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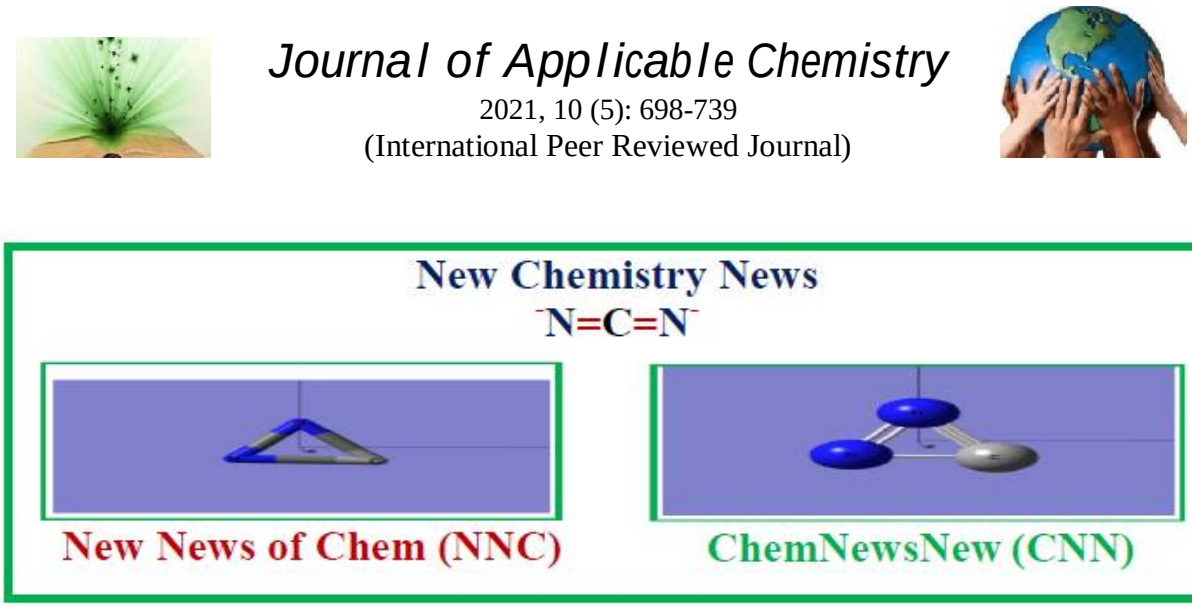

CNN –41:
Triel bonds -
Non-covalent Chemical interactions

Information Source	ACS.org ; sciencedirect.com
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Conspectus:Triel atoms (TrA: B,Al,Ga, In,Tl, Nh) belong to 13th group of 18 column chemical elements periodic table. TrA exhibitsLewis acid (LA) behavior and formscomplexes or adducts with Lewis bases (LB) i.e. molecules or compounds or π electron systems.

The strength of non-covalent bond between Tr atom and Lewis base donor atom (Ex: N in N2 or HCN) vary over a wide scale depending upon the substituents/spacers/organic moieties in both LA and LB. To one's astonishment the bond energy reaches or exceeds sometimes that of a common covalent bond. The cooperativity effect also manifests with H-,X-, Chalcogen- and Pnictogen bonds resulting in noteworthy structure, properties and functions in crystal or solution phases. The artefact is vividly felt in bio-systems, atmospheric chemistry and synthetic materials.

Keywords: Non-Covalent Chemical bonds : [Nobel gas (aerogen), Halogen,Chalcogen, Pnicogen (or Pnictogen), Tetrel, Triel , Spodium, Regium (or Coinage), alkali, alkaline earth, Hydrogen [{strong, weak}, dihydrogen, hydride]]

Layout

I Select Research Titles (2000 to 2021) in Tr-bonds

II Object oriented terminology (OOT) for Tr-bonds

Sup Inf Supplementary Information

1. Tr-bonded chemical species
2. 1. Positive ESP sphere in a single atom
2. 2 ESP contours in molecules
2. 3. σ-hole in Single Molecules
3. π-hole in a molecule
4. H bond
5. Halogen (X) bond
6. H- and X- bonds

K(nowledge)Lab
rsr.chem1979

I. Select Research Titles (2000 to 2021) in Triel-bonds

LAcid	NCC Bond	LBase
BH3 AlH3	Triel Bond	Uracil (U) Thymine (T) 5-fluorouracil (5FU)
HCl	H-Bond	

Non-covalent Chemical (NCC) bond		
Tr Element	**Interaction**	**Primary association**
B–O	Hard-hard	Charge controlled
Al–O	Soft-soft	Orbital controlled
Effect of substituents	Regioselectivity is very small	

triel bond
🕮 Strength (triel-bonded complexes) >> Strength (hydrogen-bonded ones)
🕮 Strength (Al-containing dimers) >> Strength (Boron -containing ones)
🕮 B-containing dimers (B–O triel bond) are accompanied by weak B–H···O unconventional H-bonds

Theory	DFT
Basis set	ωB97XD/6–311++G(d,p)
Software	Gaussian09
Single-point energy	MP2/6–311++G(d,p) CCSD/6-31 + G(d,p)
NBO MEPs	Reactivity descriptors global/local

KeyLrn_Bits	π–hole, B–HO H-Bond, Lewis acid, Structures and binding energies, NBO, Reactivity descriptors

TrB-01	
α-methylation and α-fluorination electronic effects on the regioselectivity of carbonyl groups of uracil by H and triel bonds in the interaction of U, T and 5FU with HCl and TrH3 (Tr = B, Al)	Journal of Molecular Graphics and Modelling, 88(2019)237-246doi.org/10.1016/j.jmgm.2019.02.006
AristoteMatondo and Renjith Thomas and Philippe Vuka Tsalu and Christian TshikalaMukeba and VirimaMudogo	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond	
	✓ Lewis acid – Lewis base interactions ✓ triel bonds ! Mechanisms of formation ! Properties ! Different coordination of trielcentres ! Strength ▪ Comparison with H-bond
	➔ Cambridge Structural Database ➔ Frequent Examples o Tetrahedral arrangements that obey the octet rule o Trivalent and hypovalenttriel structures that are characterised by the trigonal coordination as well as hypervalent triel structures possessing trigonal bipyramid and octahedral configurations
KeyLrn_Bits	Electron charge shift

TrB-02Rev	
Triel bond and coordination of trielcentres – Comparison with hydrogen bond interaction	Coordination Chemistry Reviews, 407(2020) doi.org/10.1016/j.ccr.2019.213171
Sławomir J. Grabowski	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond	Boron		
Complex	BH(CO)2/BH(N2)2 : LA	XF3/XF5 : LB	✓ X-Bond ✓ Triel Bond
	MEP | BH(CO)2/BH(N2)2 | ➔ a region with negative MEPs on the B atom in the vertical direction of the molecular plane ➔ σ-hole at the B-H bond end		
Dual role of Triel atom	✓ Boron	Lewis base	halogen bond
		Lewis acid	triel bond

Strength of X-bond	✓ IF3< BrF3< ClF3, ✓ IF5< BrF5< ClF5
Strength of Triel-bond	➔ BH(CO)2< BH(N2)2
KeyLrn_Bits	Halogen bond, Triel bond, Hypervalent halogens: boron electron donors

single-point energy
NBO MEPs
global/local reactivity descriptors

TrB-03	
Dual function of the boron center of BH(CO)2/BH(N2)2 in halogen- and triel-bonded complexes with hypervalent halogens	Journal of Molecular Graphics and Modelling, 84(2018)118-124doi.org/10.1016/j.jmgm.2018.06.017
Wenbo Dong and Yanqing Wang and Xin Yang and Jianbo Cheng and Qingzhong Li	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

		Boron	Triel Bond
	✓	✓ Haloborane salts	
triel bond donors 1-(dihaloboranyl)pyridin-1-ium compounds $P^{y+}BX2$ (X=Cl, Br and I)		**Electron donor moieties** Cl−, Br−, HCO2−, BF4− , ClO4−	
Expt Data	✓	✓ CSD (Cambridge Structural Database)	
KeyLrn_Bits		Solid state chem.	

wavefunction analysis	M06-2X/def2-QZVPD
Software	Gaussian09
Bader's theory of 'atoms in molecules'	AIMall calculation package

Geo opt	TURBOMOLE version 7.0	Constraint	C2V Symmetry group

TrB-04	
Charge-assisted triel bonding interactions in solid state chemistry: A combined computational and crystallographic study	Chemical Physics Letters, 666(2016)73-78doi.org/10.1016/j.cplett.2016.11.010
Antonio Bauzá and Xavier García-Llinás and Antonio Frontera	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond		
Methods	Modified Townes−Dailey (TD) model	To interpret and visualize measurable nuclear quadrupole coupling tensors
Principal component of the nuclear quadrupole coupling tensor	Directly related to a newquantity VPPA(or ΔP) valence p-orbital population anisotropy	
Application of VPPA	Universal measure of the ability of any element in the p-block of the periodic table (groups 13−16) to interact with nucleophiles e.g., formation of chalcogen, pnictogen, tetrel, and triel bonds	

TrB-05	
A Modified Townes-Dailey Model for Interpretation and Visualization of Nuclear Quadrupole Coupling Tensors in Molecules	J. Phys. Chem. A, 124(2020) 1176−1186
Andrew Rinald and Gang Wu	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond		
LAcid	LBase	
Complexes of TrR_3 Tr = B and Al; R = H, F, Cl, Br	N-bases	NH3 CH2NH HCN
	O-bases	CH3OH H2CO CO
Hybridization effect of N and O atoms on	strength, properties, nature of triel bond	

Hybridized	Atom	Strength of triel bond
o sp-	→ O → N	! weakest
o sp2-	→ O	! moderate
o sp3-	→ N	
o sp3-	→ O	! strongest
o sp2-	→ or N	

☞ Polarization contribution increases from sp to sp2 to sp3

☞ Most complexes are dominated by electrostatic component

TrB-06	
Influence of N‑Base and O‑Base Hybridization on Triel Bonds	ACS Omega, 5(2020) 21300−21308
Qingqing Yang, Xin Yao, and Xin Yang	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond			
Lewis-Acid	Lewis-Base	Complex	Topology
Tr = B, Al, Ga, In, Tl	HCN or N2	Tr(III)	Tetrahedral structure with the tetravalent triel atom
		TrF3.2LB	TrF3 with two ligands results in a trigonal bipyramidal structure with a pentacoordinate Tr atom

Theory	HF
Level/Functional	MP2
Basis set	Dunning-type aug-cc-pVTZ basis set
Software	Gaussian 09
basis set for o Indium o Thallium	o Aug-cc-pVTZ-PP o Effective core potential (ECP)

Probe	Atoms polarization of the NBO bonds orbital–orbital energies
TrAtom	**CQC**
B Al Ga	optimized geometries MP2/aug-cc-pVTZ level
	HF/aug-cc-pVTZ level
In T	Geom opt aug-cc-pVTZ-PP ECP
	rough NBO HF/Lanl2DZ
Software	NBO 5.0 program implemented in GAMESS

.		
Molecular electrostatic potentials		MP2/aug-cc-pVTZ and MP2/aug-cc-pVTZ-PP
	Software	AIMAll program

Tr	Energy type
B	☞ Much weaker interactions are observed compared to other triel systems ☞ because of the lower acidity of the B center relative to that of the other triel centers since stronger backbonding effect for BF3 than for the other triel trifluorides
Al	☞ Meaningful electrostatic contributions in Al complexes
Ga	☞ Most important electron charge shift is observed upon complexation

TrB-07	
Boron and other Triel Lewis Acid Centers: From Hypovalency to Hypervalency	ChemPhysChem, 15(2014) 2985 – 2993 DOI: 10.1002/cphc.201402344
Sławomir J. Grabowski	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond

LAcid	LBase	Tr bond
TrX3 Tr: B, Al; X = H, F, Cl, Br	benzene	X3Tr…Bz

Theory	MP2
Basis set	aug-cc-pVTZ
Software	Gaussian09
relativistic effects for heavier bromine atomwere not considered	
basis set superposition error (BSSE) correction applied	

Probes	
Interaction energy	Eint
Binding energy	Ebin
Deformation Energy	Edef (Ebin − Eint)

$$energy	
Interaction energy	Eint
Binding energy	Ebin
Deformation Energy	Edef (Ebin − Eint)

Quantum Theory of Atoms in Molecules^ (QTAIM)	
Software	AIMAll program
bond paths (BPs)	bond critical points (BCPs)
total electron energy density at BCP (HBCP)	electron energy density (GBCP)
	potential electron energy density (VBCP)

If	∇2ρBCP (el)ectron density concentration in inter-atomic region) is negative
Then	Energy corresponds to covalent bonds
If	∇2ρBCP (electron density concentration in inter-atomic region) > 0 (i.e. positive)
Then	Energy corresponds to ✓ ionic bonds, ✓ van derWaals interactions, ✓ other close-shell interactions like for example, not strong hydrogen bonds

TrB-08	
Triel bonds-complexes of boron and aluminum trihalides and trihydrides with benzene	Struct Chem, (2017) DOI 10.1007/s11224-017-0927-x
Sławomir J. Grabowski	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond		
KeyLrn_Bits	valence-shell electron-pair; repulsion model (VSEPR); hydrogen bond; s-hole bond; pi-hole bond; electron charge shift	

TrB-09	
Classification of So-Called Non-Covalent Interactions Based on VSEPR Model	Molecules,26(2021)4939. doi.org/10.3390/molecules26164939
Sławomir J. Grabowski	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond		

LAcid	LBase	
BCl3, BH3, AlCl3, AlH3	NCH, N2, NH3, Cl^- anion	RB…N

Theory	MP2
Basis set	aug-cc-pVTZ
Software	Gaussian16
Freq calc	MP2/aug-cc-pVTZ

KeyLrn_Bits	valence-shell electron-pair; repulsion model (VSEPR); hydrogen bond; s-hole bond; pi-hole bond; electron charge shift

Probes. CQC

🕮 Quantum Theory of Atoms in Molecules (QTAIM) 🕮 Electrostatic potentials (EPs)	AIMAll program
🕮 Natural Bond Orbital (NBO) method 🕮 Electron charge density shifts	ADF2017 program package

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{disp}.$$

DEelstat	Quasi-classical electrostatic interaction betweenunperturbed charge distributions of atoms; it is usually attractive (negative).
DEPauli,	Pauli repulsion: Energy change associated with the transformation from the superposition ofunperturbed electron densities of the isolated fragments to the wave function that properly obeysthe Pauli principle through antisymmetrisation and renormalisation of product wave function Repulsive term (positive) comprises the destabilizing interactions between electrons of the same spin on either fragment
DEorb	Orbital interaction corresponding to charge transfer andpolarization effects

TrB-10	
The Nature of Triel Bonds, a Case of B and Al Centres Bonded with Electron Rich Sites	Molecules, 25(2020) 2703 doi:10.3390/molecules25112703
Sławomir J. Grabowski	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond		

KeyLrn_Bits	electron charge shifts, chemical reaction, octet rule, hypervalency, hydrogen bond, σ-hole bond, π-hole bond

