

Chalcogen and pnictogen bonds: insights and relevance

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Hydrogen bonding (HB) and halogen bonding (XB) interactions are now well established as important noncovalent forces across different research areas. Chalcogen bonding (ChB) and pnictogen bonding (PnB) interactions are increasingly gaining attention due to their potential applications and can be added to the arsenal of the already well-established HB and XB interactions. Given the tremendous progress made by the scientific community in the understanding of ChB and PnB interactions, we aim to provide an insight into the unique characteristics of these interactions through this perspective. We also aim to discuss some important applications of ChB and PnB interactions which will provide a better understanding of the relevance of these noncovalent interactions.

Keywords: Anion recognition, catalytic activity, chalcogen and pnictogen bonds, crystal engineering, drug design, noncovalent interaction.

AN isolated atom has an isotropic distribution of electron density. However, when an atom comes together to form a molecule, a redistribution of electron density takes place which is anisotropic¹. This anisotropic distribution results in some region of the atom within a molecule being electron-rich and some other being electron-deficient. When this region of low electron density is present in an atom along with the extension of a covalent bond, it is called a σ -hole², and when this region of low electron density is perpendicular to the molecular plane consisting of the central interacting atom, it is called π -hole³. The interaction of this σ -hole or π -hole region with an electron-rich region such as lone pairs of electrons (lps) is described as the σ -hole interaction or π -hole interaction respectively^{4,5}. The presence of a σ -hole or π -hole region in an atom within a molecule is often associated with the presence of a positive electrostatic potential region in the molecular electrostatic potential maps (MESP)⁶, but not necessarily in all cases⁷. Analysis of MESP maps is crucial in the study of σ -hole and π -hole interactions, as it helps in identifying the electron donor as well as electron-donating strength of the atoms involved in the formation of electrophilic–nucleophilic interactions^{8–10}.

The concept of these hole interactions was first applied in the case of ‘halogen bonding’ (XB) interactions, where the Group 17 elements (F, Cl, Br, I) participate as an electrophilic site in the formation of a noncovalent interaction¹¹. Today, the halogen bond is considered as important as hydrogen bonding (HB) interactions¹². Several reviews have already described the importance and applications of halogen-bonding interactions^{13,14} and hence will not be the focus of this discussion.

Since the rediscovery of the halogen-bonding interactions, the concept of σ -hole and π -hole interactions has been used in establishing the formation of other types of interactions involving different atomic groups as an electrophilic species such as chalcogen bond¹⁵, pnictogen bond¹⁶, triel bond¹⁷, tetrel bond¹⁸ and aerogen bond¹⁹. The focus of this article will be on chalcogen bonding (ChB) interactions where Group 16 elements (O, S, Se, Te) and pnictogen bonding (PnB) interactions where Group 15 elements (N, P, As, Sb) participate as an electrophilic site in a noncovalent interaction respectively⁴. As discussed in a previous study⁴, chalcogens and pnictogen bonds existed long before the term ‘chalcogen bond’²⁰ and ‘pnictogen (or pnictogen) bond’¹⁶ were used in the scientific literature. A formal definition of the ChB interactions was recently (in 2019) recommended by IUPAC¹⁵ according to which ChB can be defined as ‘net attractive interaction between an electrophilic region associated with a chalcogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity’. It is also stated that pnictogen bonding interactions can be defined similarly. The definition of the chalcogen bonds and pnictogen bonds uses the same methodology as that for the definition of the HB and XB interactions, i.e. naming the interaction by referring to the atom that is participating as an electrophilic site²¹. Both chalcogen and pnictogen bonding interactions are now important categories of noncovalent interactions^{22,23}. We will explore the unique features and properties of these interactions which will be important in their overall understanding.

Both chalcogen and pnictogen bonding interactions are represented similar to halogen and hydrogen bonding interactions, i.e. $R-Z\cdots A$ (Z = hydrogen (H), halogen (X), chalcogen (Ch), pnictogen (Pn); Z is the bond donor, R is the remaining molecule and A is the bond acceptor), and

