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New Chemistry News

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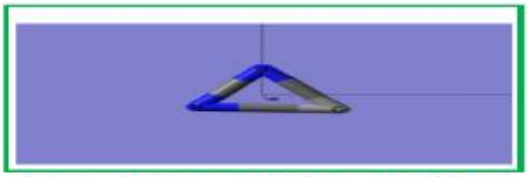

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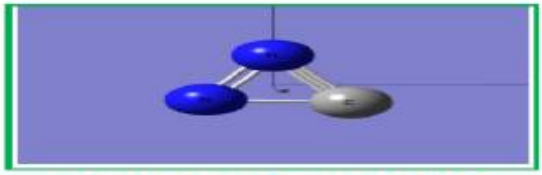


ChemNewsNew (CNN)

# CNN – 43

# *Tetrel bonds*

# *Non-Covalent interactions*



| Information Source | ACS.org ; sciencedirect.com |
|---|---|
| **K. Somasekhara Rao,**<br>**Dept. of Chemistry,**<br>**Acharya Nagarjuna Univ.,**<br>**Dr. M.R.Appa Rao Campus,**<br>**Nuzvid-521 201, India** | **R. Sambasiva Rao,**<br>**School of Chemistry,**<br>**Andhra University,**<br>**Visakhapatnam 530 003, India** |



**Conspectus:**Tetrel atoms ([TtA: C,Si Ge Sn Pb Fl]) belong to 14$^{th}$ group of 18 column chemical elements periodic table. TtA exhibits Lewis acid (LA) behaviour and forms complexes or adducts with Lewis bases (LB) i.e. molecules or compounds or π electron systems.

**History:** The non-covalent bonding interactions of group IV elements were known experimentally well before the title tetrel bond was introduced. It has a niche now in low energy patch in material world of biological, industrial and pure chemical domains.

**Methods in tetrel bonding interactions:**The sought-after approaches in these investigations comprise of preparation of tetrel bonded complex molecules, bond confirmation through spectroscopic probes, searching in crystallographic databases and computational quantum computations of species. CQC targets the of-the-shelf-available, synthetic or hypothetical set of molecular structures for feasibility/possibility exploration of tetrel and the like bonds. The Optimized

geometry,Molecular ESP map, Hirschfeld surface, NCI (Non-covalent interaction) surface and AIM are the probes widely employed to detect and confirm the non-bonding interactions.

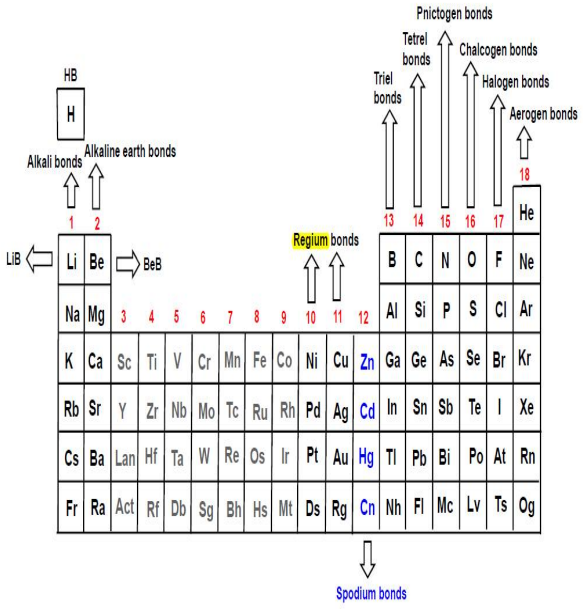
**Knowledge base:**An explainable-intelligent (Ei) knowledge-based system (KBS) for chemical speciation(CS) has been under development in this laboratory. It is amulti-layered multi-paradigm approach consisting of method bases, data bases, graphic/image basesetc. They are fabricated adaptively (manually in exploration phase) in work-flows for diverse tasks in research and learning. The series of select published research output in halogen-, hydrogen, triel-, tetrel- bonds is under active consideration in this mega system.

**Keywords:**Tetrel bonds; Non-Covalent interactions; Chemical bonds ;

| | Layout | |
|---|---|---|
| I | Tetrel bonds in chemical systems | K(nowledge)Lab<br>rsr.chem1979 |
| II | Select Research Titles from ACS (American Chemical Society) | |
| III | Select Research Titles from SD (Science Direct) | |
| IV | Supplementary Information (Sup Inf) | |
| | Tt-bonded chemical species | |
| | π interactions | |

# I. Tetrel bonds in chemical systems

| Column# | Abbrev | Abbrev | $$ bonds |
|---|---|---|---|
| | $$Bond | $$Atom | |
| 1G | HB | HA | Hydrogen |
| 18G | NgB | NgA | Nobel gas |
| 17G @ | HaB | HaA | Halogen |
| 16G @ | ChB | ChA | Chalcogen |
| 15G | PnB | PnA | Pnicogen or Pnictogen |
| | | | |
| 14G | TtB | TtA | Tetrel |



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|---|---|---|---|
| 13G | TrB | TrA | Triel |
| 12G | SPB | SPA | Spodium |
| 11G | CiB or RgB | CiA or RgA | Regium or Coinage |
| | | | |
| 1G | AkB AlkB | AkA AlkA | Alkaline |
| 2G | AEB AlkEarB | AEB AlkEarA | Alkaline-Earth |

☞ A tetrel bond is defined as an interaction between any electron donating moiety and a group 14 element (TtA) acting as Lewis acid

@ IUPAC recommened

#: column number of Chem elements in 18 Group model of periodic table

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| ACS | American Chemical Society |
| SD | Science Direct |
| RSC | Royal Society of Chemistry |

**[TtA] | [C;Si;Ge;Sn;Pb;Fl]**

# II. Select Research Titles from American Chemical Society

| | |
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| On the Importance of R–CF···O Tetrel Bonding Interactions in Biological Systems | J Phys. Chem. A, 121(2017) 5371-5376 DOI: 10.1021/acs.jpca.7b06052 |
| Xavier García-LLinás, Antonio Bauzá, Saikat K. Seth and Antonio Frontera | |
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| Inter/Intramolecular Bonds in TH5+ (T = C/Si/Ge): H2 as Tetrel Bond Acceptor and the Uniqueness of Carbon Bonds | J Phys. Chem. A, 123( 2019) 1168-1176 DOI: 10.1021/acs.jpca.8b09778 |
| Sharon Priya Gnanasekar and ElangannanArunan | |
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| Tin···Oxygen Tetrel Bonding: A Combined Structural, Spectroscopic, and Computational Study | Cryst Growth & Des 2017, 17, 7, 4021-4027 DOI: 10.1021/acs.cgd.7b00678 |
| Hussain Ullah, Brendan Twamley, Amir Waseem, Muhammed KhawarRauf,Muhammad Nawaz Tahir, James A. Platts, and Robert J. Baker | |
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| Tetrel Bonding along the Pathways of Transsilylation and Alkylation of N-Trimethylsilyl-N-methylacetamide with Bifunctional (Chloromethyl)fluorosilanes | J Phys. Chem. A, 123( 2019) 5178-5189 DOI: 10.1021/acs.jpca.9b03876 |
| Nina N. Chipanina, Nataliya F. Lazareva, Larisa P. Oznobikhina and Bagrat A. Shainyan | |
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| Tetrel bonding interactions at work: Impact on tin and lead coordination compounds (Rev) | Coordination Chemistry Reviews 384 (2019) 107–125 doi.org/10.1016/j.ccr.2019.01.003 | | | |
| Antonio Bauzá, Saikat Kumar Seth, Antonio Frontera | | | | |
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| Supramolecular Assemblies in Pb(II) Complexes with Hydrazido-Based Ligands | Crystals 2019, 9, 323; doi:10.3390/cryst9060323 | | | |
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| Systematic Elucidation of Factors That Influence the Strength of Tetrel Bonds | J Phys. Chem. A, 121( 2017) 5561-5568 DOI: 10.1021/acs.jpca.7b05300 | | | |
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| Intermolecular Interactions Involving Heavy Alkenes H2Si═TH2 (T = C, Si, Ge, Sn, Pb) with H2O and HCl: Tetrel Bond and Hydrogen Bond | ACS Omega, 5( 2020) 30210-30225 DOI: 10.1021/acsomega.0c04682 | | | |
| Yishan Chen and Fan Wang | | | | |
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| Assembly of Effective Halide Receptors from Components. Comparing Hydrogen, Halogen, and Tetrel Bonds | J Phys. Chem. A, 121 (2017) 3606-3615 DOI: 10.1021/acs.jpca.7b02305 | | | |
| Steve Scheiner | | | | |
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| Steric Crowding in Tetrel Bonds | J Phys. Chem. A, 122( 2018) 2550-2562 DOI: 10.1021/acs.jpca.7b12357 | | | |
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| Importance of π-Interactions Involving Chelate Rings in Addition to the Tetrel Bonds in Crystal Engineering: A Combined Experimental and Theoretical Study on a Series of Hemi- and Holodirected Nickel(II)/Lead(II) Complexes | Crystal Growth & Design, 19 (2019) 5869-5881 DOI: 10.1021/acs.cgd.9b00881 | | | |
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| In Situ Measure of Intrinsic Bond Strength in Crystalline Structures: Local Vibrational Mode Theory for Periodic Systems | Journal of Chemical Theory and Computation, 15( 2019) 1761-1776<br>DOI: 10.1021/acs.jctc.8b01279 |
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| Growth Pattern, Stability, and Properties of Complexes of C2H5OH and nCO2 (n = 1–5) Molecules: A Theoretical Study | ACS Omega, 5(2020) 14408-14416<br>DOI: 10.1021/acsomega.0c00948 |
| Cam-Tu Dang Phan, Nguyen Thi Ai Nhung, and Nguyen Tien Trung | |
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| Comparison of CH···O, SH···O, Chalcogen, and Tetrel Bonds Formed by Neutral and Cationic Sulfur-Containing Compounds | J Phys. Chem. A, 119 ( 2015) 9189-9199<br>DOI: 10.1021/acs.jpca.5b06831 |
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| Tetrel and Pnictogen Bonds Complement Hydrogen and Halogen Bonds in Framing the Interactional Landscape of Barbituric Acids | Crystal Growth & Design,21(2021) 642-652<br>DOI: 10.1021/acs.cgd.0c01429 |
| Vijith Kumar, Patrick Scilabra, Peter Politzer, Giancarlo Terraneo, Andrea Daolio, Francisco Fernandez-Palacio, Jane S. Murray, and Giuseppe Resnati | |
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| Potential Energy Surfaces of HN(CH)SX:CO2 for X = F, Cl, NC, CN, CCH, and H: N···C Tetrel Bonds and O···S Chalcogen Bonds | J Phys. Chem. A, 123(2019) 7270-7277<br>DOI: 10.1021/acs.jpca.9b04144 |
| Janet E. Del Bene, IbonAlkorta, and José Elguero | |
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| Carbon–Carbon Bonding between Nitrogen Heterocyclic Carbenes and CO2 | J Phys. Chem. A, 121(2017)8136-8146<br>DOI: 10.1021/acs.jpca.7b08393 |
| Janet E. Del Bene, IbonAlkorta and José Elguero | |
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| Pnictogen-Bonding Catalysis and Transport Combined: Polyether Transporters Made In Situ | JACS Au 2021, 1, 1588−1593<br>/doi.org/10.1021/jacsau.1c00345 |
| Heorhii V. Humeniuk, Andrea Gini, Xiaoyu Hao, Filipe Coelho, Naomi Sakai, and Stefan Matile | |
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| Comparison for Electron Donor Capability of Carbon-Bound<br>Halogens in Tetrel Bonds | doi.org/10.1021/acsomega.1c04085<br>ACS Omega 2021, 6, 29037−29044 |

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| Qingqing Yang, Xiaolong Zhang, and Qingzhong Li | | | |
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| Importance of #-interactions involving chelate rings in addition to the tetrel bonds in crystal engineering: A combined experimental and theoretical study on a series of hemi- and holo-directed nickel(II)/lead(II) complexes | Cryst. Growth Des (2019)<br>DOI: 10.1021/acs.cgd.9b00881 |
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| Chlorine “Equatorial Belt” Activation of CF3Cl by CO2: The C···Cl Tetrel Bond Dominance in CF3Cl–CO2 | J Phys. Chem. Letters, 12(2021)3907-3913<br>DOI: 10.1021/acs.jpclett.1c00837 |
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| Ability of IR and NMR Spectral Data to Distinguish between a Tetrel Bond and a Hydrogen Bond | J Phys. Chem. A, 122( 2018) 7852-7862<br>DOI: 10.1021/acs.jpca.8b07631 |
| Steve Scheiner | |
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| Relative Strengths of a Pnicogen and a Tetrel Bond and Their Mutual Effects upon One Another | J Phys. Chem. A, 125(2021) 2631-2641 (A: Structure, Spectroscopy, and Reactivity of Molecules and Clusters)<br>DOI: 10.1021/acs.jpca.1c01211 |
| Steve Scheiner | |
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| NMR Investigations of Noncovalent Carbon Tetrel Bonds. Computational Assessment and Initial Experimental Observation | J Phys. Chem. A, 119( 2015) 11891-11899<br>DOI: 10.1021/acs.jpca.5b10848 |
| Scott A. Southern and David L. Bryce | |
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| Experimental 13C and 1H Solid-State NMR Response in Weakly Tetrel-Bonded Methyl Groups | J Phys. Chem. C, 125( 2021) 2111-2123 (C: Physical Properties of Materials and Interfaces)<br>DOI: 10.1021/acs.jpcc.0c09832 |
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| Competition between a Tetrel and Halogen Bond to a Common Lewis Acid | J Phys. Chem. A, 125( 2021) 308-316 (A: Structure, Spectroscopy, and Reactivity of Molecules and Clusters) DOI: 10.1021/acs.jpca.0c10060 |
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| Short and Linear Intermolecular Tetrel Bonds to Tin. Cocrystal Engineering with Triphenyltin Chloride | Crystal Growth & Design, 20 (2020) 2027-2034 DOI: 10.1021/acs.cgd.9b01681 |
| Vijith Kumar, Carl Rodrigue and David L. Bryce | |
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| Weak Interactions Get Strong: Synergy between Tetrel and Alkaline-Earth Bonds | J Phys. Chem. A, 123 (2019) 7124-7132 DOI: 10.1021/acs.jpca.9b06051 |
| IbonAlkorta, M. Merced Montero-Campillo, Otilia Mó, José Elguero and Manuel Yáñez | |
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| Methane Adsorption on Heteroatom-Modified Maquettes of Porous Carbon Surfaces | J. Phys. Chem. A 2021, 125, 6042−6058 doi.org/10.1021/acs.jpca.0c11284 |
| Rylan Rowsey, Erin E. Taylor, Stephan Irle, Nicholas P. Stadie, and Robert K. Szilagyi | |
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| Azines as Electron-Pair Donors to CO2 for N…C Tetrel Bonds | J. Phys. Chem. A 2017, DOI: 10.1021/acs.jpca.7b08505 |
| IbonAlkorta, José Elguero, and Janet E. Del Bene | |
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| Ruthenium(II)-Catalyzed Regioselective 1,2-Hydrosilylation of N-Heteroarenes and Tetrel Bonding Mechanism | ACS Catalysis, 11 (2021)5885-5893 DOI: 10.1021/acscatal.1c01148 |
| Deepak Behera, Subramanian Thiyagarajan, Puthannur K. Anjalikrishna, Cherumuttathu H. Suresh, and Chidambaram Gunanathan | |
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| Rylan Rowsey, Erin E. Taylor, Stephan Irle, Nicholas P. Stadie and Robert K. Szilagyi | | | |
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| Noncovalent Interactions in Organometallic Chemistry: from Cohesion to Reactivity, a new Chapter | | | |
| Yann Cornaton and Jean-Pierre Djukic | | | |
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| Review<br>Noncovalent Bonds through Sigma and Pi-Hole Located on the Same Molecule. Guiding Principles and Comparisons | Molecules 2021, 26, 1740.<br>https://doi.org/10.3390/molecules26061740 | | |
| WiktorZierkiewicz, Mariusz Michalczyk and Steve Scheiner | | | |
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| Carbon's Three-Center, Four-Electron Tetrel Bond, Treated Experimentally | DOI: 10.1021/jacs.8b09367<br>J. Am. Chem. Soc. 2018, 140, 17571−17579 | | |
| Alavi Karim, Nils Schulz, Hanna Andersson, Bijan Nekoueishahraki, Anna-Carin C. Carlsson, Daniel Sarabi, ArtoValkonen, Kari Rissanen, JürgenGrafenstein, Sandro Kellerand Maté Erdelyi | | | |
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| Ability of Lewis Acids with Shallow -Holes to Engage in Chalcogen Bonds in Different Environments | Molecules 2021, 26, 6394.<br>https://doi.org/10.3390/molecules26216394 | | |
| RafałWysoki ´ nski 1,*, WiktorZierkiewicz 1,* , Mariusz Michalczyk 1 and Steve Scheiner | | | |
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| Dissection of the Origin of π-Holes and the Noncovalent Bonds in Which They Engage | doi.org/10.1021/acs.jpca.1c05431<br>J. Phys. Chem. A 2021, 125, 6514−6528 | | |
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| A Modified Townes-Dailey Model for Interpretation and Visualization of Nuclear Quadrupole Coupling Tensors in Molecules | dx.doi.org/10.1021/acs.jpca.0c00439<br>J. Phys. Chem. A 2020, 124, 1176−1186 | | |
| Andrew Rinald and Gang Wu | | | |
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| Comment on "Inter/Intramolecular Bonds in TH5+ (T = C/Si/Ge): H2 as Tetrel Bond Acceptor and the Uniqueness of Carbon Bonds" | J. Phys. Chem. A,<br>DOI: 10.1021/acs.jpca.9b06159 | | |
| Dominik Marx | | | |
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| Unravelling the Importance of H bonds, σ–hole and π–hole-Directed Intermolecular Interactions in Nature | J. Indian Inst. Sci.100:1 \| 43–59 (2020 A Multidisciplinary Reviews Journal |
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| Sharon Priya Gnanasekar, and ElangannanArunan | |
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| Comment on "Inter/Intramolecular Bonds in TH5+(T = C/Si/Ge): H2 as Tetrel Bond Acceptor and the Uniqueness of Carbon Bonds" | J. Phys. Chem. A, DOI: 10.1021/acs.jpca.9b07378 |
| MaramSusli, KhidhirAbdalhusseinAlhameedi, and Dylan Jayatilaka | |
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| Tetrel, pnictogen and chalcogen bonds identified in the gas phase before they had names: A systematic look at non-covalent interactions | Phys.Chem. Chem. Phys., 2017, DOI: 10.1039/C7CP02518A |
| Anthony C. Legon | |
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| Azines as Electron-Pair Donors to CO2 for N···C Tetrel Bonds | J Phys. Chem. A, 11 (2017) 8017-8025 DOI: 10.1021/acs.jpca.7b08505 |
| IbonAlkorta, José Elguero and Janet E. Del Bene | |
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| Tetrel Bonding and Other Non-Covalent Interactions Assisted Supramolecular Aggregation in a New Pb(II) Complex of an Isonicotinohydrazide | Molecules 2020, 25, 4056; doi:10.3390/molecules25184056 |
| GhodratMahmoudi 1,* , Marjan Abedi 2 , Simon E. Lawrence 3 , Ennio Zangrando 4 , Maria G. Babashkina 5 , Axel Klein 5,* , Antonio Frontera 6 and Damir A. Safin | |
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| Cooperativity in Tetrel Bonds | J. Phys. Chem. A 2016, 120, 4, 648–656 DOI: 10.1021/acs.jpca.5b11876 |
| Marta Marin-Luna, IbonAlkorta, and José Elguero | |
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# III. Select Research Titles from Science Direct

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| Origins and properties of the tetrel bond | | | Phys. Chem. Chem. Phys., 2021, 23, 5702 DOI: 10.1039/d1cp00242b | |
| Steve Scheiner | | | | |
| **PERSPECTIVE** | | TtB. | SD. | 01 |

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| Tetrel, halogen and hydrogen bonds in bis(4-((E)-(2,2-dichloro-1-(4-substitutedphenyl) vinyl) diazenyl) phenyl) methane dyes | | | 10.1016/j.dyepig.2017.12.033 Dyes and pigments, 150, 2018, 377-381 | |
| Namiq Q. Shixaliyev, Nigar E. Ahmadova, Atash V. Gurbanov, Abel M. Maharramov, Gunay Z. Mammadova, Valentine G. Nenajdenko, Fedor I. Zubkov, Kamran T. Mahmudov, Armando J.L. Pombeiro | | | | |
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| Tetrel Bonding Interactions Involving Carbon atWork: Recent Advances in Crystal Engineering and Catalysis | | | doi:10.3390/c6040060 C 2020, 6(4), 60 Journal of Carbon research | |
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| "Like-like" tetrel bonding interactions between Sn centres: a combined ab initio and CSD study | | | Dalton Trans., 2019,48, 11208-11216 doi.org/10.1039/C9DT01953G DOI: 10.1039/x0xx00000x | |
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| Comparison between Tetrel Bonded Complexes Stabilized by σ and π Hole Interactions | | | Molecules 2018, 23, 1416; doi:10.3390/molecules23061416 | |
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| Comparative Strengths of Tetrel, Pnicogen, Chalcogen, and Halogen Bonds and Contributing Factors | | | Molecules 2018, 23, 1681; doi:10.3390/molecules23071681 | |
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| Tetrel Bonding Interactions in Perchlorinated Cyclopenta- and Cyclohexatetrelanes: A Combined DFT and CSD Study | | | Molecules 2018, 23, 1770; doi:10.3390/molecules23071770 | |
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| An Ab Initio Investigation of the Geometries and Binding Strengths of Tetrel-, Pnictogen-, and Chalcogen-Bonded Complexes of CO2, N2O, and CS2 with Simple Lewis Bases: Some Generalizations | Molecules 2018, 23, 2250; doi:10.3390/molecules23092250 | | |
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| Strong Tetrel Bonds: Theoretical Aspects and Experimental Evidence | Molecules 2018, 23, 2642; doi:10.3390/molecules23102642 | | |
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| Mehdi D. Esrafili and ParisasadatMousavian | | | |
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| On the Power of Geometry over Tetrel Bonds | Molecules 2018, 23, 2742; doi:10.3390/molecules23112742 | | |
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| EphrathSolel and Sebastian Kozuch | | | |
| | TtB. | SD. | 12 |

| Quantitative Assessment of Tetrel Bonding Utilizing Vibrational Spectroscopy | Molecules 2018, 23, 2763; doi:10.3390/molecules23112763 | | |
|---|---|---|---|
| Daniel Sethio , Vytor Oliveira and ElfiKraka | | | |
| | TtB. | SD. | 13 |

| Identification of the Tetrel Bonds between Halide Anions and Carbon Atom of Methyl Groups Using Electronic Criterion | Molecules 2019, 24, 1083; doi:10.3390/molecules24061083 | | |
|---|---|---|---|
| Ekaterina Bartashevich, YuryMatveychuk and Vladimir Tsirelson | | | |
| | TtB. | SD. | 14 |

| Crystallographic and Computational Characterization of Methyl Tetrel Bonding inS-Adenosylmethionine-Dependent Methyltransferases | Molecules 2018, 23, 2965; doi:10.3390/molecules23112965 | | |
|---|---|---|---|
| Raymond C. Trievel and Steve Scheiner | | | |
| | TtB. | SD. | 15 |

| Calculation of VS,max and Its Use as a Descriptor for the Theoretical Calculation of pKa Values for Carboxylic Acids | Molecules 2019, 24, 79; doi:10.3390/molecules24010079 | | |
|---|---|---|---|
| Guillermo Caballero-García, Gustavo Mondragón-Solórzano, Raúl Torres-Cadena, Marco Díaz-García, Jacinto Sandoval-Lira and Joaquín Barroso-Flores | | | |
| | TtB. | SD. | 16 |

| Tetrel bond cooperativity in open-chain (CH3CN)n and (CH3NC)nclusters (n = 2–7): An ab initio study | Chemical Physics Letters 628 (2015) 16–20 doi.org/10.1016/j.cplett.2015.04.001 | | |
|---|---|---|---|
| Mehdi D. Esrafilia, NafisehMohammadirada, Mohammad Solimannejad | | | |
| | TtB. | SD. | 17 |

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|---|---|
| Tetrel Interactions from an Interacting Quantum Atoms Perspective | Molecules 2019, 24, 2204; doi:10.3390/molecules24122204 |
| José Luis Casals-Sainz, Aurora Costales Castro , Evelio Francisco and Ángel Martín Pendás | |
| | TtB. SD. 18 |

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|---|---|
| Intermolecular Non-Covalent Carbon-Bonding Interactions with Methyl Groups: A CSD, PDB and DFT Study | Molecules 2019, 24, 3370; doi:10.3390/molecules24183370 |
| Tiddo J. Mooibroek | |
| | TtB. SD. 19 |

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| Tetrel Bonds with -Electrons Acting as Lewis Bases—Theoretical Results and Experimental Evidences | Molecules 2018, 23, 1183; doi:10.3390/molecules23051183 |
| Sławomir J. Grabowski | |
| | TtB. SD. 20 |

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|---|---|
| Tetrel Bonding as a Vehicle for Strong and Selective Anion Binding | Molecules 2018, 23, 1147; doi:10.3390/molecules23051147 |
| Steve Scheiner | |
| | TtB. SD. 21 |

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|---|---|
| Anionic tetrel bonds: An ab initio study | Chem Phys Letters 691 (2018) 394–400 /doi.org/10.1016/j.cplett.2017.11.051 |
| Mehdi D. Esrafili, SoheilaAsadollahi, ParisasadatMousavian | |
| | TtB. SD. 22 |

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| Tetrel bonding on graphene | Computational & Theoretical Chemistry, 1147(2019) 8-12 doi.org/10.1016/j.comptc.2018.11.011 |
| Yu Zhang, Weizhou Wang, Yi-Bo Wang | |
| | TtB. SD. 23 |

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| Towards an understanding of the CO2-philicity in glycine: Deepening into the CO2:Aminoacid interactions | Chemical Physics 453-454 (2015) 1–6doi.org/10.1016/j.chemphys.2015.03.008 |
| Luis Miguel Azofra | |
| | TtB. SD. 24 |

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|---|---|
| Complexes of CO2 with the Azoles: Tetrel Bonds, Hydrogen Bonds and Other Secondary Interactions | Molecules 2018, 23, 906; doi:10.3390/molecules23040906 |
| Janet E. Del Bene, José Elguero and IbonAlkorta | |
| | TtB. SD. 25 |

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|---|---|---|---|---|
| Tetrel bonding interactions at work: Impact on tin and lead coordination compounds | Coord Chemis Rev 384 (2019) 107–125 /doi.org/10.1016/j.ccr.2019.01.003 | | | |
| Antonio Bauzá, Saikat Kumar Seth, Antonio Frontera | | | | |
| **Review** | | TtB. | SD. | 26 |