TrB-11	
Hydrogen Bonds, σ-Hole and π-Hole Bonds – Mechanisms Protecting Doublet and Octet Electron Structures	Physical Chemistry Chemical Physics, 19 (2017) 29742-29759 DOI: 10.1039/C7CP06393H
Grabowski, S. J.	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond

LAcid	LBase
TrR3 Tr = B, Al, Ga; R = H, F, Cl, Br, CH3	pyrazine

Theory	MP2 CCSD(T)
Basis set	aug-cc-pVDZ
Software	Gaussian09
ESP	WFA-SAS program
BSSE	Corrected

Inter-orbital interactions and charge transfer	Natural Bond Orbitals NBO BLYP-D3(BJ)/def2TZVPP	GenNBO 5.0 version
Positions of bond paths and their corresponding bond critical points (BCPs)	AIM analysis	
	NCI (noncovalent index) procedure	MultiWFN VMD suite of programs
Morokuma-Ziegler Energy Decomposition Analysis	BLYP-D3/ZORA/TZ2P level	ADF [68-70] package

KeyLrn_Bits	electron charge shifts, chemical reaction, octet rule, hypervalency, hydrogen bond, σ-hole bond, π-hole bond

TrB-12	
Triel-Bonded Complexes between TrR3 (Tr = B, Al, Ga; R = H, F, Cl, Br, CH3) and pyrazine	Chemphyschem . 2018,19(22):3122-3133. doi: 10.1002/cphc.201800774
Mariusz Michalczyk, WiktorZierkiewicz, and Steve Scheiner	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond

LAcid
hydrides, fluorides, chlorides of 1,8 bis(dichloroboryl)naphthalene 1,2-bis(dichloroboryl)benzene

Theory	MP2
Basis set	Dunning style aug-cc-pVTZ
Software	Gaussian16

quantum theory of atoms in molecules (QTAIM) analysis
bond-critical points (BCPs)

	Laplacian of electron density at bond-critical point	Positive	Indicates covalent bonds
	Total electron energy density at BCP, HBCP	Negative	
	Electron density at the BCPs	~0.09 – 0.11 au	
	Delocalization index (DI)	Expresses covalent character of interaction	
KeyLrn_Bits	bifurcated triel bonds; trigonal and tetrahedral configurations; interaction energy		

TrB-13	
Bifurcated Triel Bonds—Hydrides and Halides of 1,2-Bis(Dichloroboryl)Benzene and 1,8-Bis(Dichloroboryl)Naphthalene	Crystals, 9 (2019)
Sławomir J. Grabowski	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond		
LAcid	**LBase**	**Tr Bond**
TrX3 X = 5-F, Cl, Br, I	NH3 N2 HCN	B…N

TrB-14	
Two Faces of Triel Bonds in Boron Trihalide Complexes	Journal of Computational Chemistry, (2017) DOI: 10.1002/jcc.25056
Sławomir J. Grabowski	

Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

Triel Bond		
KeyLrn_Bits	Rev ; Lewis acid–Lewis base interactions; hydrogen bond; tetrel bond; pnicogen bond; triel bond; electron charge shifts	

TrB-15	
Hydrogen Bond and Other Lewis Acid–Lewis Base Interactions as Preliminary Stages of Chemical Reactions	Molecules, 25(2020) 4668 doi:10.3390/molecules25204668
Sławomir J. Grabowski	

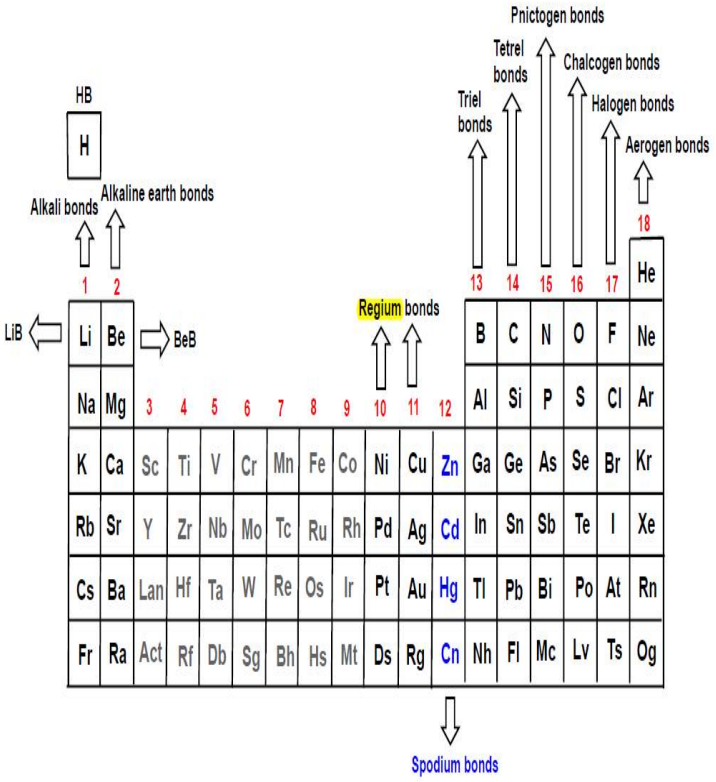
Triel bond-- Non Covalent--σ-π-holes-positive -- Lewis Acid Base interaction

II. Object oriented terminology (OOT) for Triel-bonds

column $	Abbrev	$$ Bonds
18G	NgB	Nobel gas
17G @	HaB	Halogen
16G @	ChB	Chalcogen
15G	PnB	Pnicogen or Pnictogen
14G	TTb	Tetrel
13G	TrB	Triel
12G	SPb	Spodium
11G	CiB or Rg	Regium or Coinage
1G	HB	Hydrogen

@ IUPAC recommened

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



Triel bond

triel Atom	Abbreviation	Tr At	triel atom
		Tr E	triel element (or energy)
	Atoms (or chemical elements) of Group 13 in 18 Column-Periodic table [[B, Al,] []]		
	The triel trivalent centres are categorized as hypovalent ones since they have deficiency of electrons in relation to the octet rule		
triel bonds	Abbreviation	TrB	
	The distribution of electron density between trielcentre and the electron pair of Lewis-base is called Triel bond		
	Generally classified as π-hole bonds Fits well in the concept of π -holes or σ-hole		

	A bond is a model	
	Represented with three dots as Tr…B; Ex: B…N; Al…O etc. just like a single dash (C-H) for covalent bond	
	Result of interactions of trielcentre (π -holes or σ-hole) with electron rich site of a Lewis base	
Types of triel bonds	Tr. . .B	mono-atomic Lewis base centre
	Tr. . . π	p-electrons
	Tr. . . σ	r-electrons

Interaction of Group 13 atom centres with Lewis's base	Result in stable octet structure 📖 Interactions are usually very strong → 📖 Possess numerous characteristics of covalent bonds → 📖 Sometimes classified as typical covalent bonds
Historic perspective of interaction of 13th Group elements	Before introduction of the word triel for Group 13 atoms, the complexes were called Lewis acid−base complex or a partially covalent complex Reason: binding distance is much shorter than the sum of the van der Waals radius of the atoms.

	TrB affected by
Cooperativity in TrB	TrB exhibits cooperativity with itself and other types of interactions.
Lewis bases	A weak electron donor T−H in TH(CH3)3 (T = Si, Ge, and Sn) engages in a stronger TrB bond with BH3 (>−28 kcal/mol), resulting in hydrogen transfer from the T atom to the B atom.
Substituents	Substituents affect the strength, properties, and nature of triel element interactions with Lewis bases Methyl group ➔ For the triel−hydride triel bond between o TrR3 (Tr = B and Al); R = (H and CH3) + o TtHMe3 (Tt = Si, Ge, and Sn), ▪ methyl group in triel donor molecule is electron-donating ▪ decreasing the π-hole electrostatic potential on triel atom, ➔ Weakens TrB, particularly for the B atom ➔ In contrast, the methyl substituent in the Lewis base has an enhancing effect on the TrB **F atom** ➔ The electron-withdrawing F atom in the triel donor molecule strengthens the TrB, ➔ Opposite effect is found for the electron-withdrawing F-substitution in the Lewis base ➔ BF3 has the smaller π-hole than BH3, o Former forms a stronger TrB with NH3 than the latter.

Hybridization	➔ Hybridization impose influence on the strength of NCIs
	➔ The C hybridization of the C−H bond increases its proton acidity o sp3 < sp2 <sp sequence, → ➔ Results in a stronger C−H···O hydrogen bond ➔ It also happens for TrB, if the triel atom is adjoined with different hybridized carbon atoms

σ-hole	
Def	✓ It is the region on an atom with positive ESP ← arises from an anisotropic electronic density (a physical observable) ✓ typically located along the vector of a covalent bond
	σ-hole is a real physical entity
	It is defined in terms of a partially empty σ* orbital
Uses	To visualize the interaction
Theoretical support from	Natural bond orbital analyses
Examples	Tr atoms in chemical species (moieties) Ex: Borabenzene; BX_3; Tr_2H_6;
Interaction energy	The interaction energy of σ-hole TrB in Al2H6−NH3 (−24.88 kcal/mol) << π-hole TrB in AlH3−NH3 (−32.77 kcal/mol)

π -hole	
Def	✓ It is the region with positive ESP on an atom ✓ The region is perpendicular to a portion of a molecular framewor
Size	🕮 Larger is the size of π-hole, heavier is the triel atom

	σ-hole → π-hole
Interconversion in Tr-interactions	π-hole and σ-hole on the triel atom can interconvert into each other.

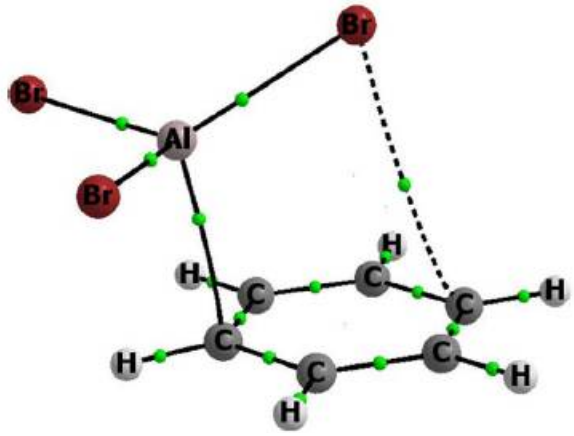
Supplementary Information
Molecular structures Triel--bonded chemical species

Sup Inf 1. Triel bonded Chemical species

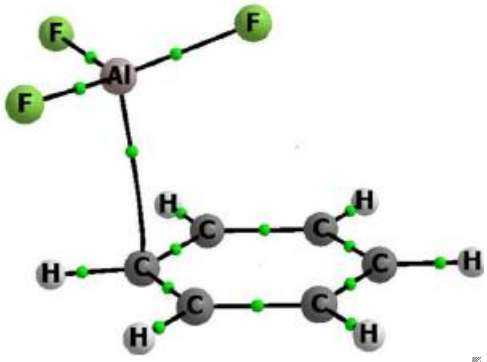
LA and LB → (SR)-A...B-(RS)

Triel Bond TrB-08

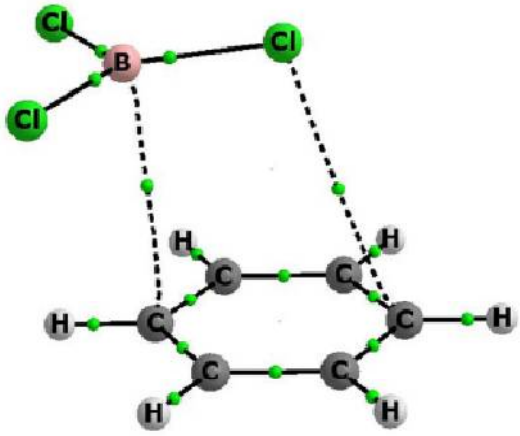
AlBr3-C6H6



AlCl3-C6H6

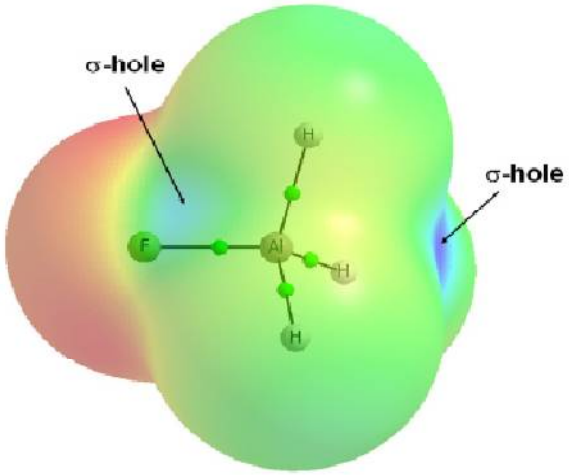


BCl3-C6H6,

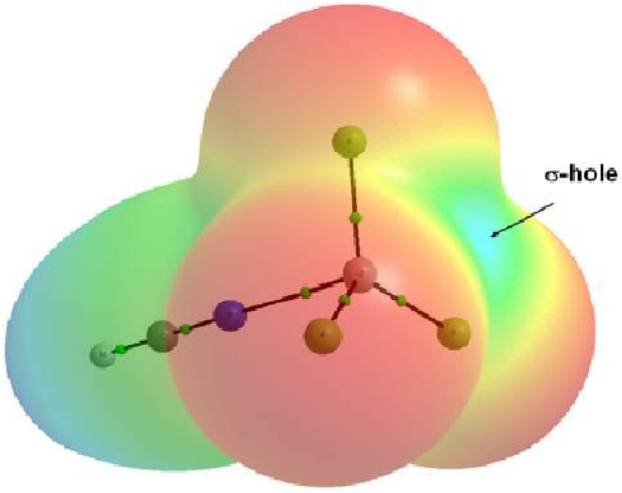


$[AlFH_3]^-$

H3Al...F Triel bond

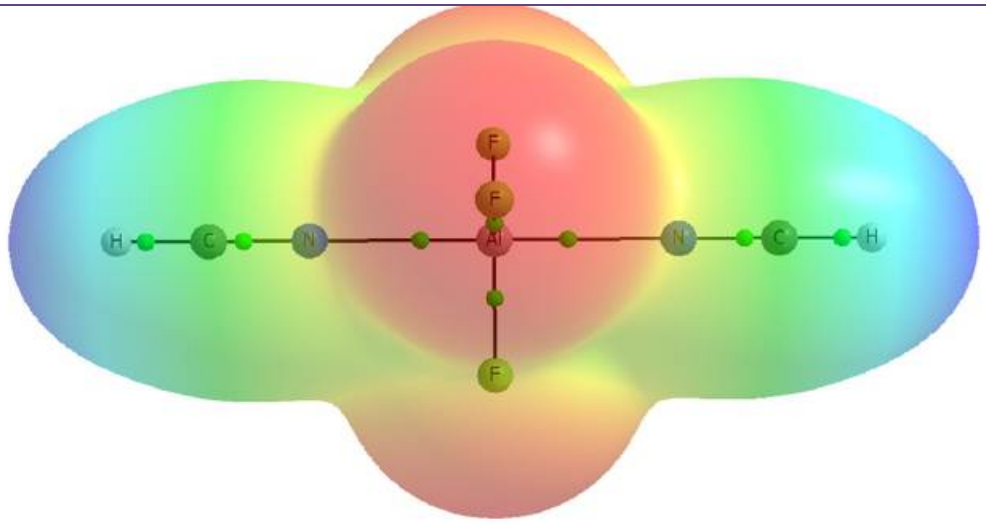


AlF3...NCH Triel bond



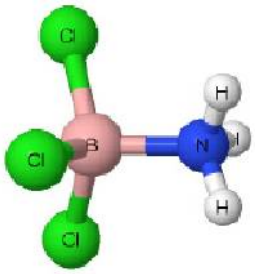
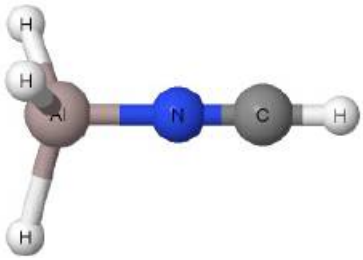
MP2/aug-cc-pVTZ level

