The S···P noncovalent interaction: diverse chalcogen bonds

Abedien Zabardasti, Hossein Afrouzi, Ali Kakanejadifard & Zahra Jamshidi


To link to this article: http://dx.doi.org/10.1080/17415993.2016.1275634

Published online: 18 Jan 2017.

Submit your article to this journal

Article views: 7

View related articles

View Crossmark data
The S···P noncovalent interaction: diverse chalcogen bonds

Abedien Zabardasti\textsuperscript{a}, Hossein Afrouzi\textsuperscript{a}, Ali Kakanejadifard\textsuperscript{a} and Zahra Jamshidi\textsuperscript{b}

\textsuperscript{a}Department of Chemistry, Lorestan University, Khorramabad, Iran; \textsuperscript{b}Department of Physical Chemistry, Chemistry and Chemical Engineering Research Center of Iran, Tehran, Iran

\textbf{ABSTRACT}

The S···P interactions in the complexes of HSX (X = F, Cl, Br, I) with PH\textsubscript{n}Me\textsubscript{3−n} (n = 0–3) have been investigated with \textit{ab initio} calculations at the MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ level of theory. The interaction energies and structural properties of intermolecular complexes have been analyzed. Results of QTAIM analysis are dealing with expand of interactions, including pure closed-shell interactions (van der Waals interactions and chalcogen bonding, YB), partially covalent closed-shell (CS; Charge Transfer) and shared-shell interactions (SS; weak covalent bond and very strong YB) for these complexes. The energy decomposition analysis (EDA) showed that electrostatic interactions are an important contributing factor for these complexes. In considering second-order contributions, the donor-acceptor pair charge transfer (CT) is most important. These findings are consistent with the Electron Localization Function (ELF) isosurface of the complexes. In each series of HSX:PH\textsubscript{n}Me\textsubscript{3−n}-chalcogen bond complexes with increasing basicity of phosphines, the stability and S···P bond strength of adducts were increased so that the HSX:PMe\textsubscript{3} (X = F, Cl, Br) complexes had very strong S···P chalcogen interactions with nearly covalent characters.

\textbf{ARTICLE HISTORY}

Received 20 October 2016
Accepted 19 December 2016

\textbf{KEYWORDS}

Chalcogen bond; methylphosphines; σ–hole interactions; HSX; interaction energy

\textbf{CONTACT}

Abedien Zabardasti \textsuperscript{a} zebardasti@yahoo.com

\textbf{Supplemental data for this article can be accessed here.} \url{http://dx.doi.org/10.1080/17415993.2016.1275634}

© 2017 Informa UK Limited, trading as Taylor & Francis Group
1. Introduction

The chemistry of noncovalent interactions has a long history [1–4]. The increasing number of studies on noncovalent interactions shows their importance. Various types of noncovalent interactions are evident in theoretical and experimental studies, including supramolecular chemistry [5], crystal engineering [6], molecular biology [7], materials [8] and the development of new pharmaceutical compounds [9]. The intermolecular interactions are responsible for the properties of liquids and the three-dimensional structures of crystals. Also, they contribute to the structure of single molecules via interactions between various segments that fold around such that they lie close to one another, for example conformations adopted by biomolecules, such as DNA, proteins and carbohydrates [10,11].

The close intermolecular contacts, which generally, occur between two centers, Lewis acid and Lewis base, are considered as noncovalent interactions [12,13]. Some of these interactions, such as hydrogen and halogen bonding, have been known for a long time, whereas the others such as chalcogen, pnicogen and tetrel bonds are newer [14–21]. The noncovalent interactions, which follow a very marked directional pattern, have been rationalized on the basis of the $\sigma$–hole concept [12].

Politzer et al. [22] have described the concept of $\sigma$–hole: a free, ground-state atom has, on the average, a spherically symmetrical electronic charge distribution. The electrostatic potential (ESP) created around the atom by its nucleus and electrons is positive everywhere, the contribution of the nucleus dominating that of the dispersed electrons. When the atom forms a covalent bond, some of its electronic charge is polarized toward the bond region, leading to the atom’s electronic density being diminished in its outer region (along the extension of the bond) but increased on its equatorial sides. Therefore the charge distribution of the atom becomes anisotropic and the ESP along the extension of the $\sigma$-bond (covalent bond) will continue to be positive. This highly directional region of positive potential is the $\sigma$-hole.

Covalently bonded atoms of Groups IV, V, VI and VII, respectively, have four, three, two and one regions of $\sigma$–holes on the extensions of the covalent bonds to these atoms. The formation of noncovalent complexes between positive $\sigma$–holes on Group IV, V, VI and VII atoms and negative sites, R—A . . . Nucleophile (negative site; e.g. lone pair of Lewis base), are called tetrel, pnicogen, chalcogen and halogen bond, respectively.

In fact, $\sigma$–hole in chalcogens designates the electron-deficient outer lobe of a half-filled $p$ bonding orbital on the Group VI atom. For example, the valence configuration of a free sulfur atom is $3s^23p_x^2p_y^3p_z^1$. The contribution of sulfur to the $R_1–S$ and $R_2–S$ bonds involves nearly pure half-filled $3p_y$ and $3p_z$ orbitals, which leads to the electron deficiencies in their outer lobes ($\sigma$–holes), and results to positive ESP along the extensions of the $R_1–S$ and/or $R_2–S$ bonds [23].

There are many theoretical studies on chalcogen bonds [24–32]. Scheiner and Adhikari [33] have compared hydrogen and halogen bonds in $S\cdots N$ interactions in $HSX:NH_3$ ($X = F, Cl, Br$). They found that the interaction energy for $S\cdots N$ chalcogen bonds indicate that they are more stable than minima containing either an $SH\cdots N$ or $NH\cdots F$ bond. In another study [34], the substituent effects on $Cl\cdots N$, $S\cdots N$ and $P\cdots N$ noncovalent bonds in $BHS:NH_3$ and $BCl:NH_3$ complexes ($B = CH_3, NH_2, CF_3, OH, Cl, NO_2$ and $F$) were examined. The effect of charge and substituent on the $S\cdots N$ chalcogen