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|---|---|---|---|---|
| Interplay between hydrogen bond and single-electron tetrel bond: H3C⋯ COX2⋯HY and H3C⋯ CSX2 · · ·HY (X = F, Cl; Y = CN, NC) complexes as a working model | Comput&Theor Chem1074, 2015, 101-106 doi.org/10.1016/j.comptc.2015.10.015 | | | |
| Zahra Rezaei, Mohammad Solimannejad, Mehdi D. Esrafili | | | | |
| | | TtB. | SD. | 27 |

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|---|---|---|---|---|
| Comparison for σ-hole and π-hole tetrel-bonded complexes involving F2C] CFTF3 (T]C, Si, and Ge): Substitution, hybridization, and solvation effects | J Fluorine Chem 207 (2018) 38–44 /doi.org/10.1016/j.jfluchem.2018.01.003 | | | |
| Wenbo Dong, Xin Yang, Jianbo Cheng, Wenzuo Li, Qingzhong Li | | | | |
| | | TtB. | SD. | 28 |

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|---|---|---|---|---|
| The differences and cooperativity between Ge (Sn)…O tetrel bonds and X (X= F, Cl, Br, and I) …O halogen bonds | Chemical Physics 534, 2020, 110748 doi.org/10.1016/j.chemphys.2020.110748 | | | |
| Yuchun Li, Xiaoting Wang, Hui Wang, Yunxiang Lu, Zhengdan Zhu, Yuxiang Ni | | | | |
| | | TtB. | SD. | 29 |

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|---|---|---|---|---|
| On the interaction of propynal with HNO, HF, HCl, H2O, CH3OH, and NH3: Red- and blue-shifting hydrogen bonds and tetrel bonds | ComputTheor Chem, 1160 (2019) 1–13 doi.org/10.1016/j.comptc.2019.05.010 | | | |
| Alfred Karpfen | | | | |
| | | TtB. | SD. | 30 |

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|---|---|---|---|---|
| Metal–tin derivatives of compartmental Schiff Bases: Synthesis, structure and application | Coord Chem Rev 395 (2019) 1–24 /doi.org/10.1016/j.ccr.2019.05.013 | | | |
| SusantaHazra, SasankasekharMohanta | | | | |
| **Review** | | TtB. | SD. | 31 |

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|---|---|---|---|---|
| General trends in structure, stability and role of interactions in the complexes of acetone and hioacetone with carbon dioxide and water | Chemical Physics 530 (2020) 110580 doi.org/10.1016/j.chemphys.2019.110580 | | | |
| Phan Dang Cam-Tu, Vu Thi Ngan, Nguyen Tien Trung | | | | |
| | | TtB. | SD. | 32 |

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|---|---|
| The Ability of a Tetrel Bond to Transition a Neutral Amino Acid into a Zwitterion | Chemical Physics Letters 731, 2019, 136584 doi.org/10.1016/j.cplett.2019.07.012 |
| Mingchang Hou, Qingzhong Li, Steve Scheiner | |

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|---|---|---|---|
| | TtB. | SD. | 33 |

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| Dependence of NMR chemical shifts upon CH bond lengths of a methyl group involved in a tetrel bond | Chemical Physics Letters 714 (2019) 61–64/doi.org/10.1016/j.cplett.2018.10.069 |
| Steve Scheiner | |

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| | TtB. | SD. | 34 |

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| Tetrel-Bonding Interaction: Rediscovered Supra-molecular Force? | Angew. Chem. Int. Ed. 2013,52, 12317 – 12321<br>DOI: 10.1002/anie.201306501 |
| Antonio Bauz, Tiddo J. Mooibroek, and Antonio Frontera | |

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|---|---|---|---|
| | TtB. | SD. | 35 |

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|---|---|
| On the σ, π and δ hole interactions: a molecular orbital overview | New J. Chem., 2018,42, 1413-1422<br>DOI: 10.1039/x0xx00000x |
| V. Angarov, S. Kozuch | |

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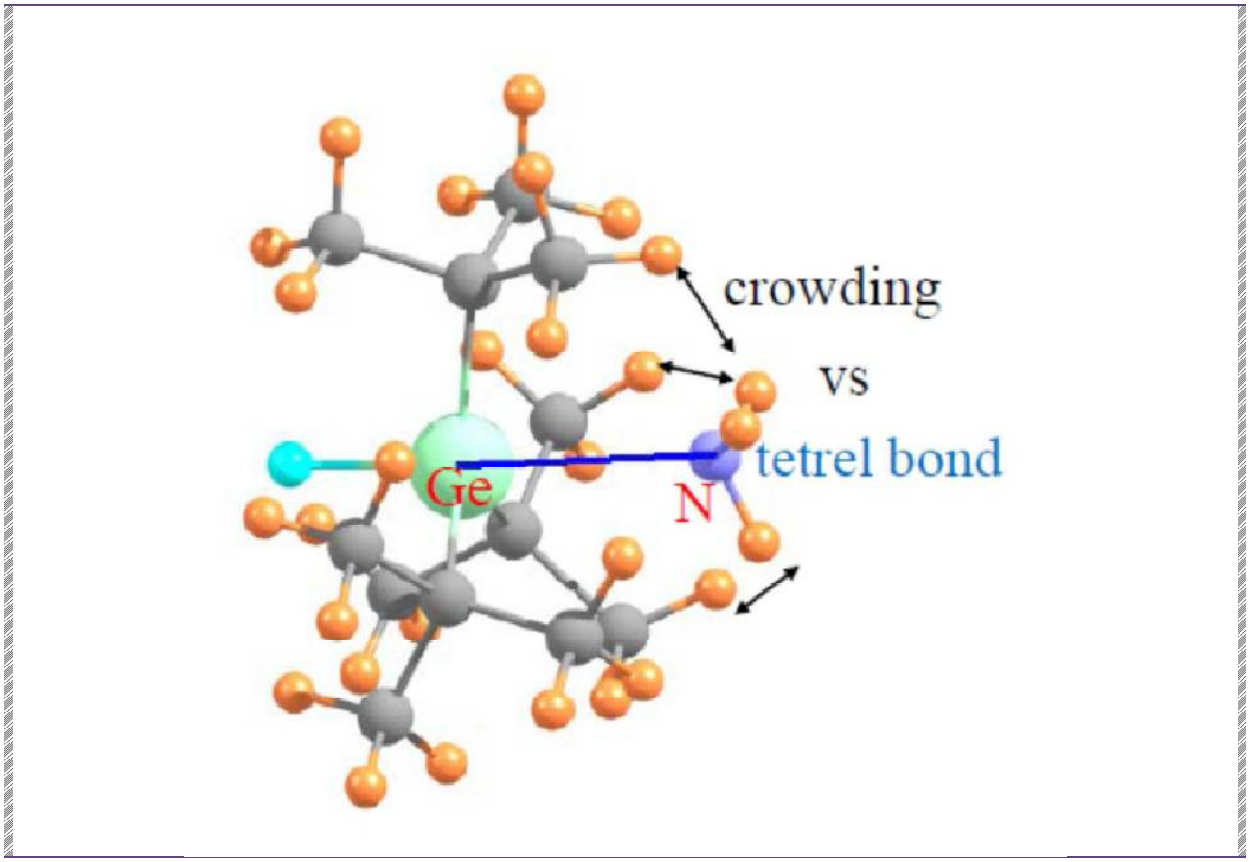
|---|---|---|---|
| | TtB. | SD. | 36 |

# IV. Supplementary Information
## Molecular structures Tetrel --bonded chemical species

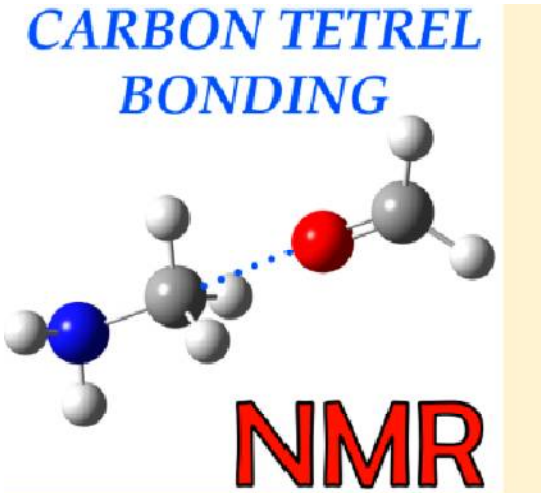
## LA and LB → (SR)-A...B-(RS )

## Tetrel Bond

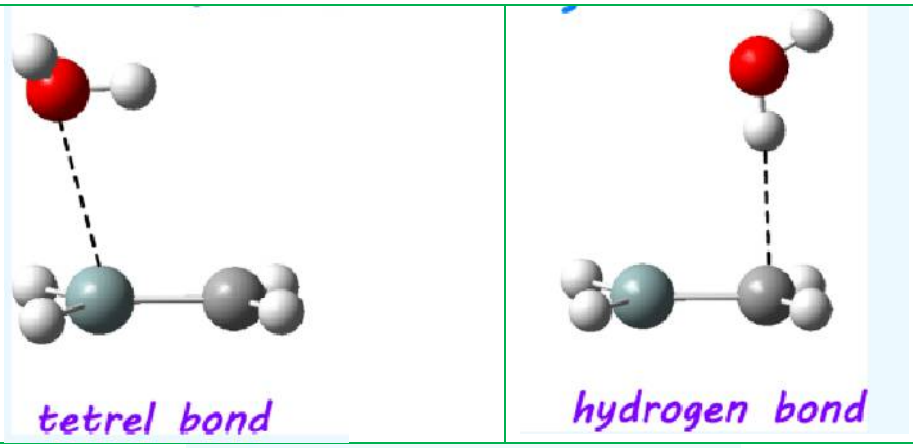
| | | | | |
|---|---|---|---|---|
| Tetrel Bond | | TtB. | ACS. | 10 |




## Tetrel Bond



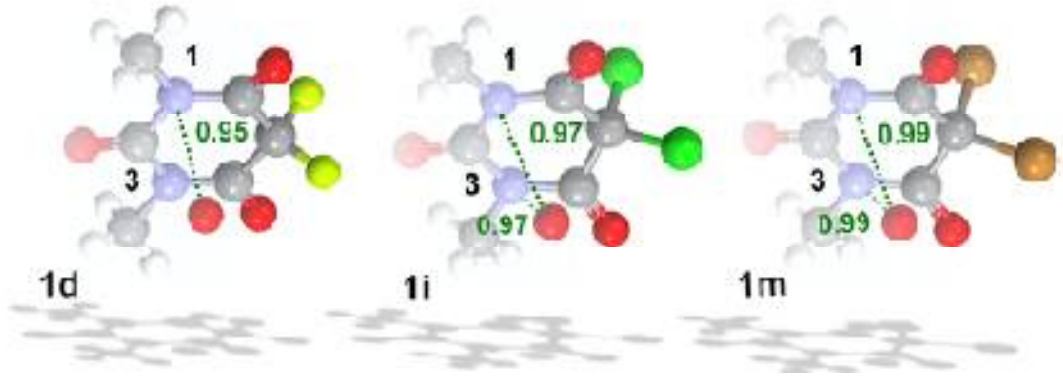

# Tetrel Bond ; HBond




Which is stronger?

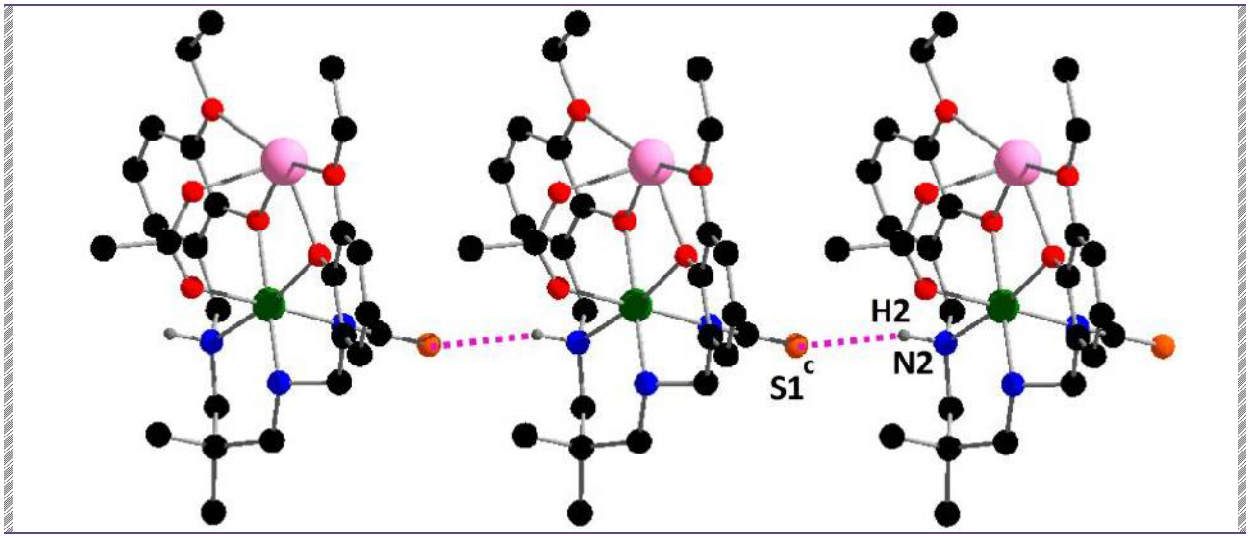
| PnicogenBond | TtB. | ACS. | 15 |
|---|---|---|---|

**5,5-difluoro-N,N-dimethyl barbituric acid (1d)**
**i5,5-dichloro (1i)**
**5,5-dibromo analogues,m (from left to right)**

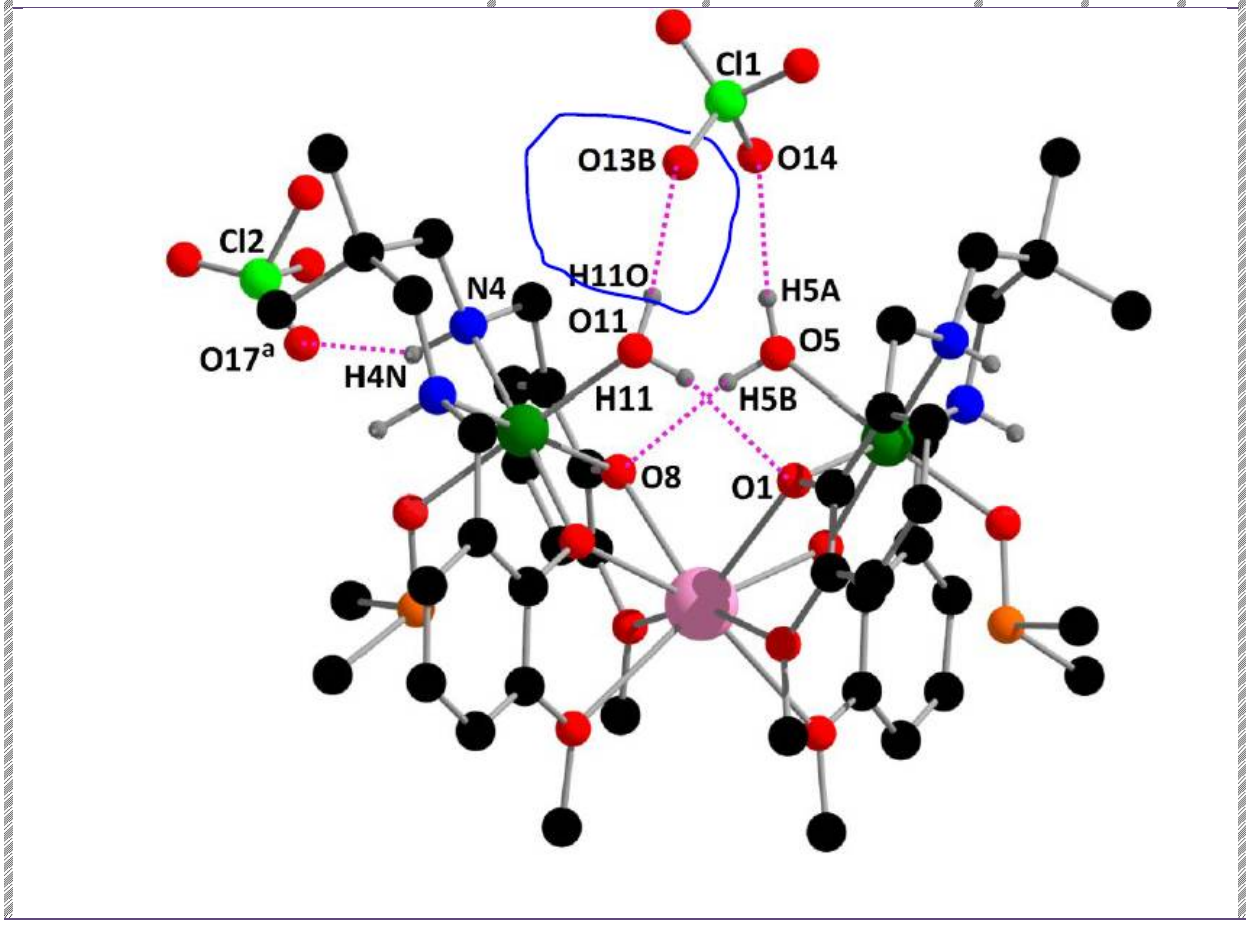



# HBond

| H-Bond | | | TtB. | ACS. | 11 |
|---|---|---|---|---|---|

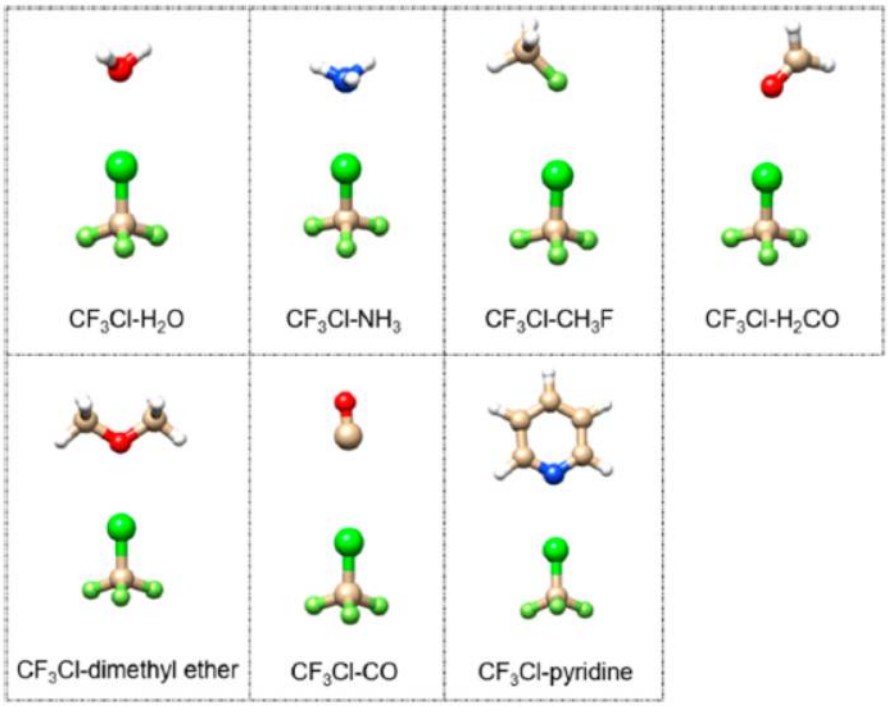



| H-Bond | | | TtB. | ACS. | 11 |
|---|---|---|---|---|---|




| Halogen Bond | | | TtB. | ACS. | 21 |
|---|---|---|---|---|---|

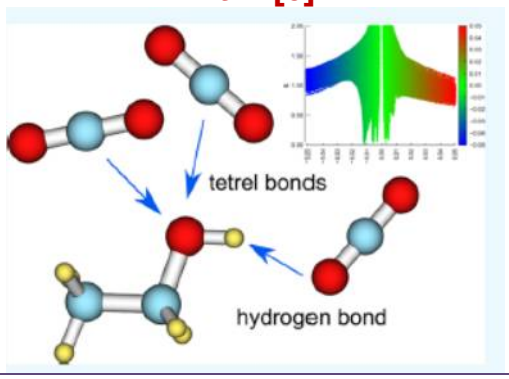
C–Cl···B (B = C, N, O or F) HaBs in complexes of CF3Cl




# Tetrel Bond ; HBond

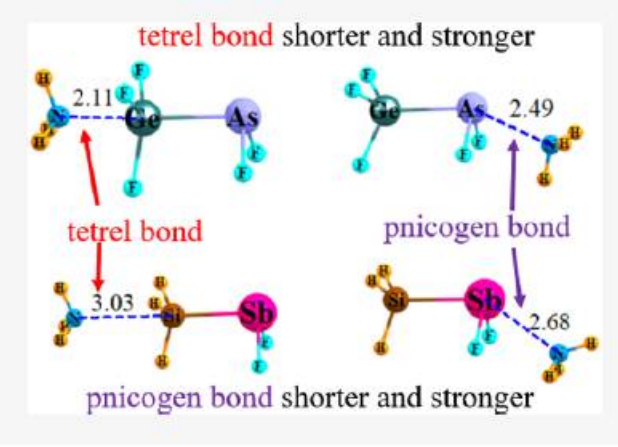
| Tetrel Bond | | TtB. | ACS. | 13 |
|---|---|---|---|---|

**TtA : [C]**



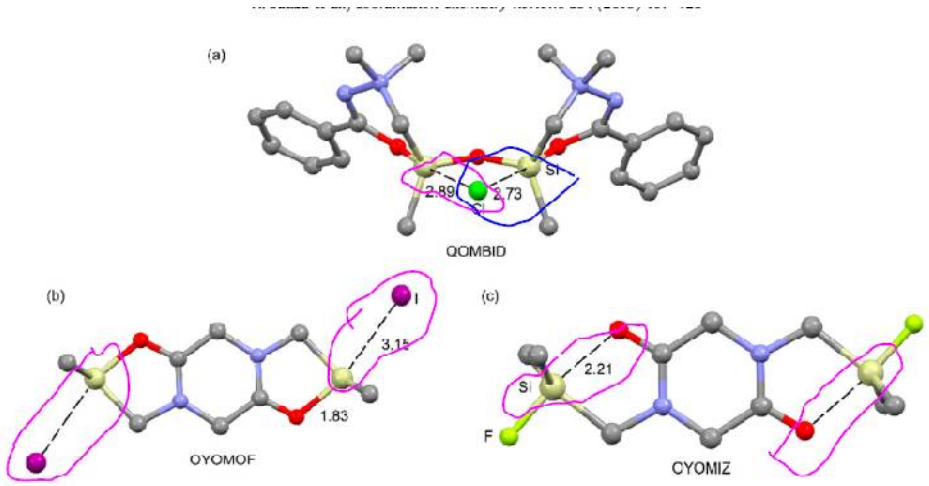

# Tetrel Bond ; Pnicogen bond

| Tetrel Bond | Pnicogen bond | TtB. | ACS. | 23 |
|---|---|---|---|---|




| Tetrel Bond + Chalcogen bond | TtB. | ACS. | 05 |
|---|---|---|---|

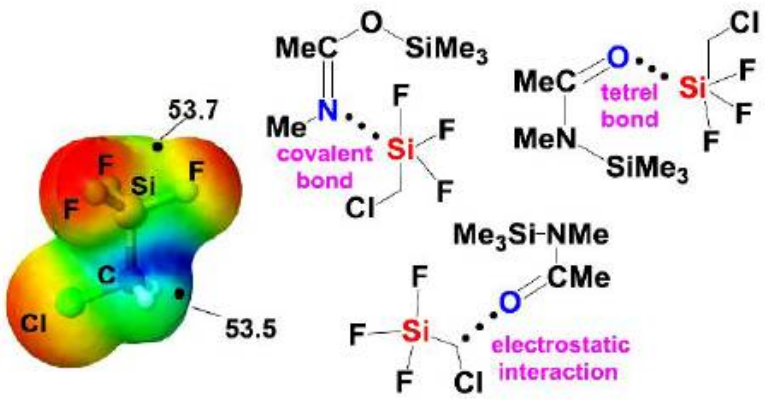
Dicyanoethene-1,2-dithiolate)-dimethyl-tin | Refcode AYADUZ




- Refcodes QOMBID (a), OYOMOF (b) and OYOMIZ (c).
- Tetrel bonds are represented as black dashed lines
- Red oxygen, pale yellow silicon, yellowish green fluorine.

| Tetrel Bond + Cov Bond + Electro-static Interaction | TtB. | ACS. | 04 |
|---|---|---|---|

