Универзитет у Београду
Факултет за физичку хемију

Nove fizičkohemijske metode

NEKOVALENTNE INTERAKCIJE

Milena Petković

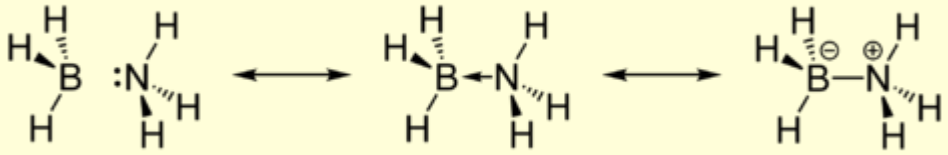
predmet: Nove fizičkohemijske metode
predavanje: Nekovalentne interakcije

?

Luisova kiselina i Luisova baza

$$A + B \rightarrow AB$$

A – Luisova kiselina (akceptor elektronskog para)
B – Luisova baza (donor elektronskog para)
AB – sistem sa nekovalentnim interakcijama



Nekovalentne interakcije (NI)

Sistemi sa nekovalentnim interakcijama:
jedinjenja koja formira bar jedan par Luisove kiseline i Luisove baze.

poreklo informacija o NI:

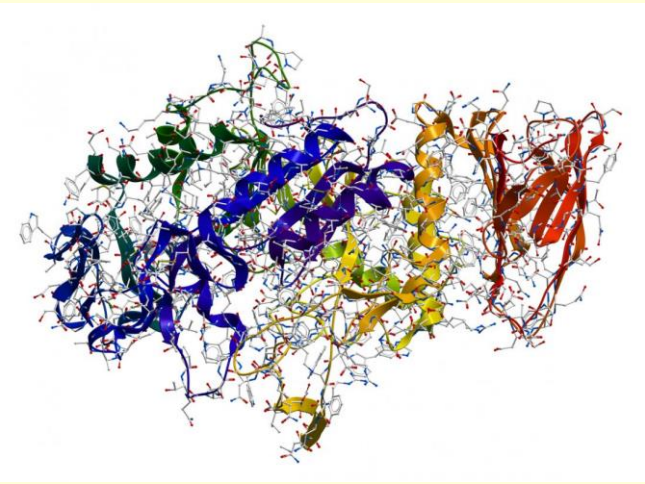
- eksperiment (kristalne strukture, spektroskopija)
- teorijski proračuni → kooperativnost

Analizirani sistemi u čvrstom i gasovitom stanju.
Problem: rastvori

Najpoznatiji predstavnici NI:

- vodonične veze
- steking interakcije

Vodonične veze: značaj



Vodonične veze: donori i akceptori

donori vodonika

atomi velike elektronegativnosti: O, N i F

- svi halogeni elementi
- većina halkogenih elemenata
- većina pnikogenih elemenata
- atomi pojedinih metala

akceptori vodonika

atomi sa slobodnim e^- parovima: O, N i F

- sistemi sa π e^-
- pojedine σ veze
- …

D–H ··· A

1) dokaz da je formirana veza;
2) dokaz da se ova veza ostvaruje preko H koji je već vezan za D.

Vodonične veze: uzroci stabilnosti

- elektrostatičke interakcije
- perturbacija elektronske strukture dveju vrsta pri njihovom približavanju i kovalentni doprinos
- sterna odbijanja

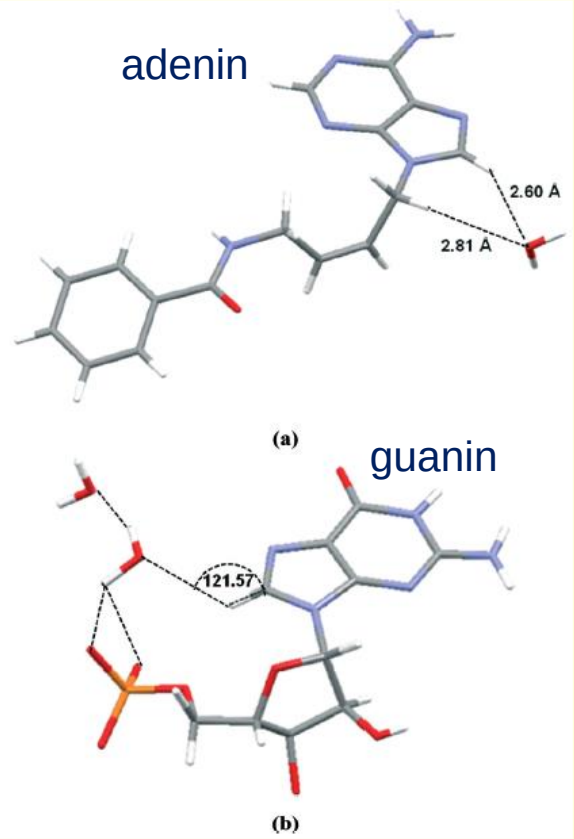
Primer netipične vodonične veze: CH···O

<u>povećanje polarnosti C-H veze</u>

- promena hibridizacije C atoma, $sp^3 \rightarrow sp$ (HC≡CH, N≡CH)
- supstituenti na C atomu koji privlače elektrone (peptidne grupe u proteinima)

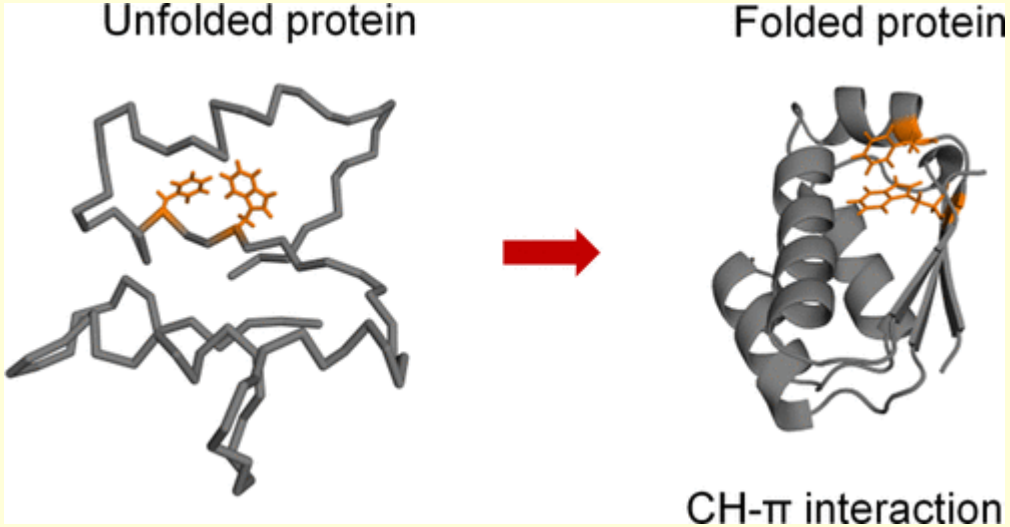
značaj:

- struktura
- mehanizmi enzimskih reakcija
- …



D. Ž. Veljković et al. *CrystEngComm.* 16, **2014**, 10089

Primer netipične vodonične veze: CH··· π

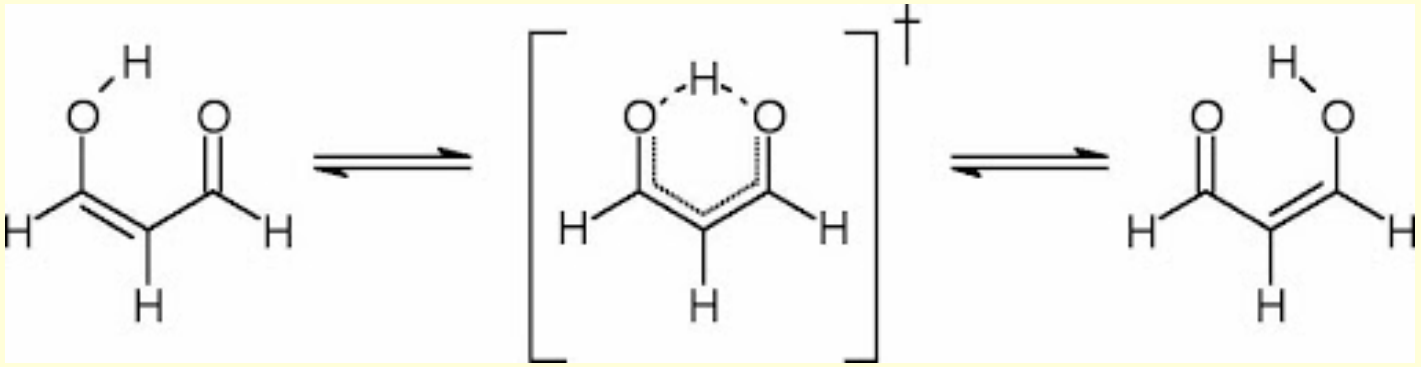


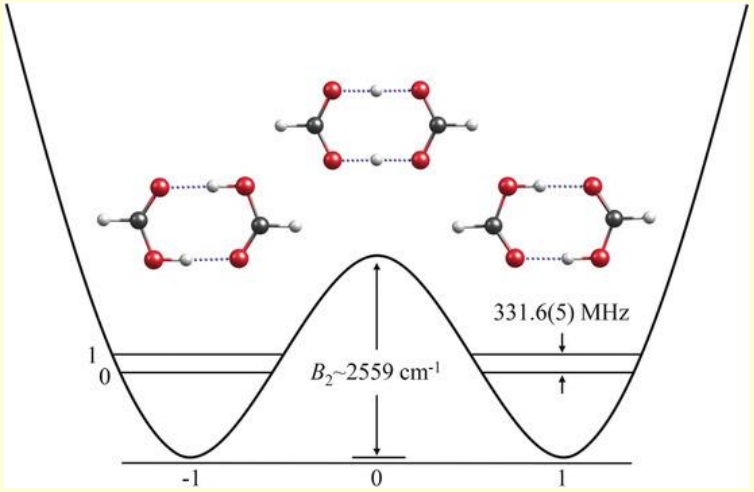
E. A. Milan-Garces et al. *J. Phys. Chem. B* 119, **2015**, 2928

Vodonične veze: prenos H

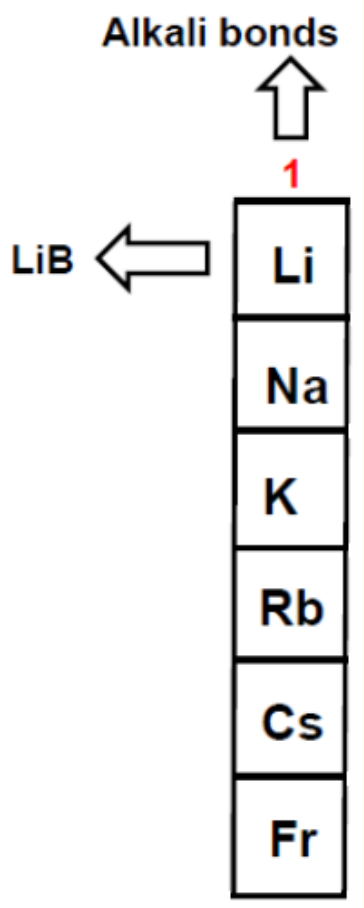
prenos:

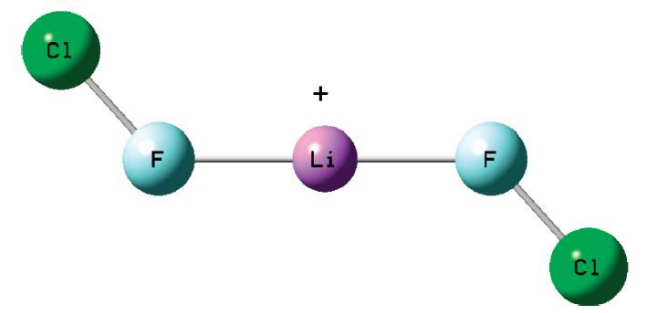
- vodonika ili protona
- intramolekulski i intermolekulski
- u osnovnom i u pobuđenim elektronskim stanjima
- jednostruki ili dvostruki
- simetričan i asimetričan
- …

