



Tetrel bonds between PySiX_3 and some nitrogenated bases: Hybridization, substitution, and cooperativity



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ABSTRACT

Ab initio calculations have been performed to study the influence of hybridization, substitution, and cooperativity on the tetrel bond in the complexes of PySiX_3 (Py = pyridine and X = halogen). The tetrel bond becomes stronger in the order of $p\text{-PySiF}_3 \cdots \text{NCH}(sp) < p\text{-PySiF}_3 \cdots \text{NHCH}_2(sp^2) < p\text{-PySiF}_3 \cdots \text{NH}_3(sp^3)$. The electron-donating group in the electron donor strengthens the tetrel bond, and this effect is mainly achieved through electrostatic and polarization interactions. Tetrel bonding displays cooperative effects with triel bonding and chalcogen bonding, characterized by shorter binding distances and greater electron densities. The cooperative effects between triel/chalcogen bond and tetrel bond have been analyzed by molecular electrostatic potentials and charge transfer. Energy decomposition indicates that many-body effects are mainly caused by polarization energy. The geometries of $\text{Si} \cdots \text{N}$ interaction and its applications in crystal materials have been characterized and evidenced by a CSD research.

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1. Introduction

Noncovalent interactions have been attracting much interest owing to their extensive applications in chemistry, physics, and biology [1–7]. For example, hydrogen bonding can stabilize biomolecular structures, modulate specificity and speed of enzymatic reactions, and construct supramolecular structures [6,7]. These noncovalent interactions are usually attributed to Lewis acid–base interactions. For instance, hydrogen bonding can be regarded as the interaction between an acidic proton and a Lewis base. To explain the formation mechanism of noncovalent interactions, Politzer and co-workers proposed the concept of “ σ -hole” [8,9], which is a region with positive electrostatic potentials (MEPs) on the outer end along X–Y bond axis. Thus, the corresponding interaction is uniformly named σ -hole interaction, such as hydrogen bonding [10], halogen bonding [8,9], chalcogen bonding [11,12], pnictogen bonding [13,14], and tetrel bonding [15].

The term “tetrel bonding” is used to describe the σ -hole interaction between the σ -hole involving the group IV atom and Lewis bases. Like hydrogen bonding, tetrel bonding also has potential applications in crystal materials, chemical reactions, and biological systems [15–18]. Hence, much attention has been

paid to tetrel bonding recently. The Lewis bases in tetrel bonding contain molecules with lone-pair electrons [19–22], anions [15,23], π -systems [24], and metal hydrides [25,26]. In general, tetrel bonding becomes stronger with increasing the tetrel atomic mass, the electron-withdrawing substituents adjoined with a tetrel atom strengthen this interaction, and it is conjunctively stabilized by electrostatic interaction and charge transfer. Interestingly, tetrel bonding exhibits cooperative effects with other interactions including hydrogen bonding [27], lithium bonding [28], and chalcogen bonding [29] or itself [30]. Recently, Esrafil et al. compared the cooperative effects between tetrel bonding and halogen/chalcogen/pnictogen bonding interactions in $\text{YH}_3\text{M} \cdots \text{NCX} \cdots \text{NH}_3$ complexes, where Y = F, CN; M = C, Si; X = Cl, SH and PH_2 [31]. The results indicated that the strength of tetrel bonding can be tuned with cooperative effects. Such synergistic effect is crucial for the applications of tetrel bonding in crystal materials, chemical reactions, and biological systems.