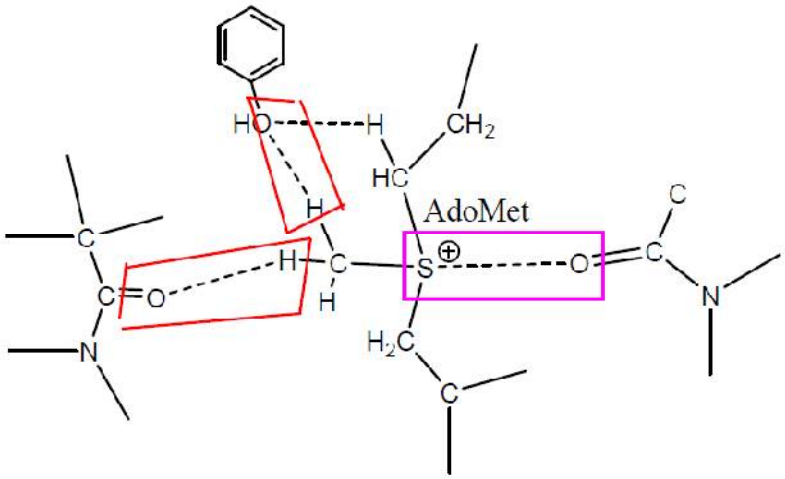
xx




## Chalcogen bond + H-bond

TtB. ACS. 14

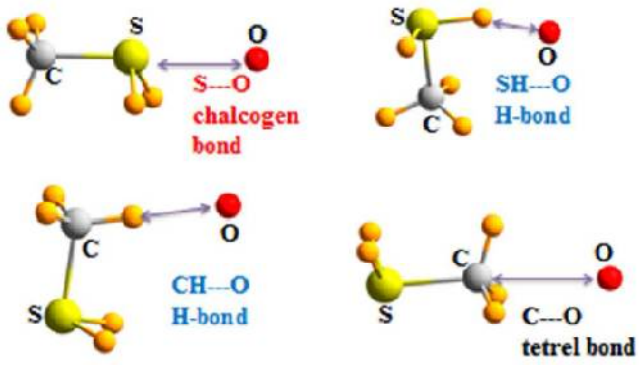
AdoMet




## Bond

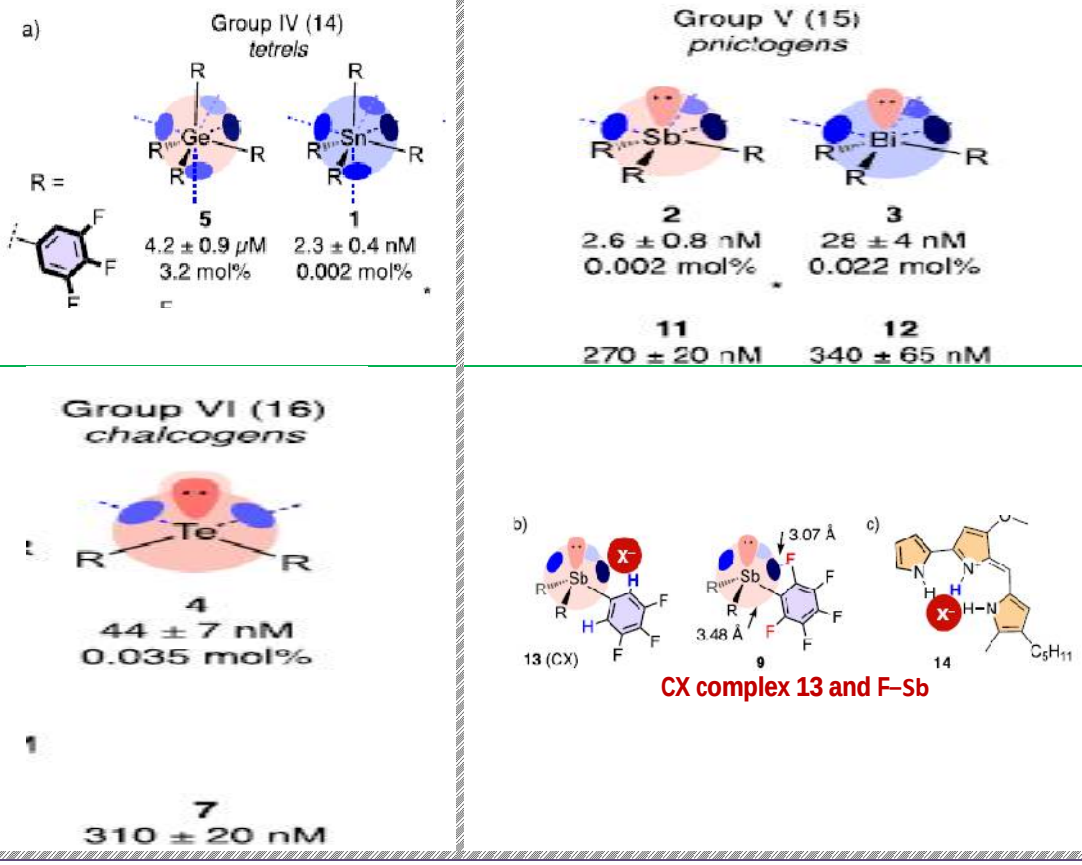
| Tetrel | Chalcogen | Hydrogen |
|---|---|---|

TtB. ACS. 14



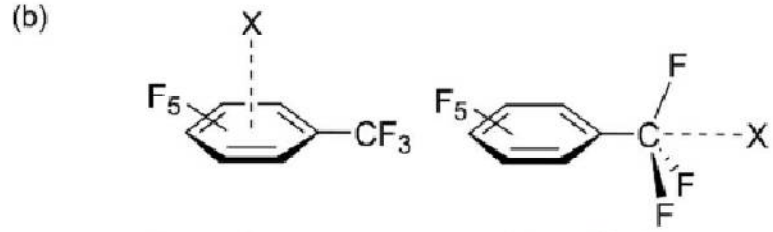

## Non_covalent Bond.

## Structure and anion transport activity of catalyst



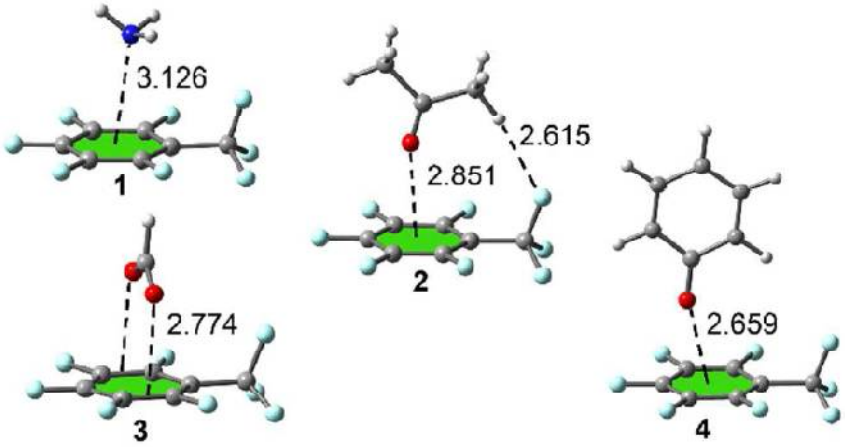


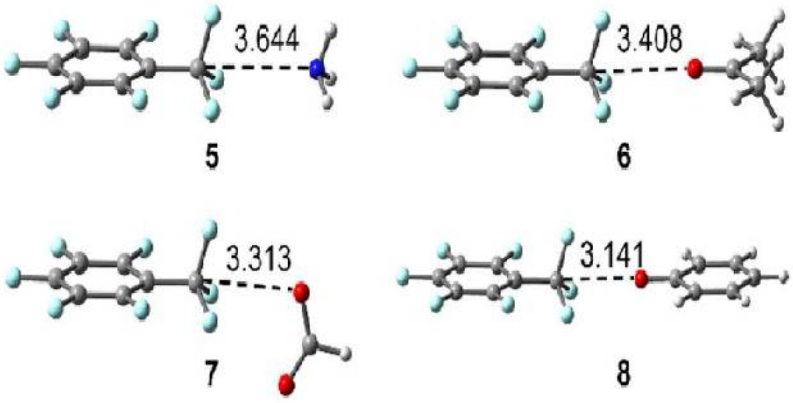

## π-hole(1–4) ; σ-hole (5–8)




1, X = $NH_3$
2, X = $CH_3COCH_3$
3, X = $HCOO^-$
4, X = $PhO^-$

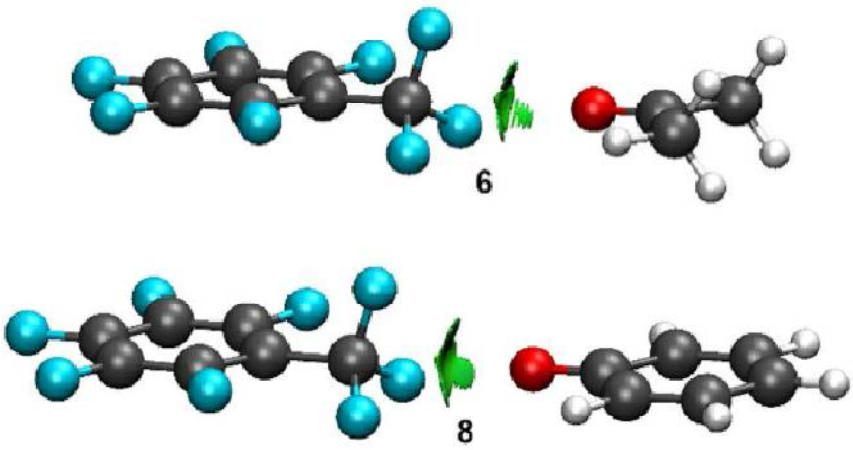
5, X = $NH_3$
6, X = $CH_3COCH_3$
7, X = $HCOO^-$
8, X = $PhO^-$



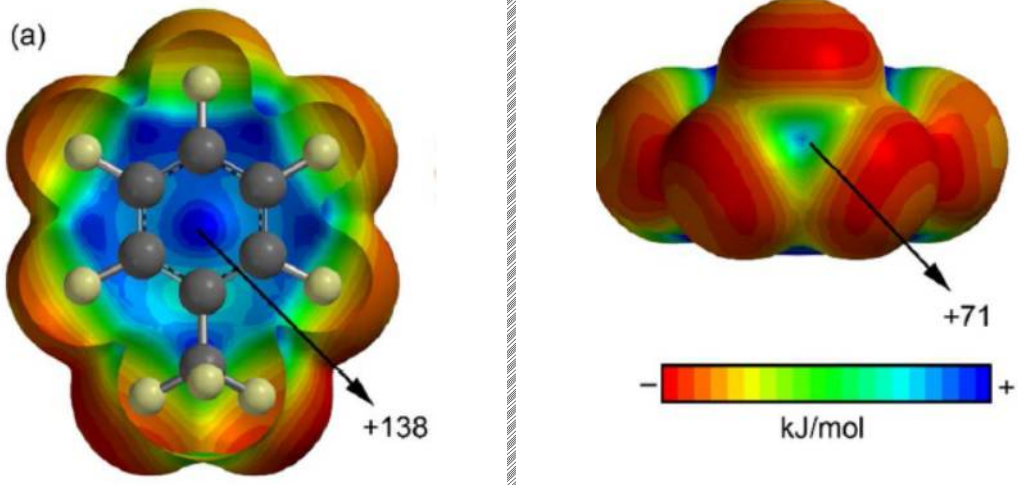




| NCI | | TtB. | ACS. | 01 |
|---|---|---|---|---|

## Complexes 6 and 8

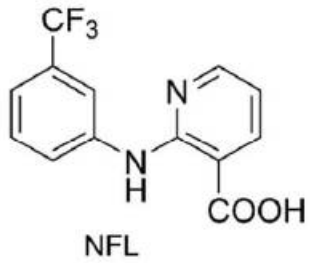



- Gradient isosurfaces are colored on a BGR scale
- based on sign (λ2)ρ over the range −0.015 to 0.015 a.u



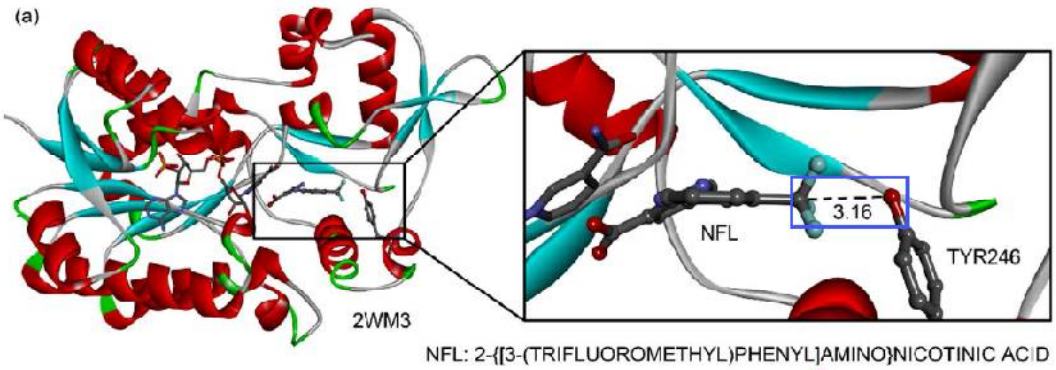



## Chemical drawing



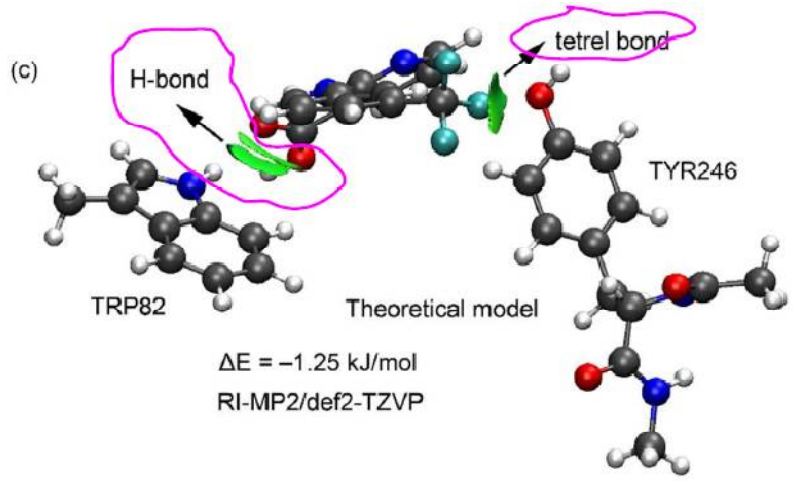

NFL

## X-ray structure of 2WM3




NFL: 2-{[3-(TRIFLUOROMETHYL)PHENYL]AMINO}NICOTINIC ACID

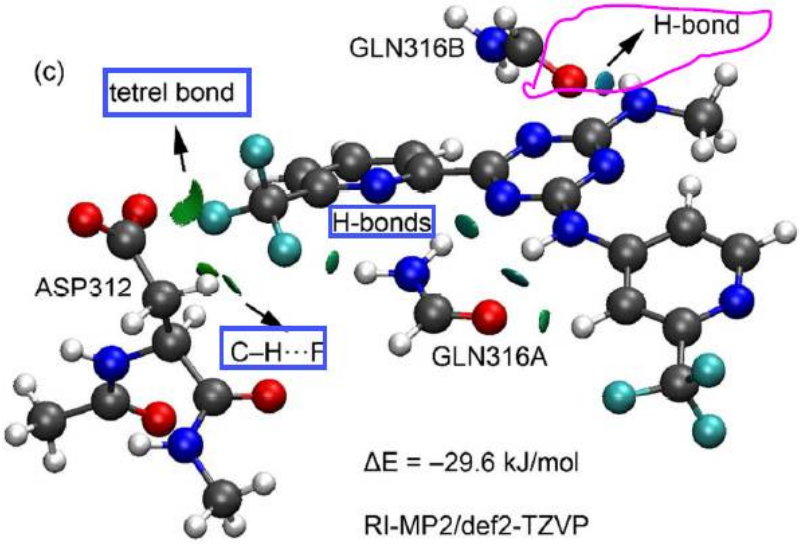
## NCIplot




| Tetrel Bond + H bond | | TtB. | ACS. | 01 |
|---|---|---|---|---|

## 2WM3 and 5I96 bonding

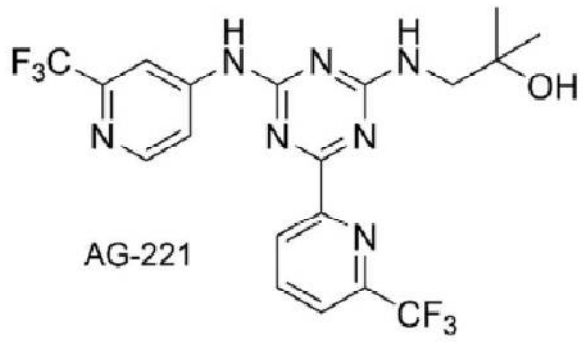
## Tetrel and Hydrogen




| Tetrel Bond + H bond | | TtB. | ACS. | 01 |
|---|---|---|---|---|

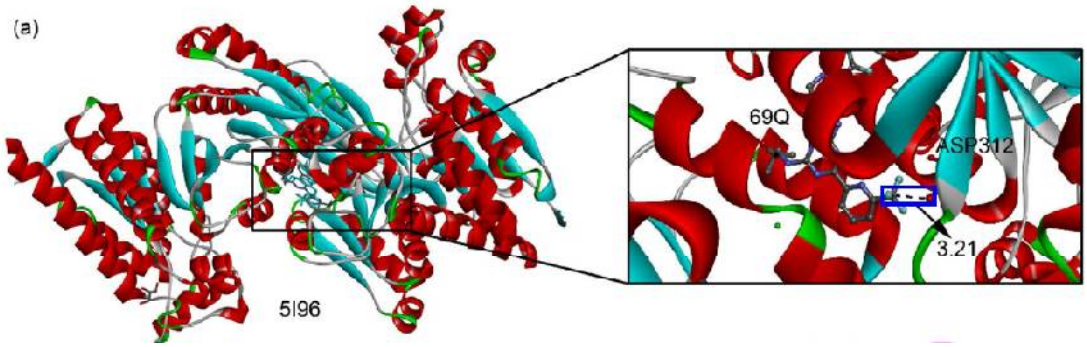
## AG 221

(b)

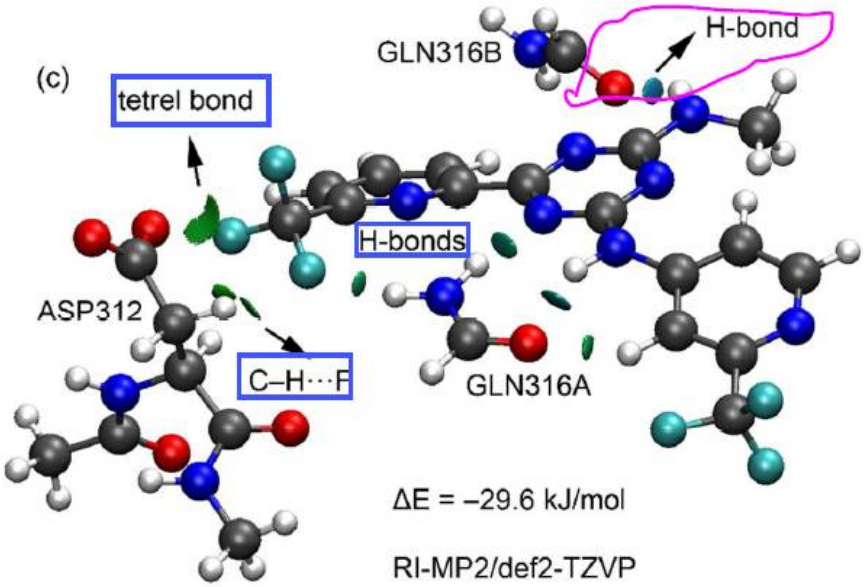



AG-221

**X-ray structure of 5196**

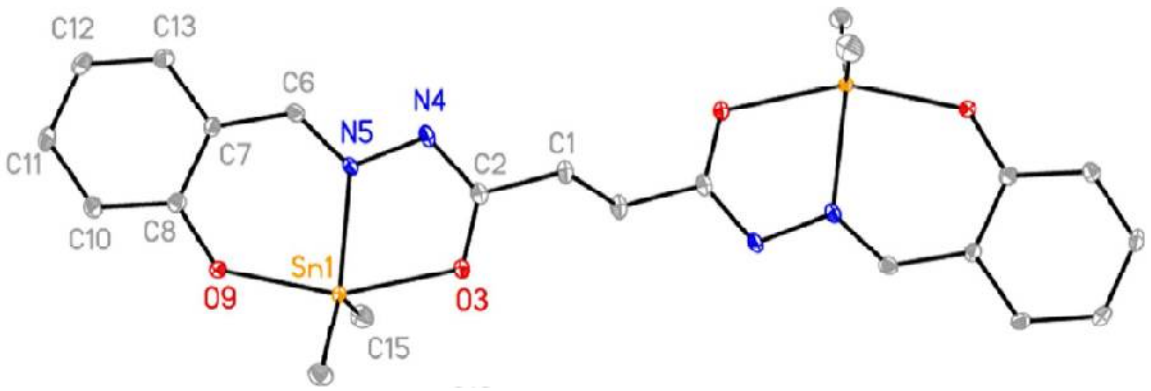



**NCIplot**




| Structure | | TtB. | ACS. | 03 |
|---|---|---|---|---|

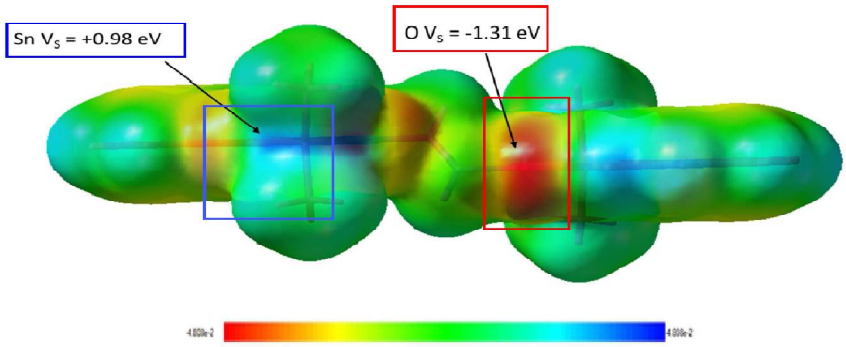
**Molecular structures of 1**




## ESP

TtB. | ACS. | 03

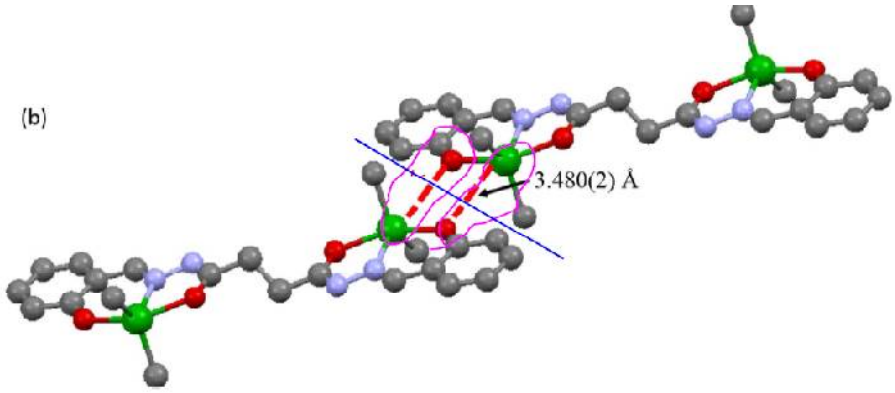
**ESP of 1'dimemapped onto 0.001 au electron density isosurface**




## Tetrel Bond

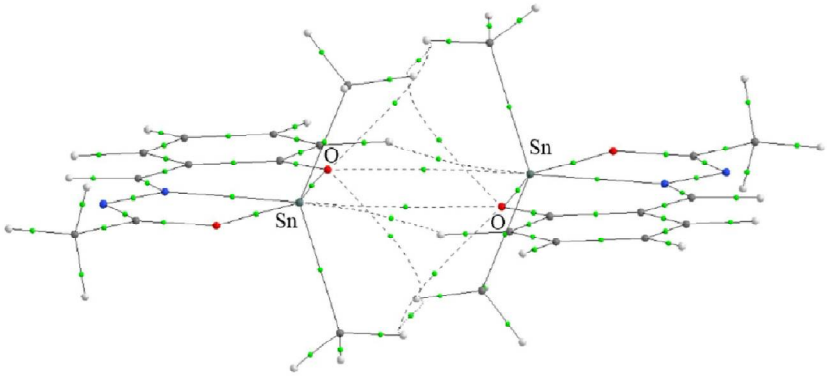
TtB. | ACS. | 03

**Dimerization of 1 via Sn...O tetrel interactions**




✓ Sn...O contacts shorter than the van der Waals radii

## Bond characteristics

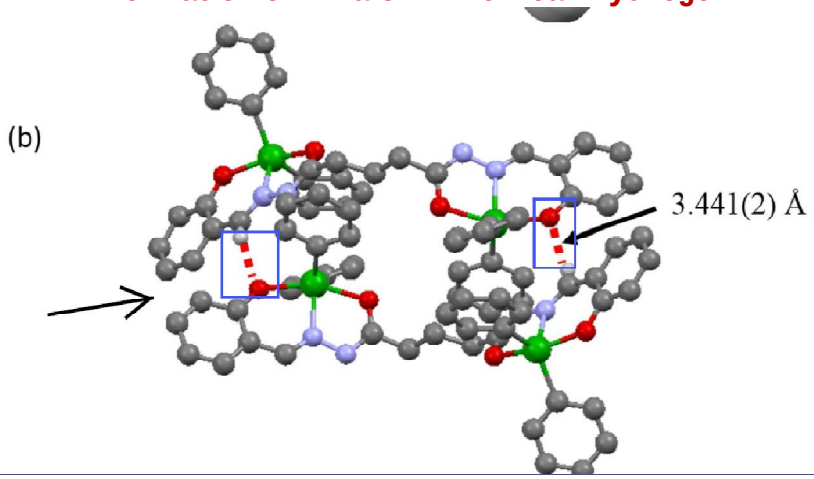



Aoms involved in tetrel bonding labeled

- Green dots→Bond critical points
- Solid lines→Intramolecular bond paths
- Dotted lines →Intermolecular bond paths

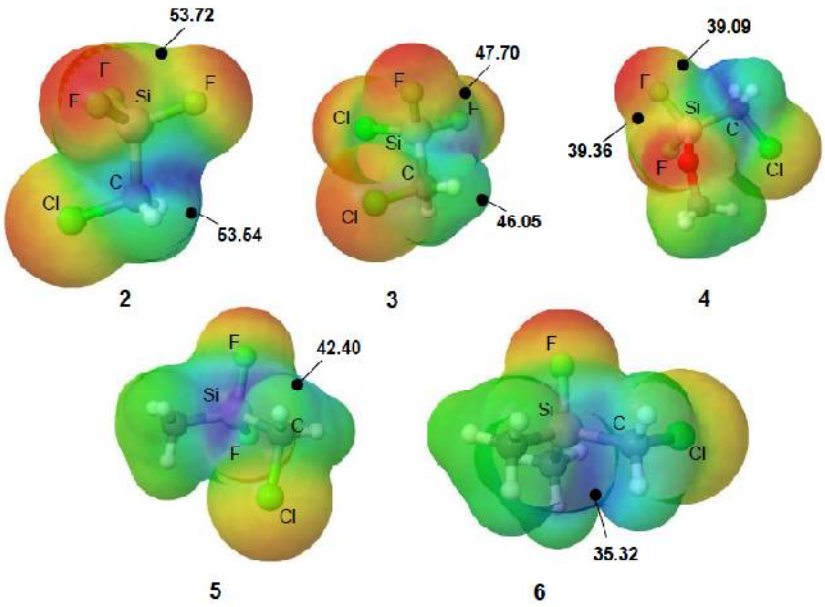
| Hydrogen Bond | | TtB. | ACS. | 03 |
|---|---|---|---|---|