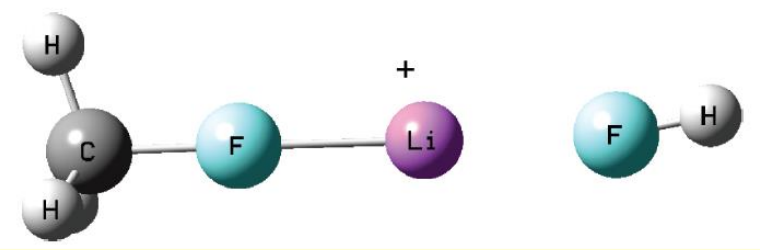


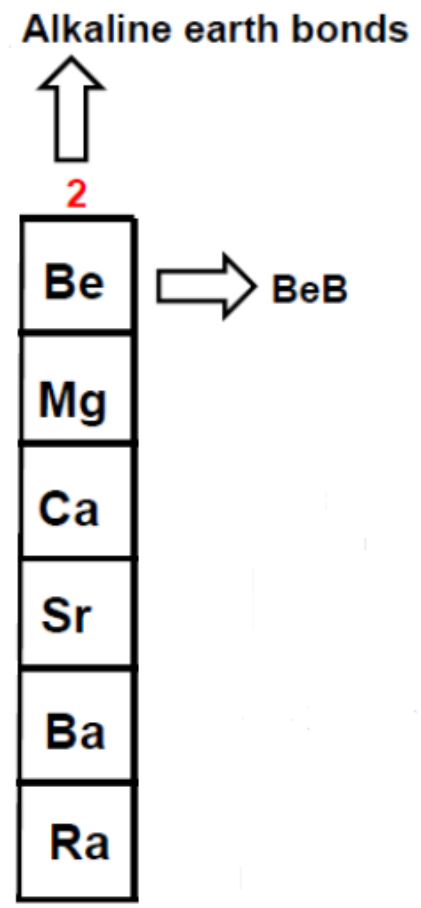


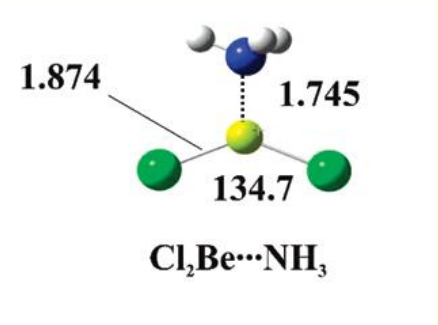
Alkalne i zemnoalkalne veze











Nova definicija → nove interakcije

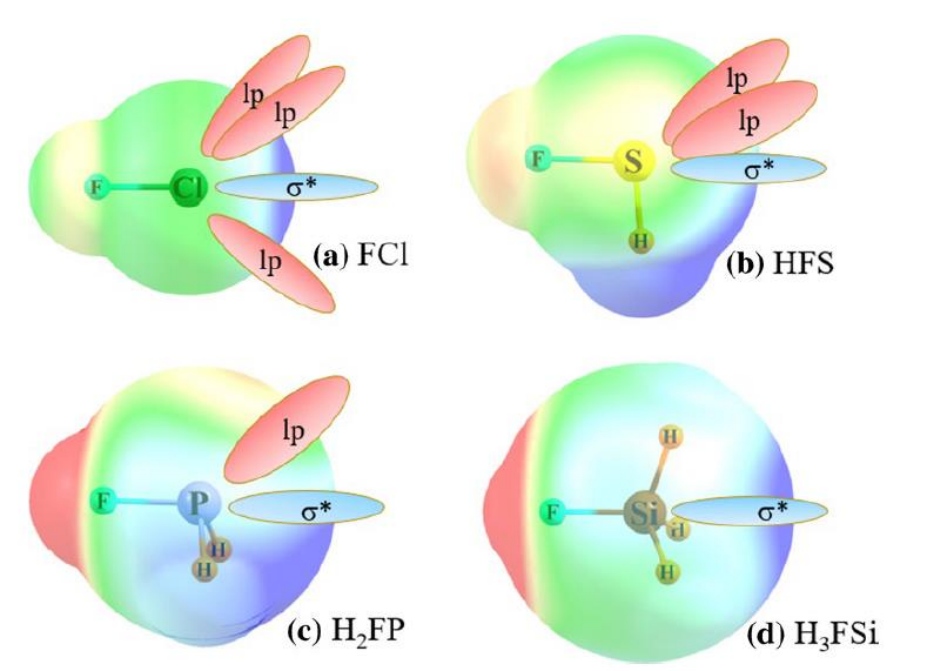
Vodonična veza: interakcija koja uključuje premošćujući atom vodonika.

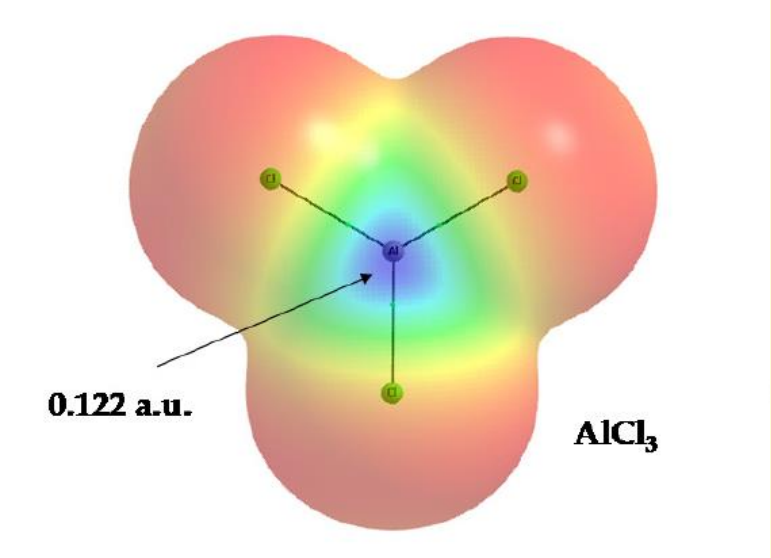
H → X

X atom 14-18. (13) grupe periodnog sistema i ima anizotropnu raspodelu naelektrisanja

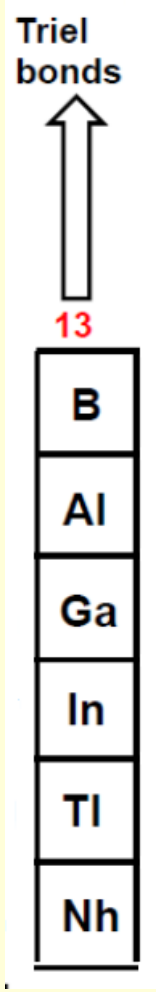
↓

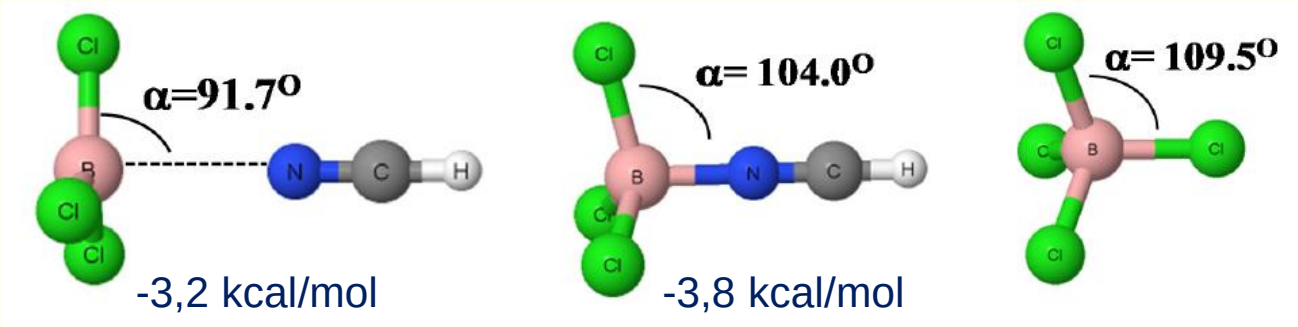
σ (π) šupljina





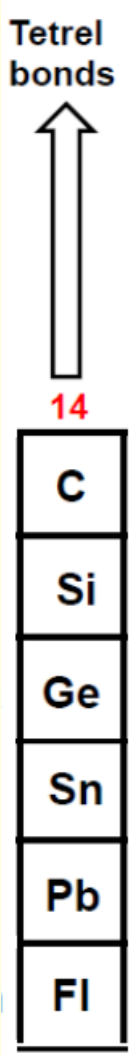
Trielne veze

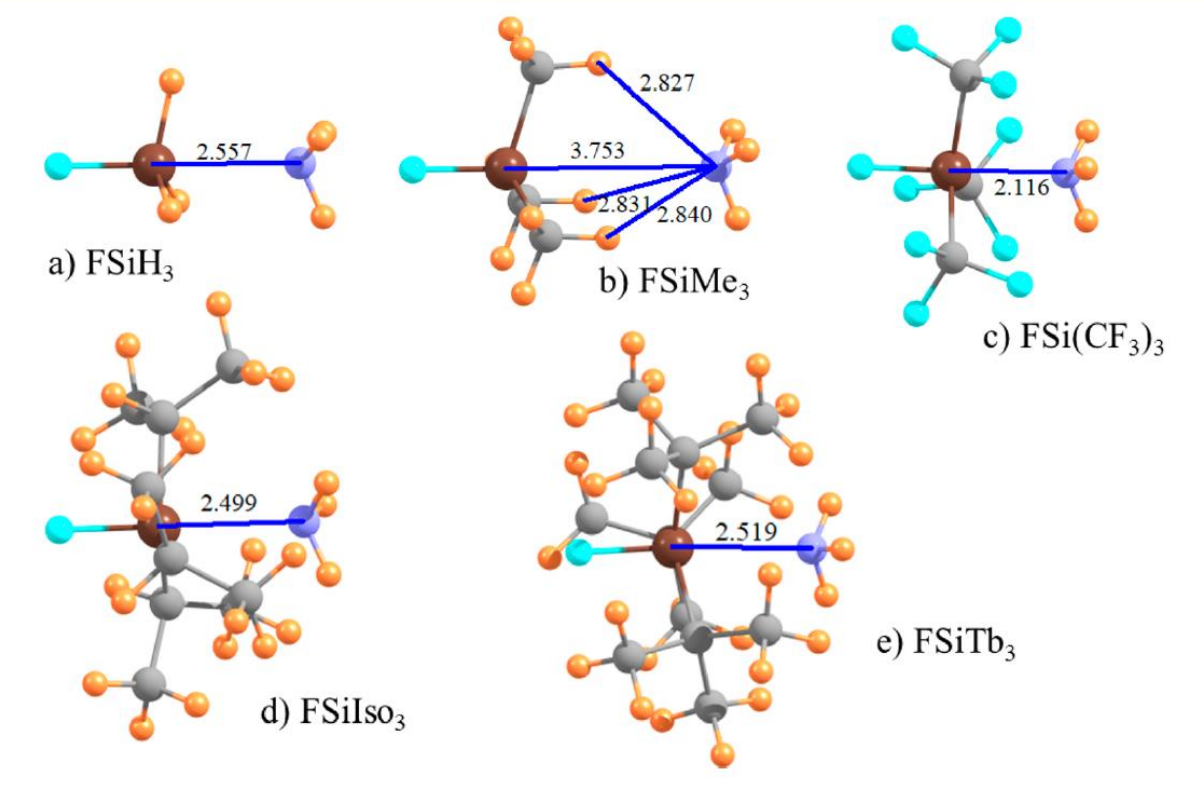




Sistem	Energija veze kcal/mol
$BCl_3 \cdots N_2$	-1,5
$AlH_3 \cdots NCH$	-17,7
$BH_3 \cdots NH_3$	-30,8
$AlCl_3 \cdots NH_3$	-38,8
$AlH_3 \cdots Cl^-$	-52,2

Tetrelne veze



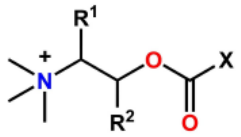


Sistem	Energija veze sa NH_3 kcal/mol
$FSiH_3$	-5,5
$FSiMe_3$	-2,2
$FSi(CF_3)_3$	-18,2
$FSiIso_3$	+0,2
$FSiTb_3$	+10,8

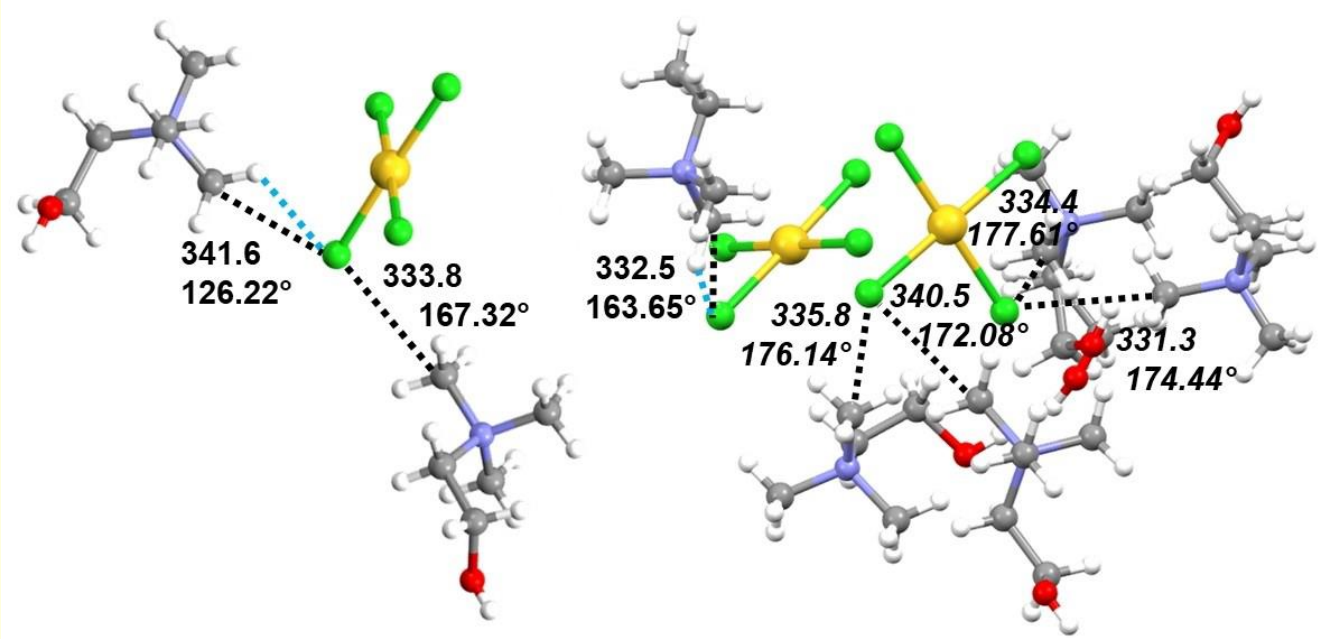
uticaj:

- veličine T atoma
- veličine supstituenta
- prirode supstituenta

Tetrelne veze u proteinima (1)



R^1	R^2	X	
H	H	CH_3	Acetylcholine
H	H	NH_2	Carbachol
H	CH_3	CH_3	Methacholine
H	CH_3	NH_2	Bethanechol
H	H	$(CH_2)_2COO(CH_2)_2N(CH_3)_3$	Succinylcholine



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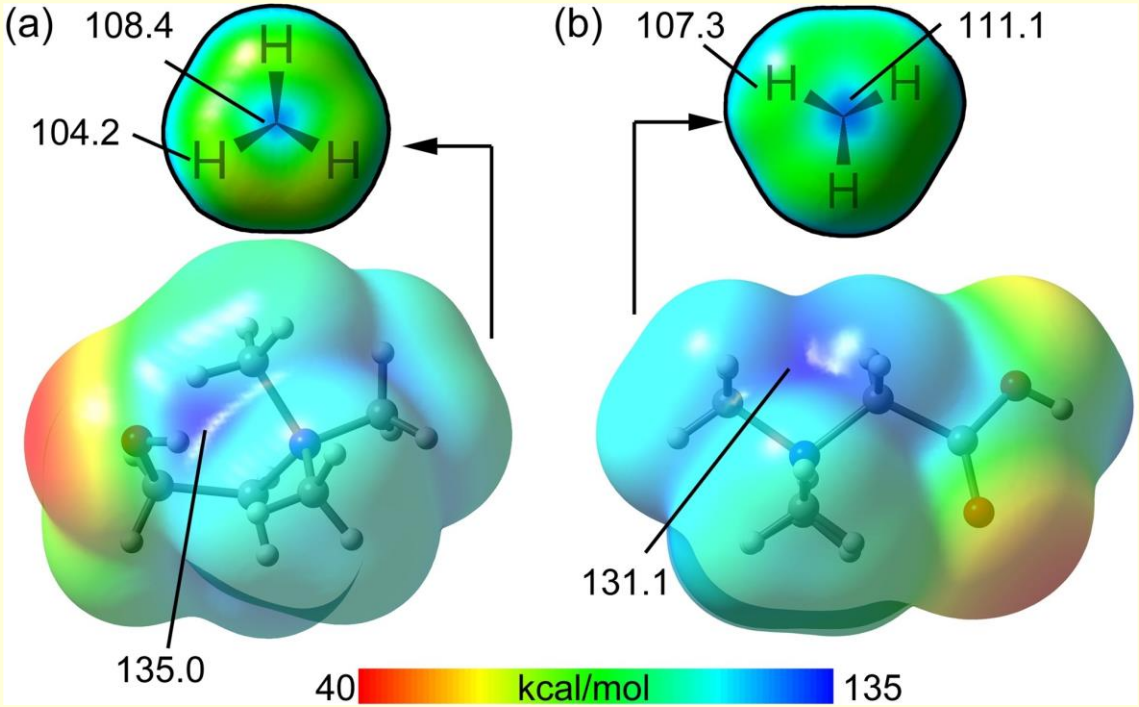
Tetrelne veze u proteinima (2)



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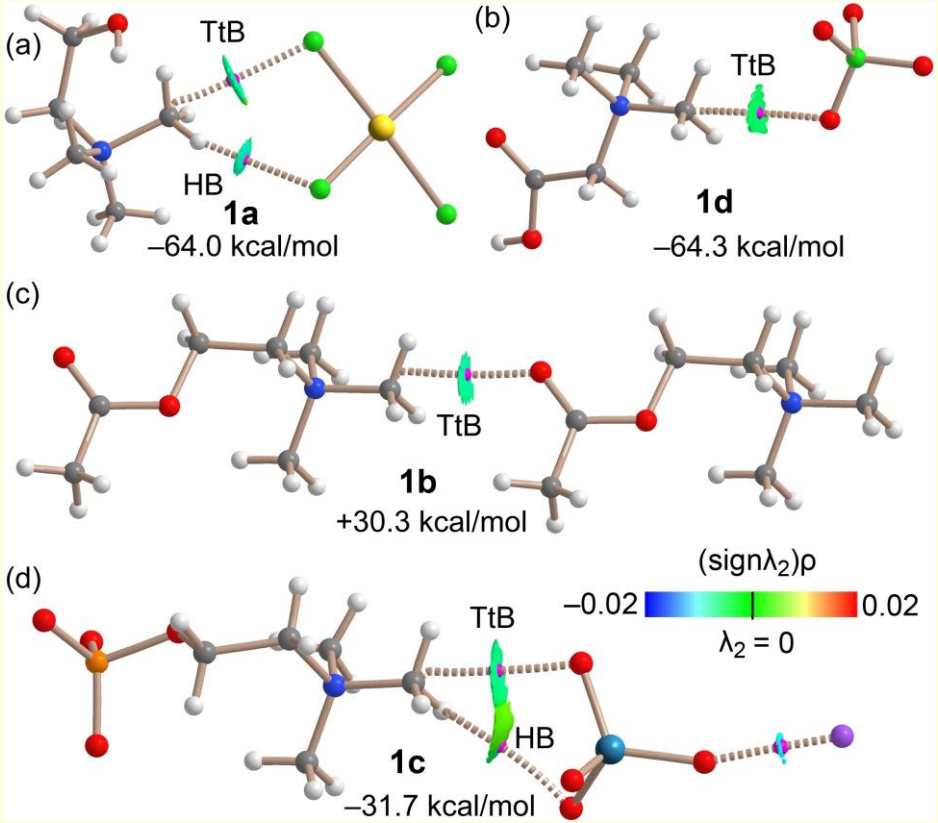
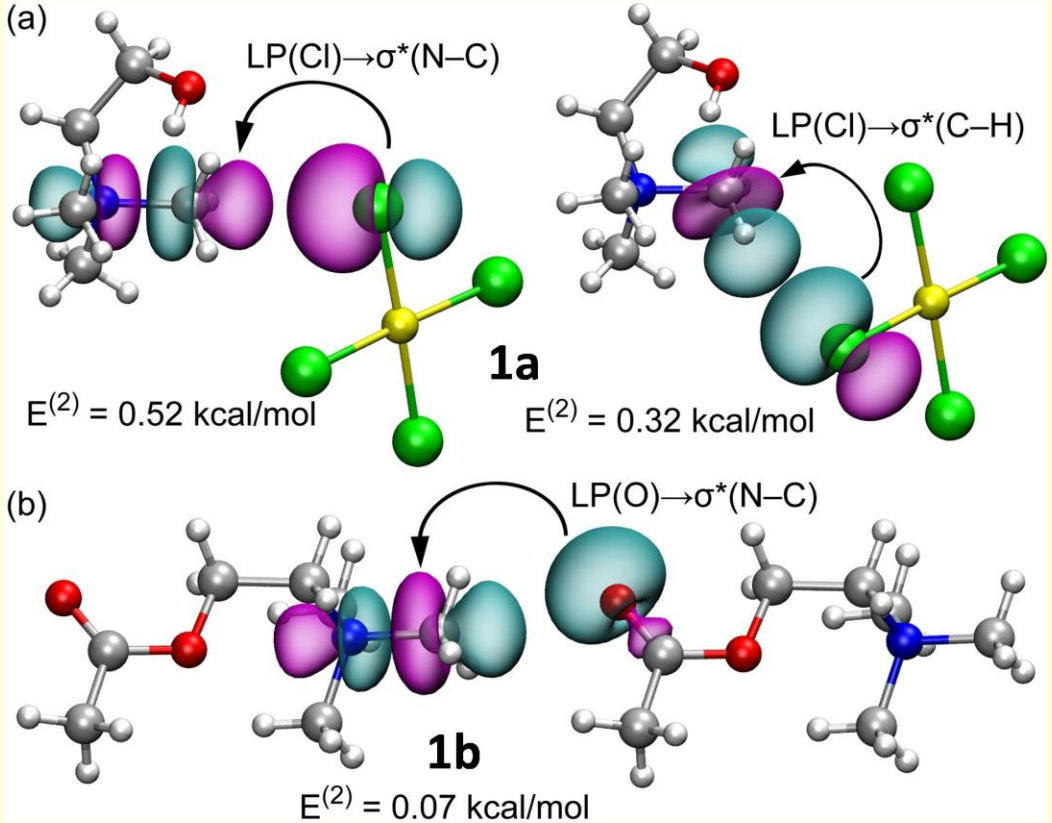
Tetrelne veze u proteinima (3)





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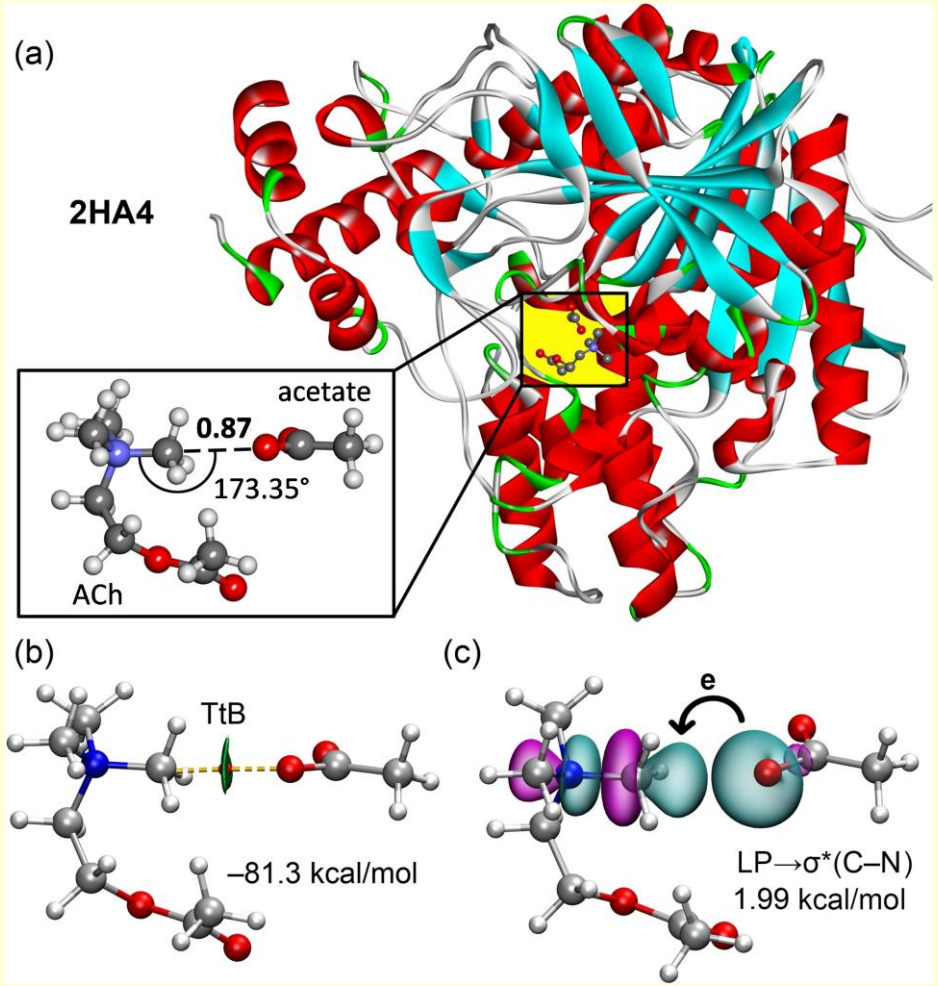
Tetrelne veze u proteinima (4)