AlF3...(NCH)2 Triel bond

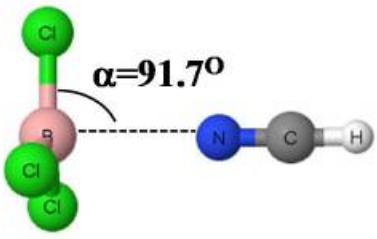
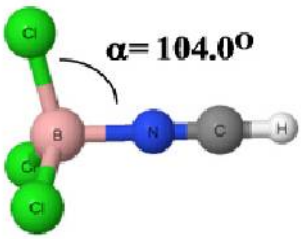
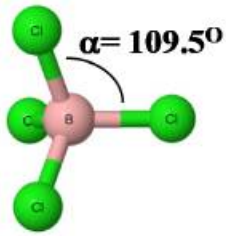


MP2/aug-cc-pVTZ level

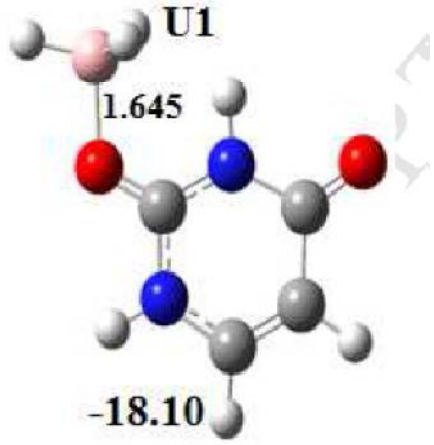
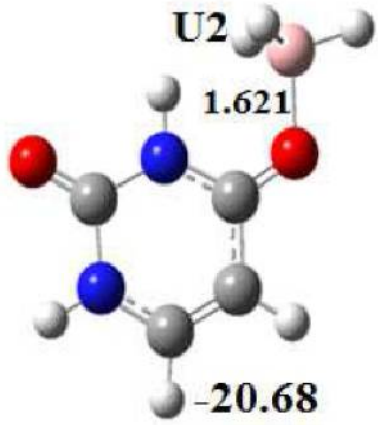
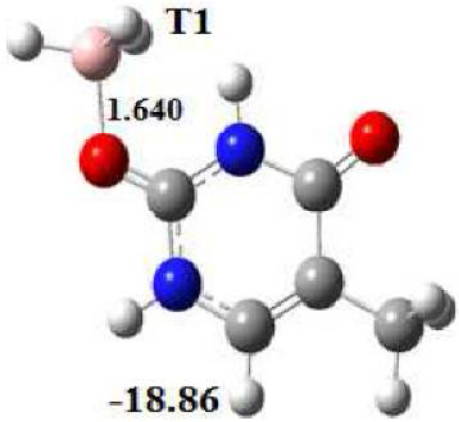
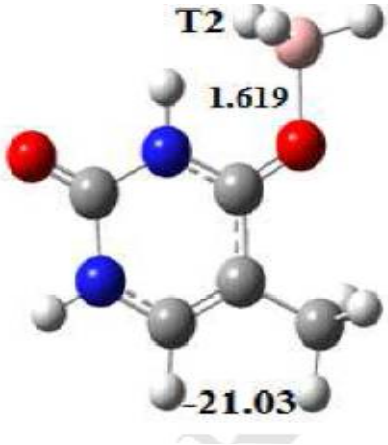
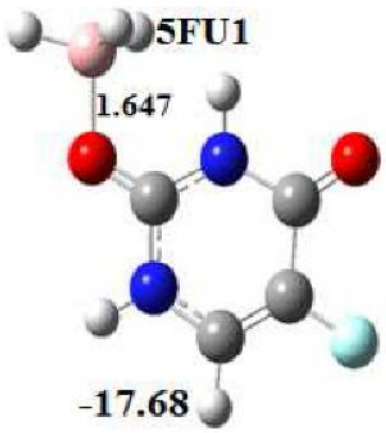
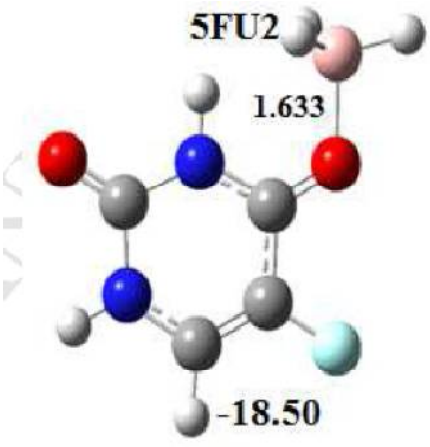
TrB-10

Cl3B...NH3 Triel bond	H3Al...NCH Triel bond
	

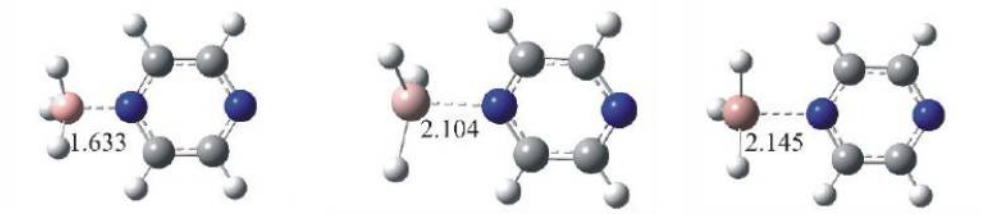
α-angle;

BCl3...NCH with longer B...N distance	BCl3...NCH with shorter B...N distance	$[BCl_4]^-$ species
		

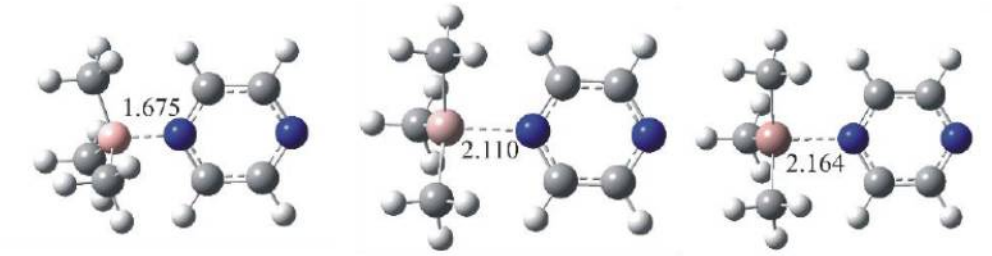
Bond length & ENergy

BH3 +U → H3-B...U1 (TrBond)	BH3 +U → H3-B...U2 (TrBond)
	
	
	

BH_3•••pyrazine AlH_3•••pyrazine GaH_3•••pyrazine



$B(CH_3)_3$•••pyrazine $Al(CH_3)_3$•••pyrazine $Ga(CH_3)_3$•••pyrazine

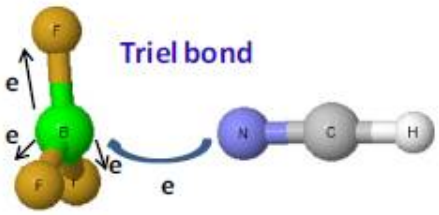


BF3 + HCN → F3-B ... N-CH | **Triel Bond** | TrB-02

A-T...B

$n_B \rightarrow \sigma_{AT}^*$

$n_B \rightarrow n_T^*$



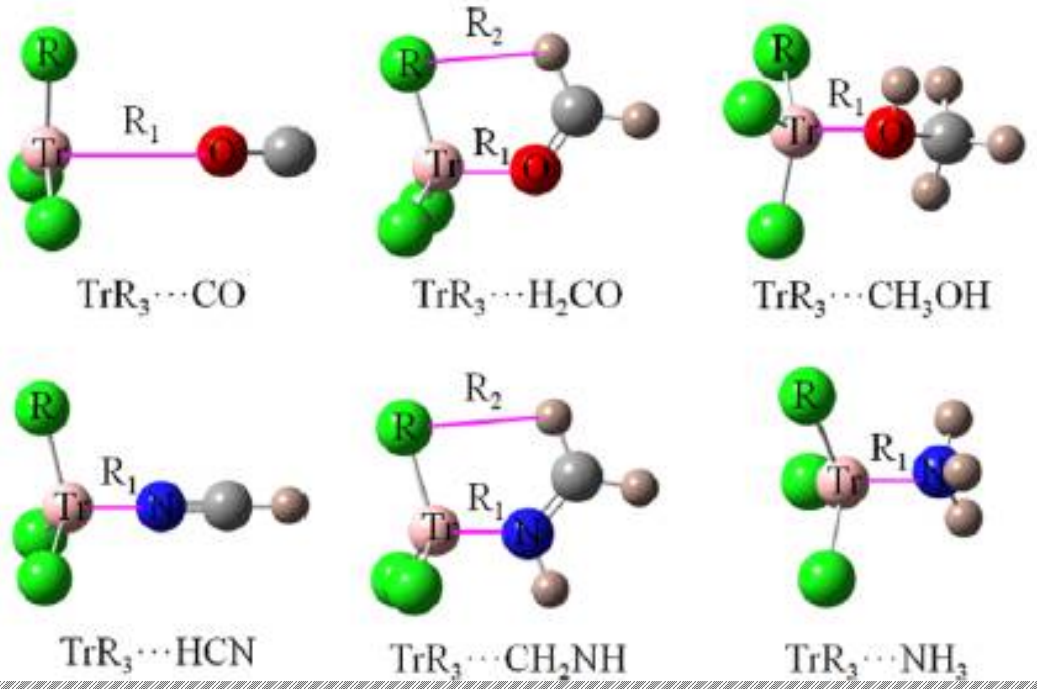
F-B...N

$n_N \rightarrow n_B^*$

FCl + NH3 → F-Cl ... N-H3

Opt Geometry –Triel complex

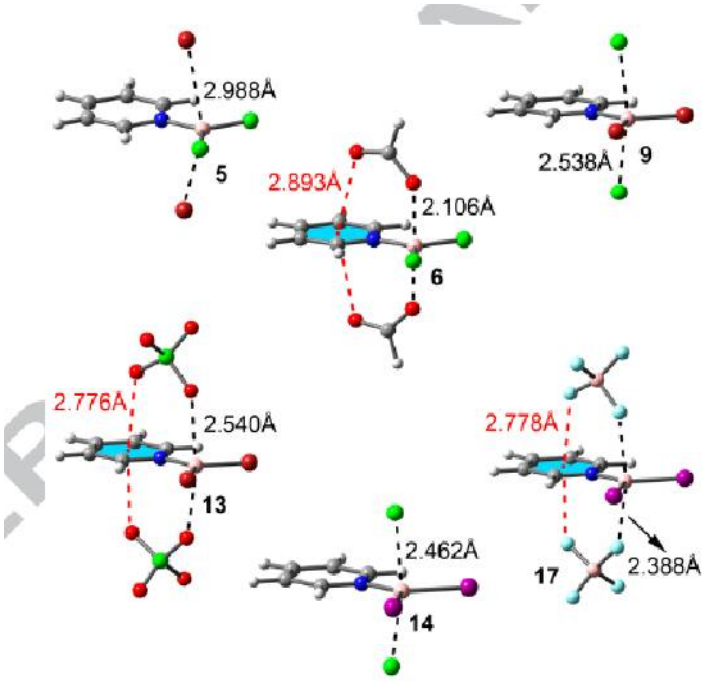
TrB-06-SI



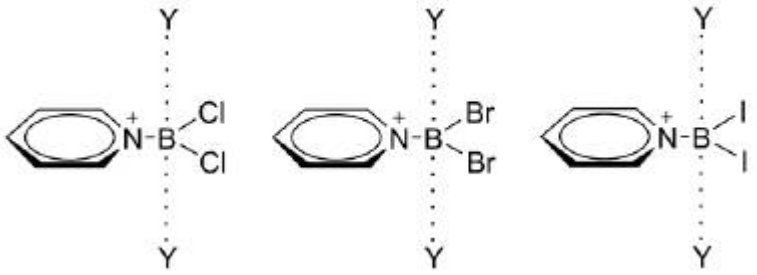
Bond length Py^+BX_2...

