

Supporting information

Revisiting conventional noncovalent interactions towards a complete understanding: From tetrel to pnictogen, chalcogen, and halogen bond

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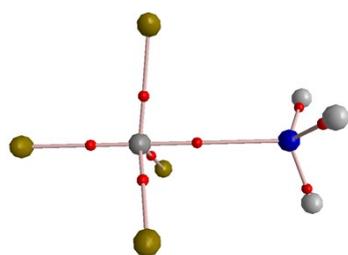
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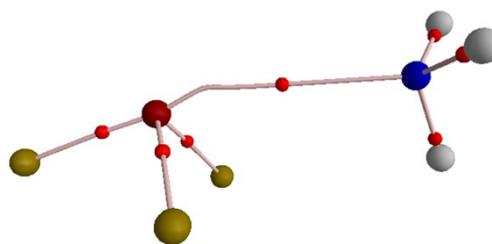
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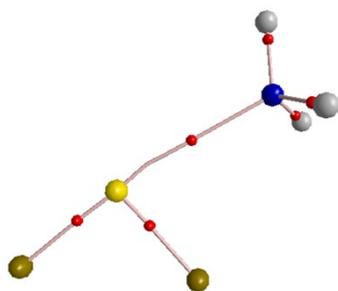
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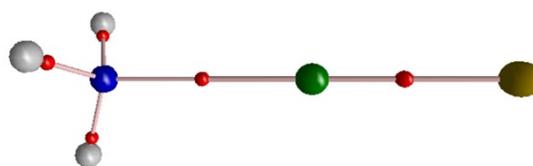
H₃N-SiF₄ TtB
(axial)



H₃N-PF₃ PniB

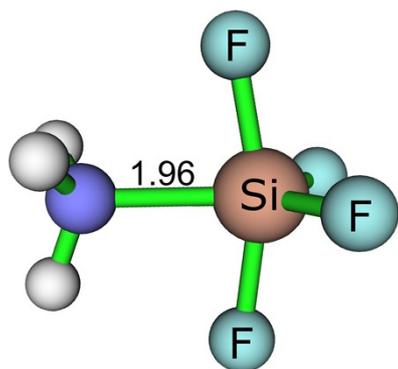


H₃N-SF₂ ChalB

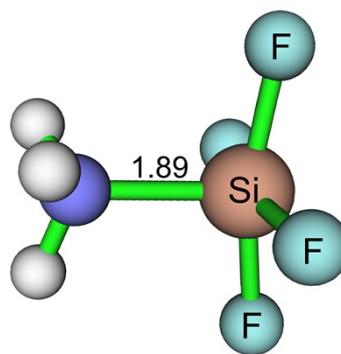


H₃N-ClF HalB

Figure S1. Topological graphs with density at MP2/aDZ of investigated complexes

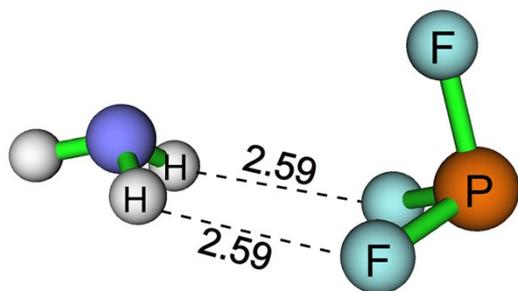


Equatorial conformer

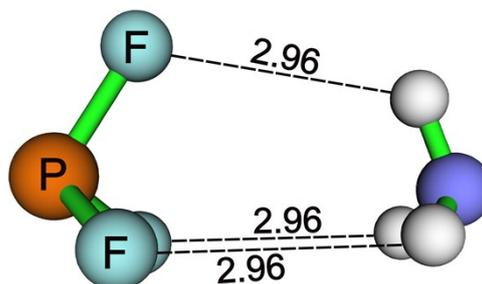


Square pyramidal conformer

a) Less stable conformers of $\text{H}_3\text{N-SiF}_4$ complex at MP2/aTZ

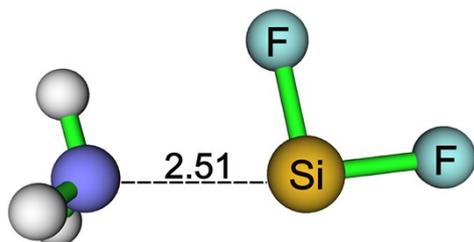


Conformer II

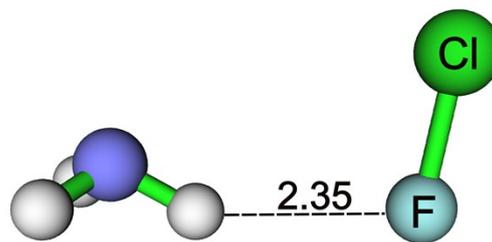


Conformer III

b) Less stable hydrogen-bonded conformers of $\text{H}_3\text{N-PF}_3$ complex at MP2/aTZ



