



Research paper

Anionic tetrel bonds: An ab initio study

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ABSTRACT

Ab initio MP2/aug-cc-pVTZ calculations were performed to investigate charge-assisted complexes formed between a series of anions ($Z^- = F^-, Cl^-, Br^-, CN^-, NC^-, N_3^-, NCS^-, SCN^-$) and CF_3X or SiF_3X ($X = F, CN$) molecules. The nature of the interaction in these complexes, termed 'anionic tetrel-bonding', is studied by molecular electrostatic potential, noncovalent interaction, quantum theory of atoms in molecules and natural bond orbital analyses. The interaction energies of these complexes span a large range, from -1.74 kcal/mol in $F_4C:SCN^-$ to -84.37 kcal/mol in $(CN)F_3Si:F^-$. The results indicate that the anionic tetrel bonds in the SiF_3X complexes have a significant covalent character.

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1. Introduction

Noncovalent interactions play a vital role in many areas of science and technology, including molecular recognition, chemical reactions, crystal engineering and regulation of biochemical processes [1–4]. Many applications of these interactions are related to their detailed information, e.g. strength, directionality and origin of the attraction. Noncovalent interactions span a wide range of binding energies, from weak van der Waals interactions between nonpolar molecules, to very strong attractions between the oppositely charged ions [5]. Though, research in this field has largely focused on the hydrogen-bonding [6]. However, in recent years consideration attention has been devoted to a specific intermolecular interaction involving halogen atoms as a Lewis acid center. This interaction, termed as 'halogen-bonding', has been extensively used in many fields of chemistry and biochemistry [7–13]. The Lewis acid property of the halogen atom in the halogen-bonding is generally explained in terms of a region of positive electrostatic potential (σ -hole) [14–19] being the consequence of the diminished electron density on the extension of the covalent bond to the halogen atom. Owing to its strength and directionality, halogen-bonding has shown potential applications in many fields like molecular folding [10,20], molecular recognition [21,22], anion binding [23–25], and in the assembly of host-guest solids [26]. Similar interactions of other covalently-bonded atoms acting as the Lewis acid center have also been characterized. Depending upon the column of the periodic table to which the Lewis center

belongs, the noncovalent interaction has been named as tetrel- (Group 14) [27–29], pnictogen- (Group 15) [30–36], chalcogen- (Group 16) [37–40] and aerogen-bonding (Group 18) [41–44]. All these interactions are relevant in chemical and biochemical systems and share many properties with each other. In fact, they can be considered as a subgroup of a general definition of σ -hole-bonding interactions. The electrostatic component of all these interactions is described in terms of the σ -hole concept. Besides, this electrostatic factor is also supplemented by a charge transfer from the electron donor into the σ^* antibonding orbital of the covalent bond involving the Group 14–18 atoms, which tends to weaken and lengthen the latter bond.

The occurrence of tetrel bonds in crystal engineering and reaction mechanisms is becoming increasingly well recognized. For instance, Mitzel et al. have reported Si...N tetrel bonding interactions in the crystalline $Si(ONMe_2)_4$ and related compounds [45,46]. Grabowski has claimed that the tetrel-bonding interaction involving carbon atom as the Lewis acid could play a critical role in the SN_2 reaction [47]. Such interactions seem to be also important in numerous biological and biochemical processes [48]. In addition, the tetrel-bonding has been studied in a large number of crystalline structures [49–52] and validated with experimental charge density analysis [53]. Moreover, there are numerous theoretical studies revealing the substitution effects on the strengths of tetrel bonds [54–59].

The potential interactions between the σ -hole regions and the anions species acting as a Lewis base have been studied previously [41,60–62]. However, to the best of our knowledge, no detailed study regarding the geometry, interaction energy and bonding properties of σ -hole regions of the Group 14 elements with anions

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is available in the literature except for the interaction between these atoms and halide anions [44,47,52,57,63,64]. In the present paper, the σ -hole interactions formed between a series of anions ($Z^- = F^-, Cl^-, Br^-, CN^-, NC^-, N_3^-, NCS^-,$ and SCN^-) and CF_3X or SiF_3X ($X = F, CN$) species acting as a Lewis acid are studied. To characterize the bonding pattern, various analyses including the molecular electrostatic potential (MEP), quantum theory of atoms in molecules (QTAIM), noncovalent index (NCI) and natural bond orbital (NBO) are applied. We believe that the results of this study can enrich our knowledge on the tetrel-bonding and may be useful in crystal engineering, supramolecular chemistry and material science.

2. Computational details

All geometry optimizations were performed at the MP2/aug-cc-pVTZ level of theory. In order to identify whether the optimized structures correspond to a true local minimum or not, the corresponding frequency calculations were also carried out at the same level. The interaction energies were computed at the same level with corrections for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise method [65]. All these calculations were performed using the Gaussian 09 suites of programs [66].