## Dimerization of 4 via O...H—C weak hydrogen




| ESP | | TtB. | ACS. | 04 |
|---|---|---|---|---|

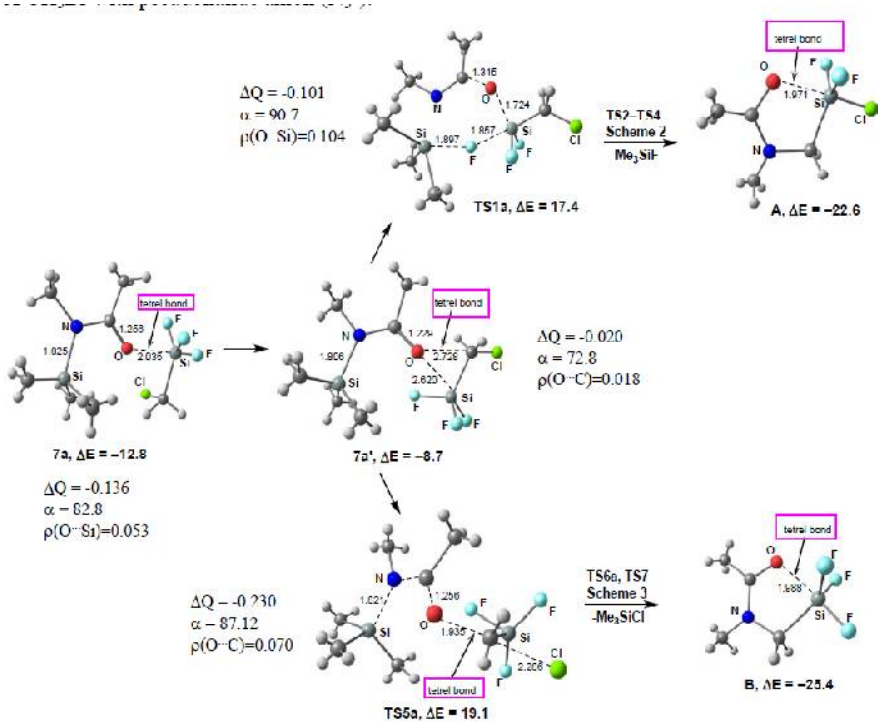
## Black dots indicate location of σ-holes




- ✓ **Silanes 2–4, two σ-holes**
- ✓ **Silanes 5 and 6 have one σ-hole at the CH2–SIF bond**

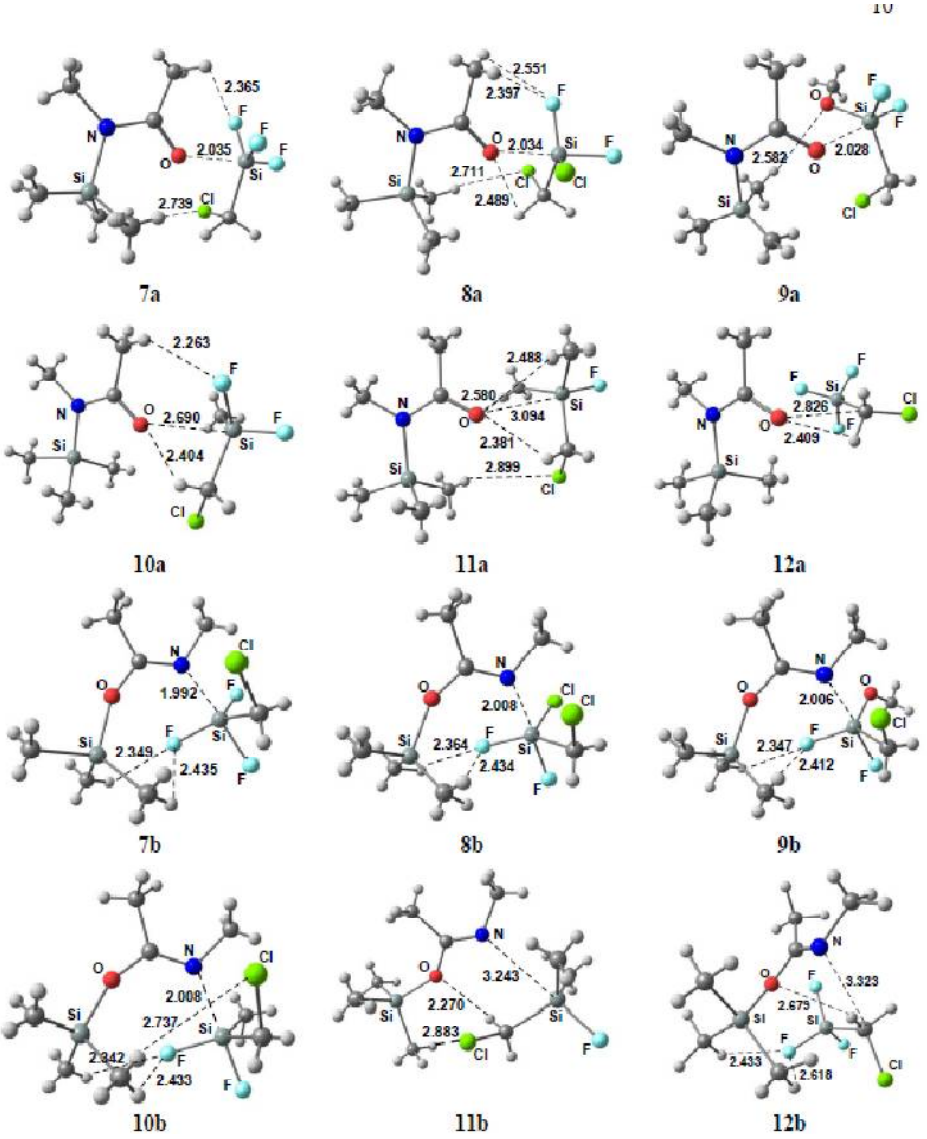


**Reaction scheme for interaction of amide 1a with silane 2**



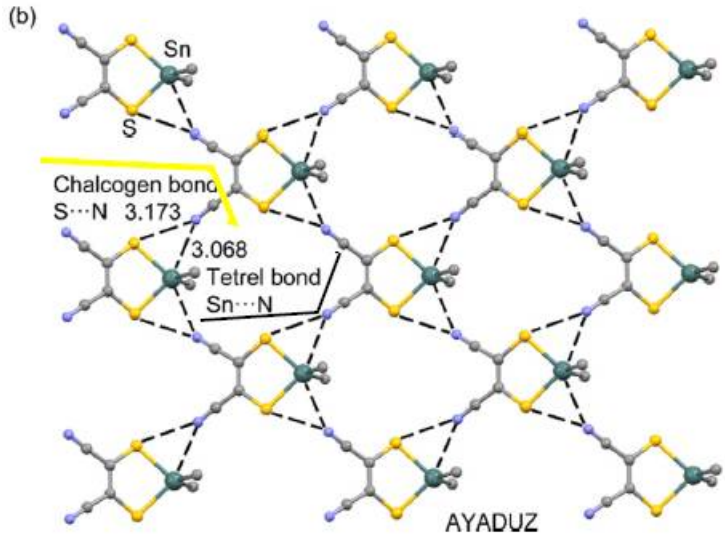

**Geom. Opt. structures of 7a–12a and 7b–12b complexes**

**(M062X/6-311G**)**




| *Tetrel Bond + Chalcogen bond* | TtB. | ACS. | 05 |
|---|---|---|---|
| dicyanoethene-1,2-dithiolate)-dimethyl-tin | refcode AYADUZ | | |

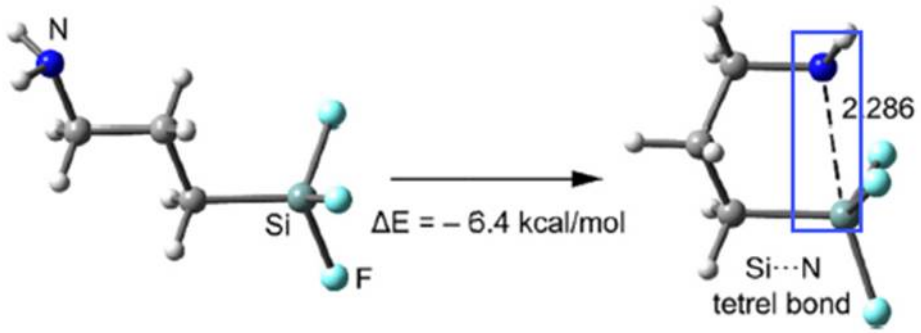
**Hydrogens have been omitted for clarity**
**Tetrel Sn...N and chalcogenideS...N bonding**



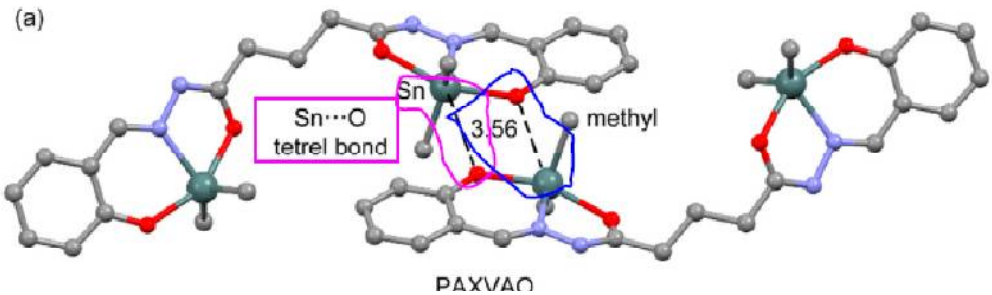

## Tetrel Bond

TtB. | ACS. | 05

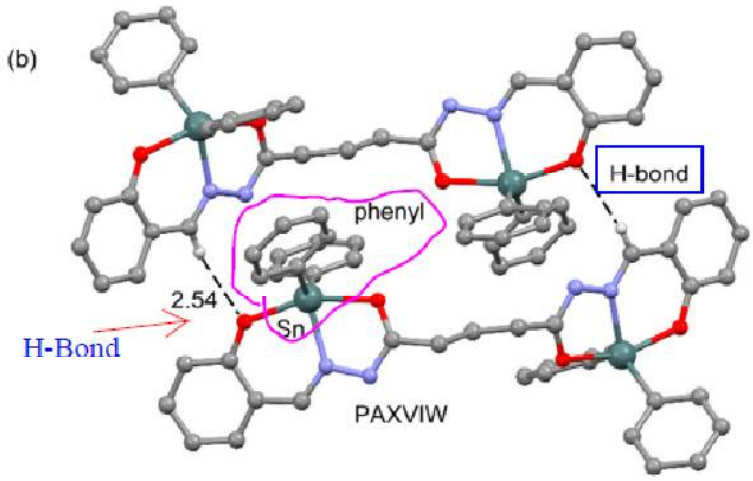
**Si...N**




**Sn...O**

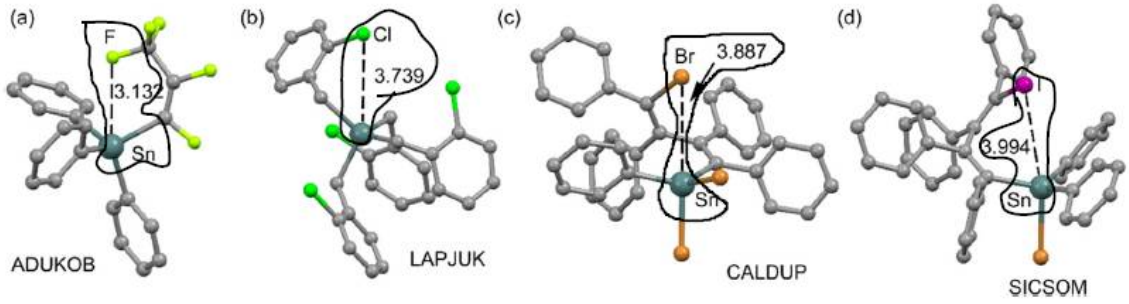



**Sn...Ph**

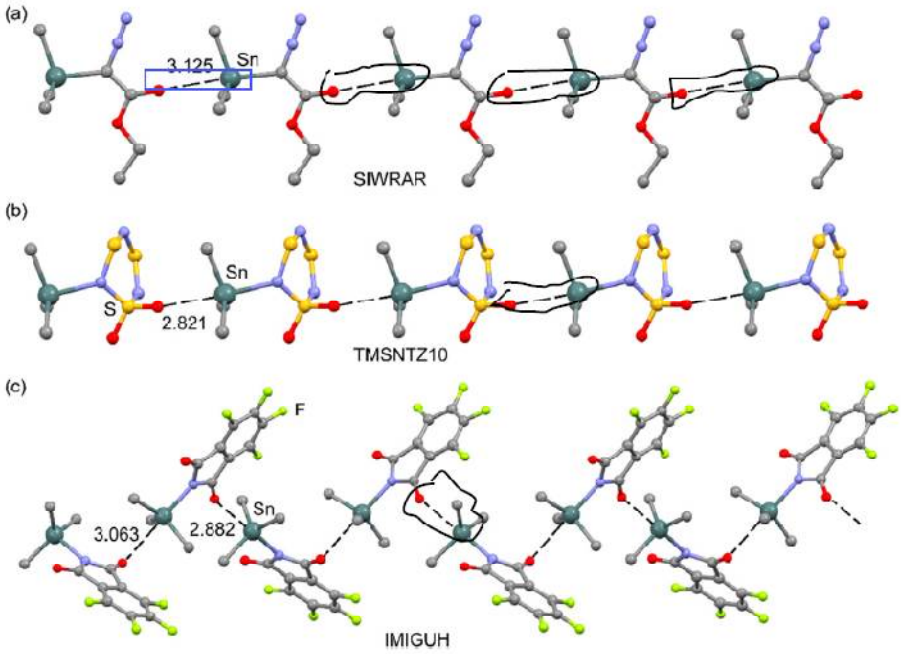



- ✓ Tetrel bonds are represented as black dashed lines;
- ✓ Refcodes PAXVAO (a) and PAXVIW (b).

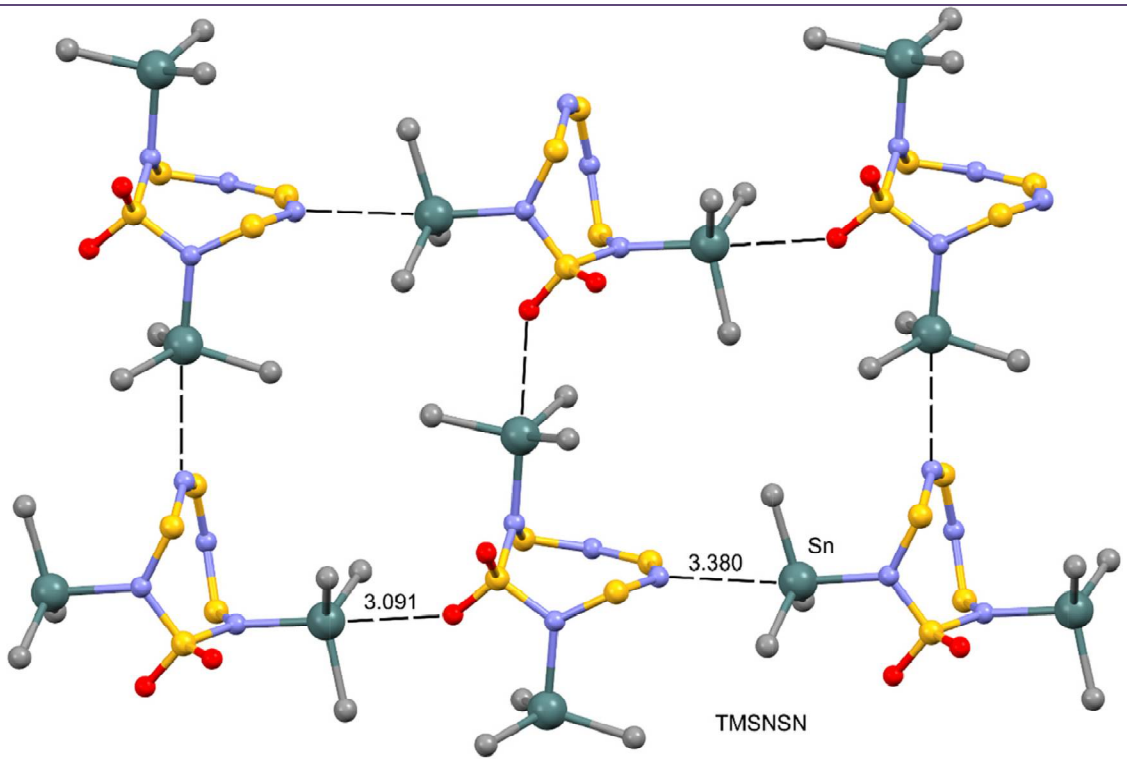
**Sn...X**



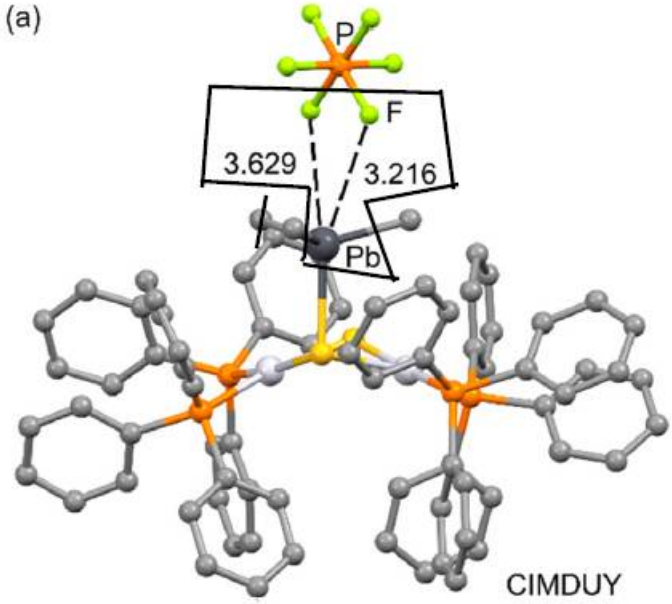

- ✓ Refcodes ADUKOB (a), LAPJUK (b), CALDUP (c) and SICSOM (d).
- ✓ Yellowish-green fluorine, green chlorine, brown bromine, purple iodine, teal tin.

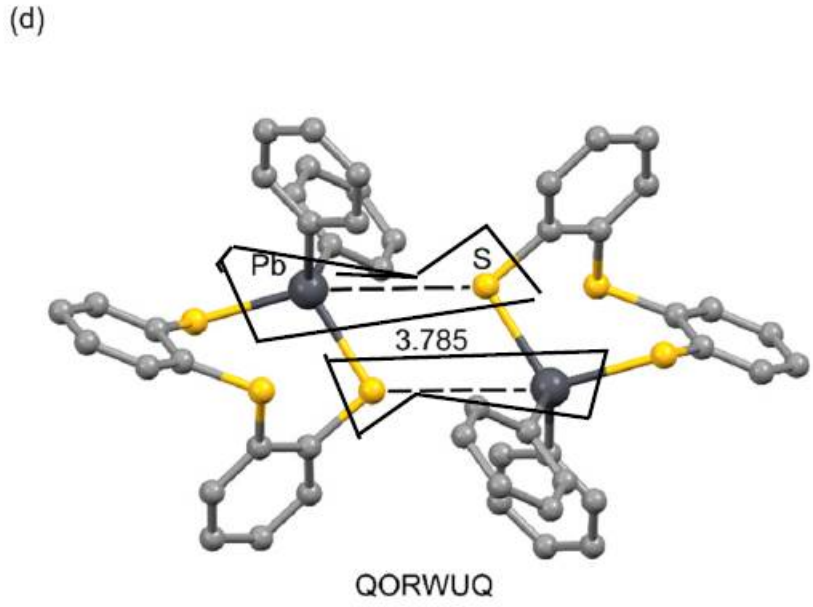



- ✓ Refcodes SIWRAR (a), TMSNTZ10 (b) and IMIGUH (c).
- ✓ Yellow sulfur

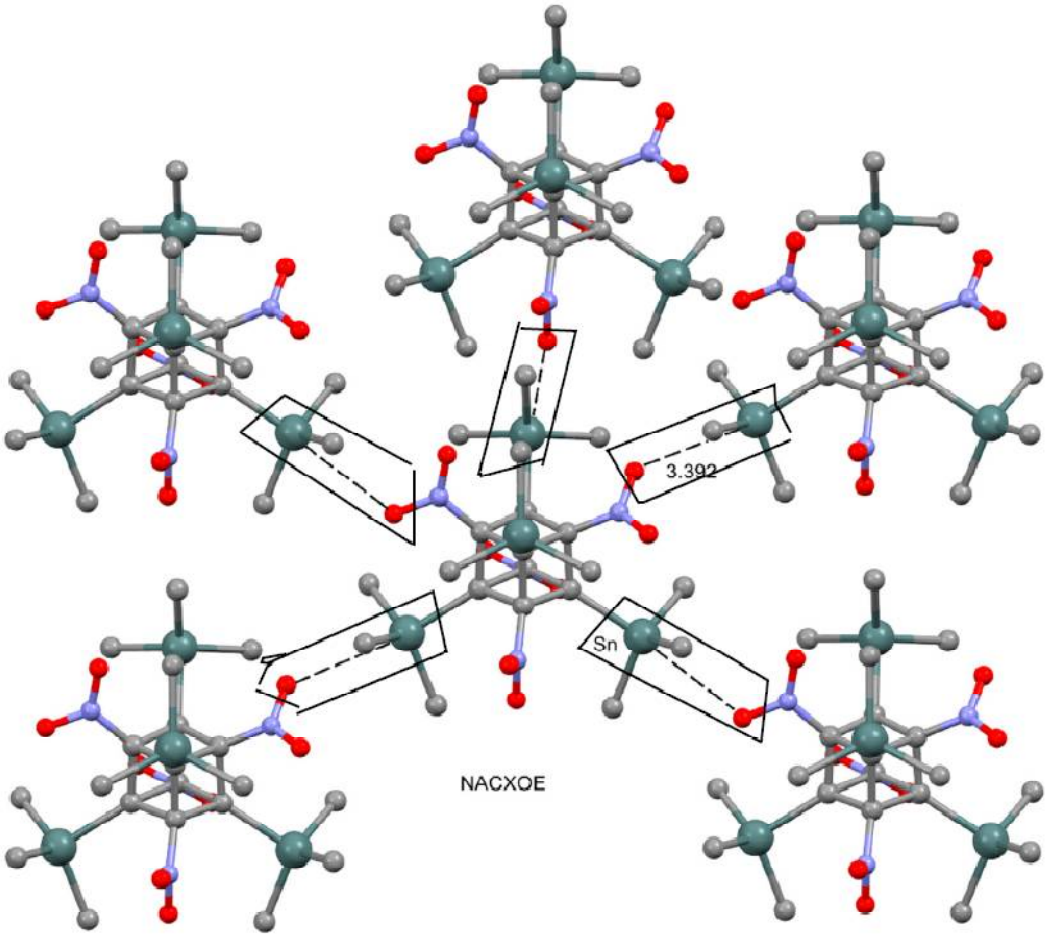



- ✓ Refcodes TMSNSN.
- ✓ Yellow sulfur



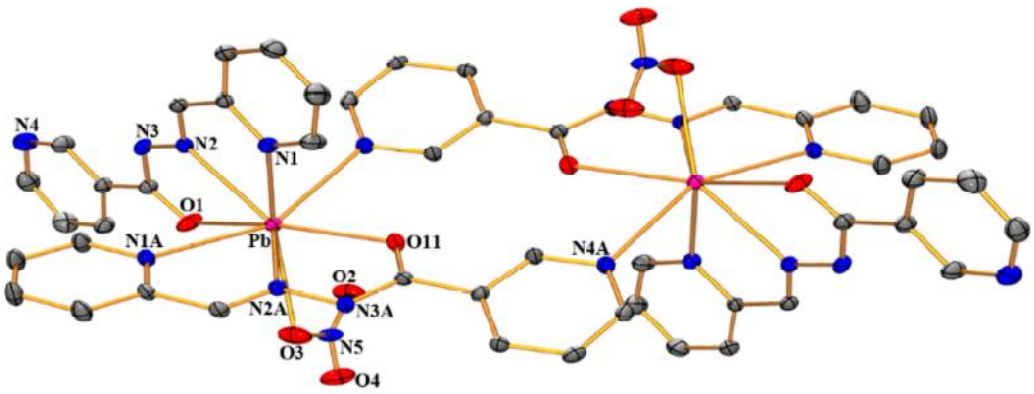




**3D assembly in refcode NACXOE**





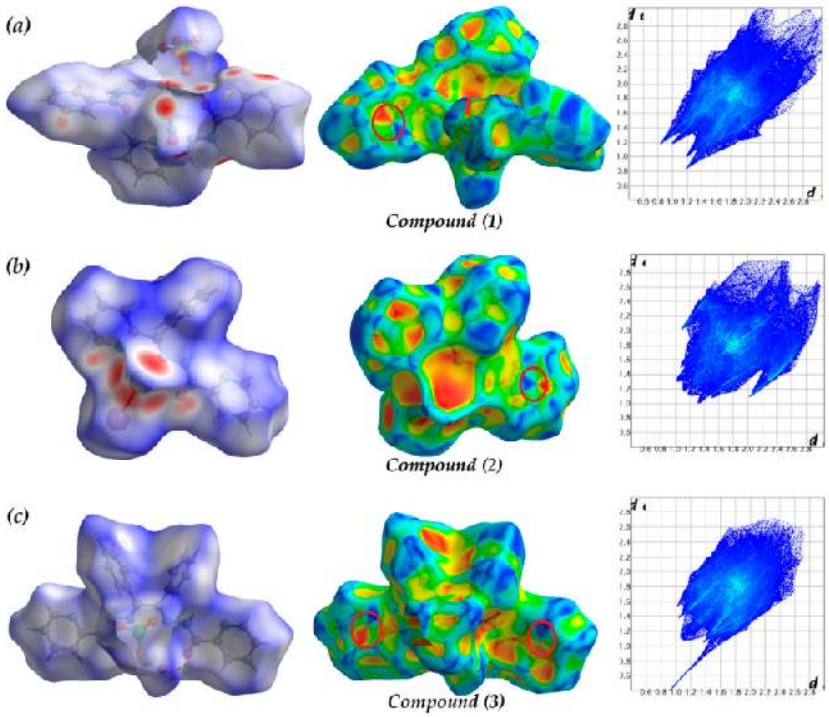

## Pb–N(4A) and Pb–O3Tetrel Bond s




- Pb–N(4A) and Pb–O3 distances are significantly longer than Sum ($R_{cov}$,)
- Two strong Pb...N4 tetrel bonds

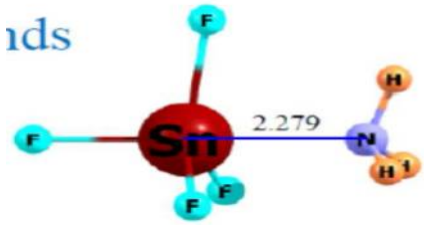
dnorm(left column), shape-index (middle column)

full fingerprint plot (right column)