M06-2X/def2-QZVPD

TrB-04



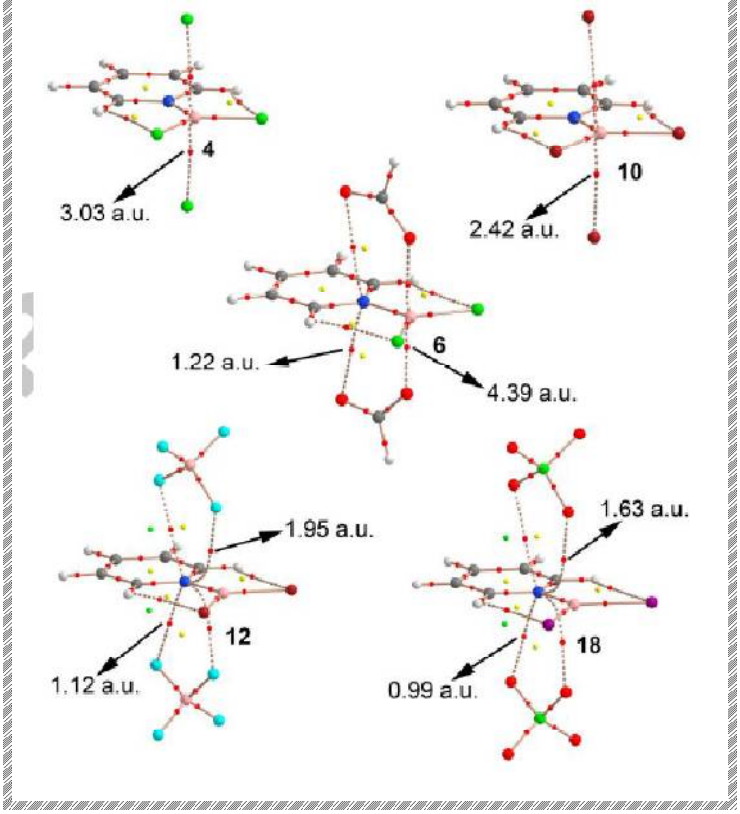
Molecules



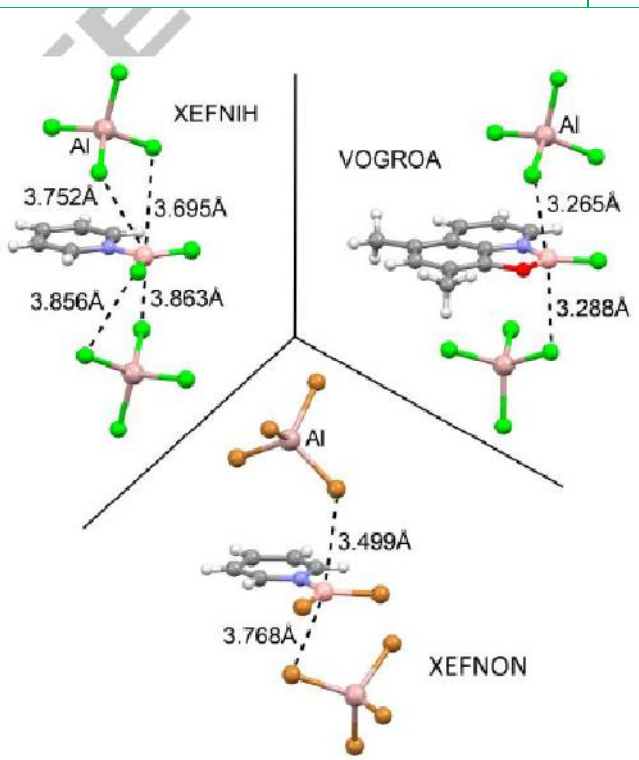
4, Y = Cl^-	**9**, Y = Cl^-	**14**, Y = Cl^-
5, Y = Br^-	**10**, Y = Br^-	**15**, Y = Br^-
6, Y = HCO_2^-	**11**, Y = HCO_2^-	**16**, Y = HCO_2^-
7, Y = BF_4^-	**12**, Y = BF_4^-	**17**, Y = BF_4^-
8, Y = ClO_4^-	**13**, Y = ClO_4^-	**18**, Y = ClO_4^-

Distribution of critical points and bond paths for complexes

TrB-04

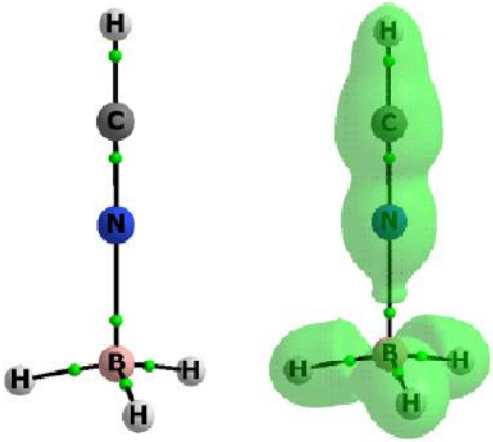


CSD Database-- solid state chemistry	TrB-04

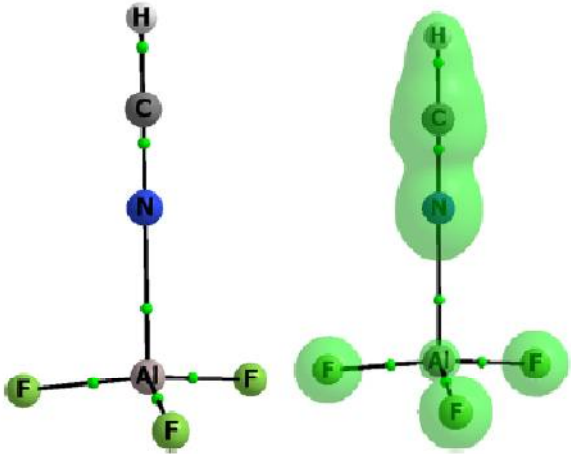


Reactive surfaces	TrB-08

BH3-NCH



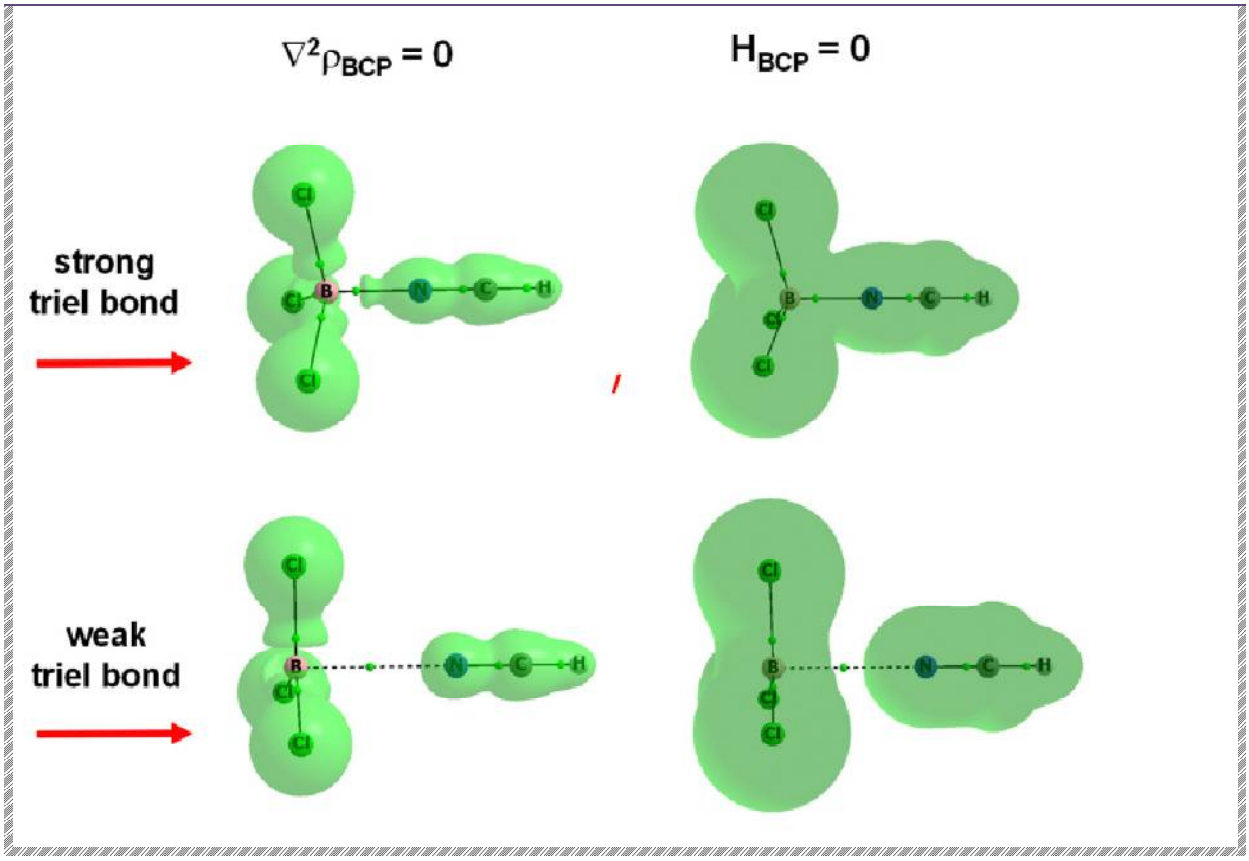
AlF3-NCH

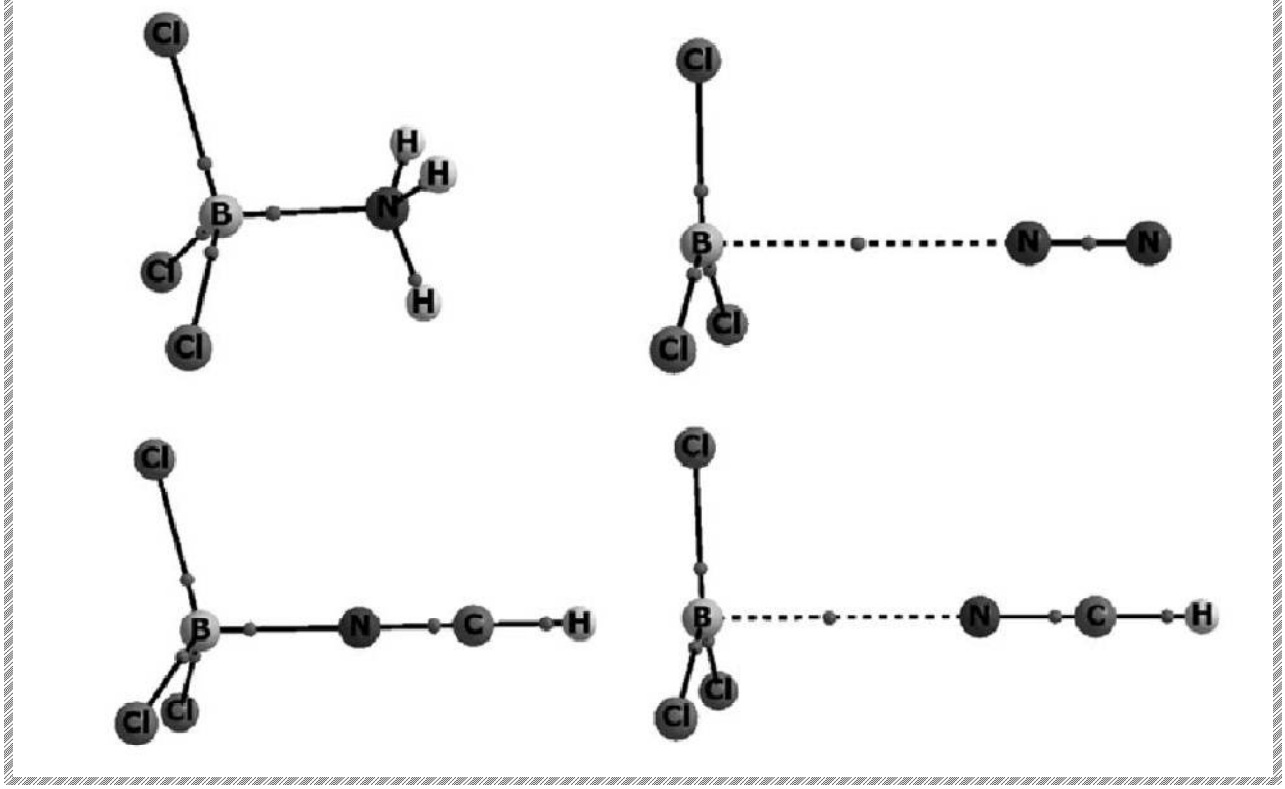


Green reactive surfaces characterize ($\nabla^2\rho < 0$) (electron charge concentration)
Solid lines : bond paths
Big circles : atomic attractors
Small circles :bond critical points

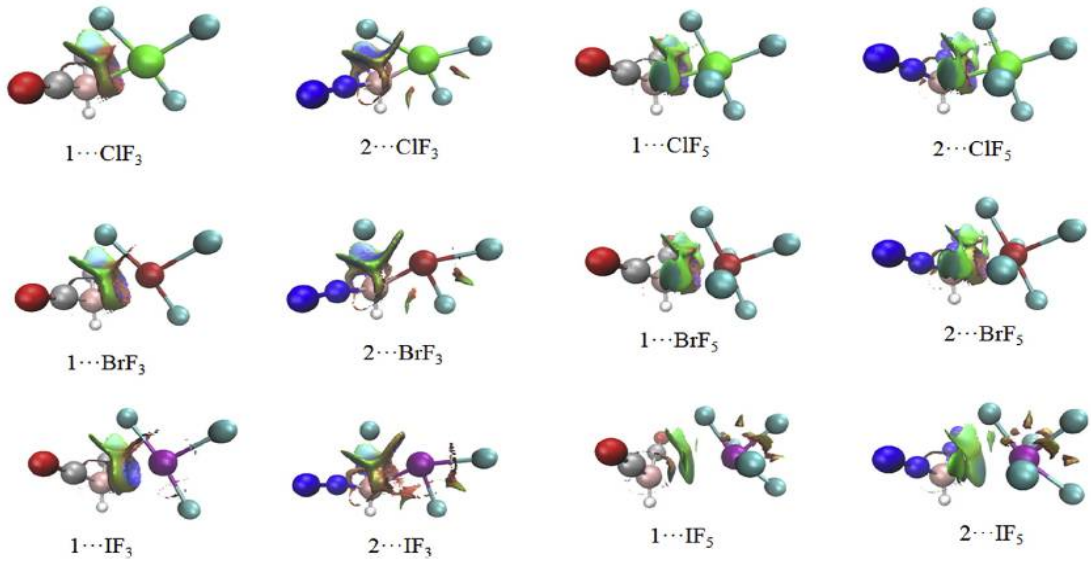
Reactive surfaces	MP2/aug-cc-pVTZ	TrB-09

Two conformations of the Cl_3B...NCH

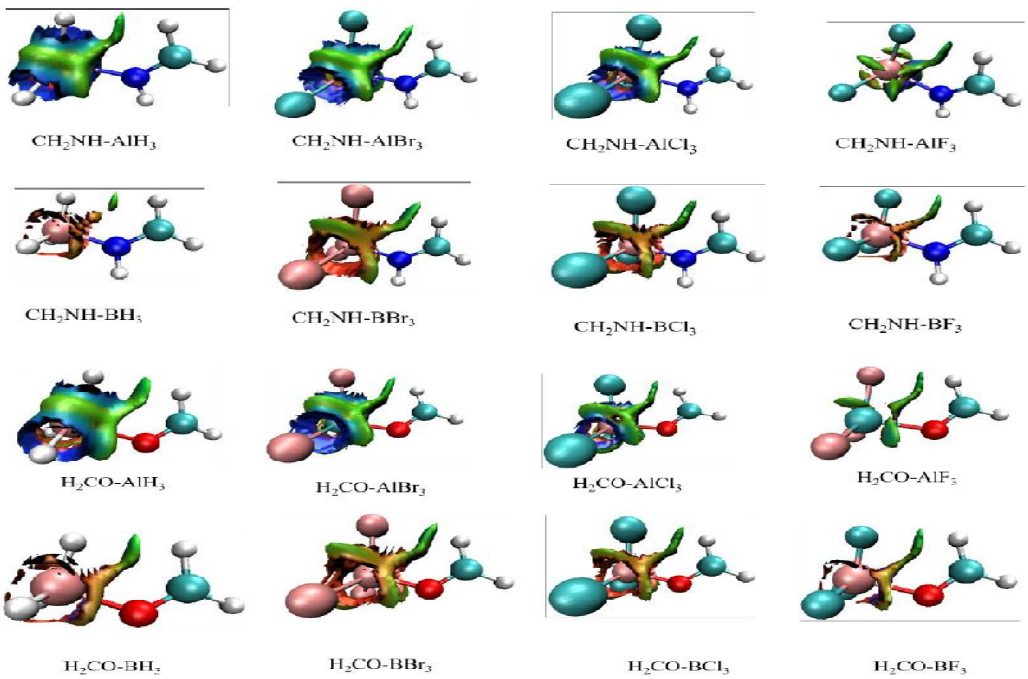

$\nabla^2\rho_{BCP} = 0$
$H_{BCP} = 0$
strong
triel bond
weak
triel bond



NCI maps of a Complexes



Blue: strong attractive interactions	Red: strong nonbonded overlap
Orange: moderate attractive interactions	Green: weak attractive interactions