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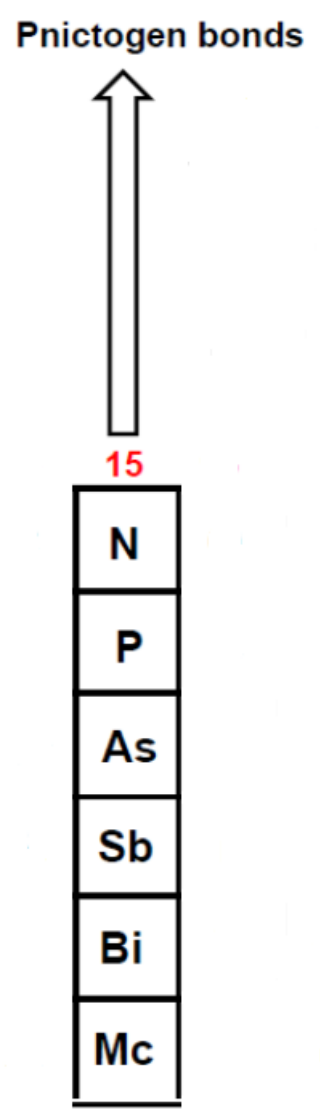
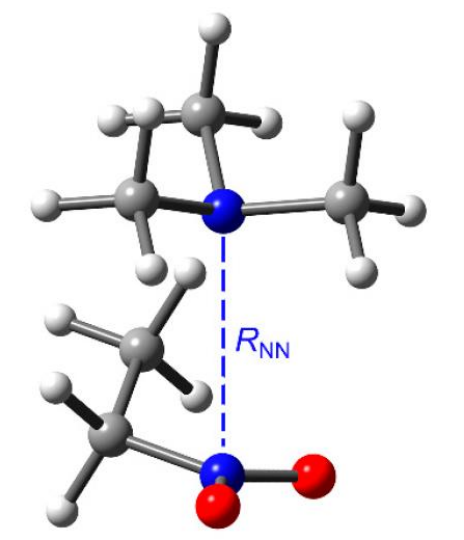
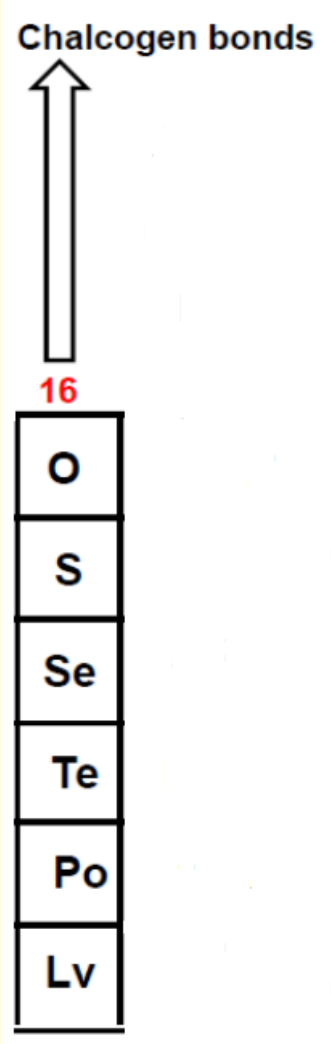
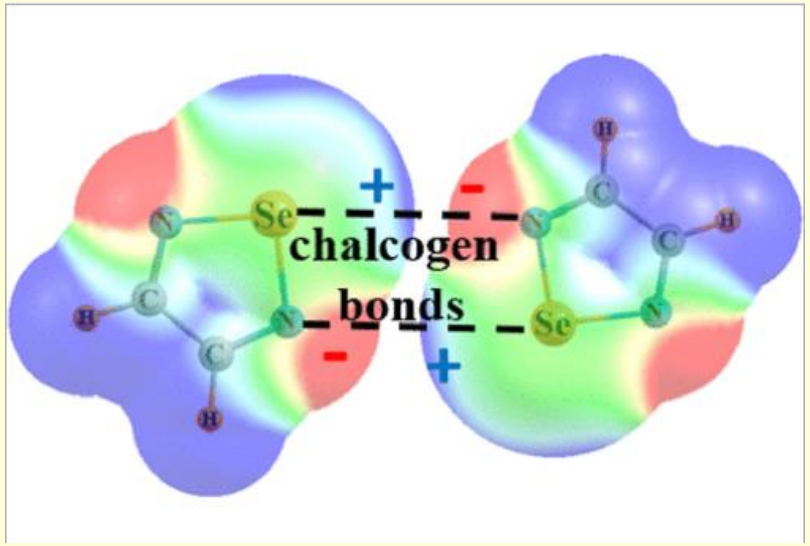
Pnikogene i halkogene veze





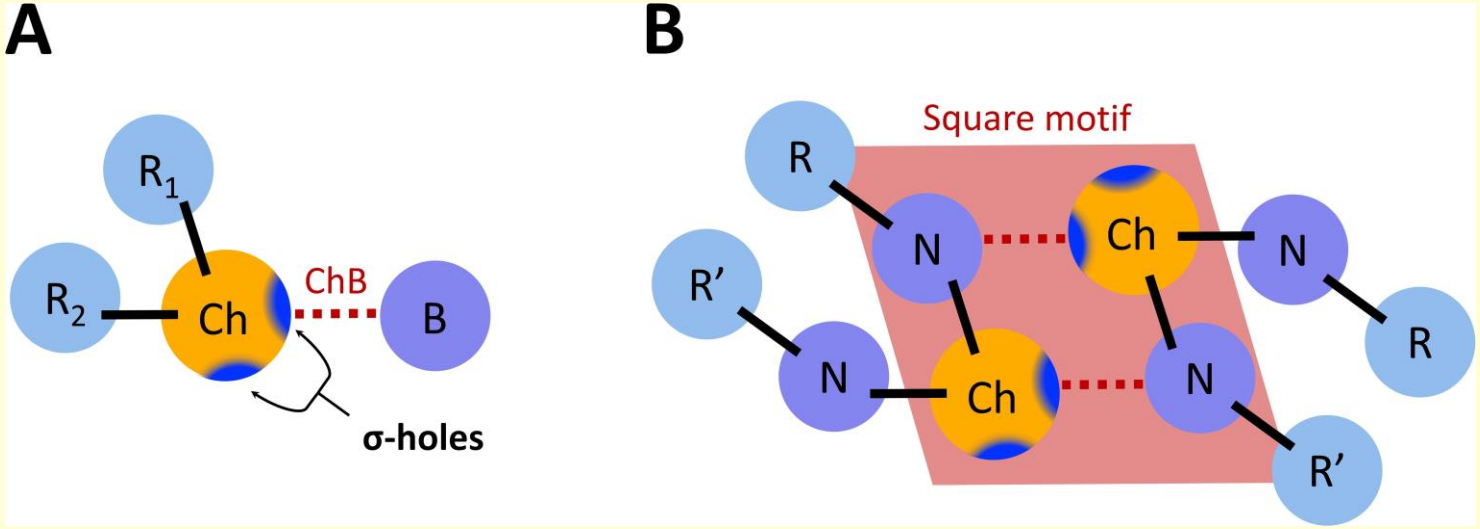




Halkogene veze: selen (1)

ključna uloga halkogenih veza u:

- molekulskom prepoznavanju
- kristalnim strukturama
- obrazovanju supramolekulskih struktura
- katalizi



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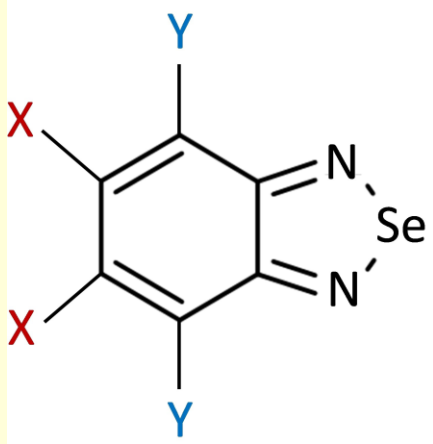
Halkogene veze: selen (2)

na svojstva halkogenih veza utiču:

- veličina supstituenta
- položaj supstituenta
- elektronegativnost supstituenta



A: X = Y = H

B: X = CH_3, Y = H

C: X = CN, Y = H

D: X = Br, Y = H

E: X = Cl, Y = H

F: X = H, Y = Br

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Halkogene veze: selen (3)

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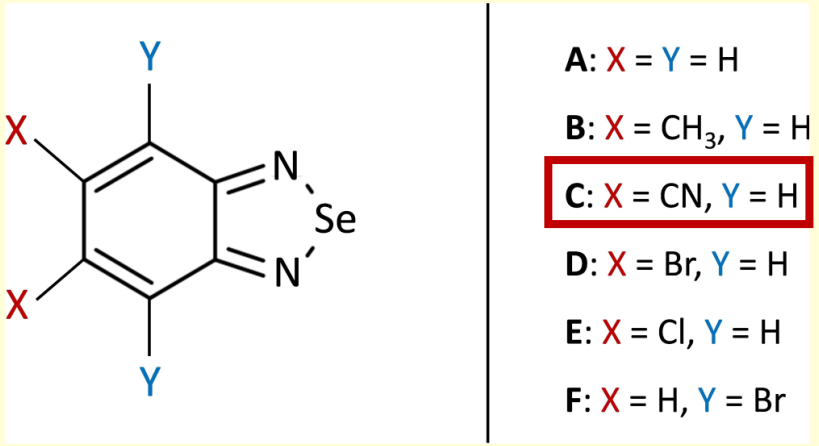

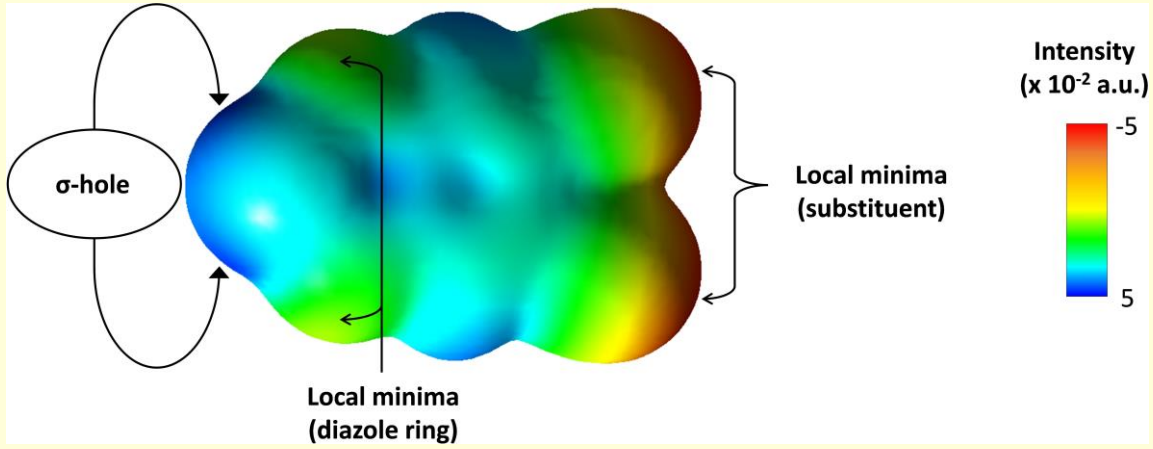

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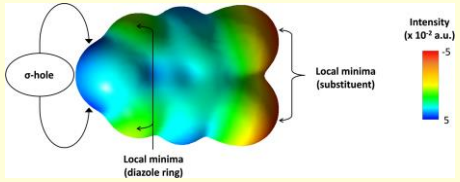
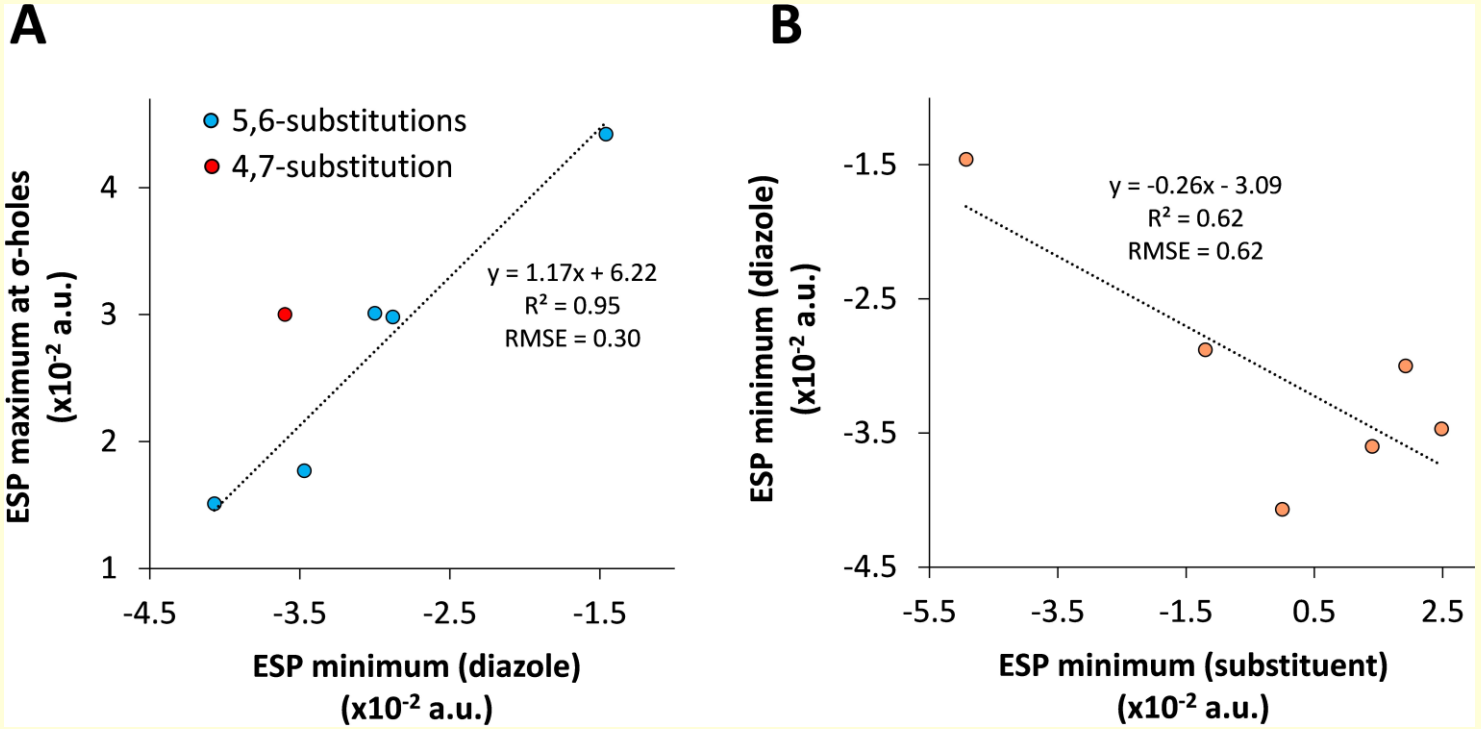
Halkogene veze: selen (4)