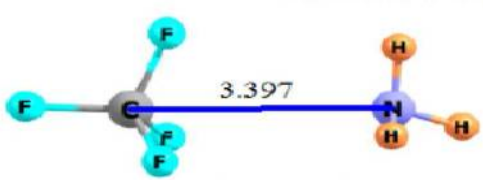



| Tetrel Bond | | TtB. | ACS. | 07 |
|---|---|---|---|---|

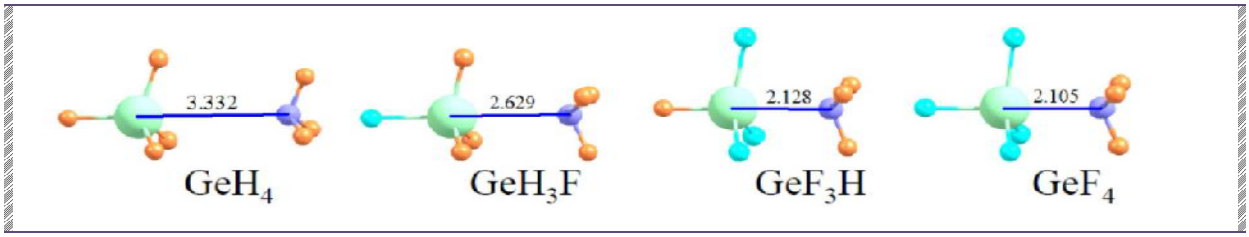
Sn...N




C...N

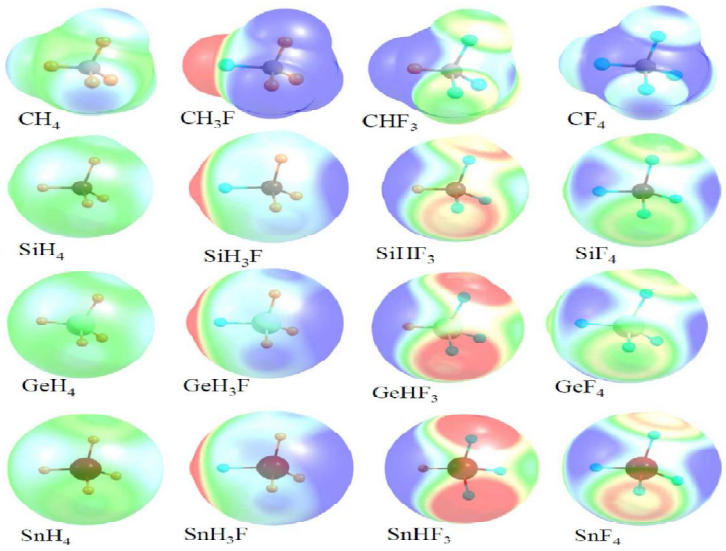



Ge...N

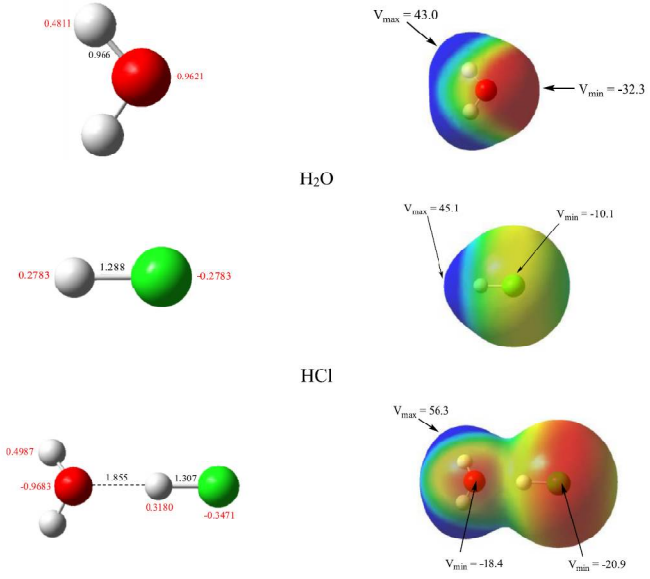



| ESP | TtA: [C; Si; Ge; Sn] | TtB. | ACS. | 07 |
|---|---|---|---|---|

$Tt H_{4-i} F_i$ ; $CH_{4-i} F_i$

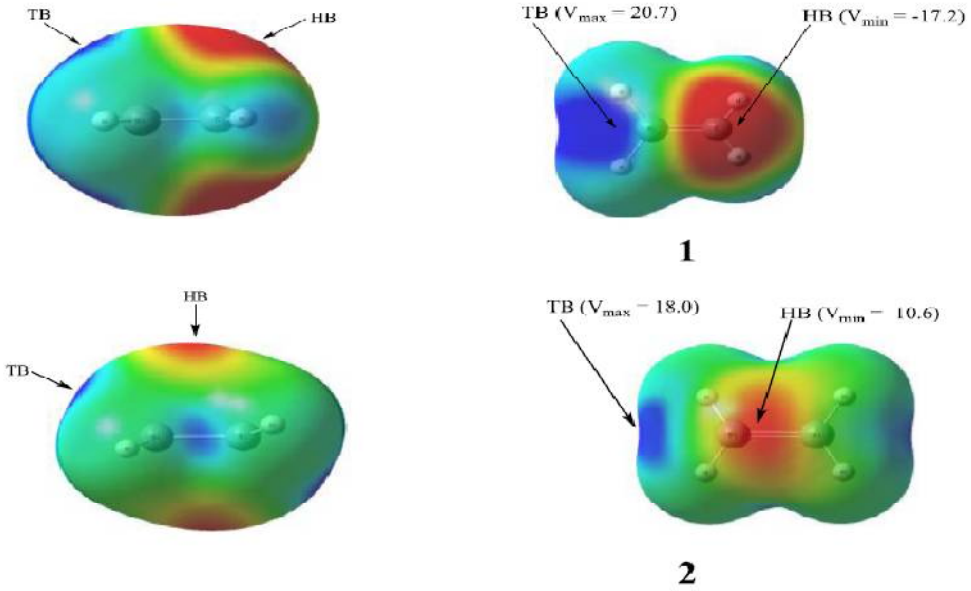


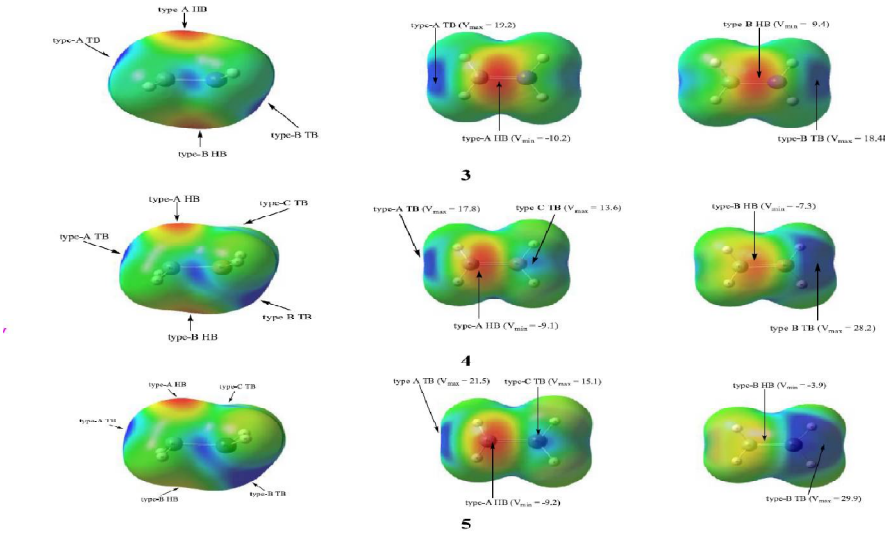

| ESP | | TtB. | ACS. | 08 |
|---|---|---|---|---|




**O...H of H2O AND HCl H-Bond**

Side view (left), top view (middle), and bottom view (right)



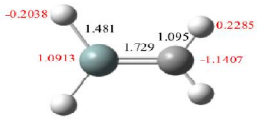




| Complex Bonding mode | Complex Bonding mode | Complex Bonding mode |
|---|---|---|
| | | |

| | | | | | |
|---|---|---|---|---|---|
| 7 (1 + $H_2O$) | TB | 21 (3 + HCl) | type-A HB | 31 (4 + HCl) | type-B HB |
| 8 (1 + $H_2O$) | HB | 22 (3 + HCl) | type-B HB | 32 (4 + HCl) | DB |
| 9 (1 + HCl) | TB | 23 (4 + $H_2O$) | type-A TB | 33 (5 + $H_2O$) | type-A TB |
| 10 (1 + HCl) | HB | 24 (4 + $H_2O$) | type-B TB | 34 (5 + $H_2O$) | type-B TB |
| 11 (2 + $H_2O$) | TB | 25 (4 + $H_2O$) | type-C TB | 35 (5 + $H_2O$) | type-C TB |
| 12 (2 + $H_2O$) | HB | 26 (4 + $H_2O$) | type-B HB | 36 (5 + HCl) | type-A TB |
| 13 (2 + HCl) | TB | 27 (4 + HCl) | type-A TB | 37 (5 + HCl) | type-A TB |
| 14 (2 + HCl) | HB | 28 (4 + HCl) | type-B TB | 38 (5 + HCl) | type-B TB |
| 15 (3 + $H_2O$) | type-A TB | 29 (4 + HCl) | type-C TB | 39 (5 + HCl) | type-C TB |
| 16 (3 + $H_2O$) | type-B TB | 30 (4 + HCl) | type-A HB | 40 (5 + HCl) | type-A HB |
| 17 (3 + $H_2O$) | type-A HB | | | 41 (5 + HCl) | type-B HB |
| 18 (3 + $H_2O$) | type-B HB | | | 42 (5 + HCl) | DB |
| 19 (3 + HCl) | type-A TB | | | | |
| 20 (3 + HCl) | type-B TB | | | | |



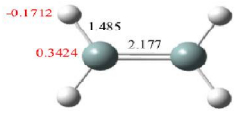
**Distances in Å, Natural charges**




$WBI_{Si-C}$ = 1.7600

D(H-Si-C-H) = 0.02°

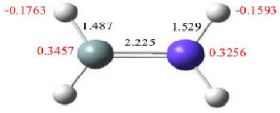
**1**




$WBI_{Si-Si}$ = 1.9145

D(H-Si-Si-H) = 30.58°

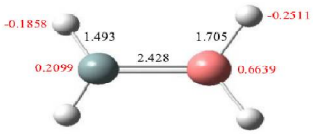
**2**




$WBI_{Si-Ge}$ = 1.8567

D(H-Si-Ge-H) = 38.19°

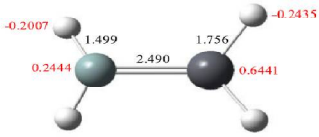
**3**




$WBI_{Si-Sn}$ = 1.6989

D(H-Si-Sn-H) = 48.45°

**4**




$WBI_{Si-Pb}$ = 1.4786

D(H-Si-Pb-H) = 56.25°

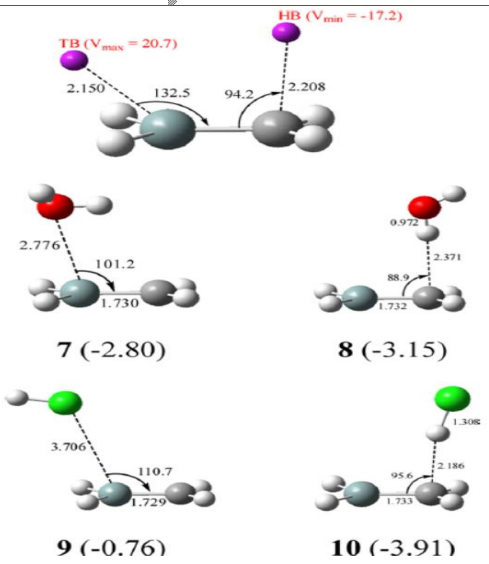
**5**

## Tetrel Bond ; H-Bond

TtB. ACS. 08

LA: H2Si⊕CiH2

LB: [H2O or HCl]

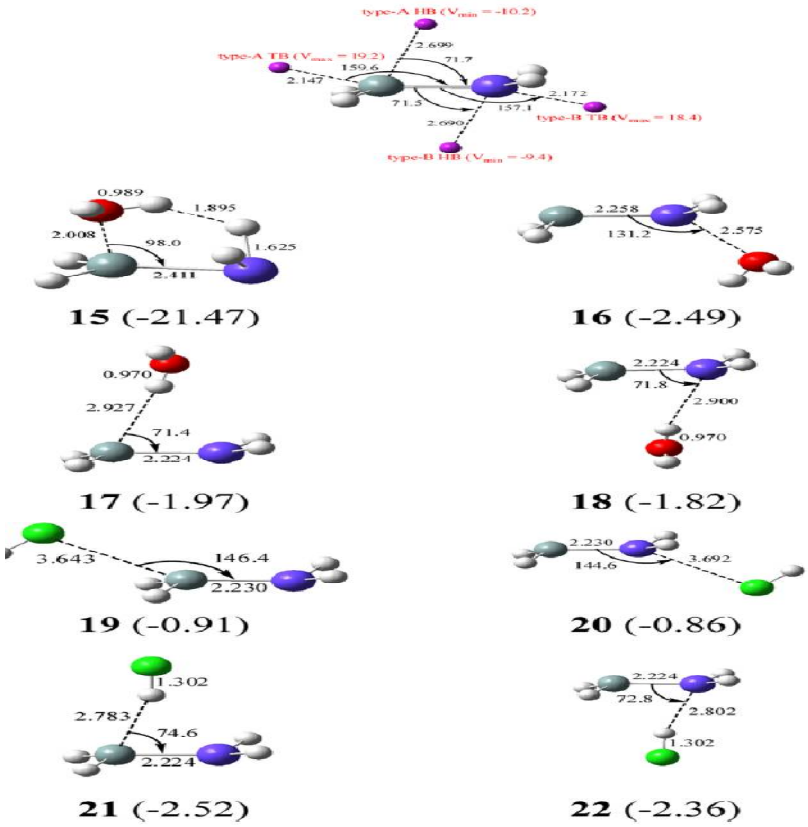


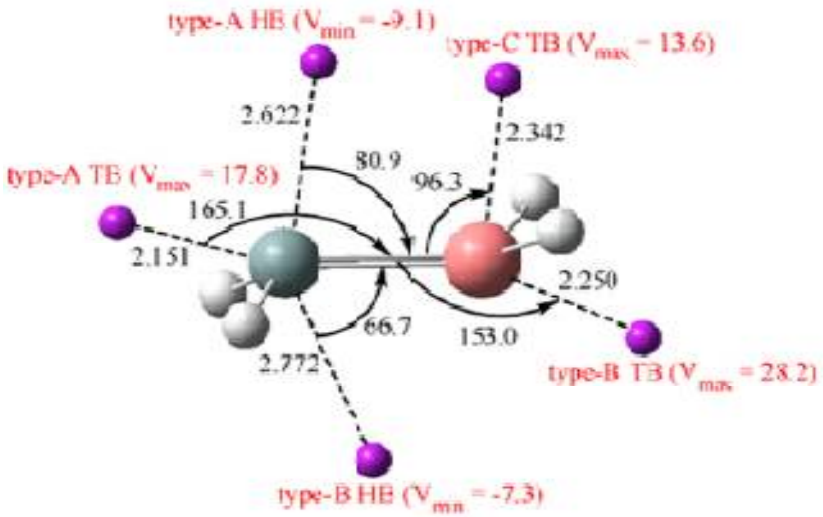

## Tetrel Bond ; H-Bond

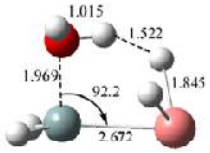
TtB. ACS. 08

LA: H2Si=GeH2

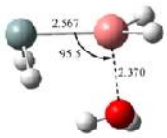
LB: [H2O or HCl]



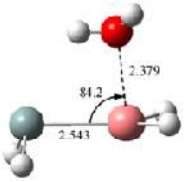


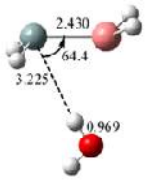

**23** (-26.89)



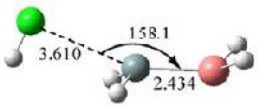

**24** (-12.89)



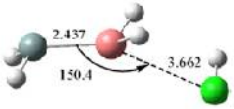

**25** (-12.33)



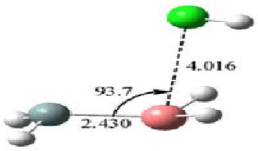

**26** (-1.70)



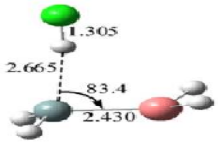

**27** (-1.01)



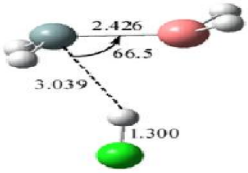

**28** (-1.40)



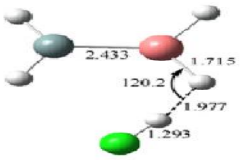

**29** (-0.58)




**30** (-2.89)



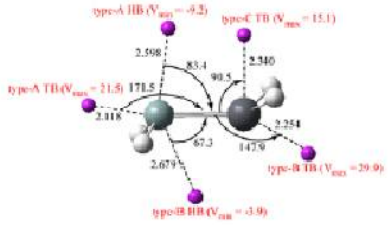

**31** (-2.29)

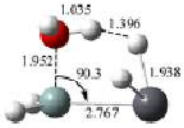



**32** (-1.41)

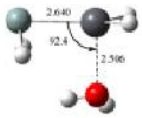
## *Tetrel Bond*

| | TtB. | ACS. | 0 |
|---|---|---|---|
| **LA: H2Si=PbH2** | **LB: [H2O or HCl]** | | |

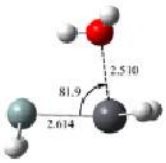




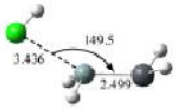

**33** (-31.52)



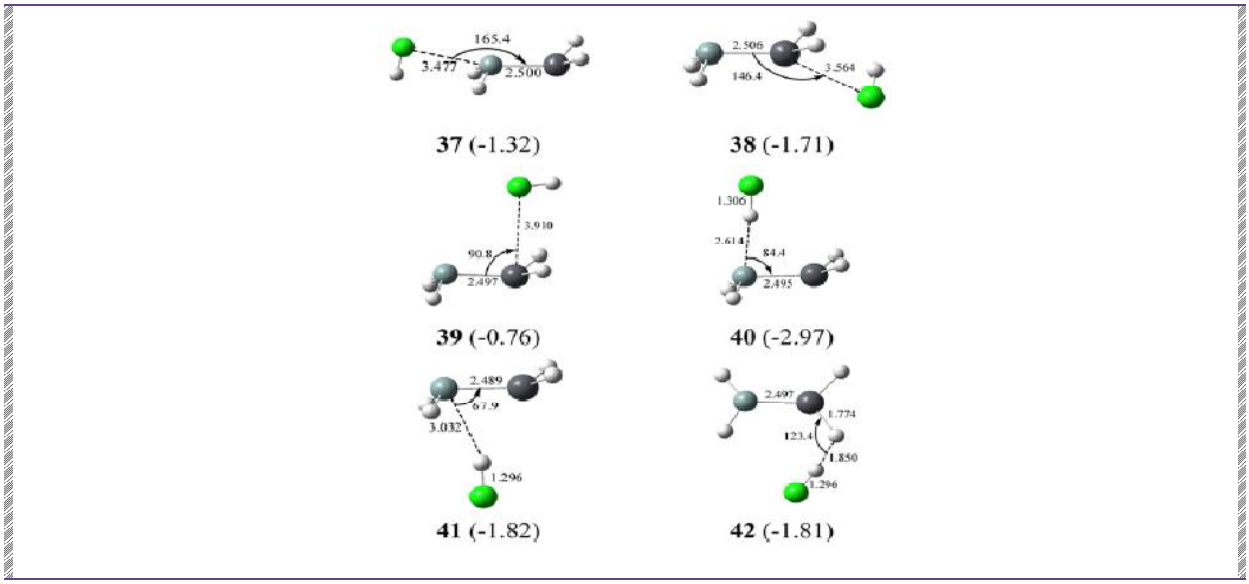

**34** (-10.76)




**35** (-10.74)

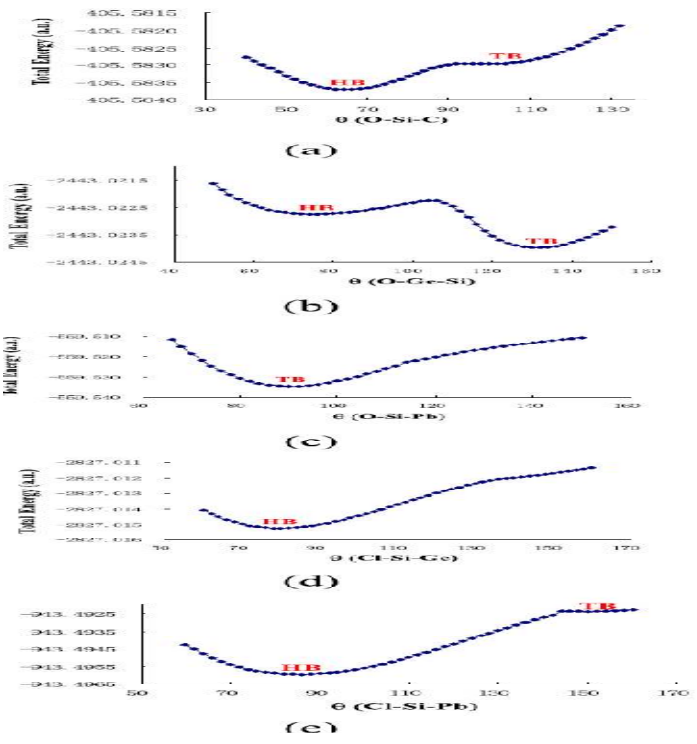



**36** (-1.51)






## Relaxed potential energy surface scans




(a) H2Si=CH2···H2O;

(b) H2Si=GeH2···H2O;

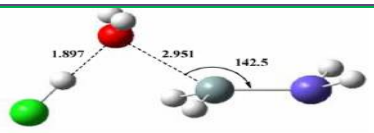
(c) H2Si=PbH2···H2O;

(d) H2Si=GeH2···HCl;

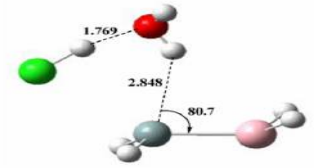
(e) H2Si=PbH2···HCl



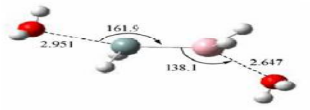
## Optimized geometries of ternary complexes



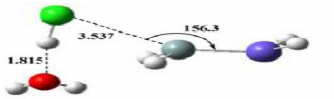

43



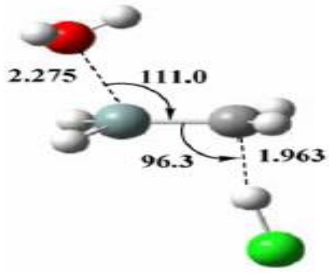

45




44



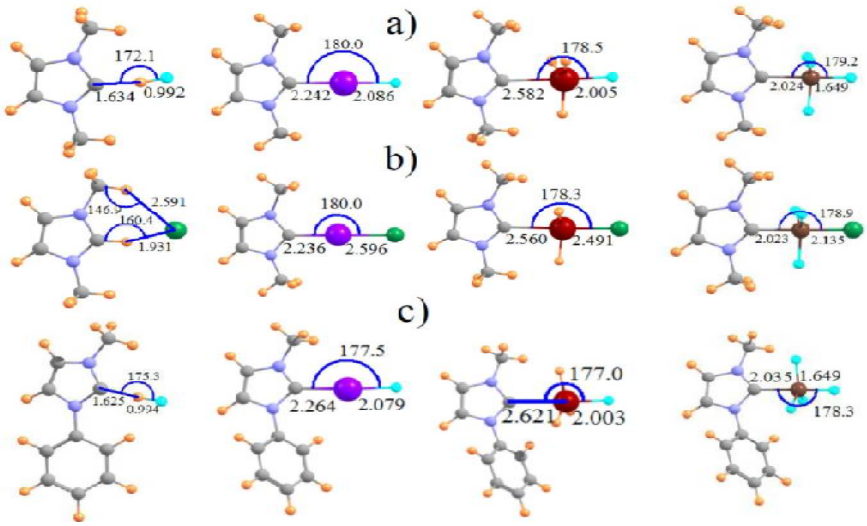

46




47

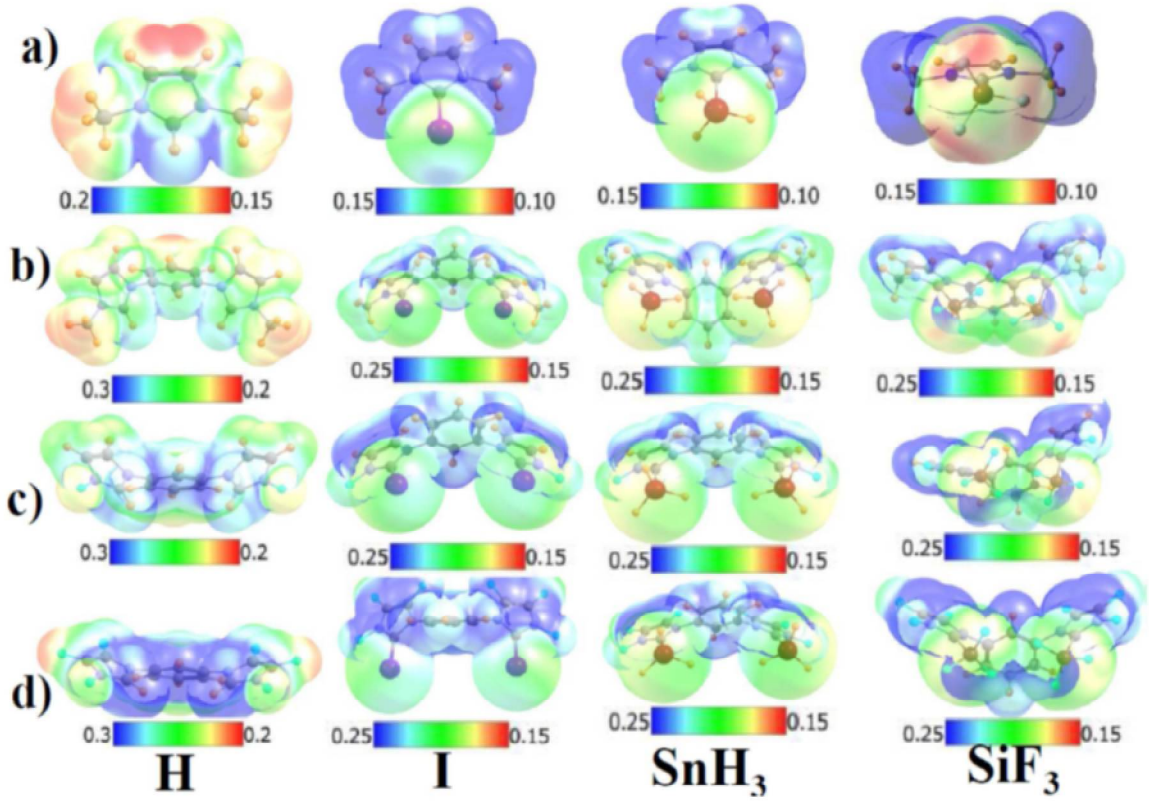
| Geom | | TtB. | ACS. | 09 |
|---|---|---|---|---|