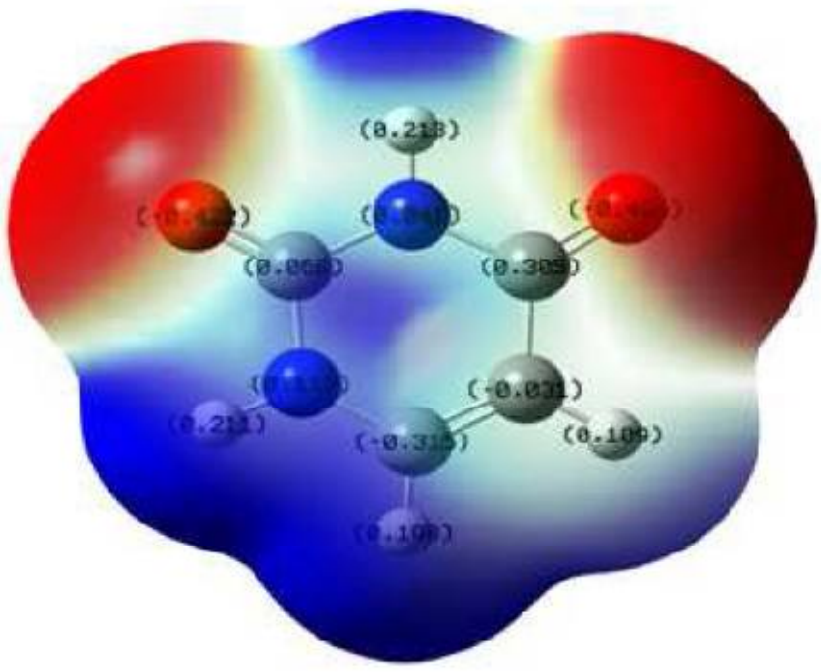
Sup Inf 2.1: Positive ESP sphere in a single atom

ESP	Be	TrB-09

positive EP sphere

Atomic Charges (based on ESP) of a molecule

ESP charges	uracil

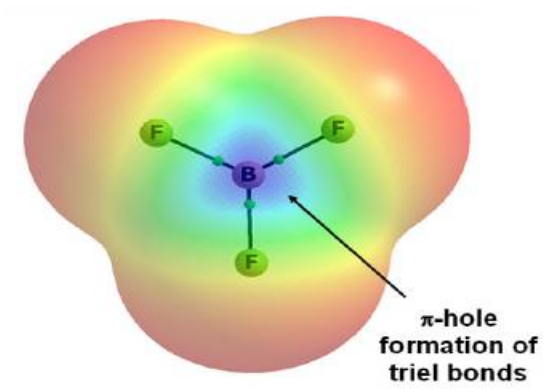


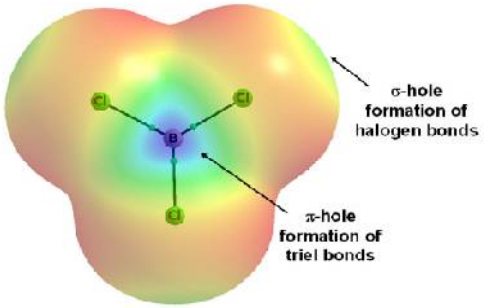
Electrostatic potential (± 31 kcal/mol)

Sup Inf 2.2: ESP contours in molecules

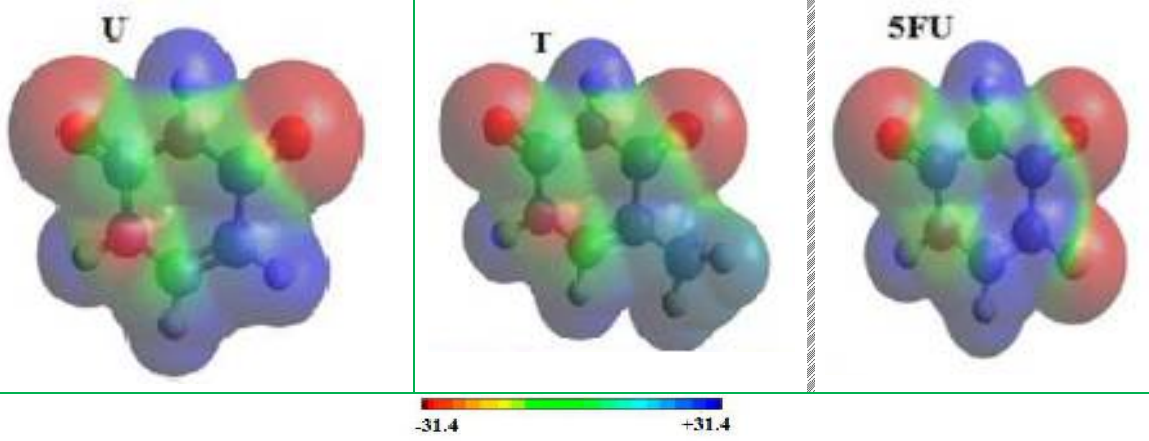
ESP TrB-09

Triel (B) atom	*Triel (B) atom; X(Cl) atoms*
BF3	**BCl3**

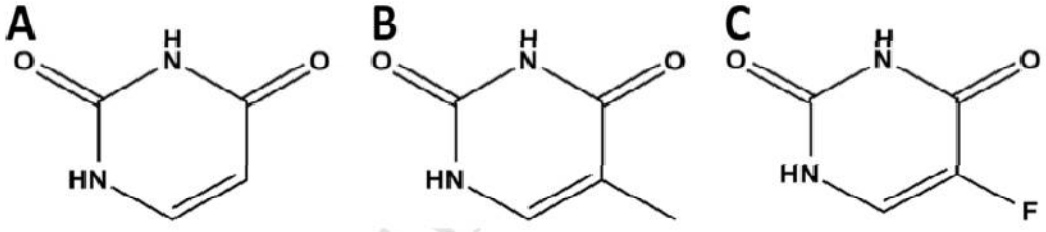


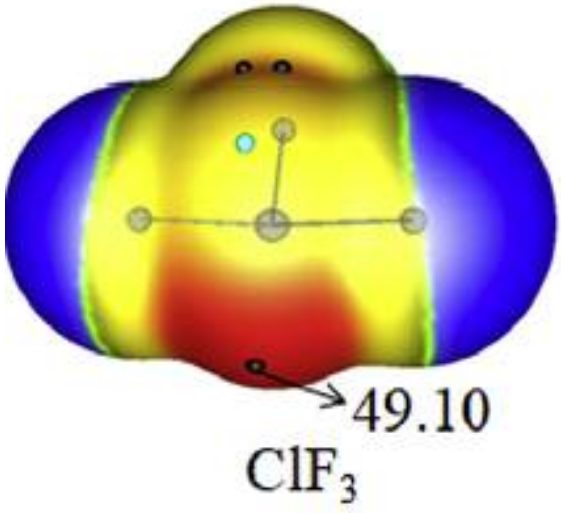


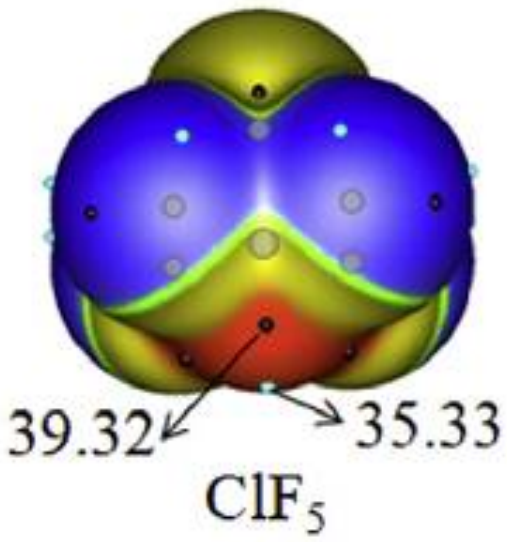
TrB-01

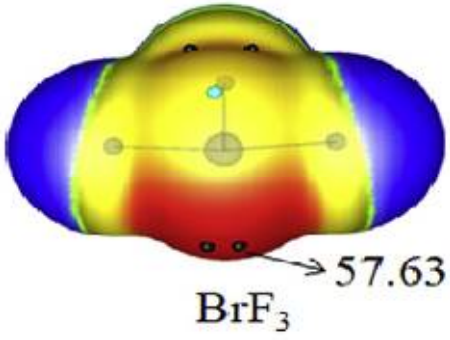


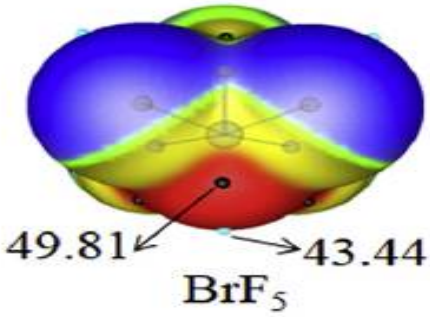
Structures of (A) Uracil, (B) Thymine, and (C) 5-fluorouracil

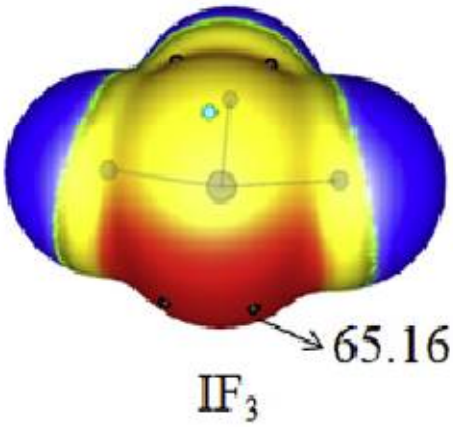


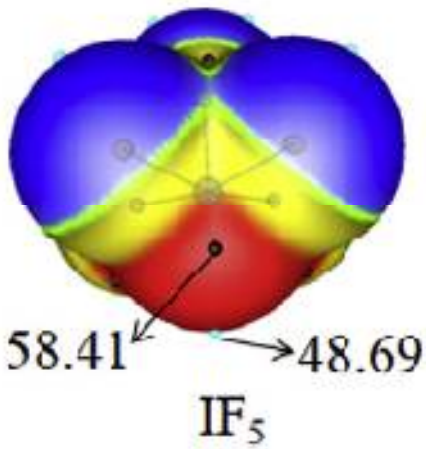




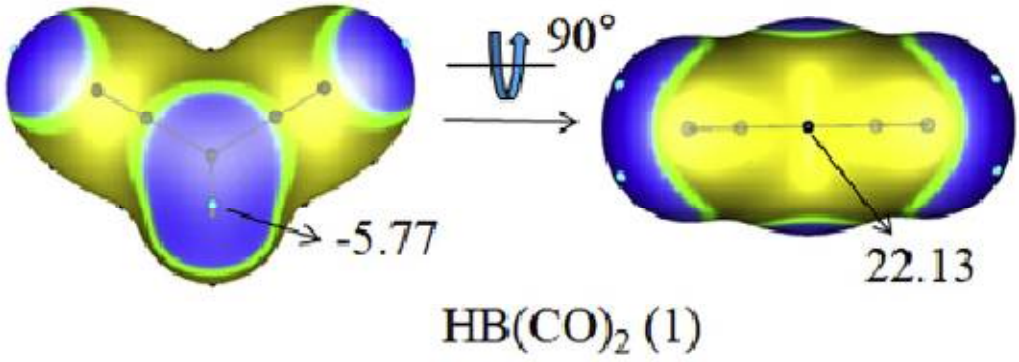




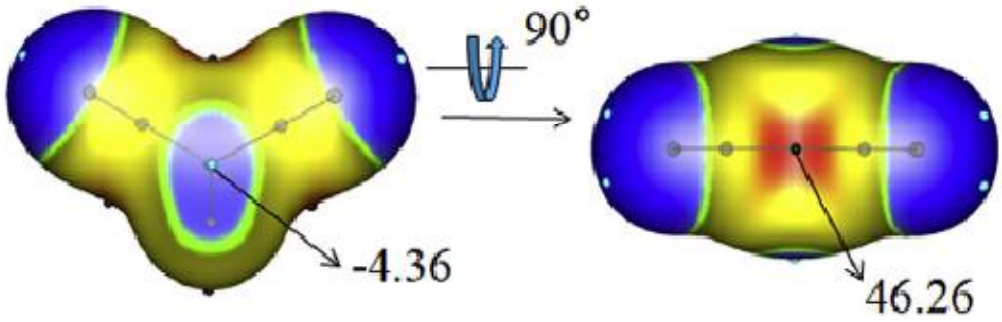




Color ranges in kcal/mol ; red, greater than 31; yellow, between 31 and 2; green, between 2 and 0, blue, less than zero.