Owing to the electron deficiency of a boron atom, the sp^2 hybridized boron atom in molecules BH_3 , BF_3 , and BCl_3 could act as a Lewis acid center to engage in Lewis acid–base interactions [32]. Very recently, Grabowski plotted the MEP maps of these molecules and found a π -hole on the B atom [33–35]. Accordingly, triel bonding is a “ π -hole” interaction involving the Group III atom [33,34], where the term π -hole describes the region with positive MEPs above the plane of a molecule. When the sp^2 hybridized boron atom forms a triel bond with Lewis bases, the triel center rehybridizes

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from sp^2 to sp^3 and presents sp^3 hybridized products, owing to the disruption of the π -hole on the triel atom [36]. In $\text{HCN} \cdots \text{HCN} \cdots \text{BF}_3$ [37], where a hydrogen bond coexists with a triel bond, the binding distance of triel bond has a larger shortening than that of hydrogen bond although the triel bond is much stronger than the hydrogen bond. A similar result was also found in $\text{XCN} \cdots \text{XCN} \cdots \text{BF}_3$ [38], where a triel bond coexists with a halogen bond. This showed that triel bonding displays a special feature in geometry when it interplays with other interaction.

In this paper, PySiX_3 (Py = pyridine and X = F, Cl) is chosen to act as a Lewis acid (the σ -hole on the Si atom) and a Lewis base (the N atom of pyridine ring) to bind with a series of nitrogenated bases (NCLi, iminazole, NHCH_2 , NH_3 , NH_2Me , NHMe_2 , NCH, NMe_3 , and N_2) and three molecules having a π -hole (BF_3 , BCl_3 , and SO_3), respectively. The reason for selecting the molecule PySiX_3 is that pyridine and its derivatives as well as the groups involving Si are often used as a building block in crystal engineering [39,40]. We firstly explained the formation of tetrel bonding and triel bonding by analyzing the MEP maps of these molecules, then we focused on the effects of hybridization and substitution on tetrel bonding, and finally we discussed the cooperativity between tetrel bonding and triel/chalcogen bonding. To unveil the mechanism of cooperative effect between tetrel bonding and triel/chalcogen bonding, we performed an analysis for these complexes in views of molecular electrostatic potentials, atoms in molecules (AIM), natural bond orbital (NBO), and energy decomposition.

2. Theoretical methods

The equilibrium structures of complexes and monomers were optimized at the MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels of theory. Frequency calculations at the MP2/aug-cc-pVDZ level were performed to ensure that the optimized structures are minima on the potential energy surfaces. Interaction energies were calculated as the difference between the energy of the complex and the energy sum of the monomers. The counterpoise procedure of Boys and Bernardi [41] was used to perform the basis set superposition error (BSSE) correction for the interaction energies. All calculations were carried out using the Gaussian 09 program [42].

Molecular electrostatic potentials (MEPs) at the 0.001 electrons Bohr^{-3} contour of electronic density were calculated at the MP2/aug-cc-pVTZ level using the wave function analysis–surface analysis suite (WFA-SAS) program [43]. Natural bond orbital (NBO) analysis was implemented at the HF/aug-cc-pVTZ level via NBO 5.0 version [44] to analyze orbital interaction and charge transfer. Topological properties were derived from the theory of atoms in molecules (AIM) at the MP2/aug-cc-pVTZ level with the AIM2000 software [45]. To gain an insight into the nature of the investigated intermolecular interactions, we performed the energy decomposition analysis (EDA) using the GAMESS program [46].

3. Results and discussion

3.1. Tetrel- and triel-bonded dyads

3.1.1. MEPs

Fig. 1 shows the structures of complexes $\text{BF}_3 \cdots p\text{-PySiX}_3$ and $p\text{-PySiX}_3 \cdots \text{NZ}$ (NZ = NCLi, im, NHCH_2 , NH_3 , NH_2Me , NHMe_2 , NCH, NMe_3 , and N_2), both of them are combined with a triel bond and a tetrel bond, respectively. To have an understanding for the formation of both interactions, the MEP maps of molecule $p\text{-PySiF}_3$ are plotted in Fig. 2. As expected, the N atom of $p\text{-PySiF}_3$ has the most negative MEP (blue region), which is about two times in magnitude as much as that on the F atom (-15.45 kcal/mol). Thus the N atom of $p\text{-PySiF}_3$ could form a triel bond with the B atom of BF_3 , where