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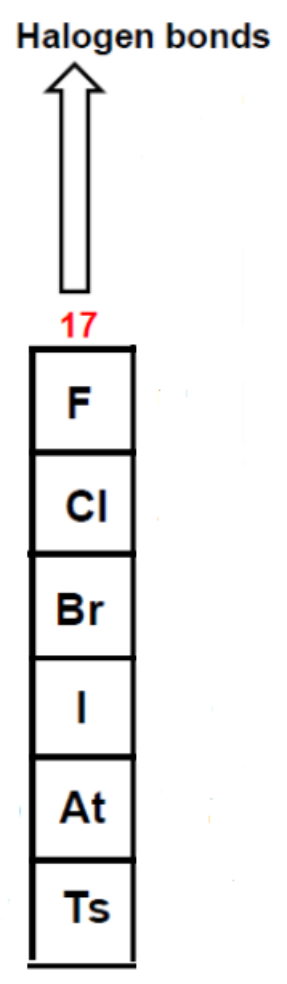
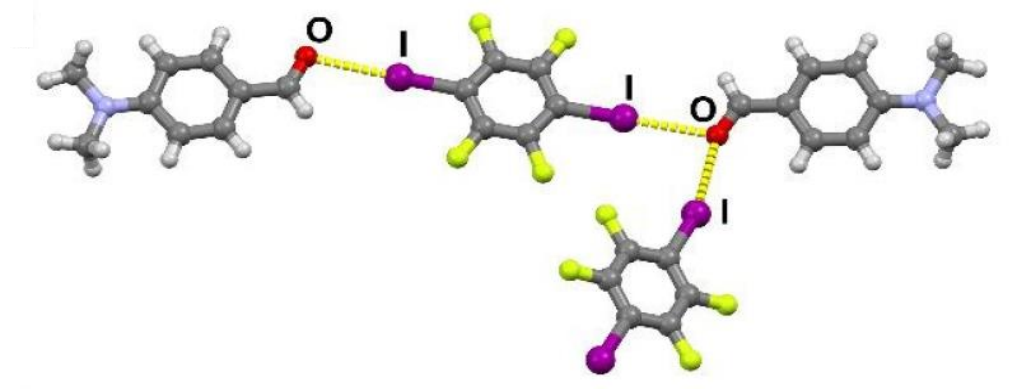
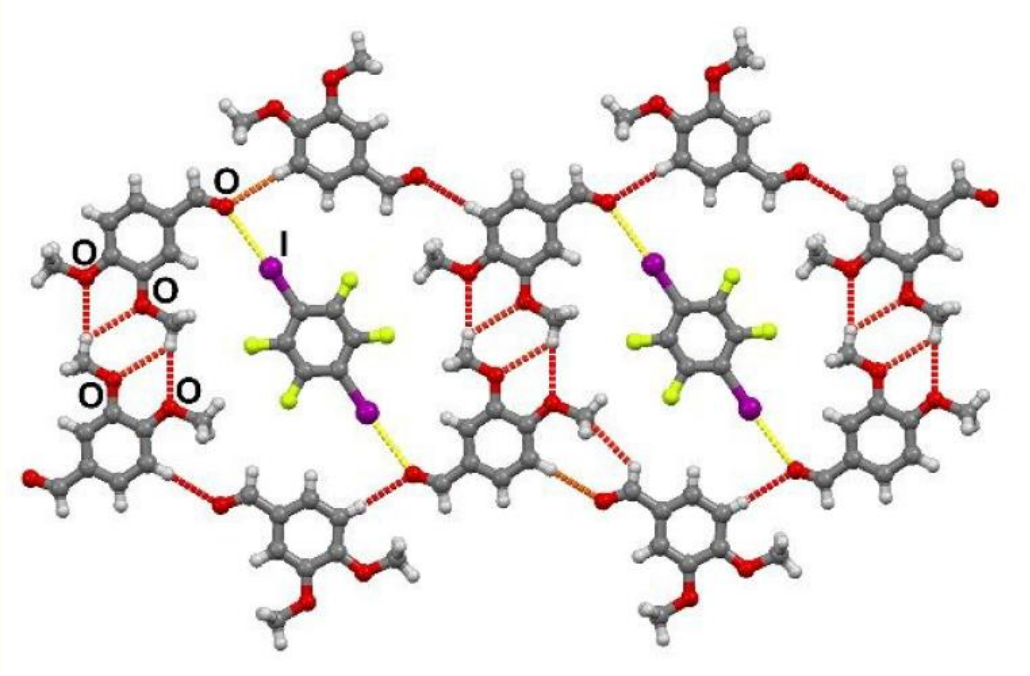
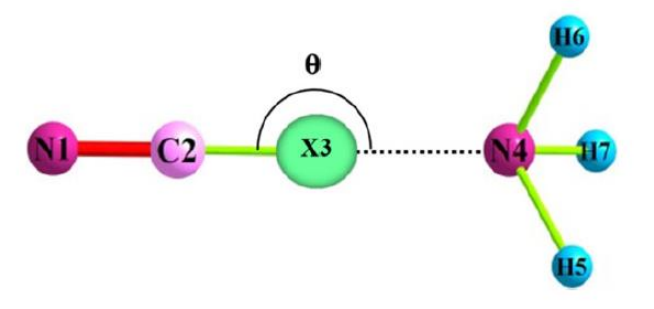
Halogene veze

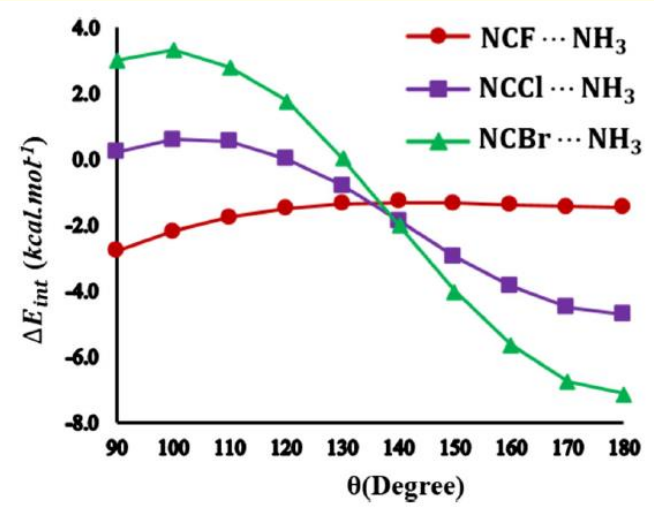


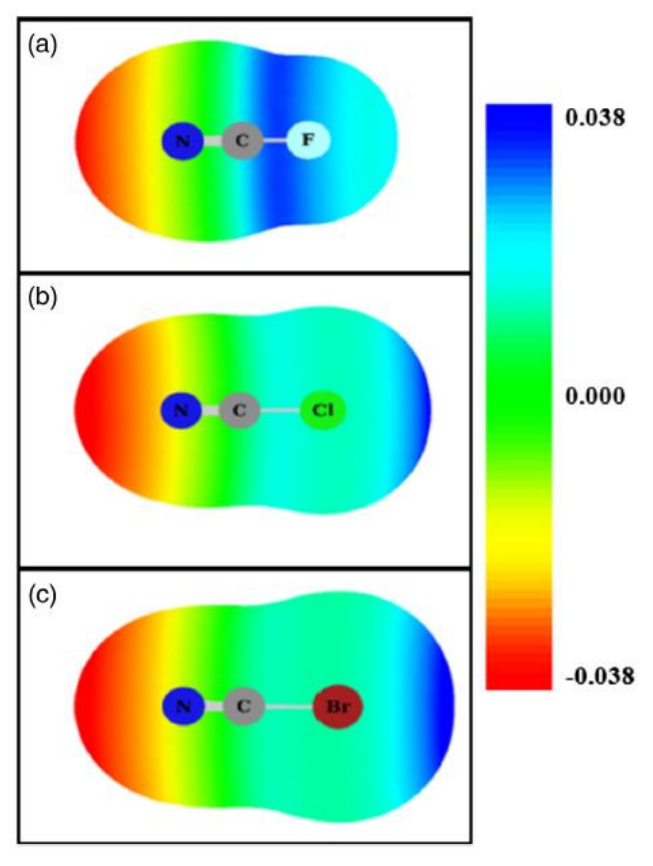




NCX···NH_3 dimeri (1)







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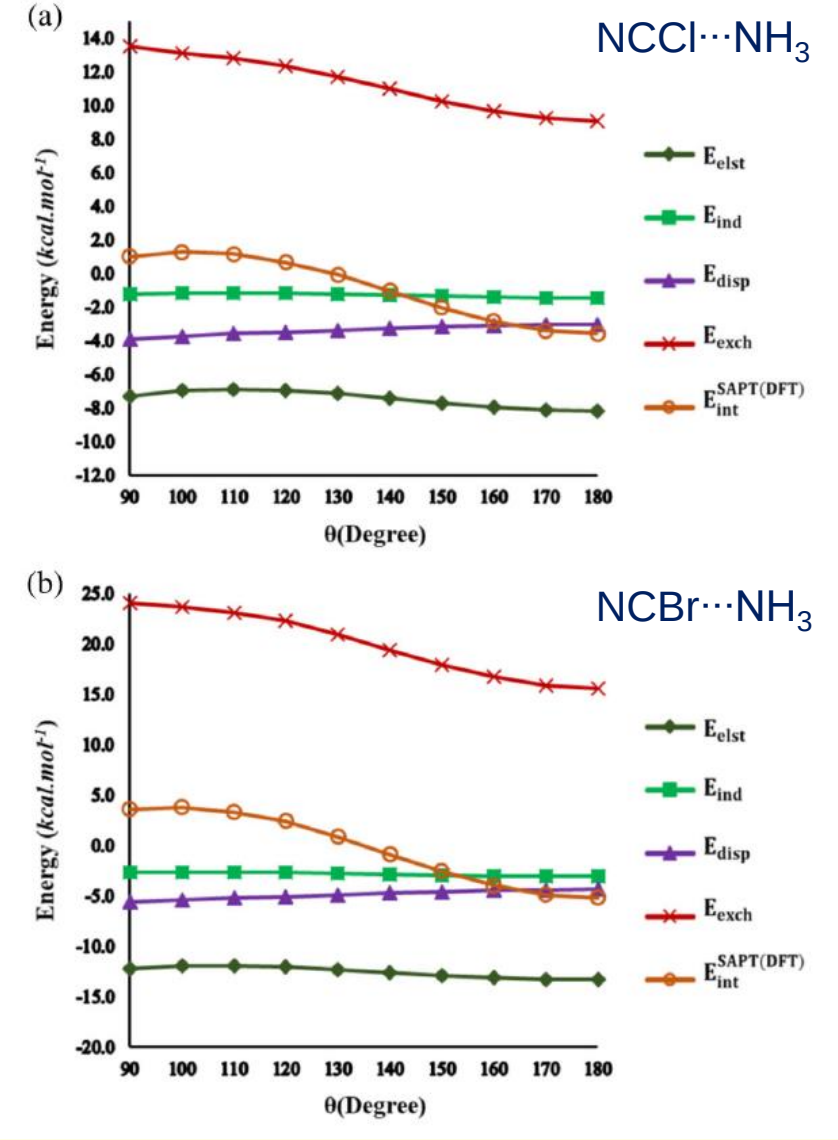
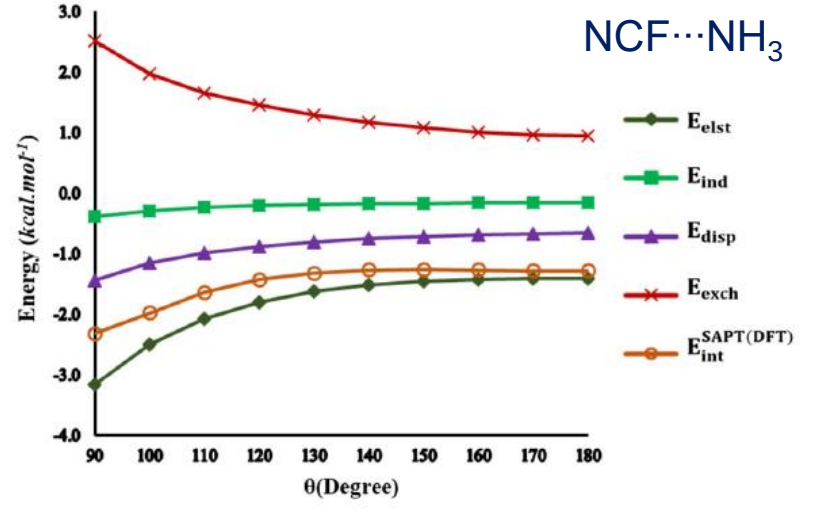
NCX···NH_3 dimeri (2)