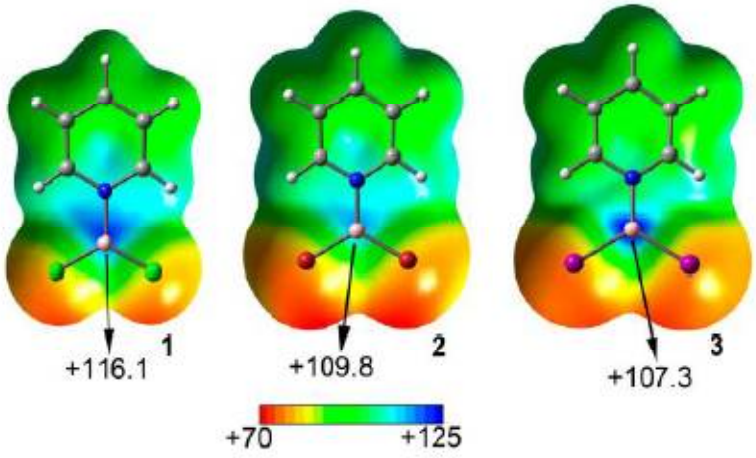
$HB(CO)_2$ (1)



$HB(NN)_2$ (2)

ESP | Py^+BX_2 (X=Cl, Br and I) | TrB-04

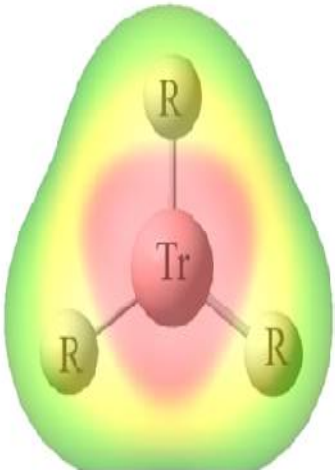
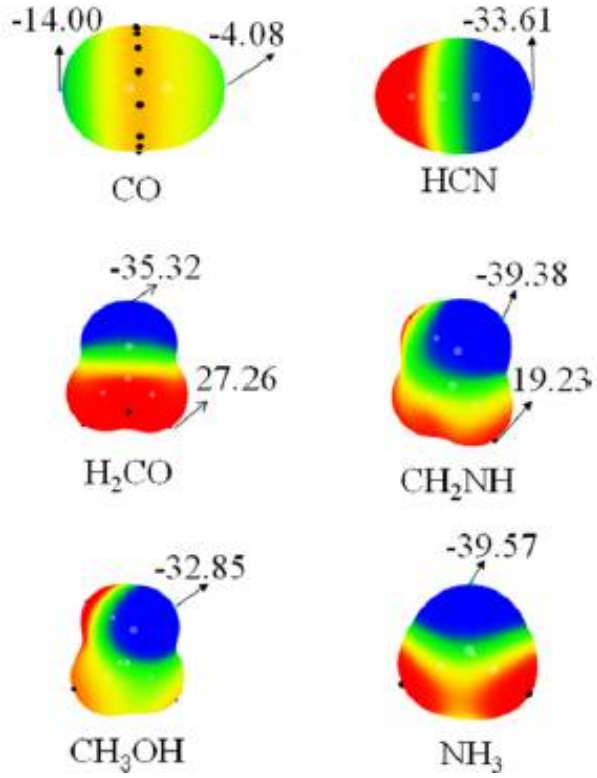
1-(dihaloboranyl)pyridin-1-ium compounds (triel bond donors LA

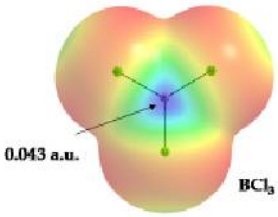
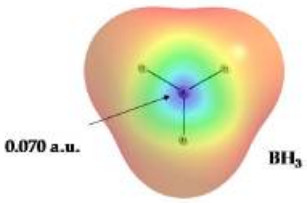


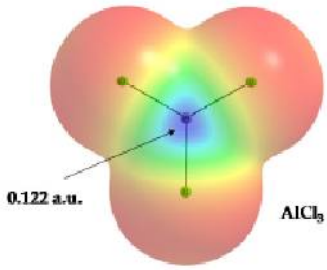
1, X = Cl
2, X = Br
3, X = I

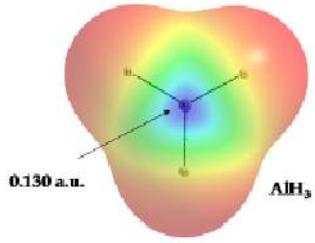
Electron rich molecules

Cl^-, Br^-, HCO_2^-, BF_4^-, ClO_4^-

ESP	TrB-06
TrR3 (Tr = B, Al; R = H, F, Cl, Br)	Electron donors (Lewis bases)
	

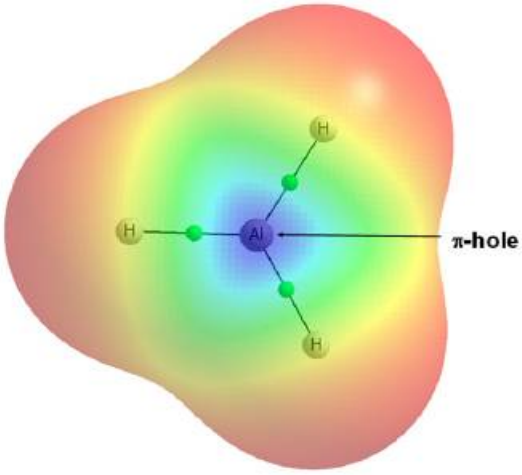
ESP	TrB-10
	



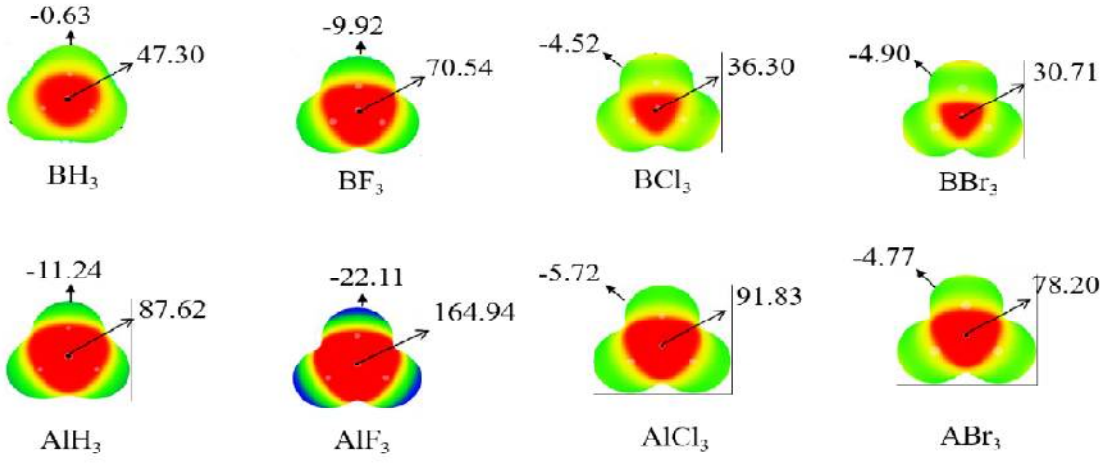


ESP TRb-09

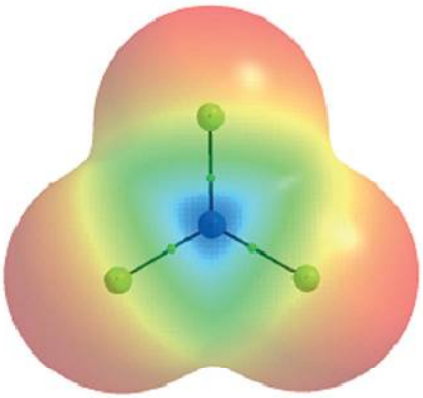
[AlH_3]

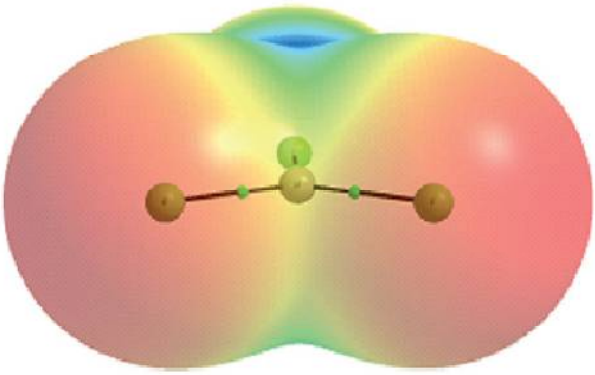


ESP TrX3 TrB-06-SI



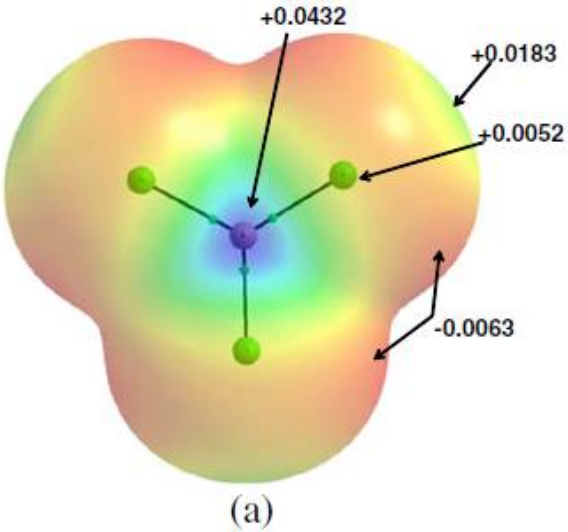
ESP	AlF3	two orientations	TrB-07



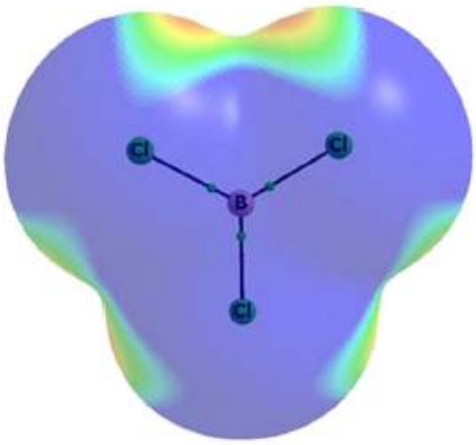


ESP	TrB-08

BCl3

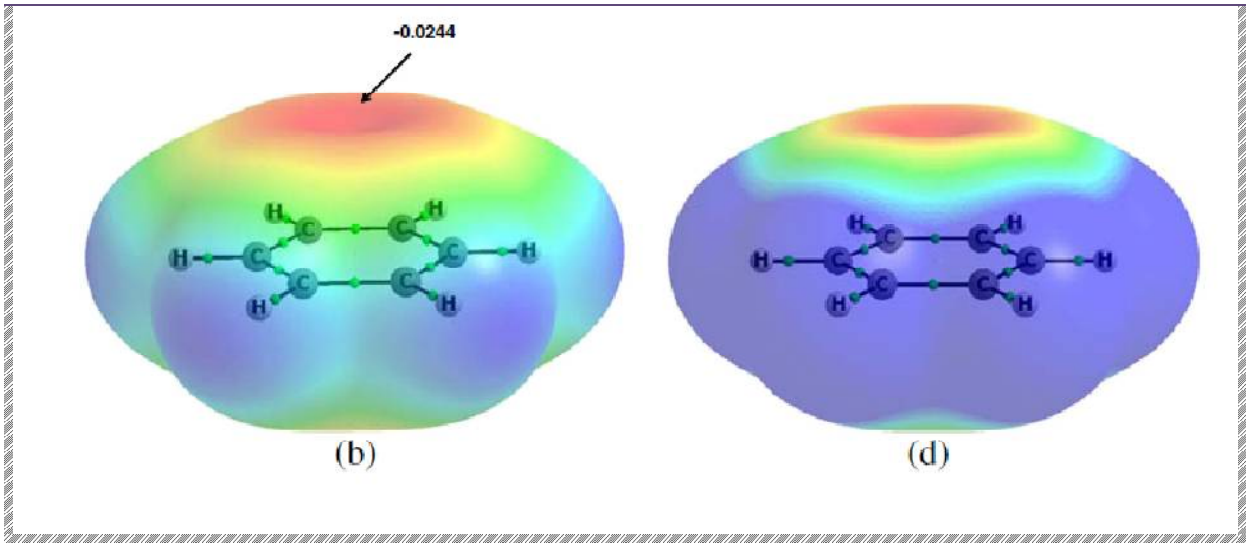


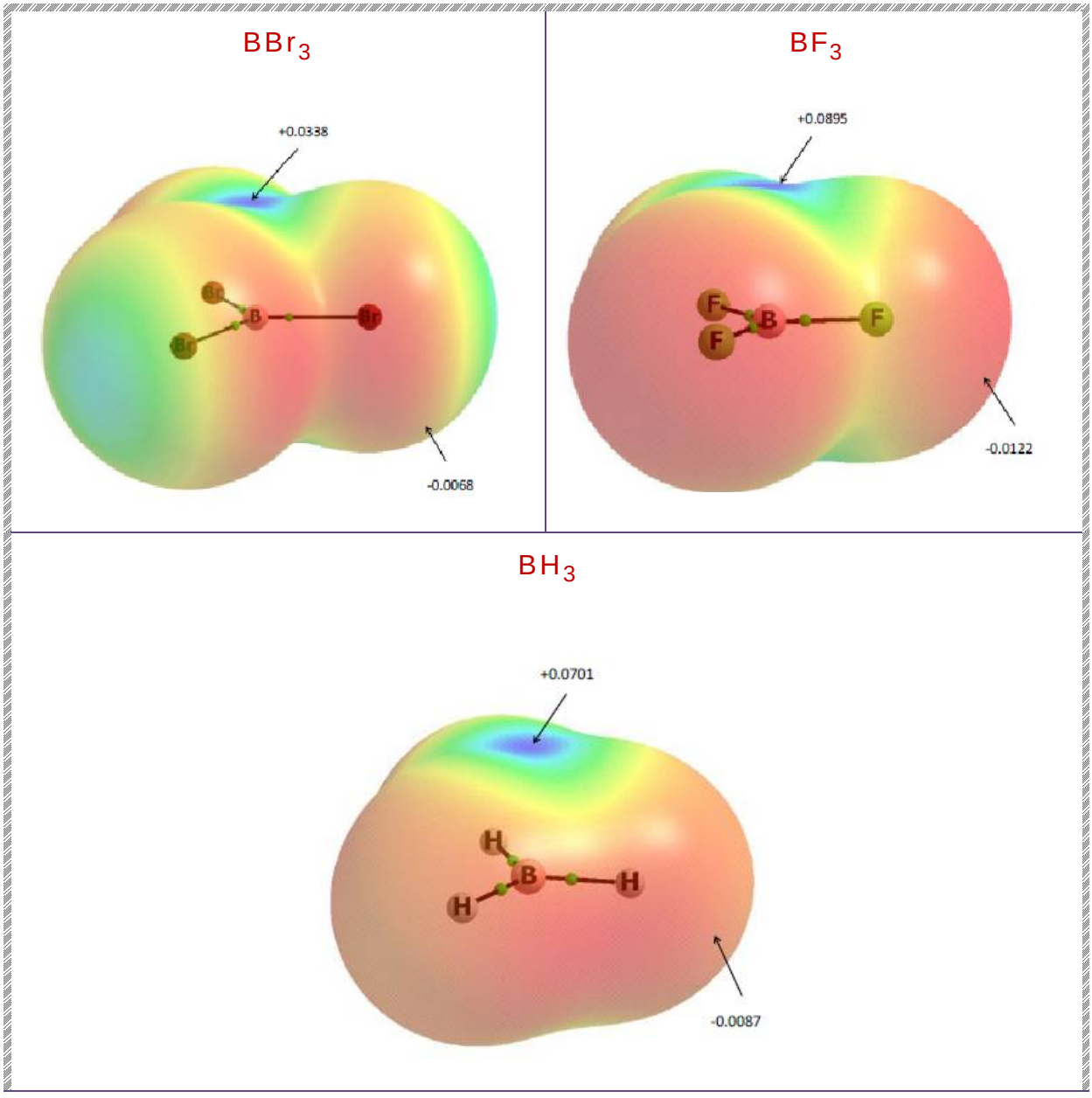
(a)