**a) F- and b) Cl- with ImH+ and its I, SnH3, and SiF3-substituted derivatives.**



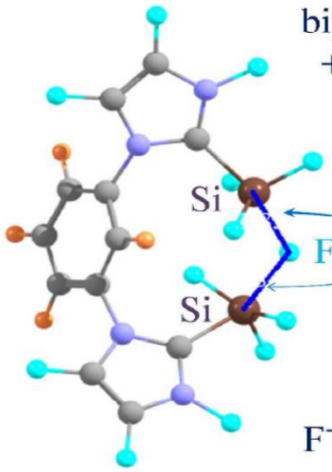

**c) Complexes of F- with phenyl-substituted receptors**

**a) ImR+, b) R-Im-Bz-Im-R+2, c) R-ImF-Bz-ImF-R+2, d) RImF3-Bz-ImF3-R+2**






**Si...F**




bipodal receptor
+ $F^-$

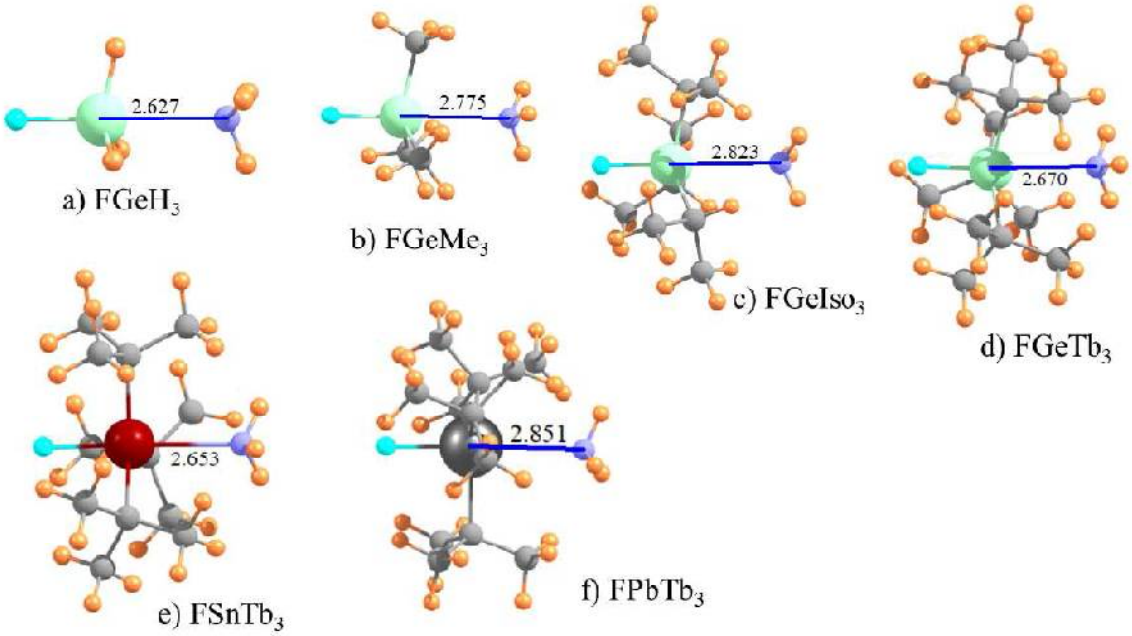
tetrel bonds

binding energy
= 250 kcal

$F^-/Cl^-$ selectivity = $10^{28}$

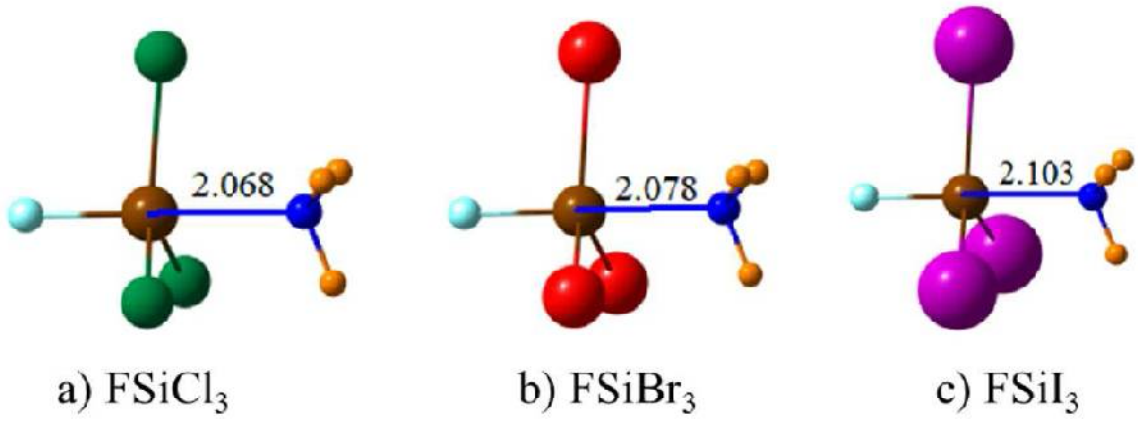
| Geom Opt. | TtA : [Ge, Sn, Pb] | LB: [N of NH3] | TtB. | ACS. | 10 |
|---|---|---|---|---|---|

**Complexes with Tt_Bond**

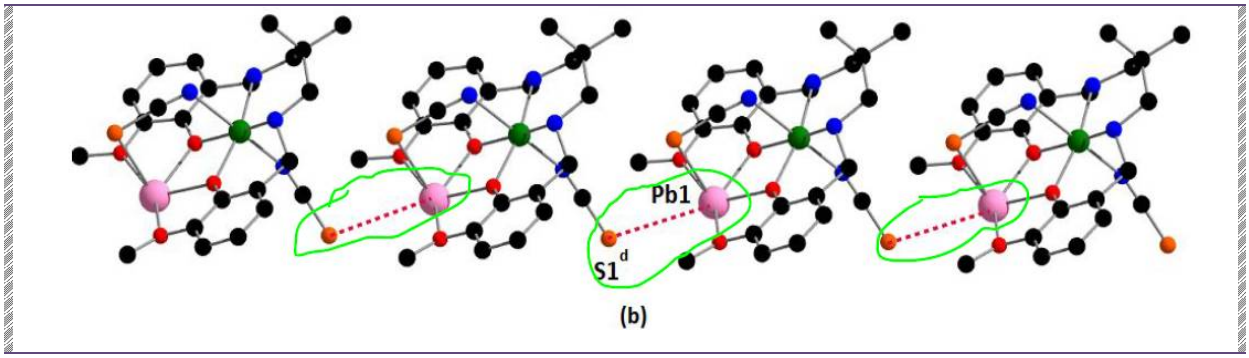



| Geom Opt. | TtA : Si;<br>Mol: SiX3; X : [ Cl;Br;I] | LB: [N of NH3] | TtB. | ACS. | 10 |
|---|---|---|---|---|---|

**Si Complexes with Tt_Bond**

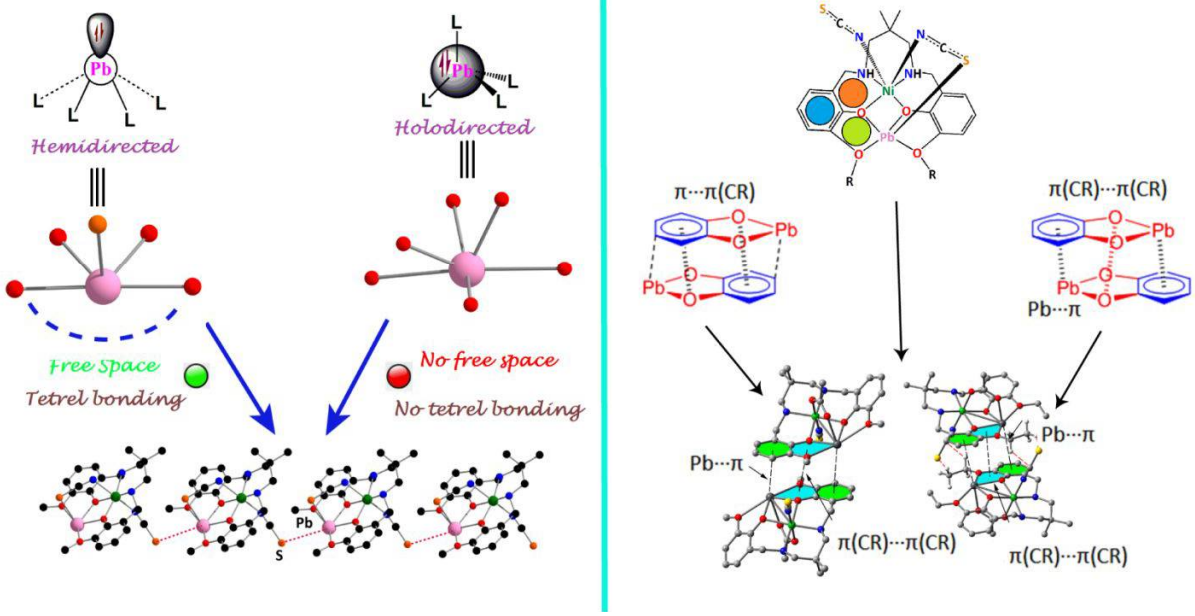



| Tetrel Bond | TtA : Pb; | LB: [S of SCN] | TtB. | ACS. | 11 |
|---|---|---|---|---|---|



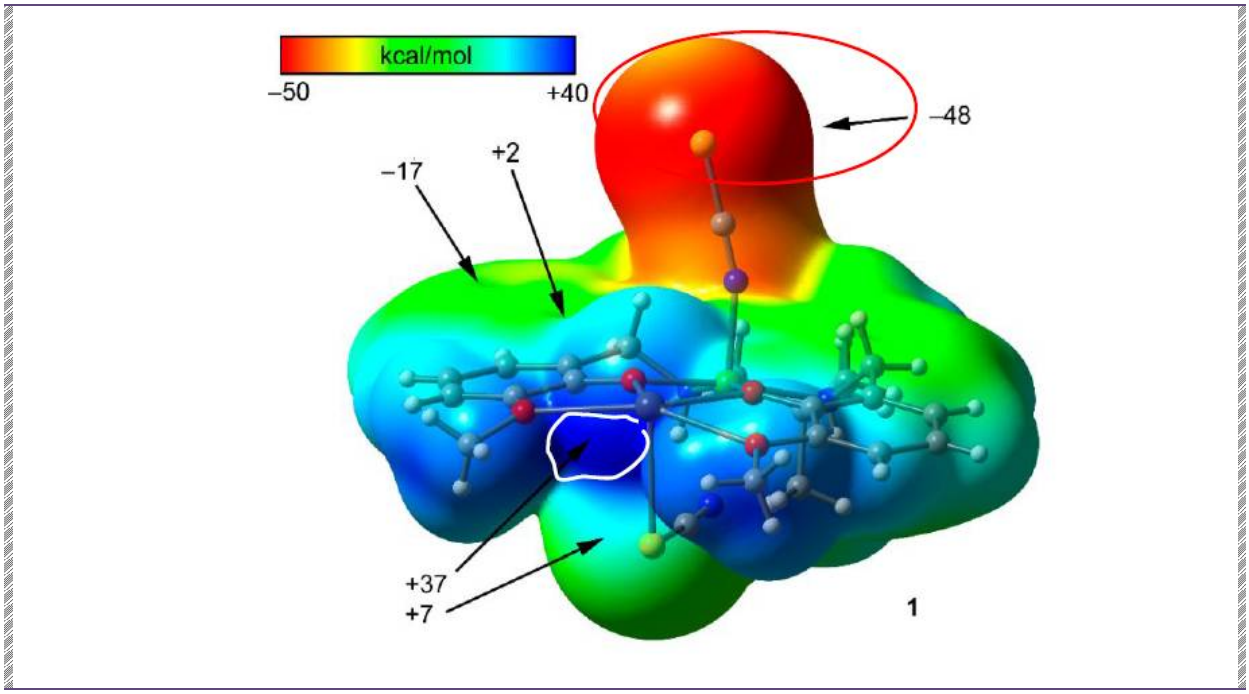

| (Pb)Tetrel Bond<br>Pb-π;<br>π···π Interactions | TtA : Pb; | TtB. | ACS. | 11 |
|---|---|---|---|---|

Supramolecular interactions in crystal engineering

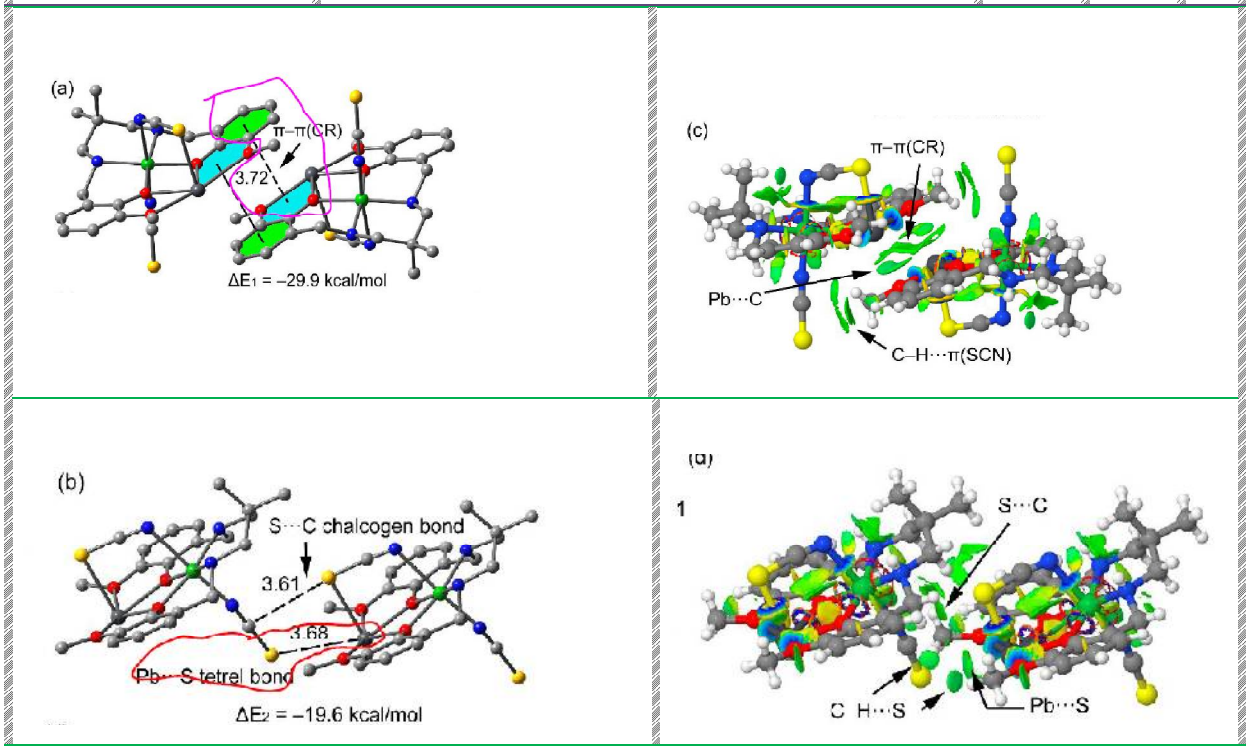



| ESP | PBE0/def2-TZVP | TtB. | ACS. | 0 |
|---|---|---|---|---|

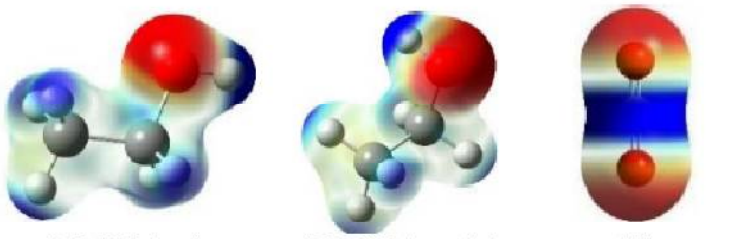
σ-holes



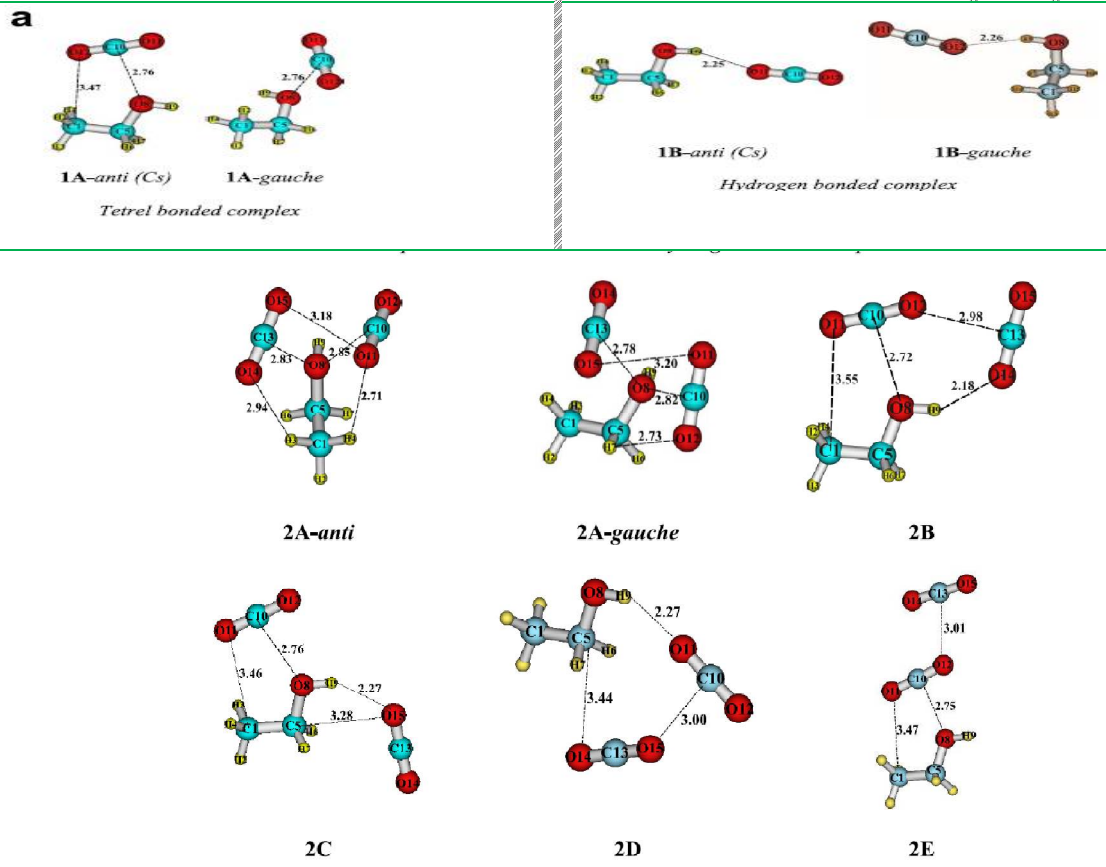

| NCI | | TtB. | ACS. | 11 |
|---|---|---|---|---|




| ESP | MP2/aug-cc-pVTZ | TtB. | ACS. | 13 |
|---|---|---|---|---|

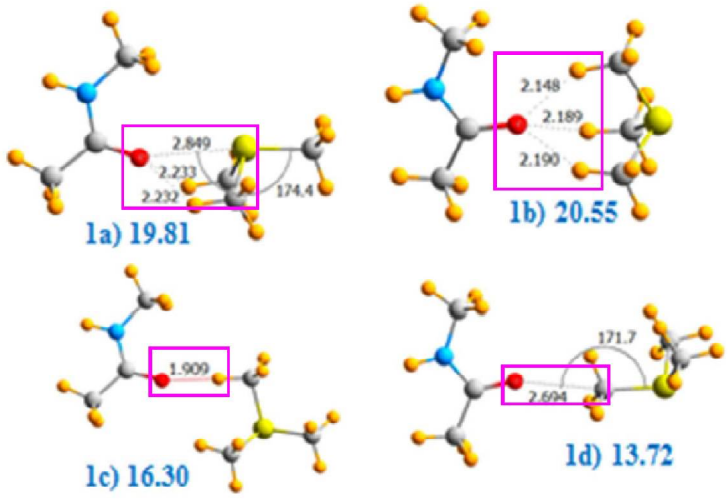



**TtA : [C]** | TtB. | ACS. | 13

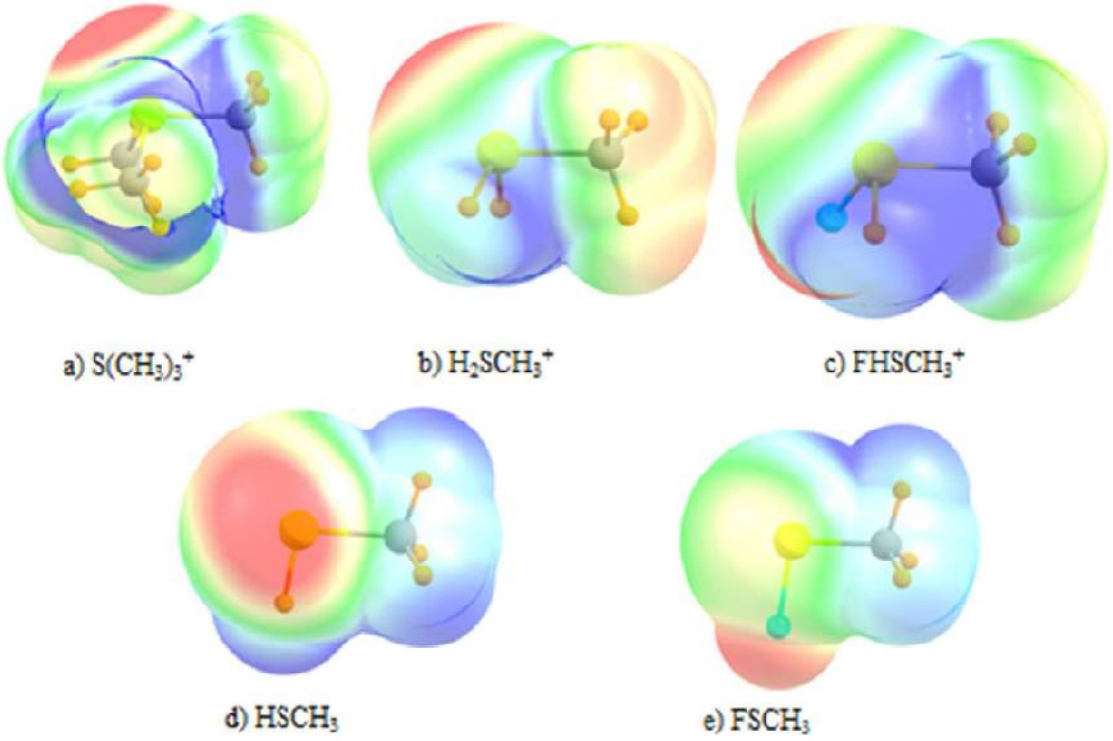



Optimized structures of C2H5OH···nCO2 (n = 1, 2)

## NMA with (CH3)3S+



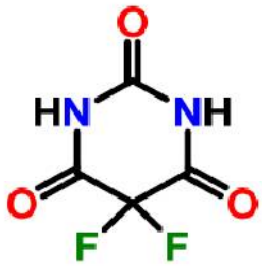


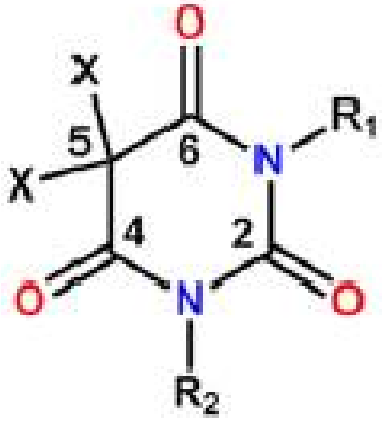




**Extrema a) 0.16 - 0.20; b) and c) 0.18 - 0.25; d) ±0.03, e) ±0.05 au.**

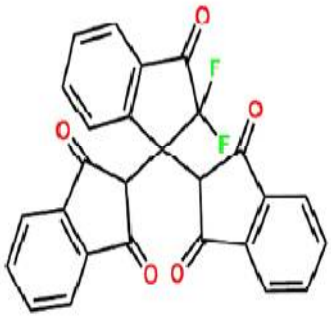


**5,5-Difluoro barbituric acid**





5,5-Dihalobabrbituric



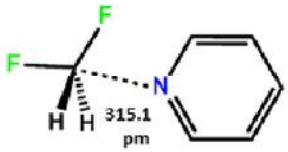
Indandione Derivative

| | X | $R_1$ | $R_2$ |
|---|---|---|---|
| 1a | F | H | H |
| 1b | F | $CH_3$ | H |
| 1c | F | $C_2H_5$ | H |
| 1d | F | $CH_3$ | $CH_3$ |
| 1e | F | $C_2H_5$ | $C_2H_5$ |
| 1f | Cl | H | H |
| 1g | Cl | $CH_3$ | H |
| 1h | Cl | $C_2H_5$ | H |
| 1i | Cl | $CH_3$ | $CH_3$ |
| 1j | Br | H | H |
| 1k | Br | $CH_3$ | H |
| 1l | Br | $C_2H_6$ | H |
| 1m | Br | $CH_3$ | $CH_3$ |
| 1n | H | $CH_3$ | H |

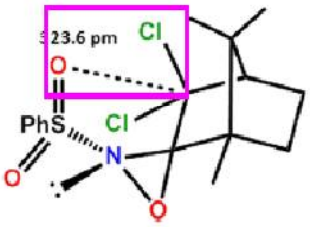
## *Tetrel Bond*

TtB. ACS. **15**

**Freon-32**



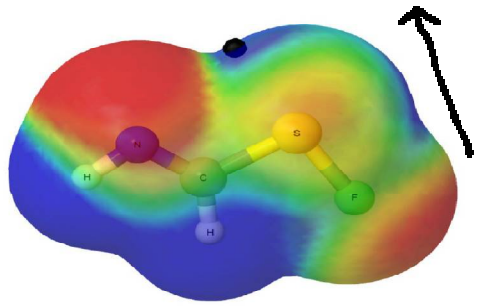

**(+)-N-Phenylsulfonyl-3,3-camphoryloxaziridine**



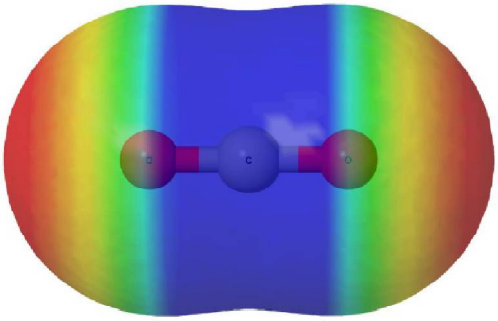

## *ESP*

TtB. ACS. **16**

**HN(CH)SF** | **CO2**



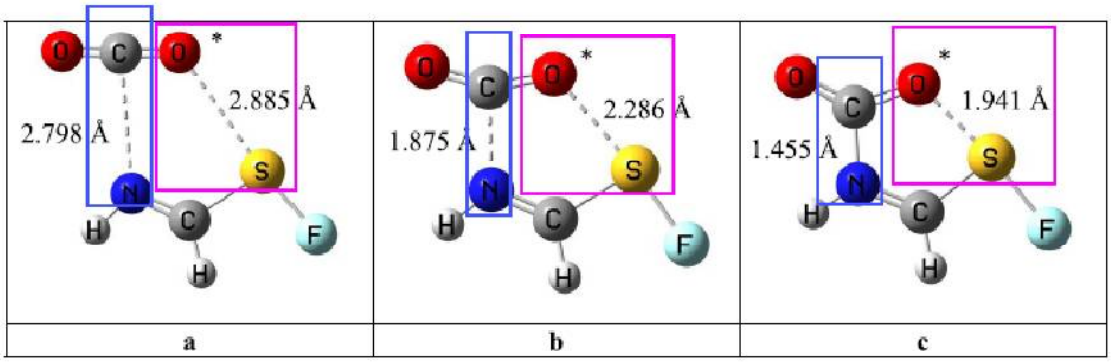
➔ σ-hole along the S-F bond in HN(CH)SF is indicated with a black dot