c) *Eclipsed conformer* of $\text{H}_3\text{N-SF}_2$



d) Hydrogen bonded-structure of $\text{H}_3\text{N-ClF}$

Figure S2. Secondary structures of investigated complexes at MP2/aTZ level

Two other conformers of H₃N-SiF₄, including *equatorial* and *square pyramidal* geometries, stated by Chehayber *et al.*¹, were also reoptimized at MP2/aTZ high-level of theory to accurately investigate their stabilities and electronic properties (cf. Figure S2). Their binding energies are positive, 5.10 and 11.92 kJ.mol⁻¹, respectively, at MP2/aTZ. Both *equatorial* and *square pyramidal conformer* occur an imaginary frequency of -43.14 cm⁻¹ and -125.83 cm⁻¹.

The *hydrogen-bonded* conformers (**II** and **III**) of NH₃-PF₃ both are less stable than H₃N-PF₃ PniB one. Indeed, their E_b+ZPE+BSSE values at MP2/aTZ are slightly negative, i.e. -0.56 and -1.64 kJ.mol⁻¹, respectively. The AIM analyses show the conformer **II** exhibits three intermolecular interactions, including a PF...N HalB and two NH...F hydrogen bonds. Their ρ(rc) values at BCPs are 1.9 × 10⁻³ a.u, 5.8 × 10⁻³ a.u, and 5.8 × 10⁻³ a.u, respectively; and all significantly lower than that of N...P PniB (18.5 × 10⁻³ a.u). The conformer **III** occurs two imaginary frequencies (-49.49 and -49.47 cm⁻¹) at MP2/aTZ.

The *eclipsed* structure of H₃N-SF₂ model exhibits the stabilization energy of -21.2 kJ.mol⁻¹ at MP2/aTZ, reasonably approximate to that of the *staggered* one (-21.1 kJ.mol⁻¹). However, one imaginary frequency is found in the *eclipsed* conformer (-57.15 cm⁻¹), where H_α atom of NH₃ vibrates towards the outside of the C_s symmetry plane. Thus, the *eclipsed* structure could be recognized as a transition state moving towards the more stable *staggered* conformer.

The H₃N-CIF *hydrogen-bonded* structure exhibits an binding energy of -1.38 kJ.mol⁻¹ at MP2/aTZ.

1. Chehayber JM, Nagy ST, Lin CS. Ab initio studies of complexes between SiF₄ and ammonia. *Can J Chem.* 1984;62(1):27-31. doi:10.1139/v84-006

Table S1. $V_{s,min}$ and $V_{s,max}$ values (kcal.mol⁻¹) of isolated monomers derived from Multiwfn at MP2/aTZ

Isolated monomers	$V_{s,min}$	$V_{s,max}$
NH₃	-37.267252	26.530416
		26.516305
		26.524880
ClF*	-10.899116	47.815127
SF₂	-11.484665	45.237921
	-11.467289	45.232004
PF₃	-11.311841	39.768458
	-11.267542	39.654171
	-11.269485	39.613856
SiF₄	-9.805767	57.264031
	-9.776024	57.161980
	-9.804366	56.949983
	-9.788675	57.243163

* This structure exists maxima points around the F atom, which form a ring in perpendicular to the F-Cl bond

Table S2. Contribution of different components to interaction energies of noncovalent complexes using high order SAPT2+(3)dMP2 approach (kJ.mol⁻¹) at aTZ

	SiF₄-NH₃ TtB	PF₃-NH₃ PniB	SF₂-NH₃ ChalB	ClF-NH₃ HalB
Electrostatic	-330.66	-50.89	-103.60	-162.05
Induction	-135.79	-13.27	-45.35	-103.41
Dispersion	-62.00	-19.89	-31.90	-40.28
Exchange	402.81	65.49	150.34	257.93
E _{elst} /E _{int} (SAPT)	3.39	3.40	2.74	2.63
E _{ind} /E _{int} (SAPT)	2.16	1.49	0.71	1.08
E _{disp} /E _{int} (SAPT)	0.84	1.05	1.07	0.49
E _{exch} /E _{int} (SAPT)	-5.39	-4.93	-3.53	-3.21