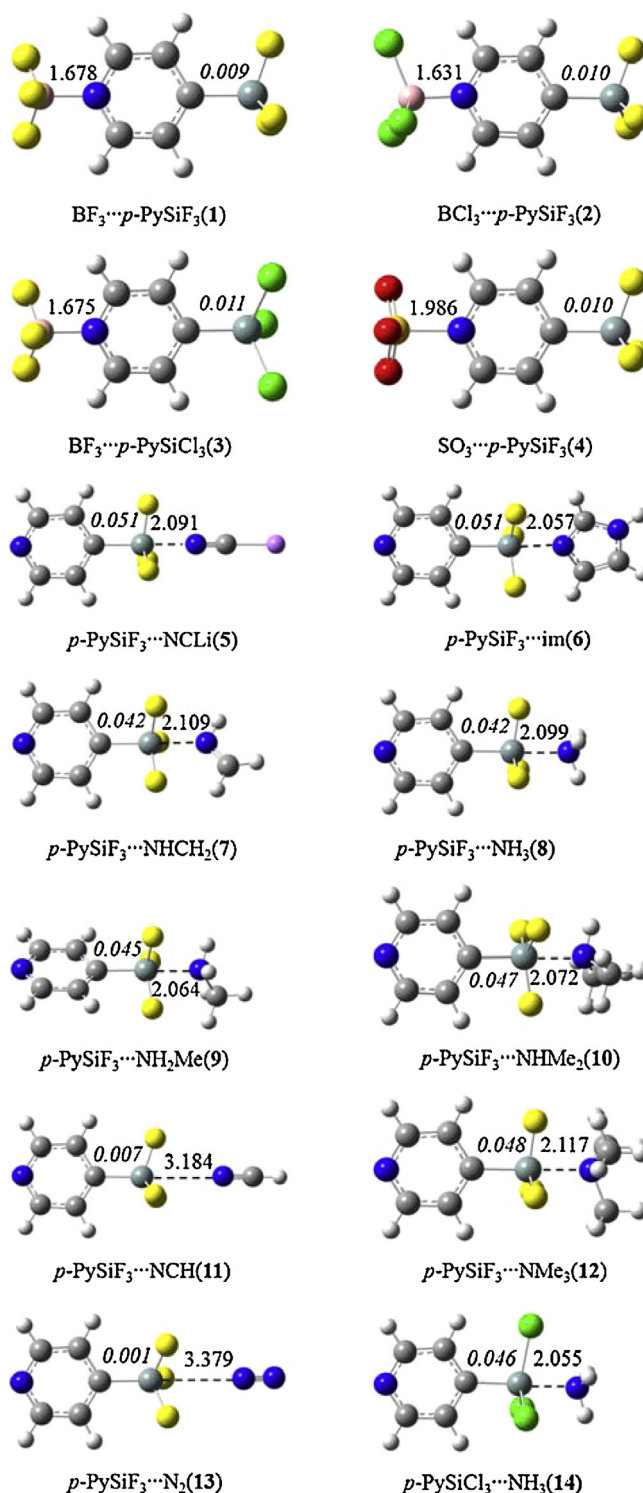


Fig. 1. Optimized structures of triel/chalcogen- and tetrel-bonded dyads of $p\text{-PySiX}_3$ with the binding distances and the change of C–Si bond length (italic) in angstrom.

a π -hole is present on the B atom [33,34], as shown in Fig. 2. On the other hand, four red regions with positive MEPs (σ -holes) are found on the surfaces of Si tetrahedroid, and all of them can participate in a tetrel bond with the nitrogen bases. However, we only focus on the σ -hole along the C–Si axis although it has a little smaller MEP than other σ -holes.

Table 1 presents the most negative MEP on the N atom ($V_{\text{min,N}}$) and the most positive MEP on the Si atom along the C–Si axis

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