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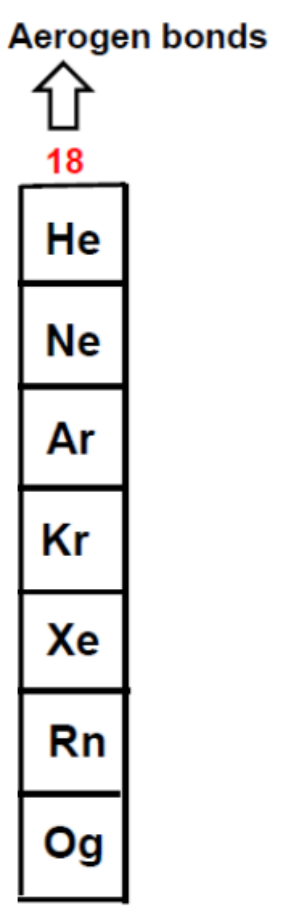
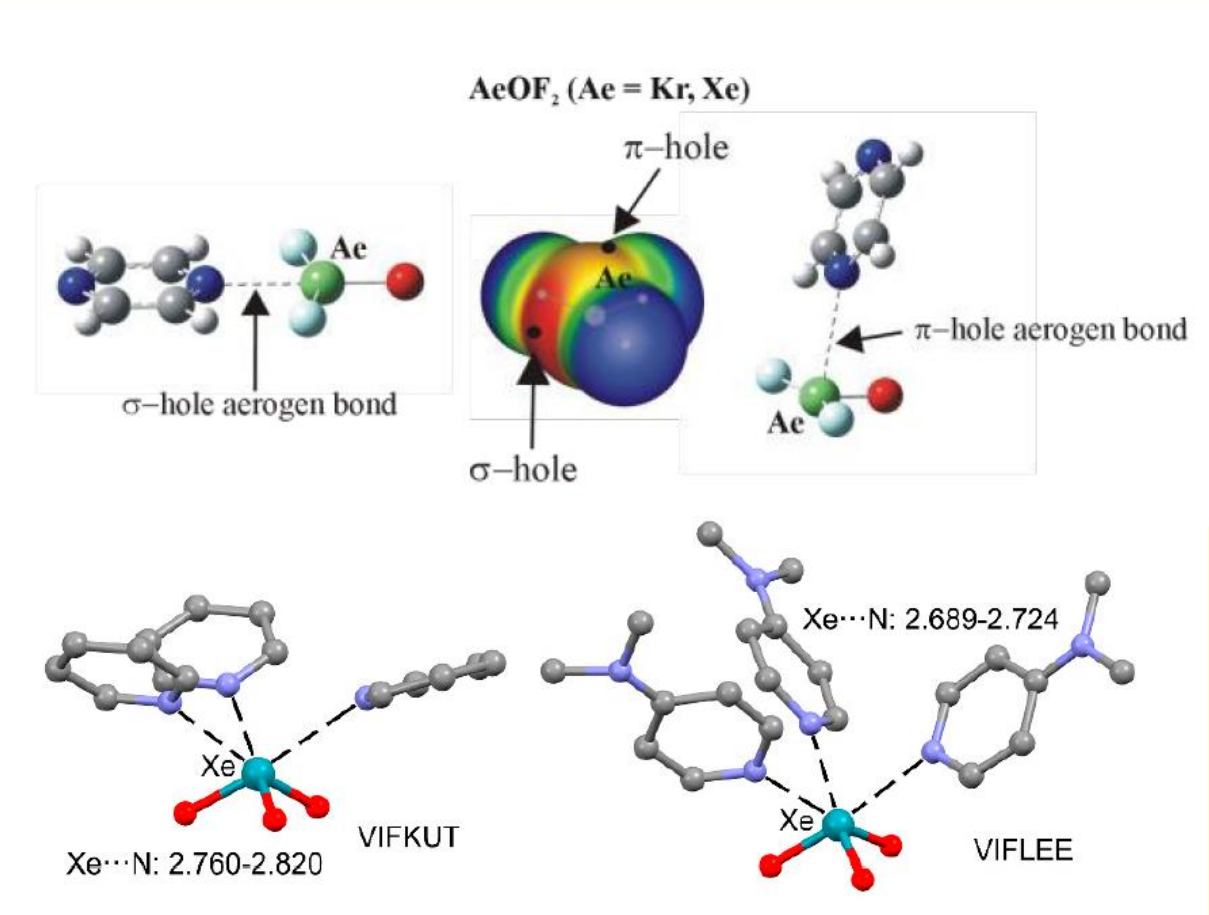
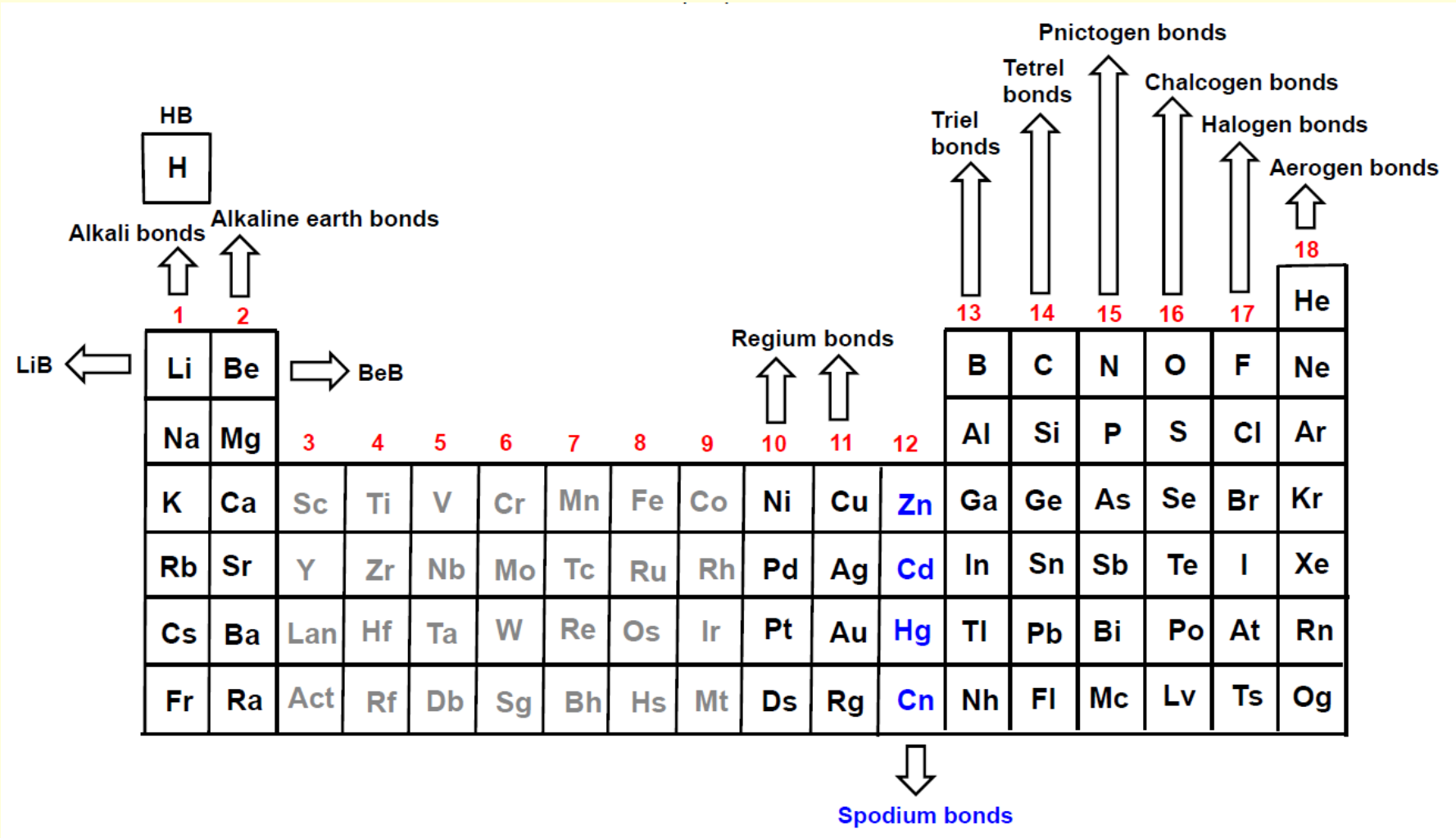
Aerogene veze





Naziv tipa NI potiče od Luisove kiseline



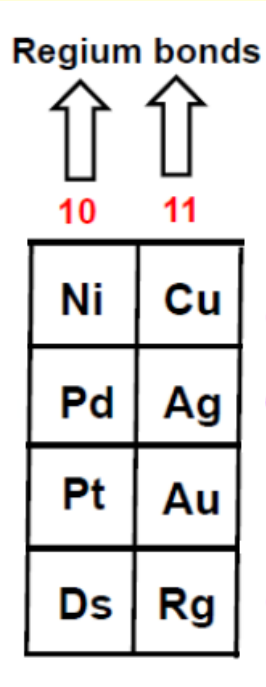
Luisove baze

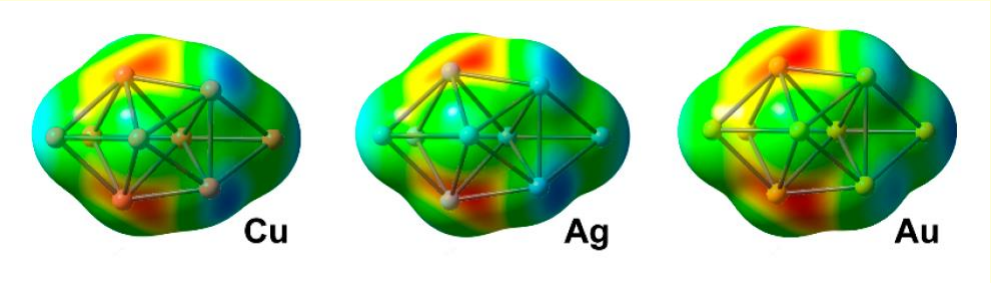
anjoni

neutralni molekuli:

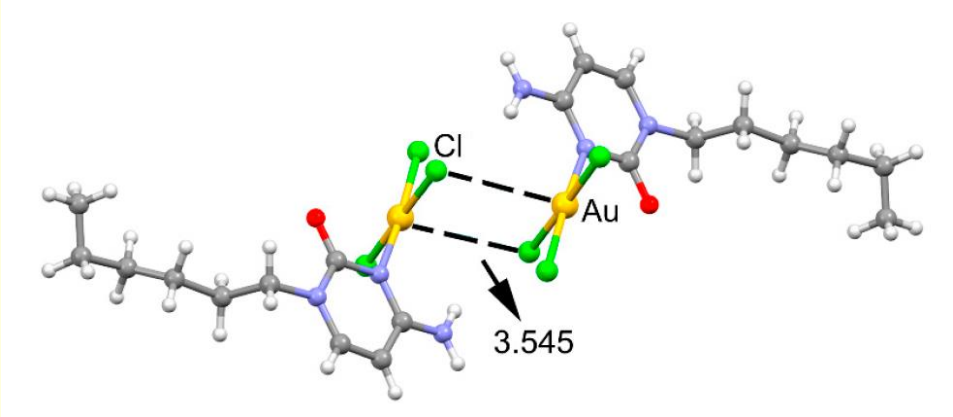
- atomi
- višestruke veze
- aromatični prstenovi
- funkcionalne grupe

Regijumske veze



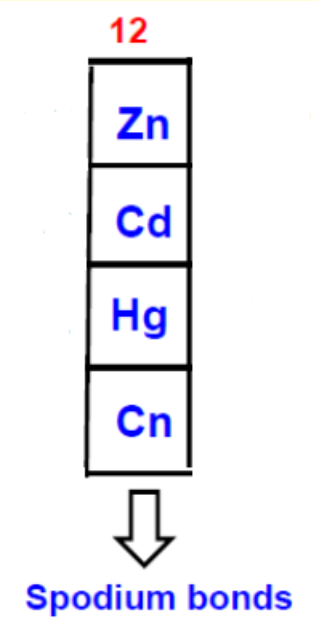


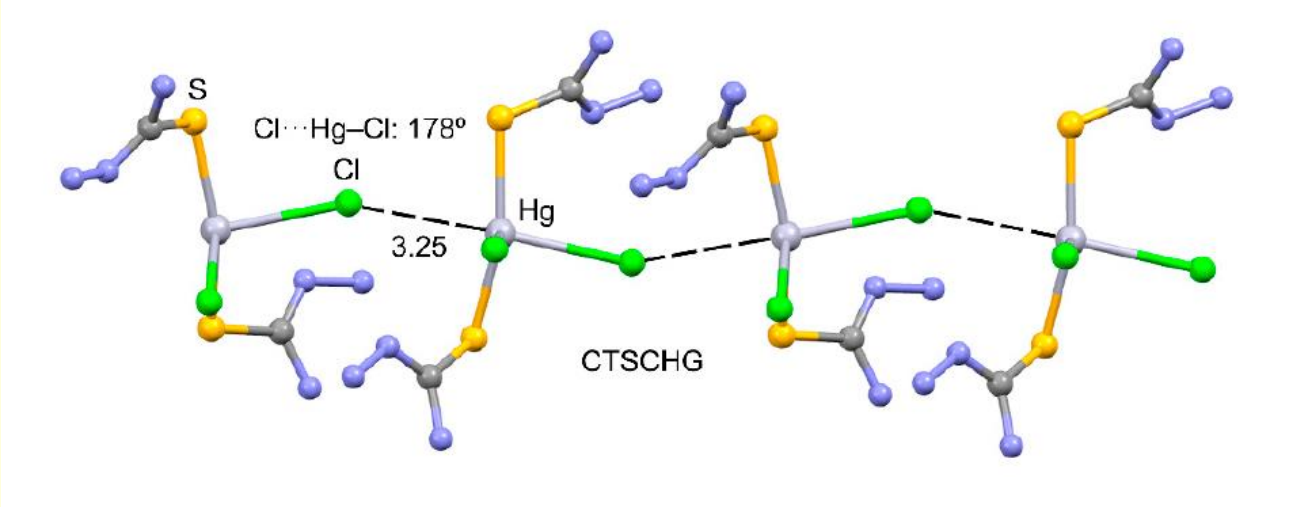
klasteri (nema NI)