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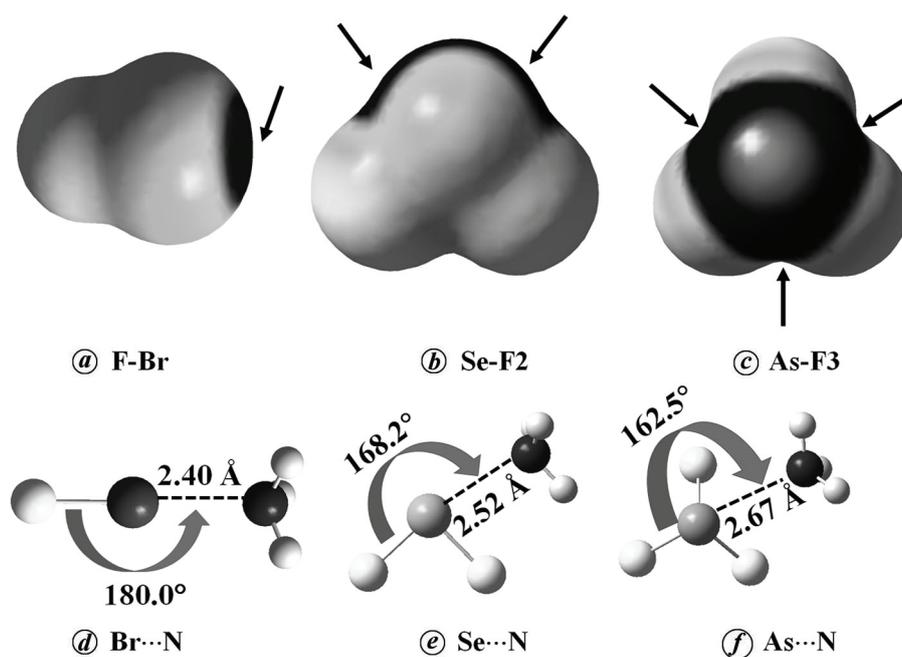


Figure 1. Possible region of the σ -hole in case of (a) monovalent halogen ($X = \text{Br}$), (b) divalent chalcogen (Se) and (c) trivalent pnictogen ($\text{Pn} = \text{As}$) represented by the blue region, (marked by arrows) in the molecular electrostatic potential map. (d–f) Representative example of (d) halogen bonding ($\text{Br}\cdots\text{N}$), (e) chalcogen bonding ($\text{Se}\cdots\text{N}$) and (f) pnictogen bonding ($\text{As}\cdots\text{N}$). All calculations are done at MN15/DEF2DZVP using G09 (ref. 28).

also share several of their characteristics such as strength, directionality and cooperativity^{2,24}. Due to these features, chalcogen and pnictogen bonding interactions are suitable alternatives to not only halogen-bonding, but also to hydrogen-bonding interactions. In comparison to monovalent halogens (Figure 1 a), divalent chalcogen can have two (Figure 1 b) while a trivalent pnictogen can have three possible regions of σ -holes (Figure 1 c), each along with the extension of σ -covalent bond (Figure 1). This allows chalcogen and pnictogen atoms to simultaneously form multiple chalcogen and pnictogen bonding interactions. Specifying valency is important here because all these bonding interactions are possible with donor atoms of different valencies as well^{25–27}. All the calculations are done at MN15/DEF2DZVP level using G09 (ref. 28).

Similar to halogen bonds, in most cases of chalcogen and pnictogen bonding interactions, the bond acceptor tends to approach the donor chalcogen/pnictogen atom along with the extension of the σ -covalent bond, leading to preference towards a highly directional $\angle\text{A-Z}\cdots\text{D}$ bonding angles²⁹. However, there are cases which have shown that linear directionality is not always a necessary condition for the formation of chalcogen or any other noncovalent interaction. For example, charge density studies on chalcogen containing phthalic anhydrides $\text{C}_8\text{O}_2\text{H}_4\text{Ch}$ ($\text{Ch} = \text{S}, \text{Se}, \text{Te}$) revealed the presence of $\text{C}-\text{Ch}\cdots\text{O}$ chalcogen-bonding interaction with $139^\circ < \angle\text{C}-\text{Ch}\cdots\text{O} < 146^\circ$ (ref. 30). The presence of these chalcogen

bonds could not be explained completely from the σ -hole concept, which is electrostatically driven. However, in the study³⁰, the distribution of $L(r)$ critical points around the chalcogen atom revealed the presence of additional charge-depleted (CD) sites capable of participating in chalcogen-bonding interactions, apart from those which are present along with the extension of $\text{C}-\text{Ch}$ covalent bond. This shows that apart from electrostatics, energy terms such as dispersion, induction and exchange-repulsion can have a non-negligible contribution towards the overall stability of such noncovalent interactions. Similar observations have also been made in the case of halogen-bonding interaction³¹. These observations implicate that high directionality is not a necessity for the occurrence of these interactions and attention should be paid during analysis to not miss the presence of such unique cases of noncovalent interactions.