The MEP maxima and minima values were obtained with the Wave Function Analysis–Surface Analysis Suite (WFA–SAS) [67] using the MP2/aug-cc-pVTZ generated wavefunctions. The NBO analysis was performed at the with the MP2/aug-cc-pVTZ level by means of the NBO 5.0 package [68]. The electron densities of the complexes were analyzed using the QTAIM methodology [69]

using the AIM2000 [70] program. The noncovalent interaction index (NCI) [71] and electron density difference (EDD) analyses were performed with the help of MultiWFN [72].

3. Results and discussion

As noted above, the formation of a tetrel-bonding interaction largely arises from the electrostatic attraction between the positively charged σ -hole on the tetrel atom and the negative region on the Lewis base. As Fig. 1 indicates, the MEPs on the 0.001 au electron density isosurfaces of CF_3X and SiF_3X ($X = F, CN$) show a small region of positive potential (σ -hole) over the central atom, along the extension of the covalent C–X or Si–X bond. The formation of these positive regions is due to the shift of electron density around the central atom towards the electron-withdrawing F or CN group. Clearly, a larger positive MEP of the σ -hole is associated with the Si atom when the X substitution is hold. Besides, for a given tetrel atom, the CN group exhibits a larger σ -hole potential compared to the F one. It is interesting to note that the MEP analysis of CF_3CN and SiF_3CN molecules in Fig. 1 also indicates the presence of σ -hole regions on the extension of the C–F or Si–F bonds. As evident, the MEP value associated with the Si–F bonds of SiF_3CN is slightly smaller than that of Si–CN one. Thus, from the MEP analysis, it should be expected that SiF_3CN forms the most stable σ -hole interaction compared to CF_4 , CF_3CN and SiF_4 molecules.

The geometric and energetic parameters of the anionic tetrel-bonded complexes are listed in Table 1. The fully optimized geometries of these complexes are given in Fig. S1 of Supporting Information. As seen, all these complexes show a linear X–C··· Z^- or X–Si··· Z^- arrangement, thus indicating that the interaction is

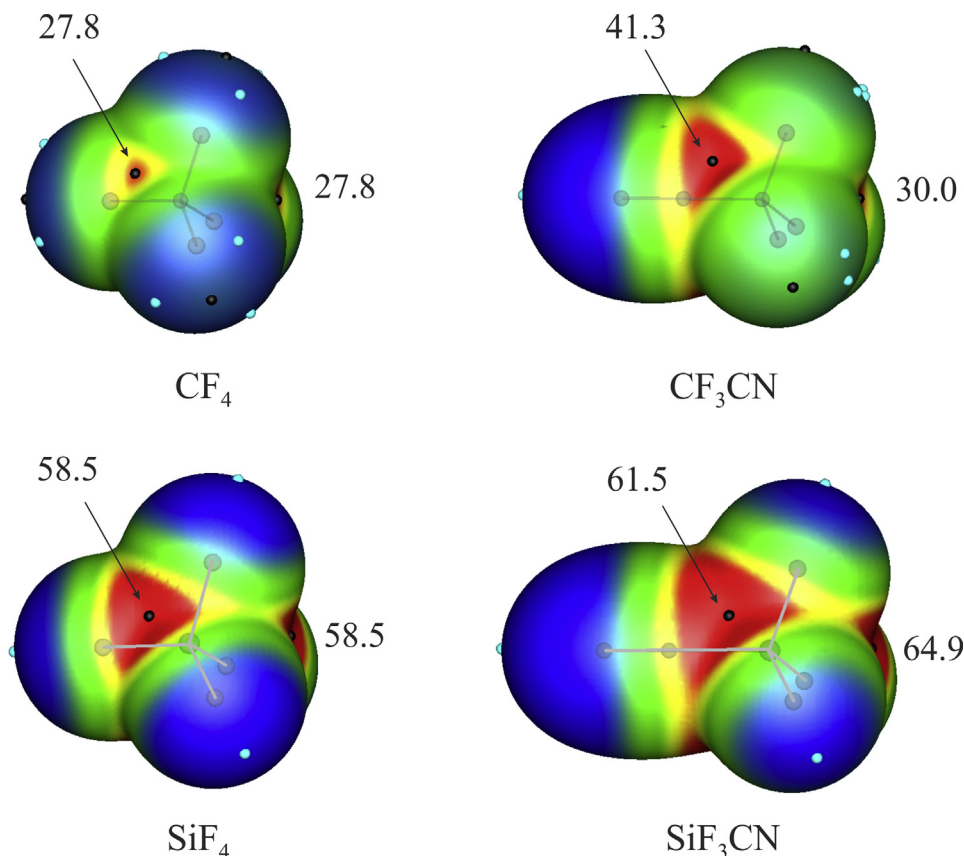


Fig. 1. Calculated MEP onto the van der Waals surface of CF_3X and SiF_3X ($X = F, CN$). The color code for MEP plots, in kcal/mol, is: red > 25; 25 > yellow > 15; 15 > green > 0 and blue < 0. The locations of the σ -holes are indicated with black circles, and their values are given in kcal/mol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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