trihloro-(1-heksilcitozin)srebro(III) kompleks

Spodijumske veze



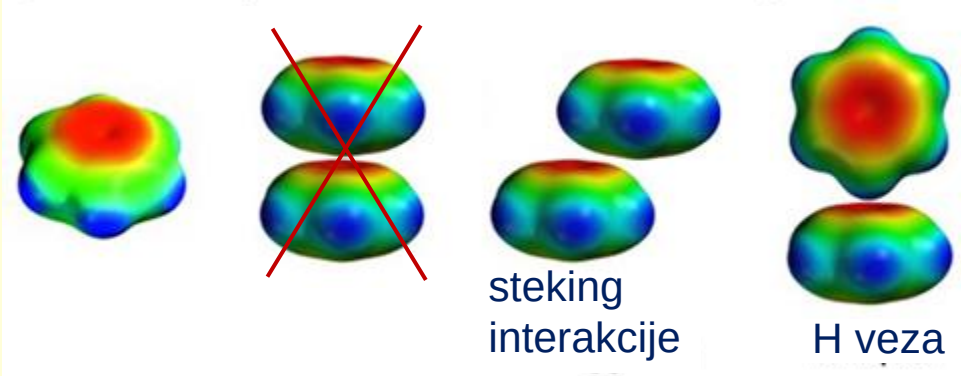


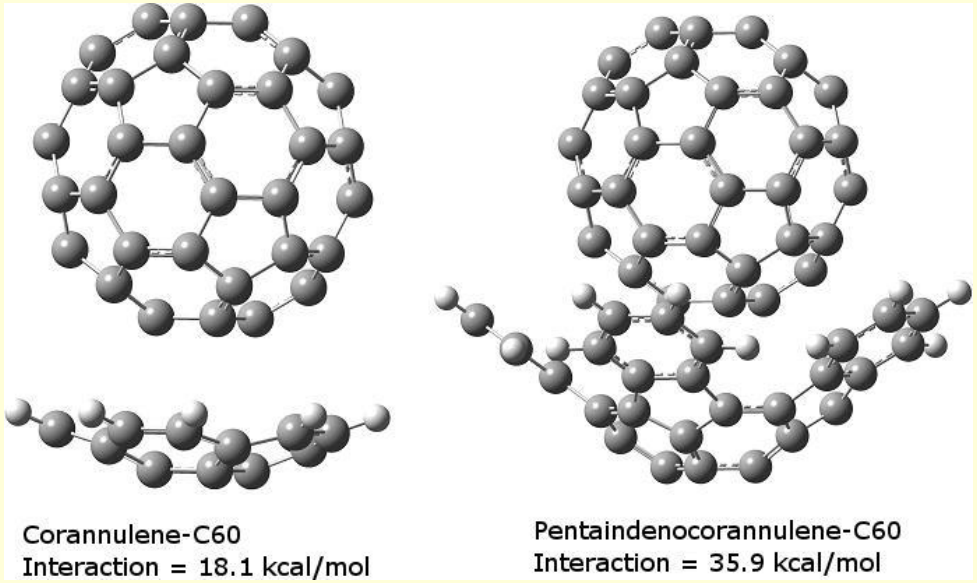
ZnO – spodium (lat)

Hg-Cl veza:

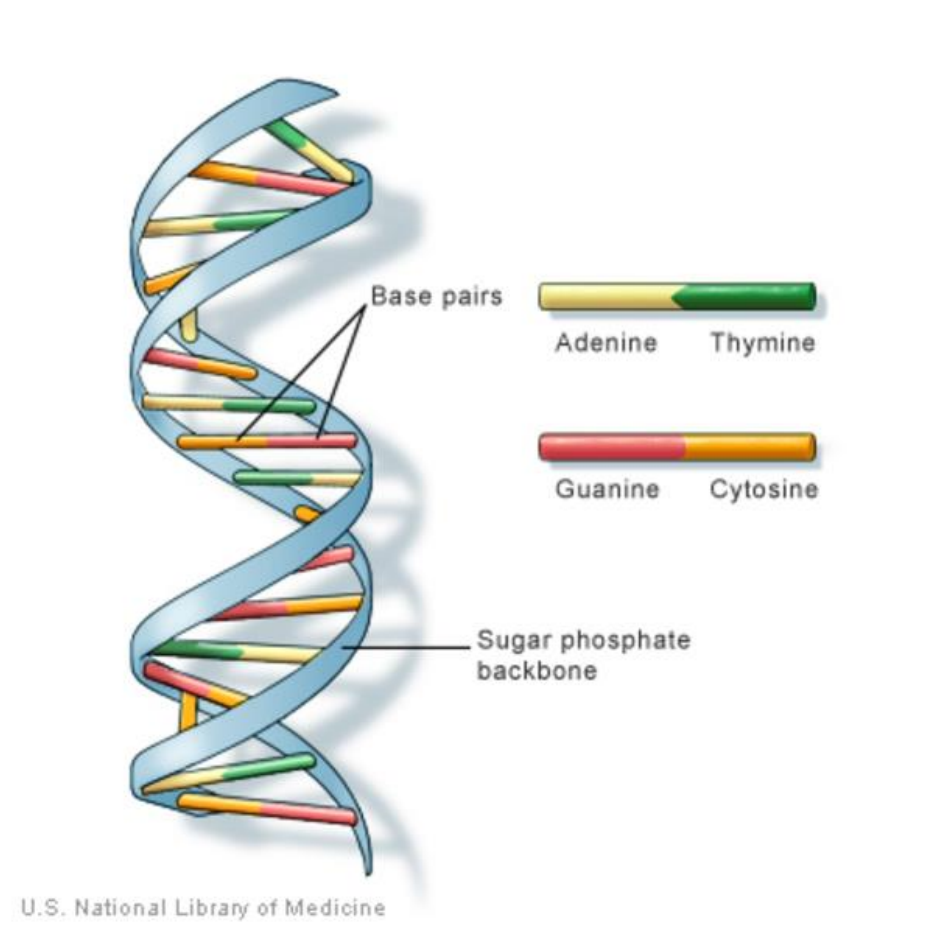
- zbir van der Valsovih radijusa: 3,30 Å
- dužina Hg···Cl veze: 3,25 Å
- zbir kovalentnih radijusa: 2,39 Å

Steking interakcije

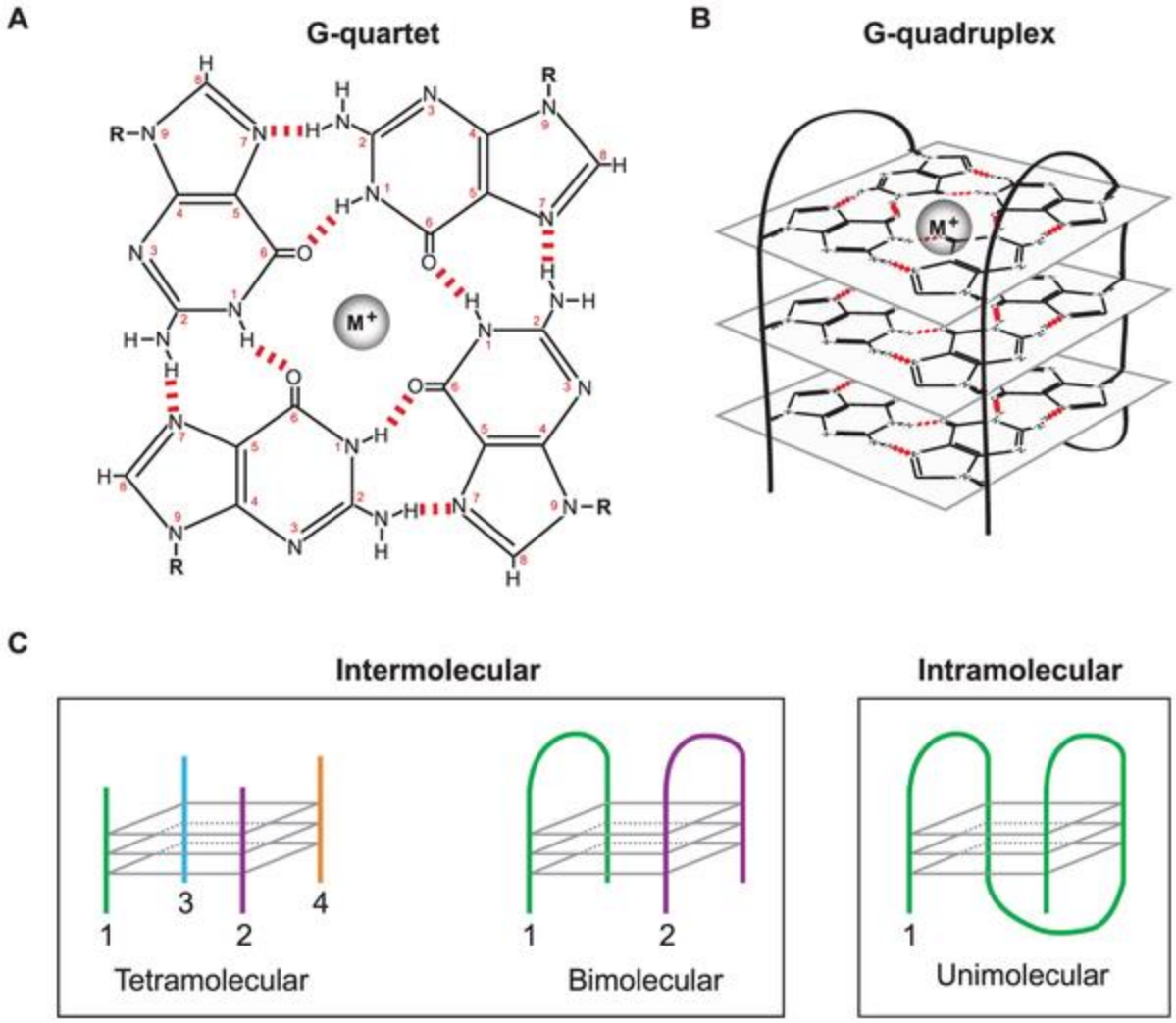




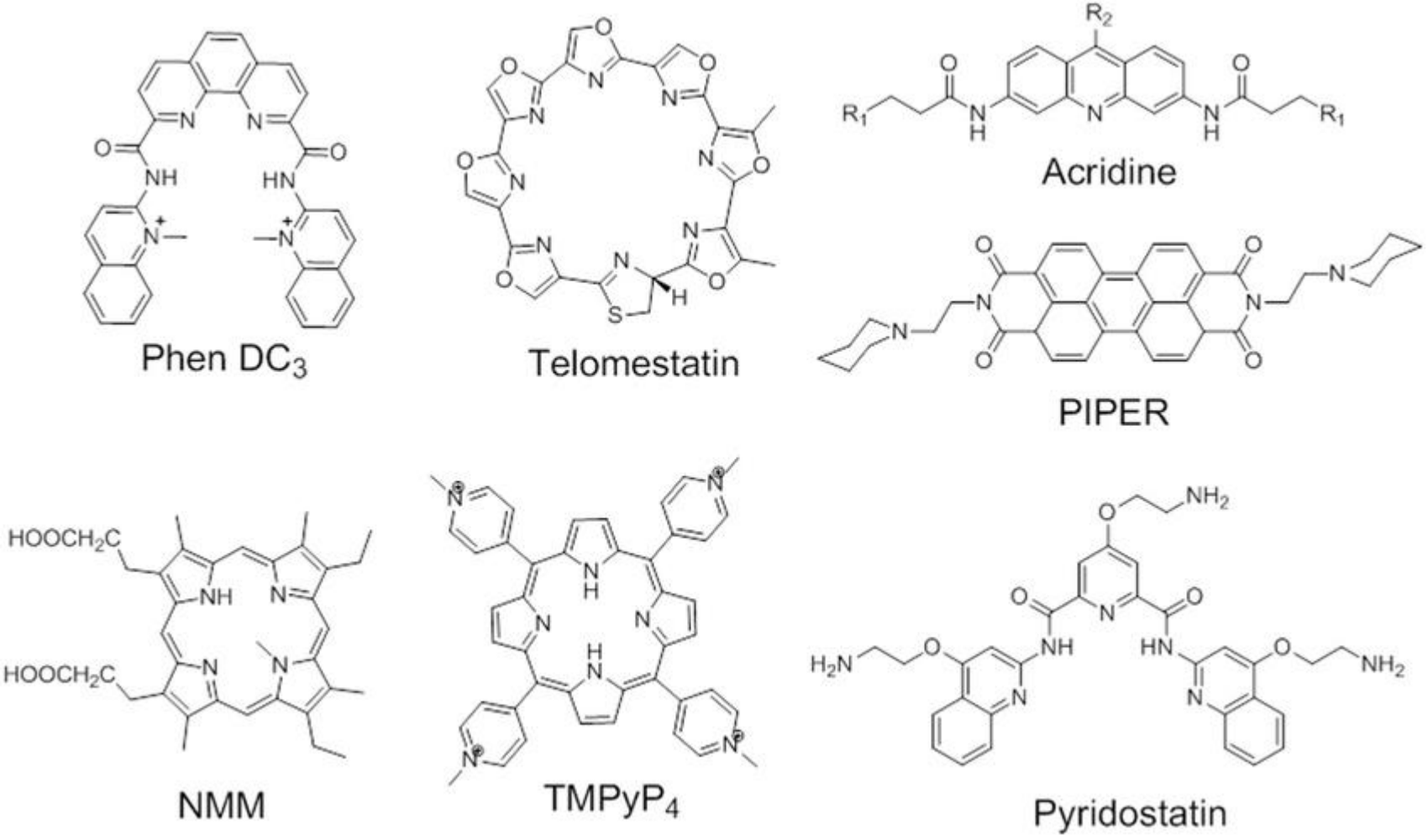
Primer: DNK


Base pairs
Adenine
Thymine
Guanine
Cytosine
Sugar phosphate backbone
U.S. National Library of Medicine