## Tetrel Bond

TtB. ACS. 16

**HN(CH)SF:CO2**



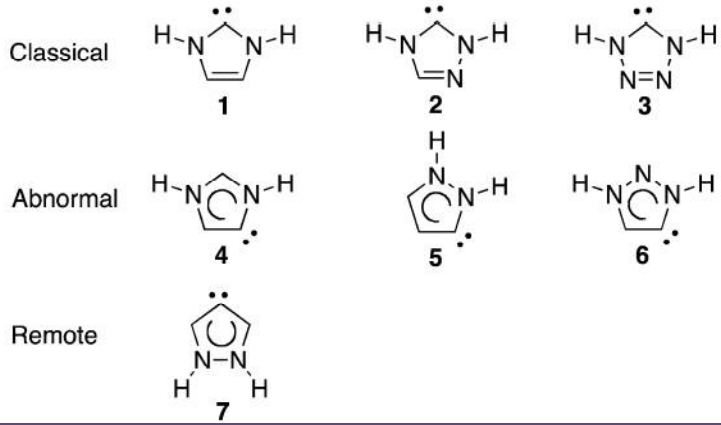

- (a ) complex, (b) transition structure, and (c) molecule
- Atom O2 is indicated with an asterisk

## Structure

**LB: [N of NH3]**

TtB. ACS. 17

**NHCs (Nitrogen Heterocyclic Carbenes)**

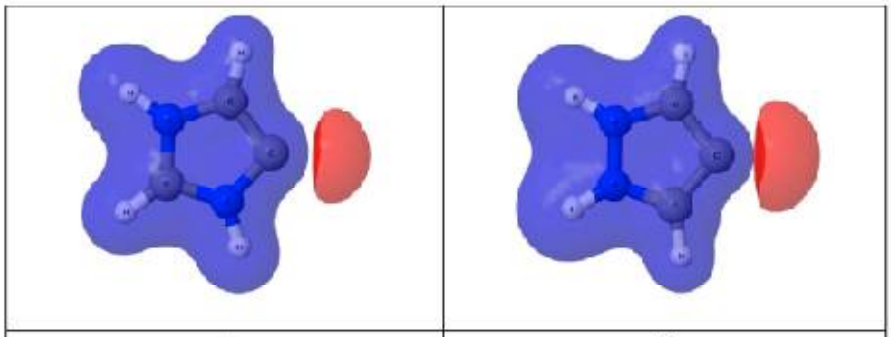



## ESP

**Ab initio MP2/aug'-cc-pVTZ**

TtB. ACS. 17

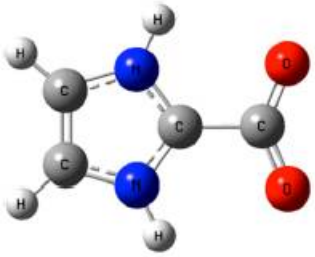
**isosurfaces forNHCs 4 and 7**



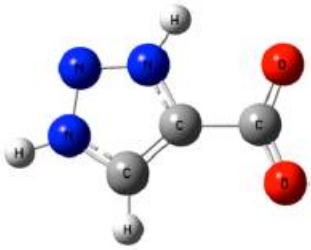
4 | 7



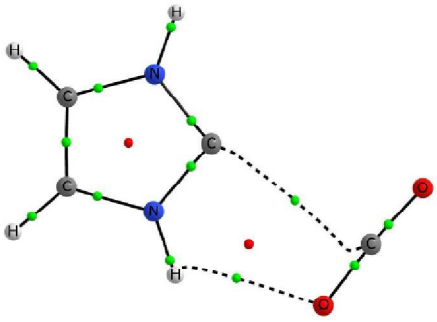
**Molecules 1-CO2 and 6-CO2**

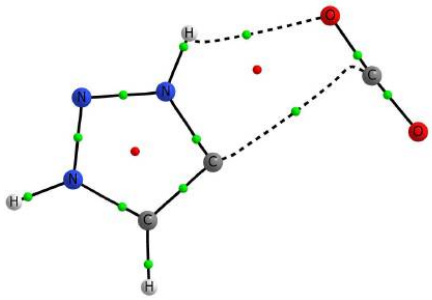


$1\text{-}CO_2$

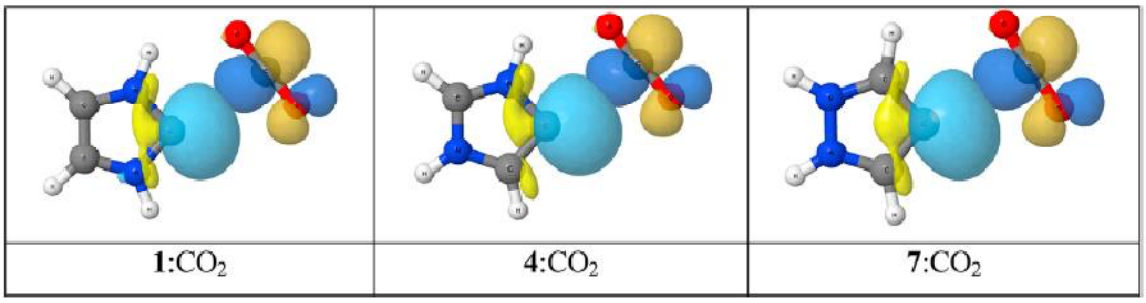


$6\text{-}CO_2$



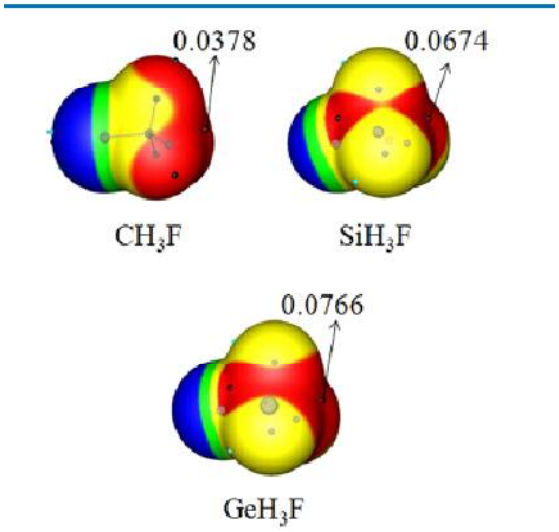


**Orbitals involved in the $C4_{lp} \rightarrow \pi^* C1-O_3$ charge transfer for 1:CO2, 4:CO2, 7:CO2**



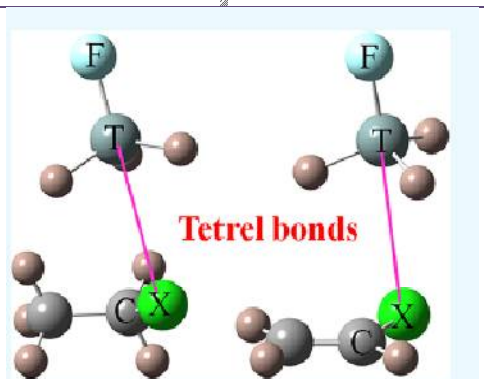
$1{:}CO_2$ | $4{:}CO_2$ | $7{:}CO_2$

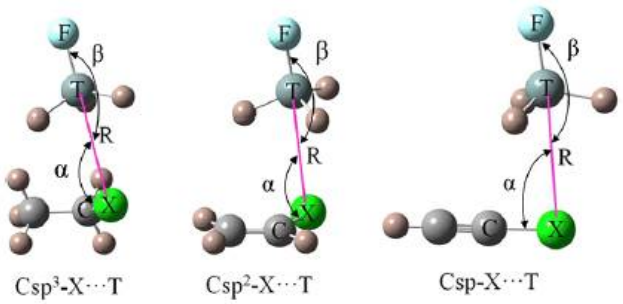
**ρ = 0.001**



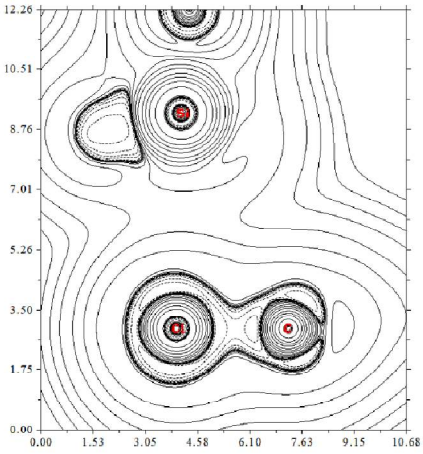

- ✓ **Red, greater than 0.02;**
- ✓ **Yellow, between 0.02 and 0;**
- ✓ **Green, between 0 and −0.02;**
- ✓ **Blue, smaller than −0.02**





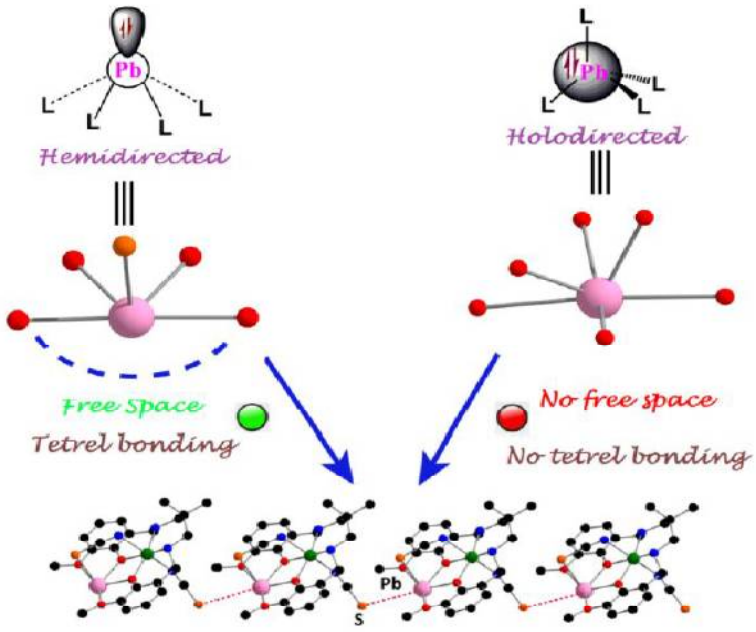



**Laplacian contour of CH2=CHCl···SiH3F**



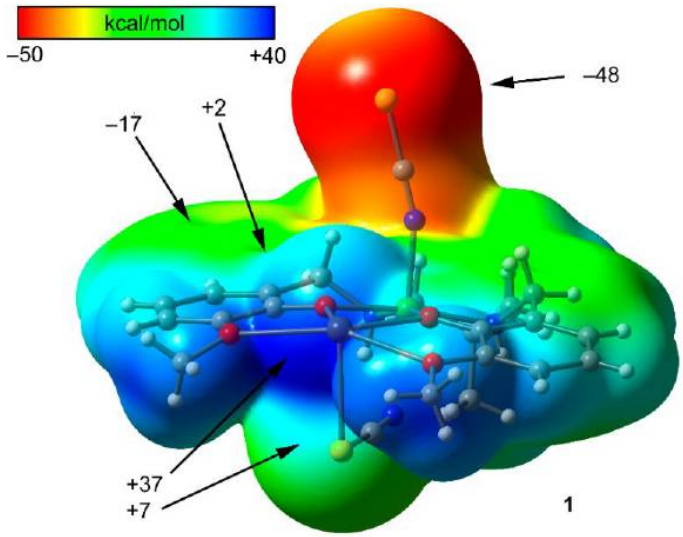

## Tetrel Bond





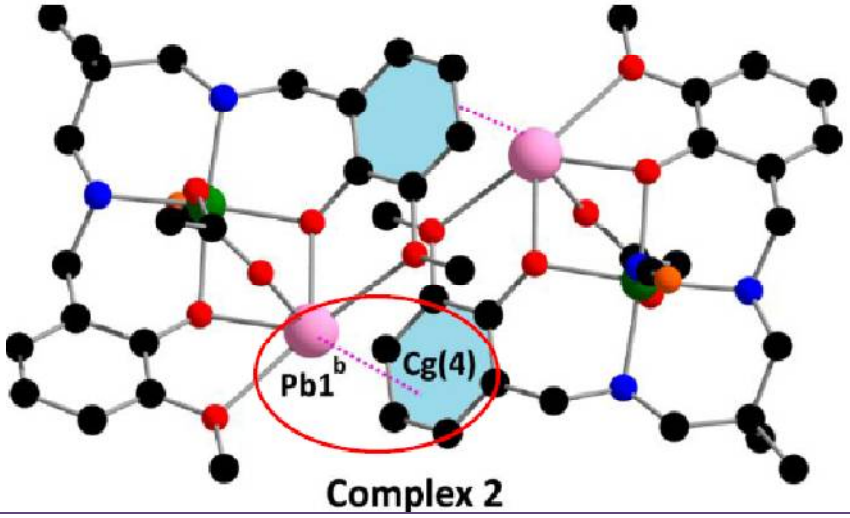
## ESP

**PBE0/def2-TZVP**

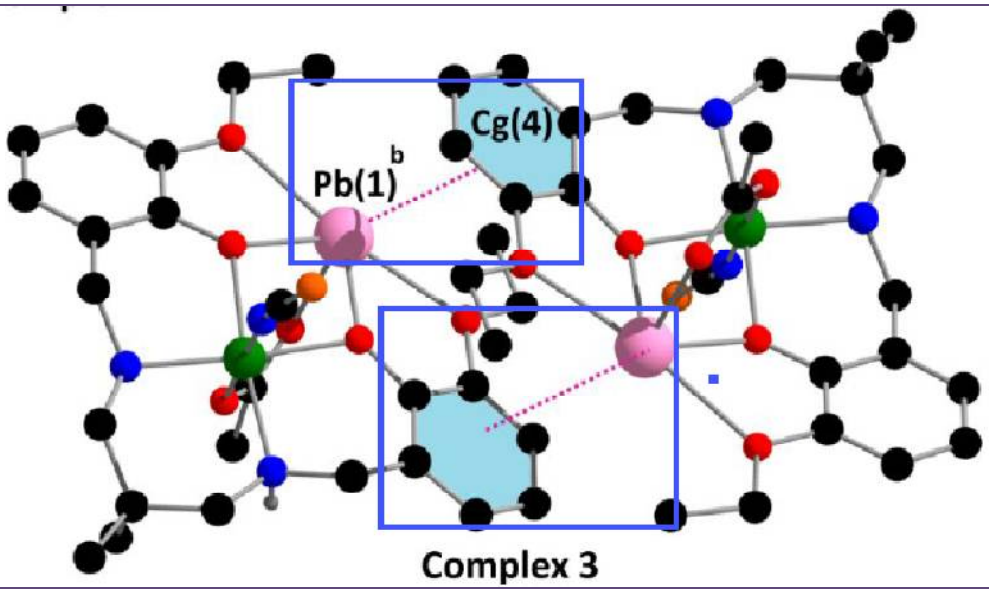





## Cation···π interactions

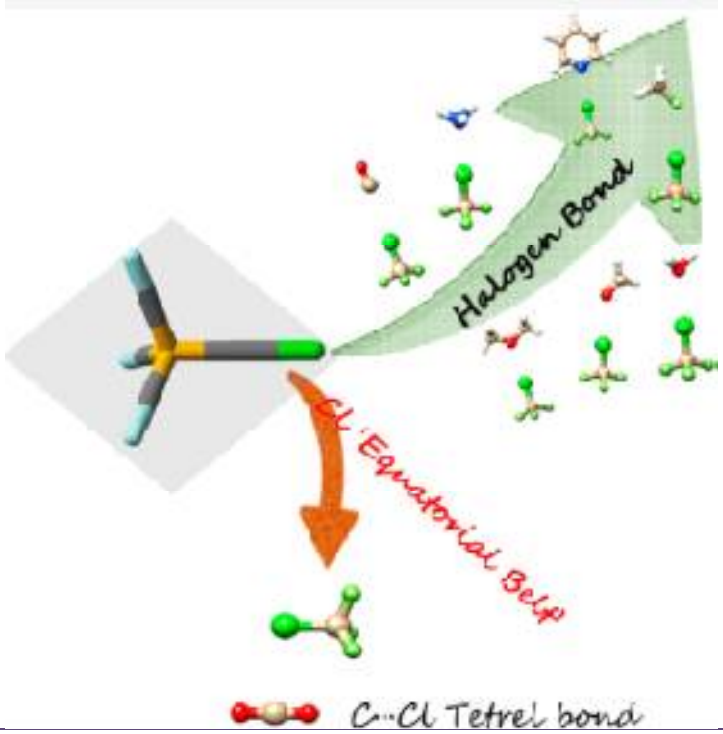



Complex 2

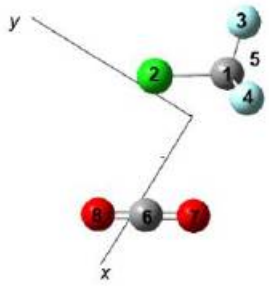



Complex 3

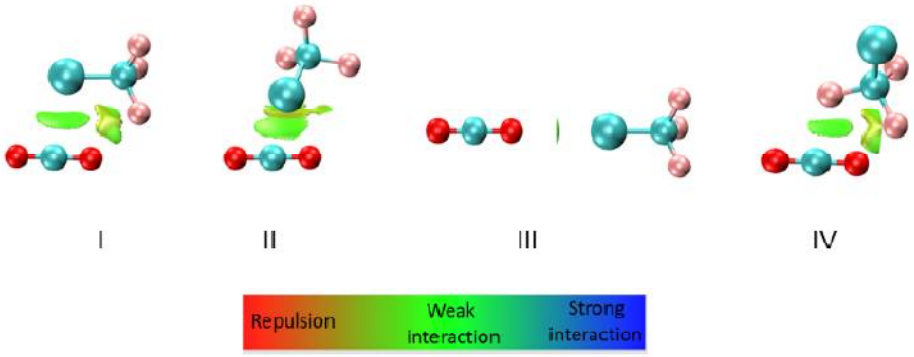





**Structure of CF3Cl-CO2 isomer**



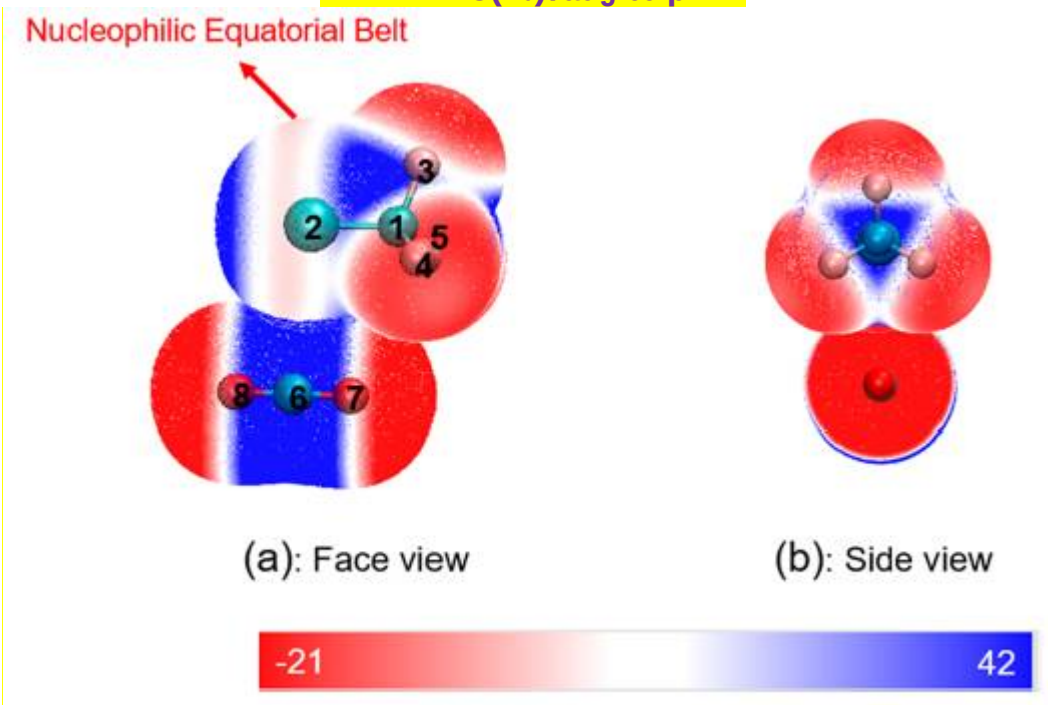

## NCI isosurfaces




## ESP



B2PLYP-D3(BJ)/aug-cc-pVTZ




- ✓ **Electrostatic complementary interactions and**
- ✓ **Penetration of van der Waals surface between CF3Cl and CO2**

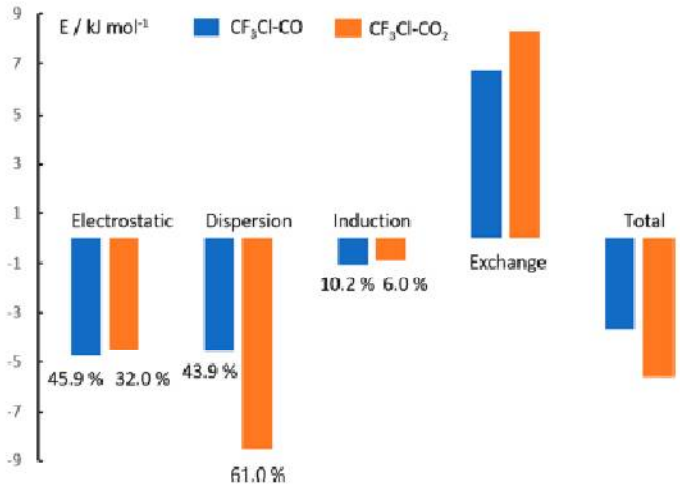
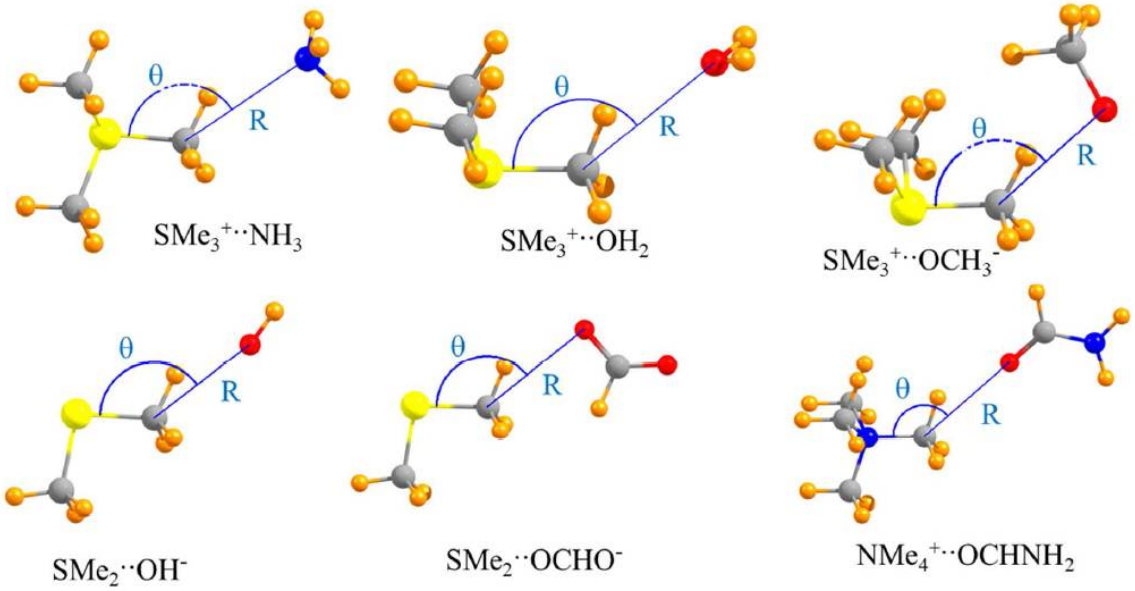


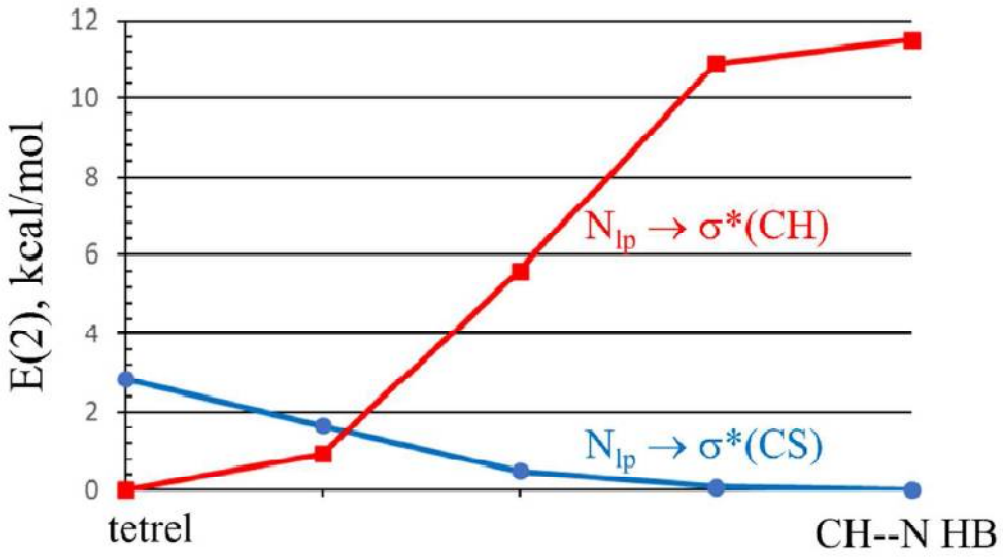

Figure 5. Summary of the SAPT energy contributions for the complexes of $CF_3Cl{-}CO$ and $CF_3Cl{-}CO_2$.