The local electronic environment around the central Ch or Pn atom determines the strength of the σ -hole or π -hole, which in turn affects the strength of the formed noncovalent interaction. The local electronic environment around the central atom can be altered by changing the atom or functional group attached to the atom. Gas-phase analysis of dimeric systems showed that for a given nucleophile (e.g. NH_3), the strength of the $\text{S}\cdots\text{N}$ chalcogen bond and $\text{P}\cdots\text{N}$ pnictogen bond can be directly correlated with the strength of the σ -hole^{32,33}. Substitution also plays a crucial role in the formation of π -hole-directed

chalcogen bonds and pnictogen bond interactions^{34,35}. In fact, utilizing appropriate substituents, even the electronegative oxygen and nitrogen atoms which are usually utilized as a nucleophile can participate as an electrophilic centre in the formation of chalcogen and pnictogen bonding interaction respectively. Gas-phase analysis of $\text{FH}_2\text{N}:\text{NH}_3$ dimeric system revealed the formation of a weak $\text{F}\cdots\text{N}\cdots\text{N}$ pnictogen bonding interaction³⁶. The existence of nitrogen-centered $\text{N}\cdots\text{Cl}$ pnictogen bonding interaction was also confirmed from high-resolution X-ray charge density analysis³⁷. In our previous study on chalcogen and pnictogen bonds, we examined the formation of $\text{N}\cdots\text{O}$ noncovalent interactions in $\text{XYZN}:\text{OXY}$ systems ($X/Y/Z = \text{F/Cl}$), where we observed that these $\text{N}\cdots\text{O}$ interactions can be tuned to be a chalcogen bond or pnictogen bonding interaction, depending on the strength of the electron-withdrawing substituent attached directly to the interacting atoms³⁸. Another ab initio study similarly established the formation of oxygen-centred chalcogen-bonding interaction with different nucleophilic species³⁹. Therefore, substitution is a useful tool to modify the electron-density distribution around the central chalcogen and pnictogen atoms, which in turn can be utilized in modifying the nature and characteristics of chalcogen and pnictogen bonding interactions.

Chalcogens and pnictogens also have a dual donor-acceptor character, similar to halogens, due to the presence of electron-deficient holes (either σ -hole or π -hole) which act as an electron acceptor as well as the presence of lps which can act as an electron donor during the formation of noncovalent interactions^{40,41}. As discussed above, these donor-acceptor regions can be modified using appropriate substitutions. While studies involving chalcogen or pnictogen, as either electrophile or nucleophile are present in abundance, there are interactions where chalcogen or pnictogen can simultaneously behave as an electron-donor and electron-acceptor in the formation of the same interaction. While the previously discussed $\text{N}\cdots\text{O}$ interactions were very weak and dispersive³⁸, orbital analysis revealed that in some dimeric complexes, $\text{N}\cdots\text{O}$ interaction had simultaneous characteristics of both chalcogen as well as pnictogen bonding interactions. In another study, we analysed $\text{Se}\cdots\text{P}$ noncovalent interaction in $\text{XHSe}:\text{PH}_3$, $\text{H}_2\text{Se}:\text{PH}_2\text{X}$ and $\text{XHSe}:\text{PH}_2\text{X}$ dimers using ab initio calculations⁴². While chalcogen bonding was prominent in $\text{XHSe}:\text{PH}_3$ and pnictogen bonding were more prominent in $\text{H}_2\text{Se}:\text{PH}_2\text{X}$ complexes, simultaneous chalcogen and pnictogen bonding behaviour was observed in $\text{XHSe}:\text{PH}_2\text{X}$ complexes. The stability of $\text{Se}\cdots\text{P}$ interaction in some $\text{XHSe}:\text{PH}_2\text{X}$ complexes was relatively higher than the other two sets of complexes. This is because in the case of $\text{XHSe}:\text{PH}_2\text{X}$, both σ -hole and lps associated with Se and P atoms were able to participate in the interaction simultaneously. Hence stronger and more stable chalcogen and

pnictogen bonding interactions can be achieved if the donor-acceptor property of the central chalcogen or pnictogen atom can be activated simultaneously.