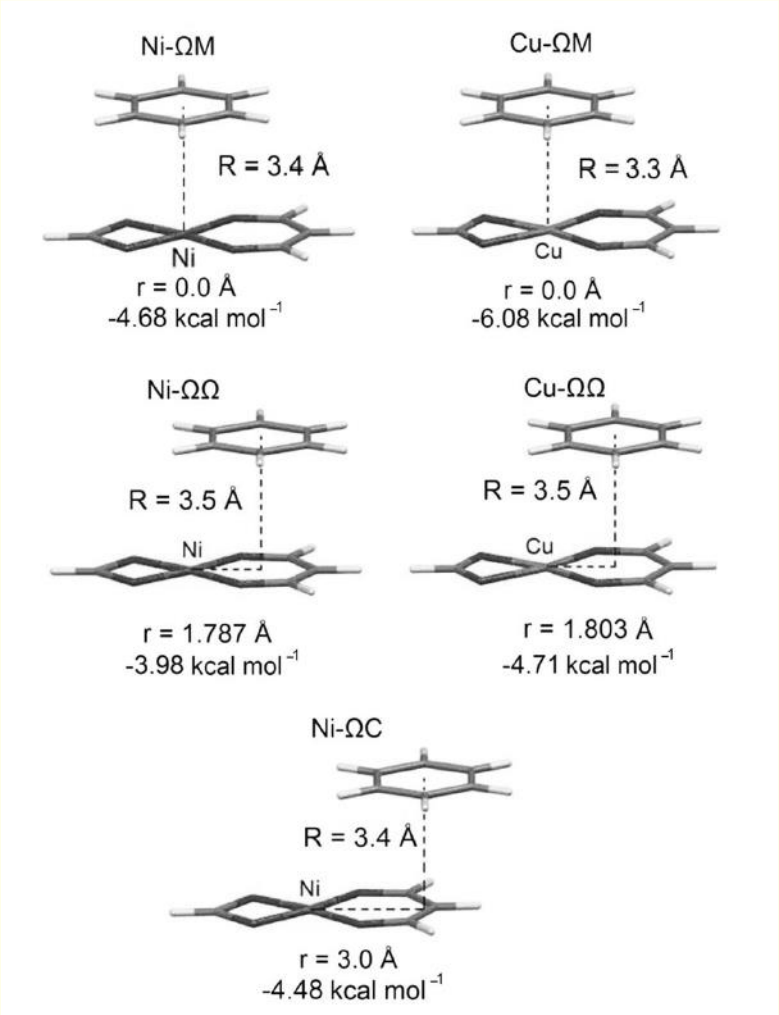
Primer: kvadrupleks guanina



Primer: kvadrupleks guanina – ligandi



Steking interakcije i helatni prstenovi



$E_{benzen\text{-}benzen}$ = -2.73 kcal/mol

D. Malenov et al. *ChemPhysChem* 15, **2014**, 2468

Steking interakcije i koordinacija sa prelaznim metalima

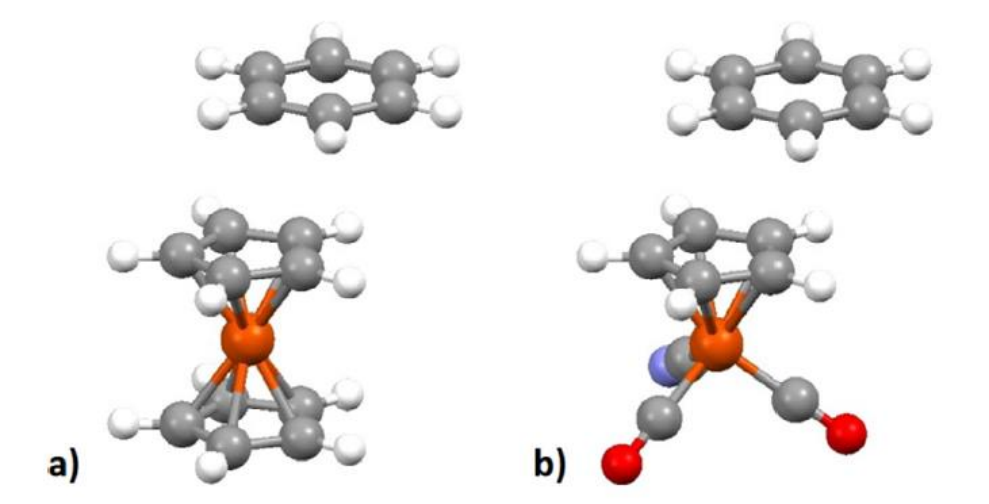
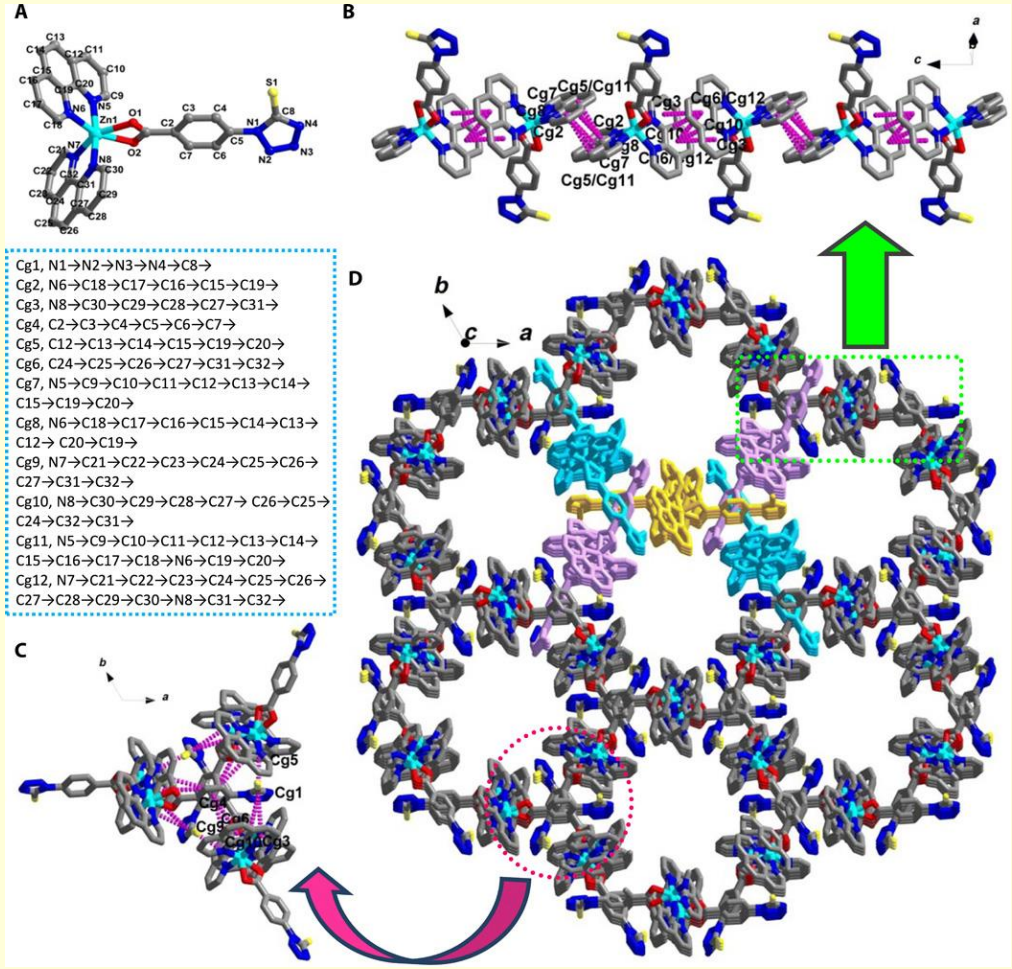


Fig. 32. Parallel-displaced geometries of stacking interactions between uncoordinated benzene and a) sandwich [$FeCp_2$], b) half-sandwich [$FeCp(CN)(CO)_2$].

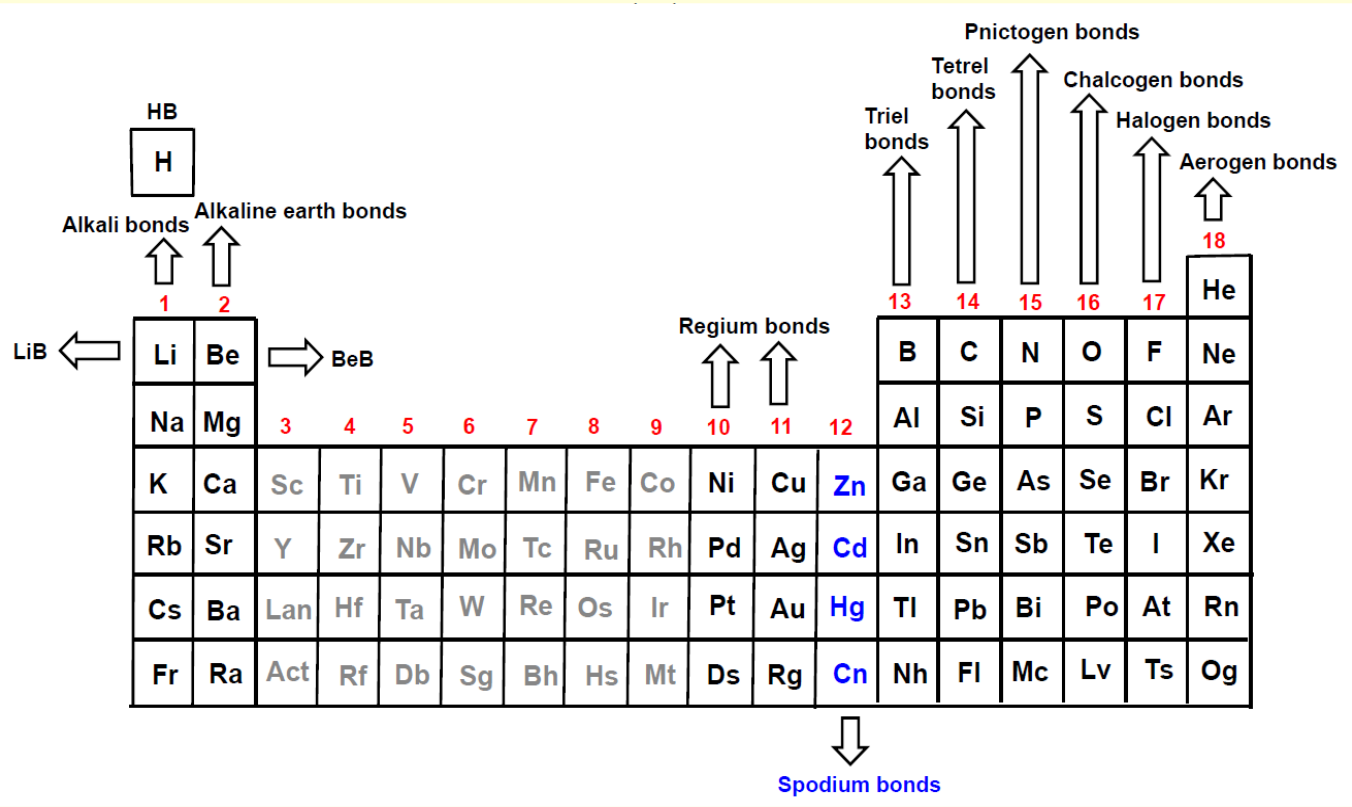
D. Malenov, S. Zarić, *Coord. Chem. Rev.* 419, **2020**, 213338

Primer: porozne supramolekulske strukture



Deng et al. *Sci. Adv.* 6, **2020**, eaax9976

Vrste nekovalentnih interakcija



- steking interakcije

Apstrakt

Napisati apstrakt o tetrelnim vezama na osnovu radova koji nisu prikazani u ovoj prezentaciji.