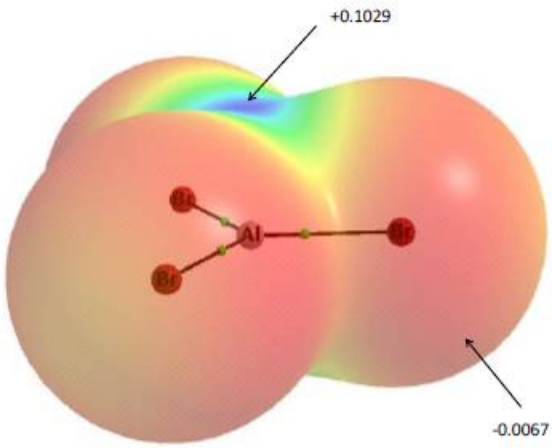
(c)

benzene

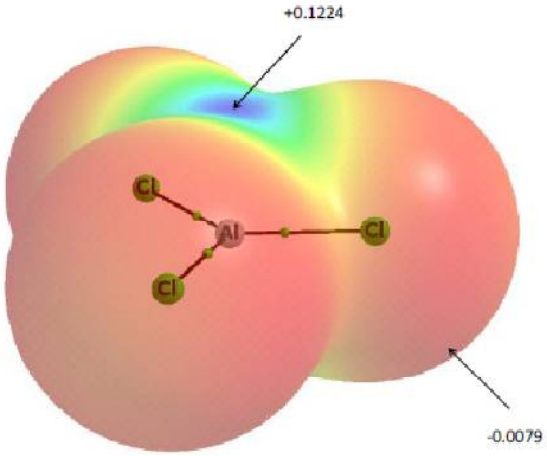

-0.0244
(b)
(d)


BBr_3
+0.0338
-0.0068
BF_3
+0.0895
-0.0122
BH_3
+0.0701
-0.0087

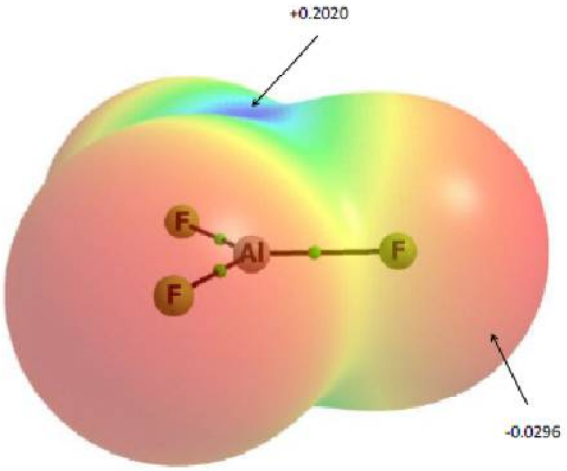
AlBr3



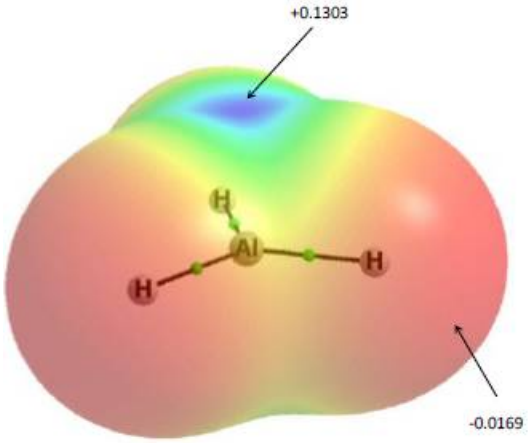
AlCl3



AlF3



AlH3

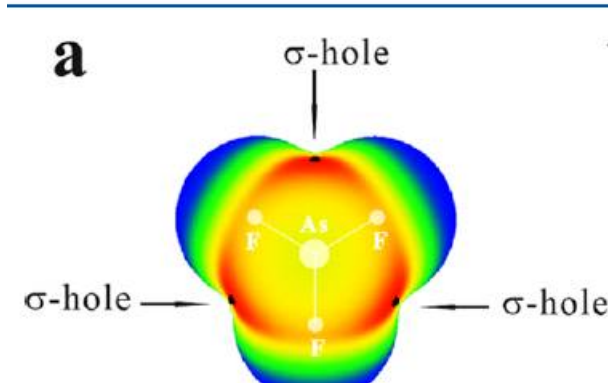


Sup Inf 2.3: σ-hole in Single Molecules

σ-holes	Π-hole	MP2/ccpVDZ

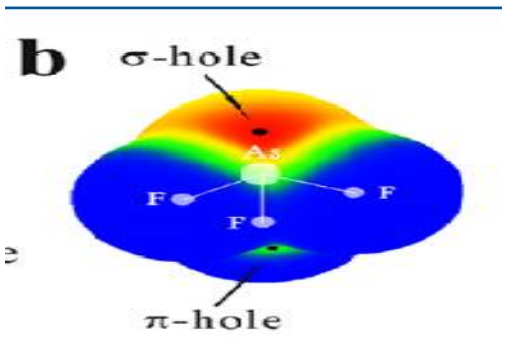
AsF3

(a) top view



AsF3

(b) bottom view

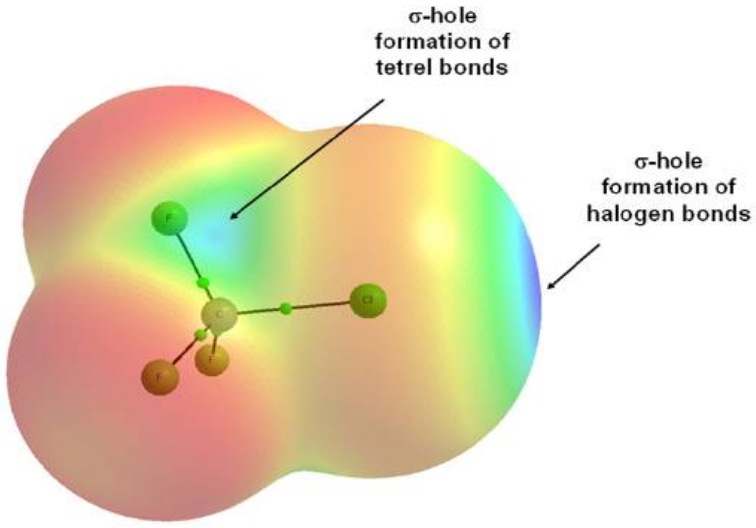


red > 35 (+ve)	blue < 0(-ve)	green [0 to 15];	yellow [15 to 35];

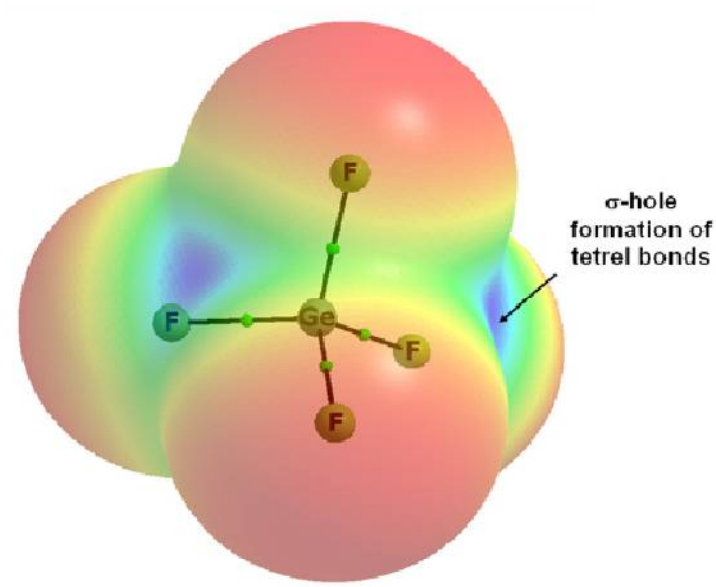
How Many Pnicogen Bonds can be Formed to a Central Atom Simultaneously?
Ref: Rafał Wysokiński, Wiktor Zierkiewicz, Mariusz Michalczyk, and Steve Scheiner, J. Phys. Chem. A 2020, 124, 10, 2046-2056; https://dx.doi.org/10.1021/acs.jpca.0c00257

ESP	MP2/Aug-cc-pVTZ	TrB-09

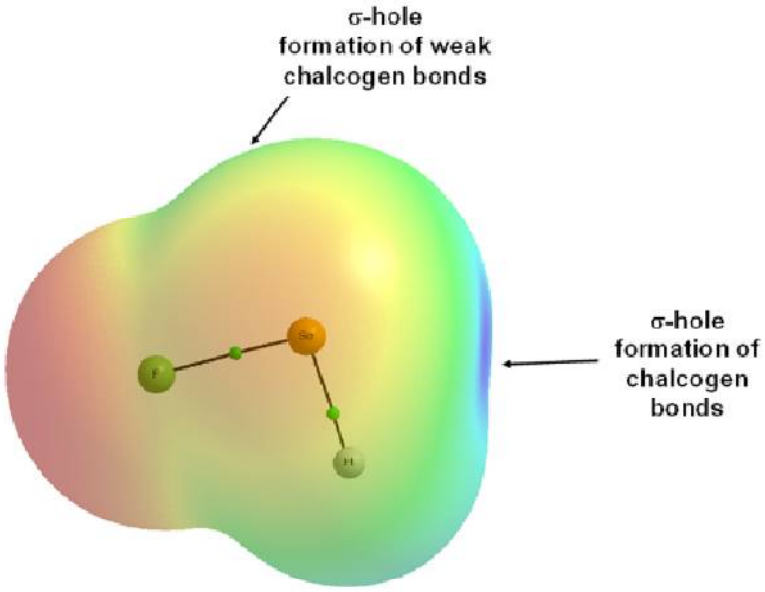
F3CCl



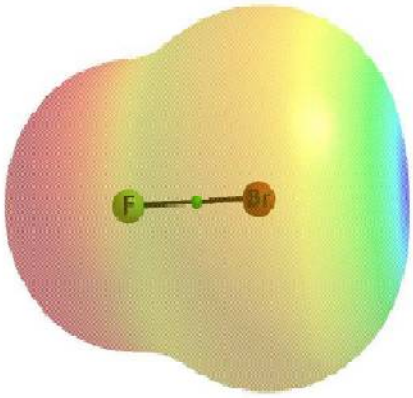
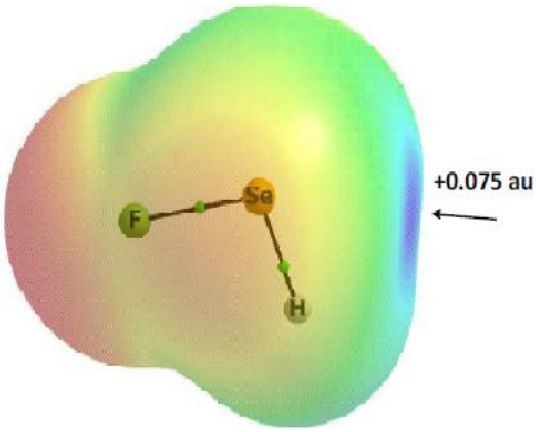
GeF4

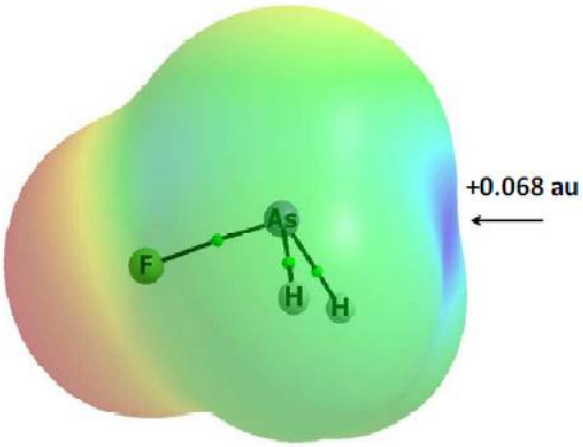
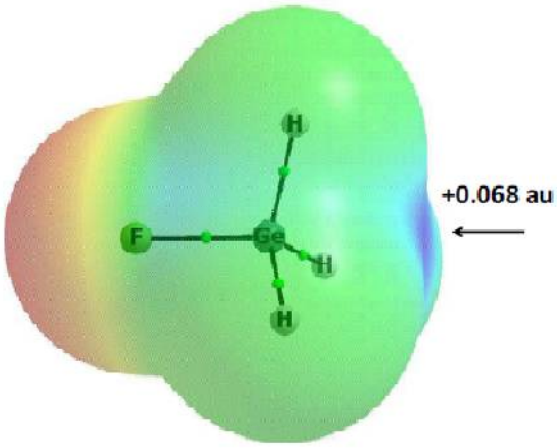


SeFH



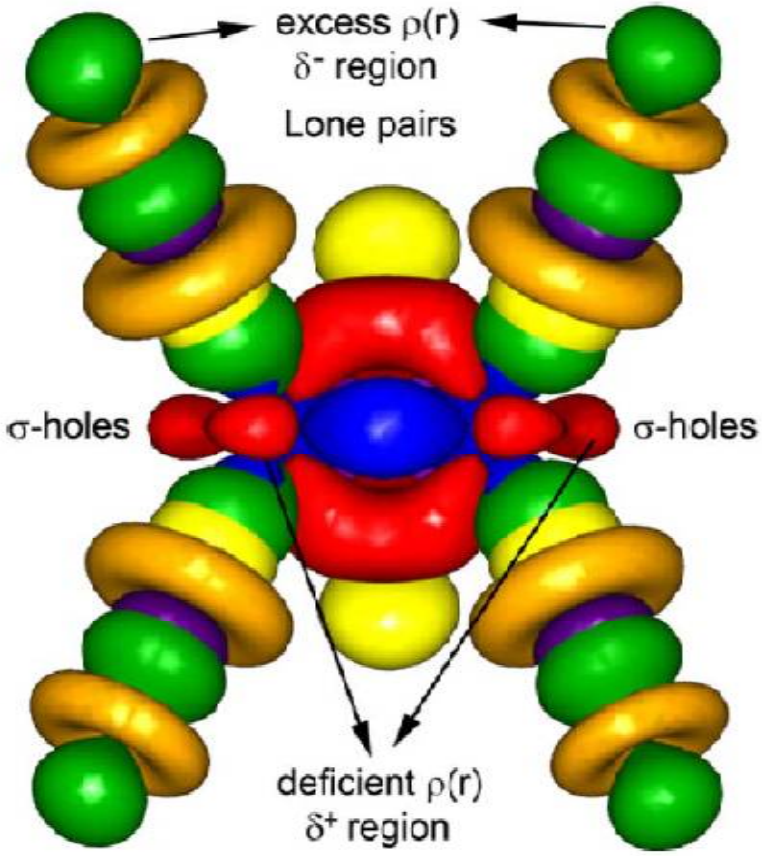
maximum positive EP (blue); minimum negative EP (red)

