-dimensional networks with chalcogen bonds between selenium or tellurium atoms and cyano nitrogens (Fig. 1) [48,49]. The Se···N≡C separations are 281.3 and 283.5 pm, the Te···N≡C are 274.5 and 275.8. A meaningful way of comparing separations involving different pairs of atoms is by means of their normalized contacts, Nc. This is the ratio between an observed separation and the sum of the van der Waals radii of the two atoms [50]. For $Se(CN)_2$ and $Te(CN)_2$, the Nc values are 0.80 and 0.76, respectively. The shortness of these separations, is a consequence of the strong electron-attracting power of the cyano group, which makes the σ-hole potentials at chalogen atoms remarkably positive [51]. Similarly, quite short PBs [52] and XBs [53–56] are formed when the cyano group is appended to, or nearby, an element of Group 15 and 17 of the periodic table.

Fluorine is the most electronegative (electron-attracting) atom and its presence in a molecule remarkably increases the σ-hole potentials of nearby atoms and their tendencies to interact attractively with negative sites in the gas, liquid or solid phases [27,46,57]. For instance, the gas phase XBs formed by the chlorine of interhalogen X–Cl are stronger when X = F than when X = Cl[26b] and the co-crystals of SiF_4 with pyridine [58] and amine [59] derivatives have Si···N TBs as short as 204.1 pm (Nc = 0.63). $Si(CH_3)_4$ does not form analogous co-crystals.

In this review, we will show that close contacts [60] between covalently-bonded Group 15 atoms and negative sites (e.g. Lewis bases) are quite common in the crystal structures of fluorinated derivatives of the Group 15 atoms [61]. Close contacts are commonly taken as

indications of attractive interactions, although this may not necessarily be always the case [41]. We will show that the directionalities and separations of these interactions are convincing experimental evidences that linking a fluorine to a pnictogen atom increases its σ-hole electrophilicity to the point that PB formation may become a determinant of the lattice structures in crystalline solids. Structures from the Cambridge Structural Database (CSD) [62] will demonstrate that PB formation is a fairly general heuristic principle for predicting some short contacts in the crystal structures of compounds containing fluorinated pnictogen atoms, particularly when polyfluorinated. Antimony trifluoride (Swart's reagent) is widely used for the fluorination of both inorganic and organic chloro-compounds and it has some industrial applications [63]. Also antimony pentafluoride is a particularly interesting compound, being the starting material for the synthesis of fluoroantimonic acid, probably the strongest known acid. The recognition of their tendency to form PBs may become a valuable tool to anticipate some structural features of crystalline solids containing these important compounds.

Numerous papers have been published on the modelling of PB [64–72]; of particular relevance to this review are those discussing the effect of the nature of pnictogen atom substituents on PB strength [44,57,73,74]. Papers presenting experimental evidences of PB presence are much less common [75–78]. The collection of single crystal X-ray structures analysed in this paper demonstrates that the PB presence in crystals of compounds belonging to specific structural classes is fairly general. This suggests that a convenient design of the used tectons, may allow PB to be used as a reliable tool in crystal engineering.

2. PBs in trivalent and monofluorinated derivatives

N-Fluoro-*N*-(2,4,6-trinitrophenyl)-*t*-butylamine [79] is the only compound present in the CSD where a trivalent nitrogen atom is bound to one fluorine and two carbon atoms. The conformation adopted by this derivative in the solid is determined by an intramolecular N···O contact (276.5 pm, Nc = 0.90) involving the oxygen atom of one nitro group *ortho* to the N–F moiety [80].

In crystals of fluoro-diphenyl-antimony(III), strong intermolecular SbF interactions bridge adjacent $SbPh_2F$ units and form infinite chains of where fluorine and antimony atoms alternate (Fig. 2) [81]. If both the fluorine atoms bound to antimony are taken into account, antimony atoms in the chain adopt a seesaw geometry; alternatively the geometry
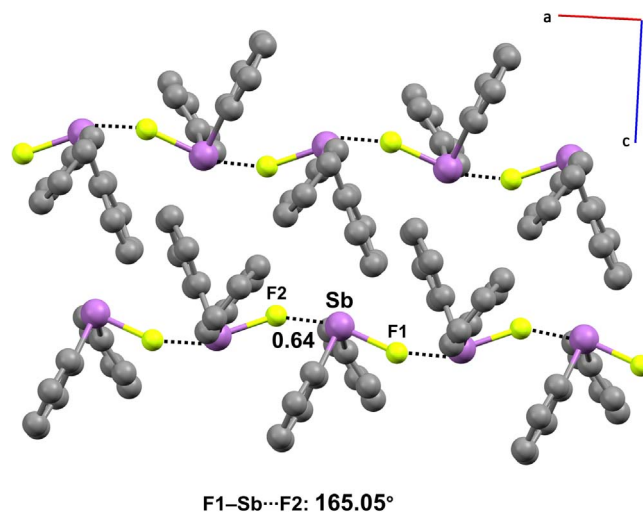

F1–Sb···F2: **165.05°**

Fig. 2. Ball and stick representation of two infinite chains in crystalline fluoro-diphenyl-antimony(III). PBs are black dotted lines, hydrogens have been omitted for clarity. The Nc value is reported close to the interaction. Color code: Grey, carbon; yellowish green, fluorine; violet, antimony. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)