Applications

Crystal engineering

Both chalcogen and pnictogen bonds are increasingly utilized in crystal engineering as the molecular linker stabilizing the three-dimensional arrangement of molecules in crystal structures. The existence of both these interactions in the different crystal structures is well established by high-resolution X-ray charge density analysis^{30,37,43}. The chalcogen bond in crystalline solids is already considered as a world parallel to halogen bonds⁴⁴, and pnictogen bonding is also slowly and steadily gaining prominence as a useful supramolecular interaction⁴⁵. Like halogen bonds, chalcogen and pnictogen bonds are also involved in the formation of unique supramolecular synthons⁴⁶. Analysis of the crystal structures of several antioxidant ebselen derivatives revealed the formation of unusually short $\text{Se}\cdots\text{O}$ chalcogen bonds which not only result in the formation of conserved supramolecular synthons, but also play an important role in $\text{Se}\cdots\text{N}$ bond cleavage (Figure 2a)⁴³. The alkoxide cage structures are interlinked to others via the formation of $\text{Pn}\cdots\text{O}$ ($\text{Pn} = \text{P, As, Sb, Bi}$). A study revealed that depending on the Pn

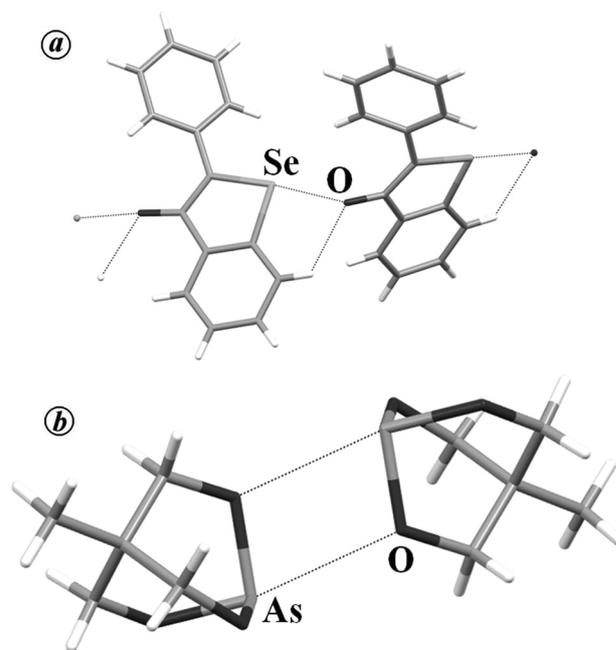


Figure 2. *a*, Chalcogen bond present in ebselen derivative (REFCODE: SENG0H02). *b*, Pnictogen bonding observed in alkoxide cage (REFCODE: BORNE). Structures retrieved from the CSD database⁵².

atom involved, these alkoxide cages formed several unique dimeric or trimeric supramolecular synthons (Figure 2b)⁴⁷. Experimental studies have also reported the preservation of the same supramolecular synthon by replacing the bond-donor atom from the same group of elements or even with a bond donor atom from a different element group⁴⁴. In crystalline solids, both chalcogen and pnictogen bonding can be promoted by fluorination^{48,49}. This is because the presence of a strong electron-withdrawing group will further enhance the strength of the σ -hole or π -hole region, which will lead to a stronger bonding interaction. Both chalcogen and pnictogen bonding interactions have been efficiently utilized in designing co-crystals as well^{50,51}. All these analyses support the notion that chalcogen and pnictogen bonding interactions are as important as hydrogen and halogen bonding in crystal engineering. It is important to mention here that the dimers represented in Figure 2 were retrieved from the CSD database⁵².

Anion recognition and catalysis

Due to the possibility of the simultaneous presence of multiple bond-donor sites whose strength can be enhanced or suppressed by appropriate substitution, chalcogen and pnictogen bonding interactions are an appropriate tool for anion recognition⁵³ as well as for catalytic activity. Anion recognition with chalcogen and pnictogen bonding has been observed for monodentate, multidentate as well as charged ligands⁵³. It has been observed that under a similar electronic environment, the strength of anion recognition followed the trend of pnictogen bond > chalcogen bond > halogen bond. This is because polarization increases from right to left in the periodic table, resulting in a more efficient bonding interaction in the case of pnictogen bonding. For example, chloride (Cl^-) binding with $\text{Sb}(\text{C}_6\text{F}_5)_3$ via pnictogen bonding ($K_D = 19 \pm 7 \mu\text{M}$) was stronger than Cl^- binding with $\text{Te}(\text{C}_6\text{F}_5)_2$ via chalcogen bonding ($K_D = 470 \pm 70 \mu\text{M}$), which in turn was stronger than Cl^- binding with $\text{I}(\text{C}_6\text{F}_5)$ via halogen bonding ($K_D = 1370 \pm 30 \mu\text{M}$; Figure 3)^{54,55}. As expected,