ESP	σ-holes	TrB-11
		

1,1,2,2-tetracyanocyclopropane (TCCP)

octupoles, quadrupoles, and dipoles



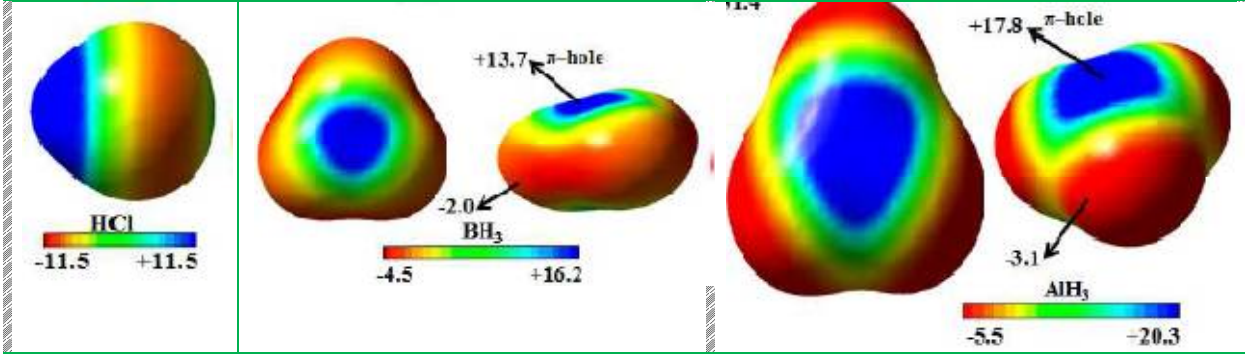
Blue, green, and violet indicate positive (electron excess, δ^-),

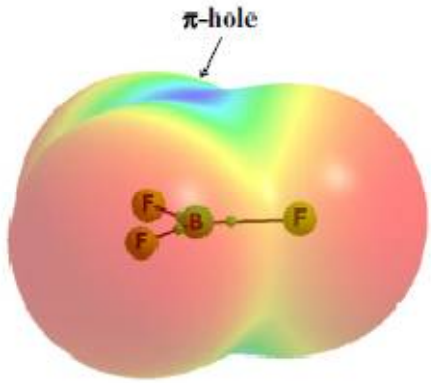
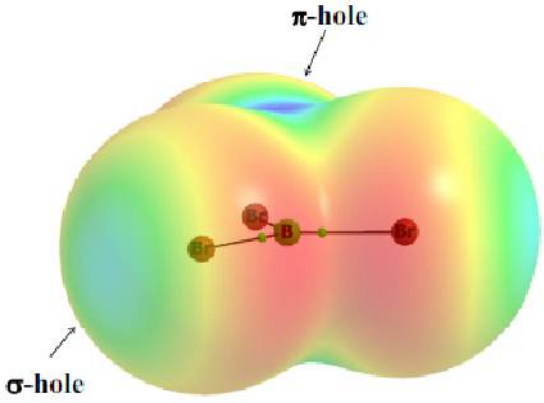
red, orange, and yellow indicate negative (electron deficiency, δ^+)

Sup Inf 3: π-hole in a molecule

B, Al

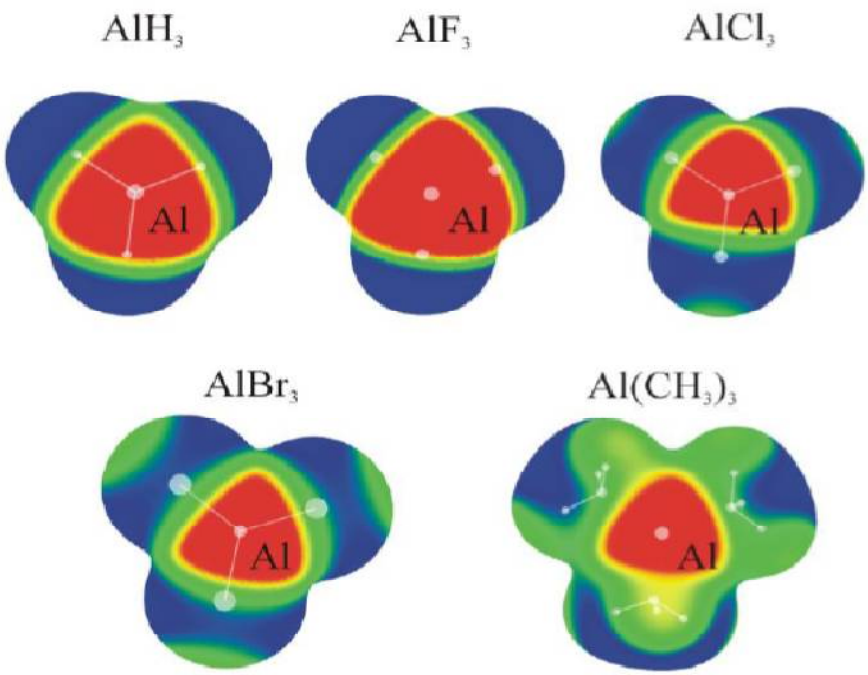
TrB-01

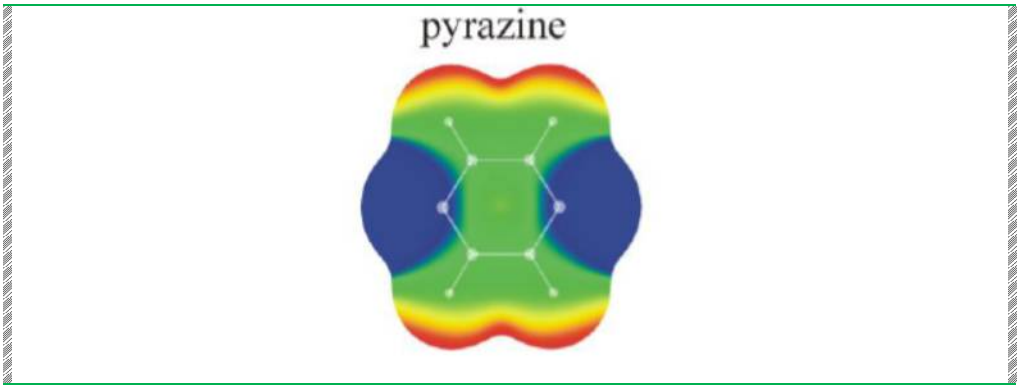


BF3	BBr3
	

Symbol (graphic)	Correspond to
Solid lines	Bond paths
Big circles	Atomic attractors
Small circles	Bond critical points
Blue	+ve π
Red	-ve σ

π-hole donors	AlR_3 (R = H, F, Cl, Br, CH_3)	MP2/aug-cc-pVDZ	TrB-12
blue below 0 kcal/mol		red greater than 15	





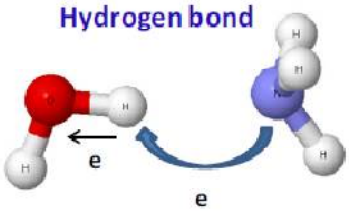
Sup Inf 4: *H bond*

H2O + NH3 → HO-H ... N-H3

Type of interaction (up)
Orbital-orbital overlap (below)

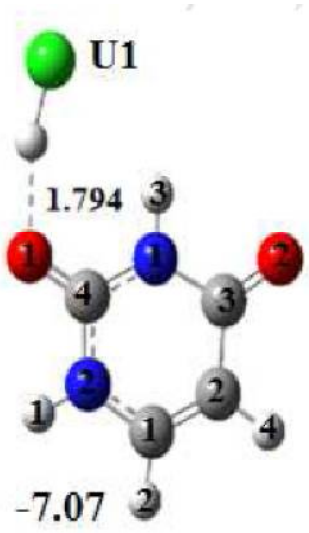
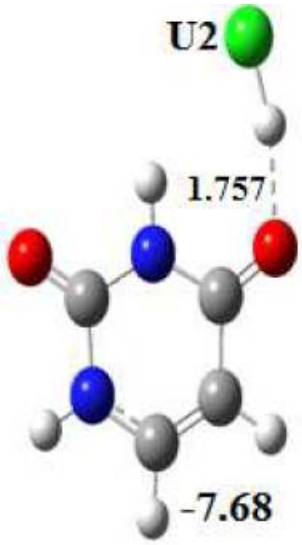
A-H...B
$n_B \rightarrow \sigma_{AH}^*$

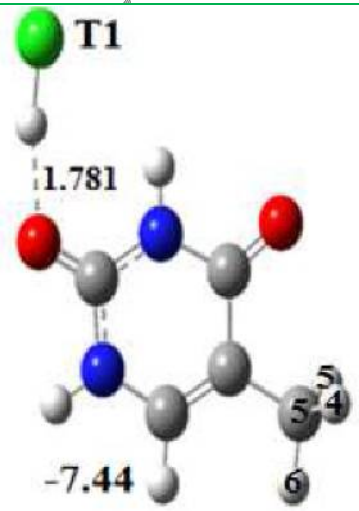
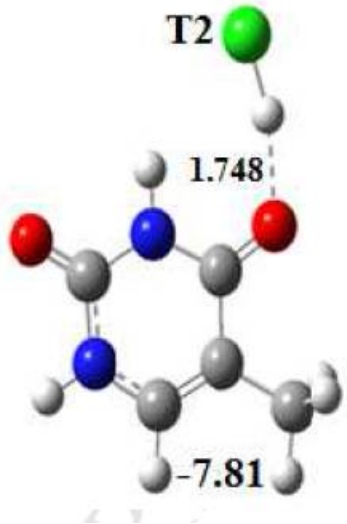
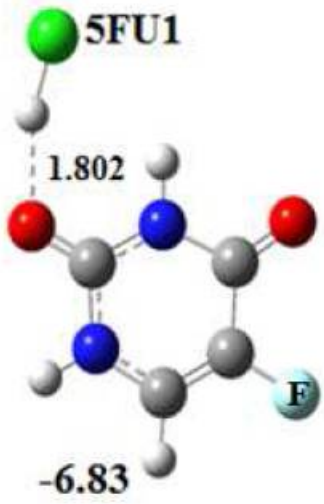
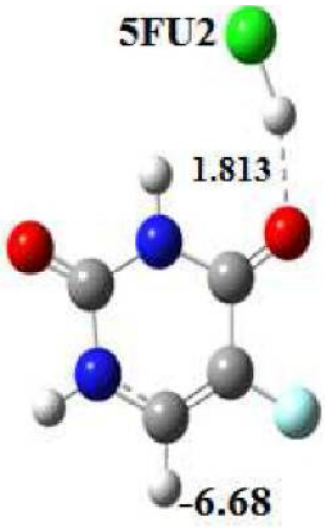
Hydrogen bond



Type of interaction (up)
Orbital-orbital overlap (below)

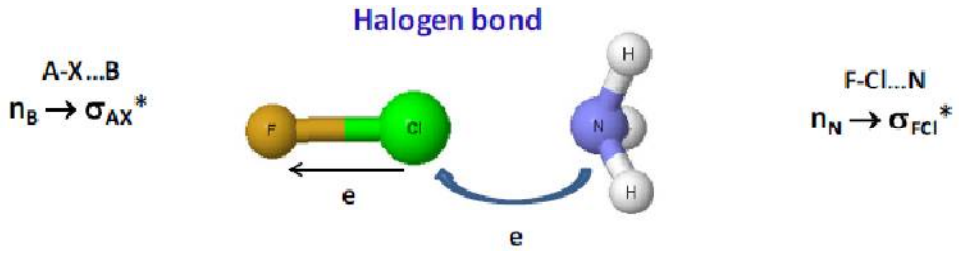
O-H...N
$n_N \rightarrow \sigma_{OH}^*$

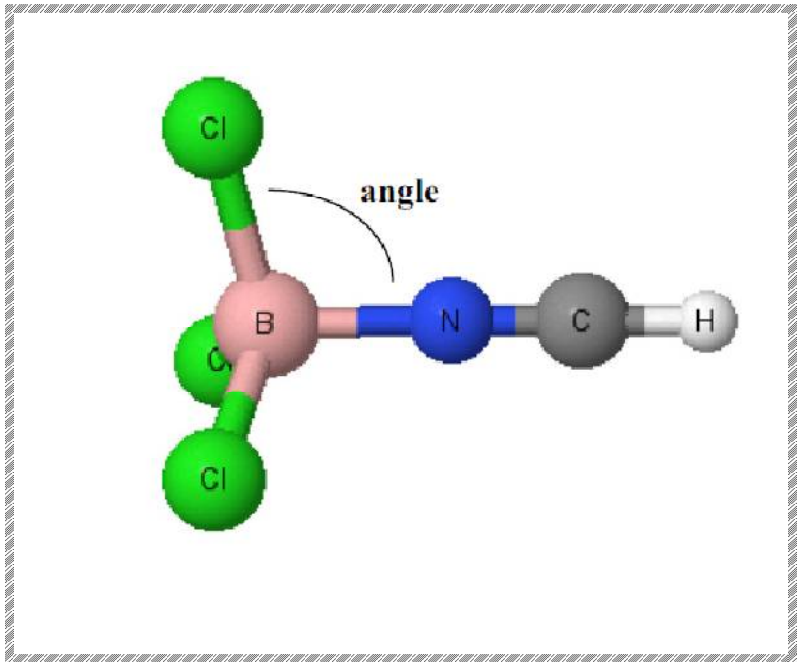
H bond	TrB-01
HCl+U→ Cl-H...U1 (HBond)	**HCl+U→ Cl-H...U2 (HBond)**
	

H bond	**ωB97XD/6-311++G(d,p)**	TrB-01
		
		

Sup Inf 5: *Halogen (X) bond*

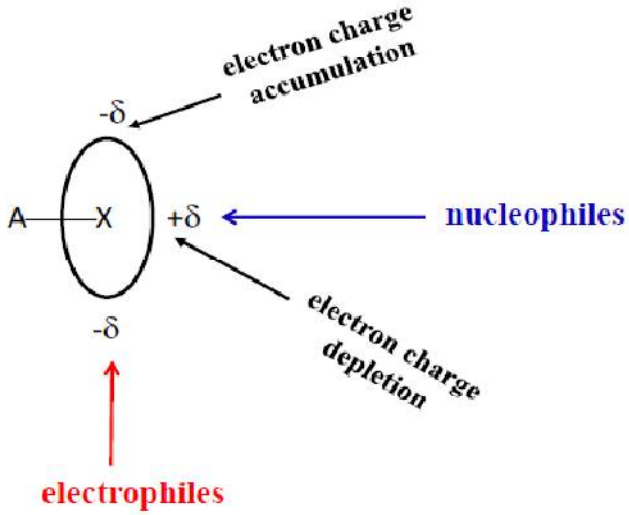
FCl + NH3 → F-Cl ... N-H3





TrB-09

Dual role of halogen atom as Lewis acid and Lewis base centre



Sup Inf 6: *H- and X- bond*

TrB-11

Central atom – Lewis acid

Central atom – Lewis base

$A\text{-}H^{+\delta}\cdots B$ ----> $A\text{-}H^{+\delta}\cdots{}^{-\delta}H\text{-}B$ <----- $A\cdots{}^{-\delta}H\text{-}B$

Hydrogen bond

Dihydrogen bond

Hydride bond

$A\text{-}X^{+\delta}\cdots{}^{-\delta}H\text{-}B$

Halogen-hydride bond

$A\text{-}X^{+\delta}\cdots B$ ----> $A\text{-}X^{+\delta}\cdots{}^{-\delta}X\text{-}B$ <------ $A\cdots{}^{-\delta}X\text{-}B$

Halogen bond

Dihalogen bond

Halide bond

formation of
H-bond, X- bond, … etc