| **Tetrel Bond** | | TtB. | ACS. | 22 |
|---|---|---|---|---|
| | **LA: [SMe3+, NMe4+, SMe2]** | **LB: [NH3, OH2, OCHNH2, OCH3-, OH-, HCOO]** | | |

**SMe3 ... LB [NH3; OH2; OR]**



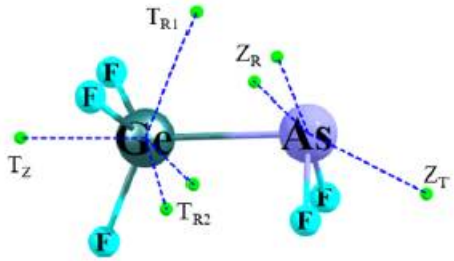

**SMe3 ... NH3 system -- NBO**




- **NBO values of E(2) for charge transfer**
  - **From N lone pair to σ*(CS) (blue curve)**
  - **To σ*(CH) red curve antibonding orbitals for SMe3+···NH3 system**

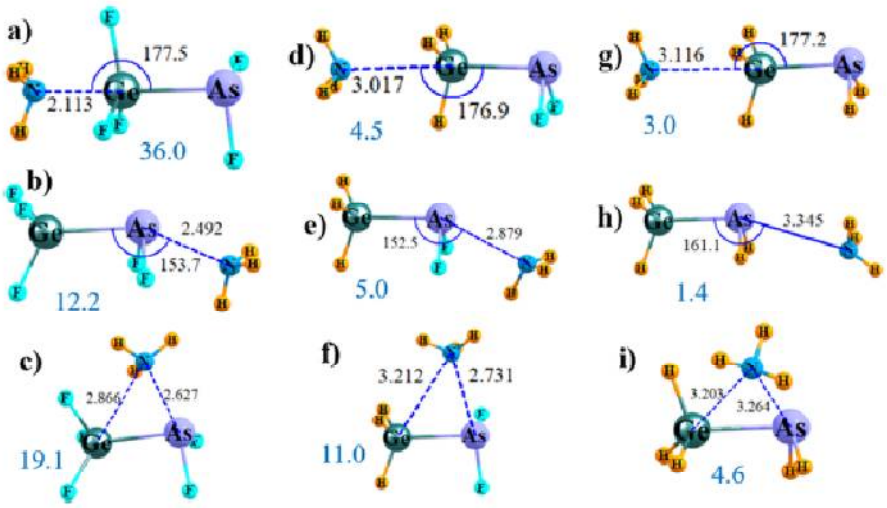
| ESP | | TtB. | ACS. | 23 |
|---|---|---|---|---|

**Isodensity surface**




| Tetrel Bond | LA: [Ge] | TtB. | ACS. | 23 |
|---|---|---|---|---|

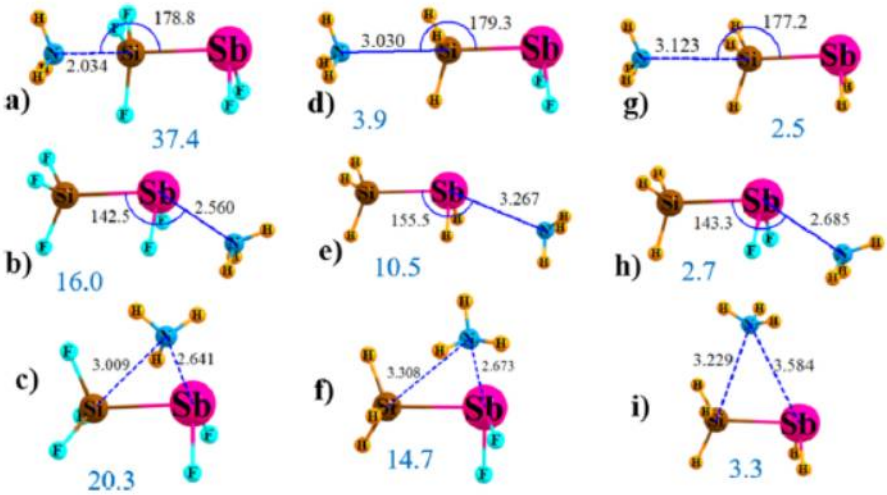
**LA...LB**




| LA | LB |
|---|---|
| (a–c) GeF3AsF2 | NH3 |
| (d–f) GeH3AsF2 | |
| (g–i) GeH3AsH2 | |



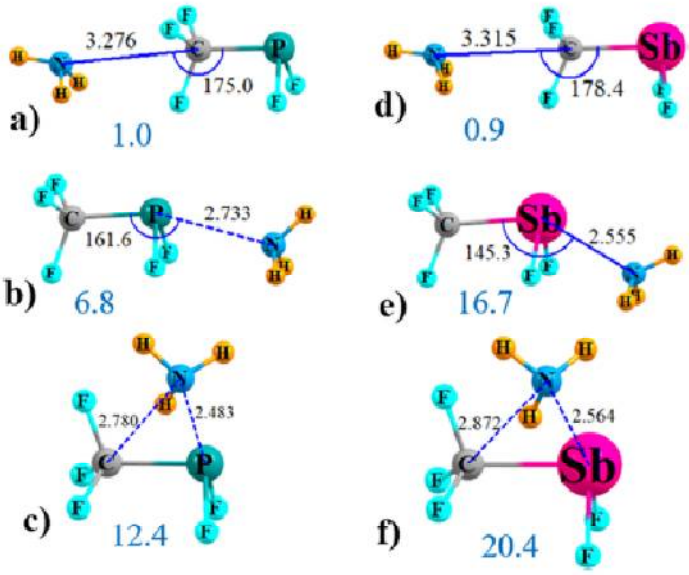
**LA...LB**




| LA | LB |
|---|---|
| (a–c) SiF3SbF2 | NH3 |
| (d–f)SiH3SbF2 | |
| (g–i) SiH3SbH2 | |

| Picogen Bond | LA: [Sb; P] | TtB. | ACS. | 23 |
|---|---|---|---|---|

**LA...LB**

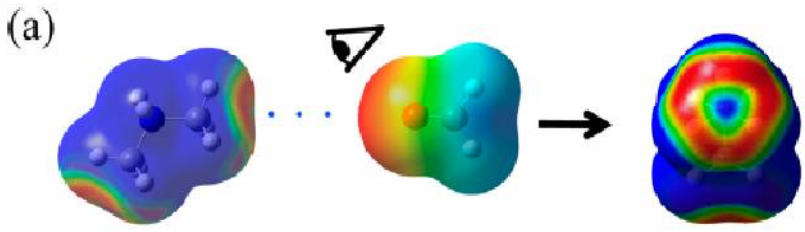



| LA | LB |
|---|---|
| (a–c) CF3PF2<br>(d–f) CF3SbF2 | NH3 |

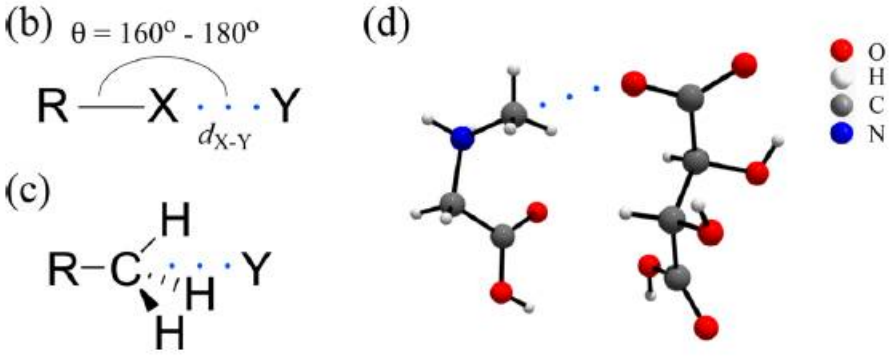
| ESP | +ly charged dimethylammonium (left) | Formaldehyde (center) | TtB. | ACS. | 24 |
|---|---|---|---|---|---|

**CAM-B3LYP/6-311++G(d,p)**

- ✓ σ-hole is present on the methyl carbon
- ✓ adjacent to the C–Nσ-bond, ESP: 0.179 au



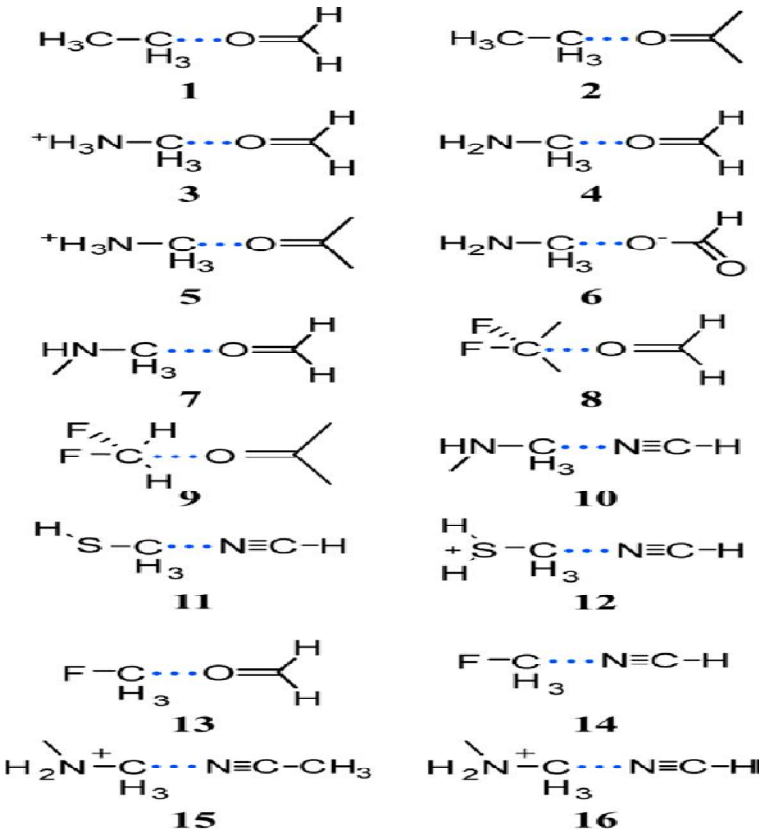

| Tetrel Bond | | TtB. | ACS. | 24 |
|---|---|---|---|---|




- (b) General schematic of a tetrel bond
  - ✓ R is a covalently bonded atom or functional group
  - ✓ X is the tetrel bond donor (X = C, Si, Ge, Sn, or Pb),
  - ✓ Y is the tetrel bond acceptor.
  - ✓ D(X−Y) is smaller than the sum of the van der Waals radii of interacting atoms
- (c) Carbon tetrel bond involving a methyl carbon.
- (d) Example of a carbon tetrel bond occurring in crystal structure of sarcosinium tartrate



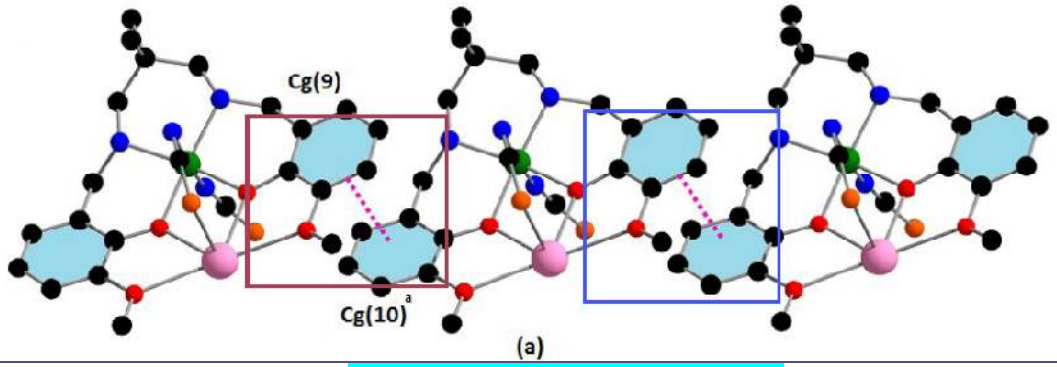
| LA | LewisBase |
|---|---|
| Methyl carbons | Oxygen-containing or nitrogen-containing functionalgroups |



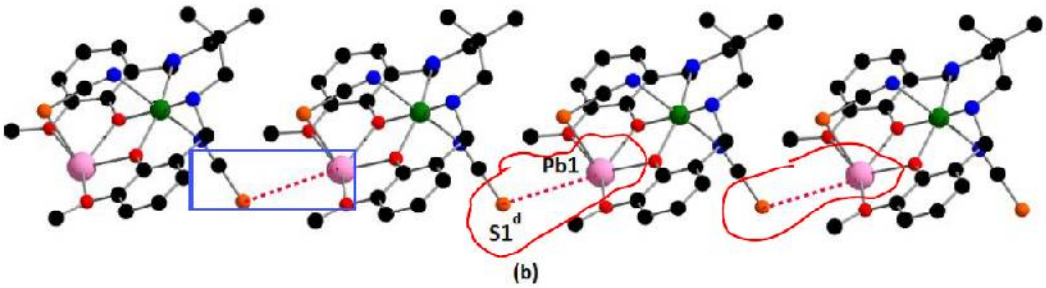
# π interactions



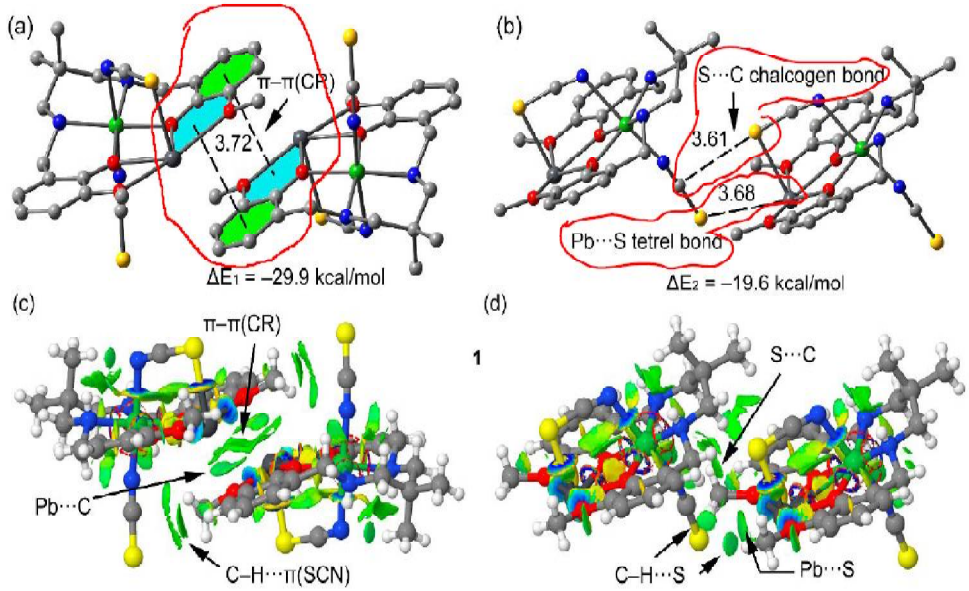
π···π interactions -- complex 1




Pb···S interactions --- complex 1



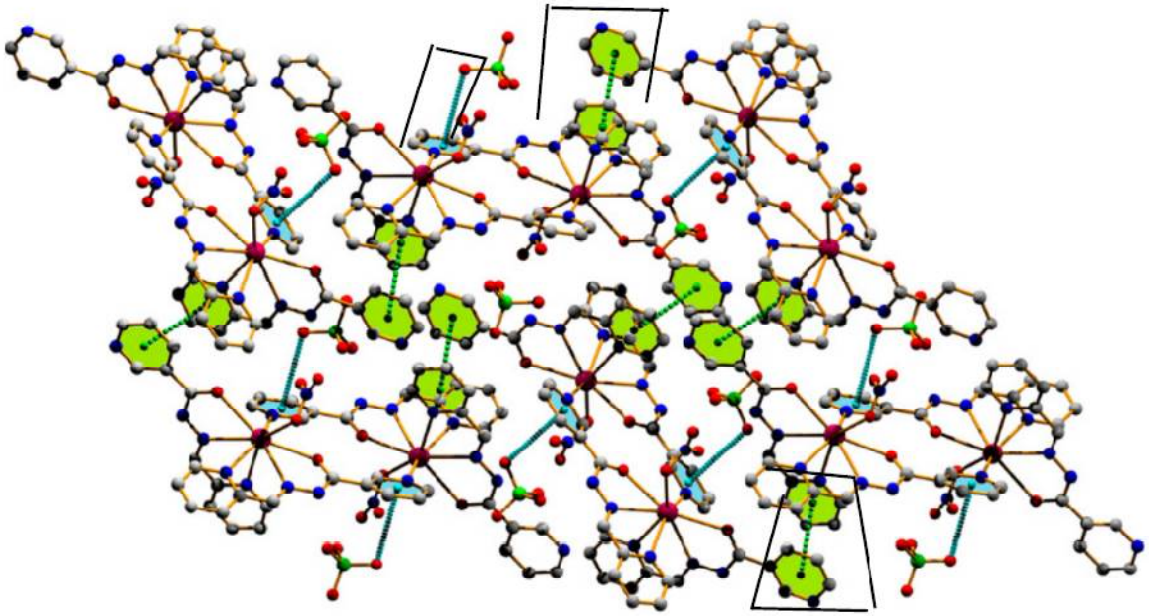

(a,b) Theoretical modelsthe non-covalent interactions



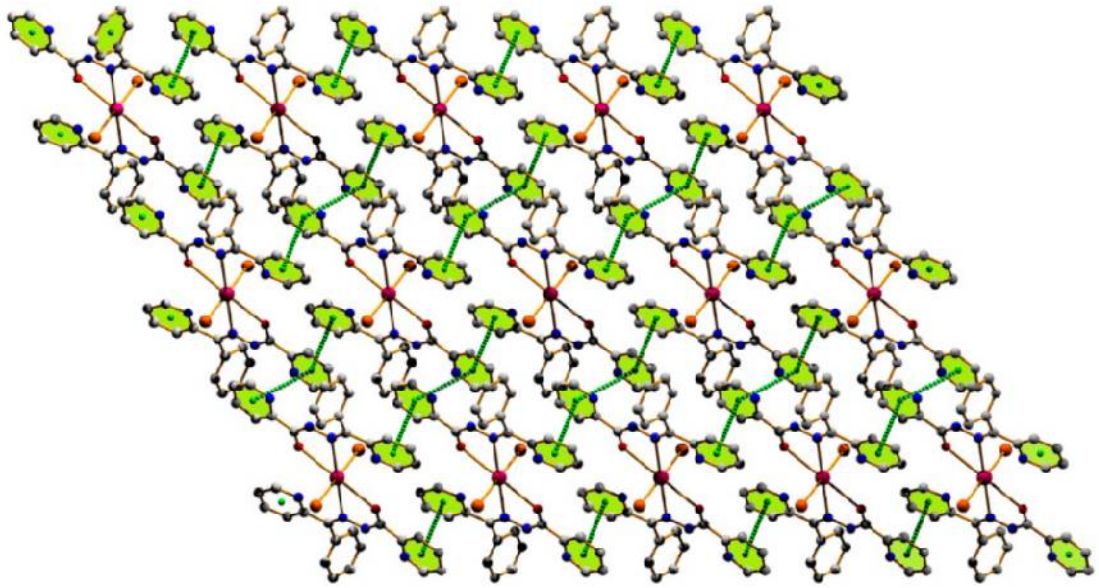

(c,d) NCI plots

| Anion...π; π...π interactions | TtB. | ACS. | 06 |
|---|---|---|---|

**Anion...π**

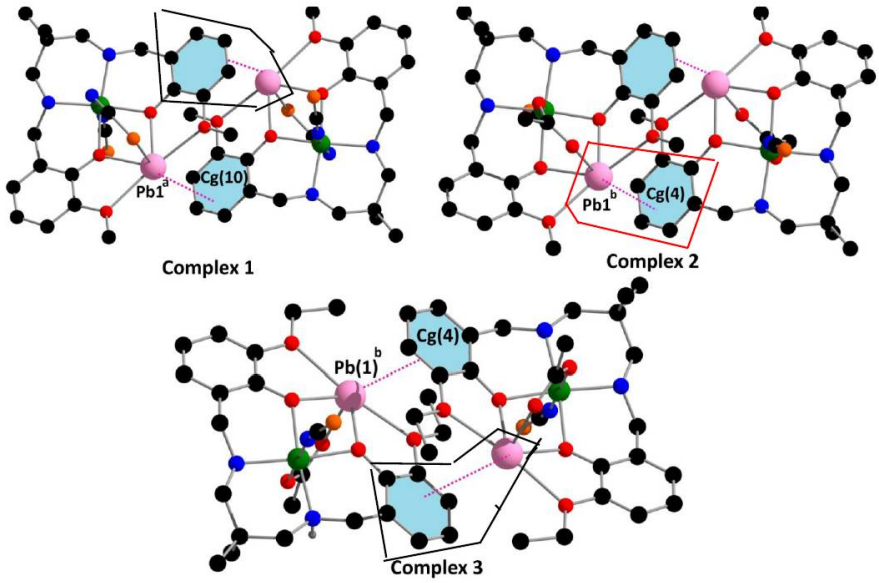


**Mixture of π...πstacking forces.**

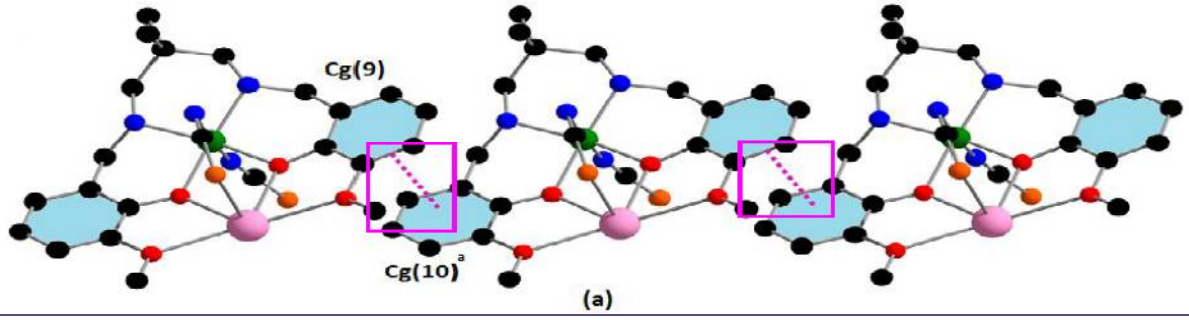


| Cation···πinteractions | TtA : Pb; | TtB. | ACS. | 11 |
|---|---|---|---|---|

**xx**

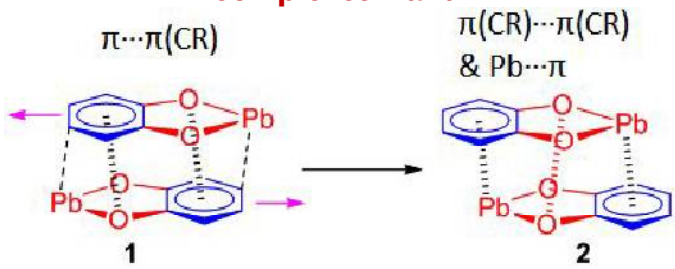



| π···π Interactions | | | TtB. | ACS. | 11 |
|---|---|---|---|---|---|

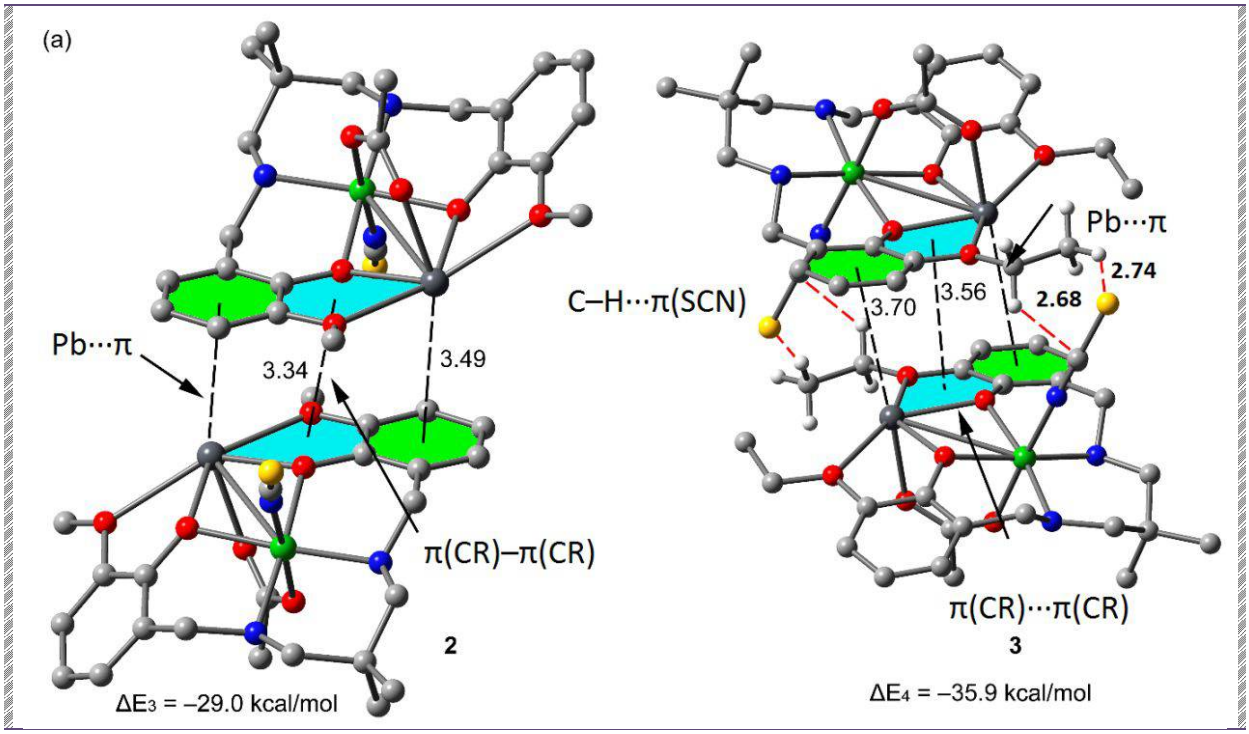



| π···stacking assemblies | TtB. | ACS. | 11 |
|---|---|---|---|

**Complexes 1 and 2**




**Theoretical models**


(a)
Pb···π
3.34
3.49
π(CR)–π(CR)
2
ΔE3 = –29.0 kcal/mol
C–H···π(SCN)
Pb···π
2.74
3.70
3.56
2.68
π(CR)···π(CR)
3
ΔE4 = –35.9 kcal/mol