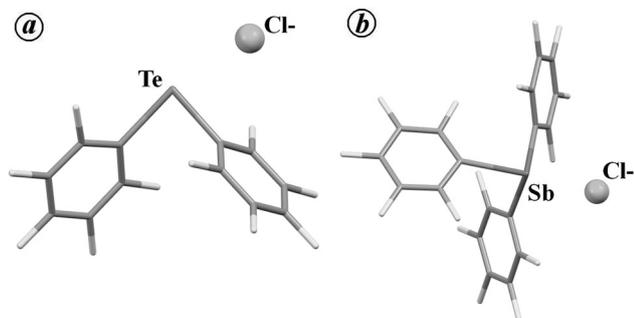


Figure 3. *a*, Cl^- binding with $\text{Te}(\text{C}_6\text{H}_5)_2$. *b*, Cl^- binding with $\text{Sb}(\text{C}_6\text{F}_5)_3$ in gas phase.

anion binding was weaker for the lighter atoms compared to their heavier counterparts, again following the trends in polarizability. The substitution also affected the strength of anion binding. The chloride binding with $\text{Sb}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{H}_5)$ was weaker compared to that observed with $\text{Sb}(\text{C}_6\text{F}_5)_3$ (ref. 54). This is because the presence of additional electron-withdrawing fluorine in $\text{Sb}(\text{C}_6\text{F}_5)_3$ compared to that in $\text{Sb}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{H}_5)$ enhances the strength of σ -hole on Sb, resulting in stronger chloride-binding. This is consistent with the observation that the presence of electron-withdrawing groups promotes the strength of these hole interactions. The study of Reissert-type substitution of isoquinoline catalysed by chloride-binding catalysis via different σ -hole interactions showed that pnictogen bond was more efficient compared to chalcogen and halogen bonds in accelerating the reaction⁵⁶. In another study, benzodiselenazoles was reported to be a useful scaffold in chalcogen-bonding catalysis⁵⁷. Pnictogen-bonding catalysis has been also used efficiently for brevetoxin-type polyether cyclization⁵⁸. Several detailed review articles have extensively explored the role of chalcogen and pnictogen bonding interactions in catalysis^{54,59}. All these studies show that both chalcogen and pnictogen bonding interactions are viable alternatives to halogen and hydrogen bonding interactions in anion transport and catalysis.

Protein and drug design

Given that chalcogens, especially sulphur atoms are present in all proteins as cysteine (Cys) and methionine (Met) amino-acid residues, the possibility of the presence of chalcogen bonds in proteins is naturally expected⁶⁰. Chalcogen bonds, such as $\text{S}\cdots\pi/\text{S}\cdots\text{O}/\text{S}\cdots\text{N}/\text{S}\cdots\text{S}$ interactions, play an important role in the functionality as well the stability of several different proteins. Chalcogen bonds can also influence the interaction of the proteins with ligands and hence play a crucial role in structure-based drug design. Replacement of sulphur with heavier chalcogen such as selenium in protein scaffolds will probably result in the presence of stronger chalcogen-bonding interactions, given the higher donor capability of heavier chalcogens⁶¹. In comparison to chalcogen bonds, the possible presence of pnictogen bonding interactions in proteins seems to be unexplored and presents an opportunity for detailed studies.

Summary and outlook

While chalcogen and pnictogen bonds share several of their characteristics with hydrogen and halogen bonding interactions, it is only in the past decade or so that these two interactions have become the focus of several theoretical and experimental studies. While chalcogen and pnictogen bonding interactions are not still as much

explored as halogen or hydrogen bonding interactions, they are appropriate alternatives to halogen and hydrogen bonding interactions in terms of their directionality, strength and cooperativity. They also have some unique features such as the presence of multiple donor sites, higher possibility of deviation from linear geometry and simultaneously acting as a bond donor and bond acceptor within the same noncovalent interaction, which further increases their relevance with possible applications. While chalcogen and pnictogen bonding interactions were initially investigated in gas-phase and crystalline solids, it is now well understood that these interactions can play important role in other research areas as well. While some progress has been made, the next step will be to understand the role of these interactions in materials science and biological systems in order to contribute to the design of new materials.

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ACKNOWLEDGEMENT. R.S. and D.C. thank Indian Institute of Science Education and Research Bhopal for infrastructure and research facilities.

Received 5 January 2021; revised accepted 8 March 2021

doi: 10.18520/cs/v120/i12/1848-1853