CAPVT IIa

Vezno, nevezno (ali ne i bezvezno)

Međumolekulske interakcije

- Interakcija permanentnih dipola (Keesomova sila)
- Interakcija permanentnog i induciranog dipola
- Interakcija induciranih dipola (disperzna, Londonova sila)
- Jaka vodikova veza
- Slaba vodikova
- Halogenska veza
- Međuhalogenska veza

- Interakcija π—π
- Interakcija π—kation
- Interakcija π—anion
- Interakcija π—halogen
- Interakcija π—halkogen (O, Te)
- Interakcija π—N
- N–H··· Cl_2–M
- Interakcija halkogen—halkogen
- ...

Najjednostavnije međumolekulske interakcije

- Interakcija permanentnih dipola (Keesomova sila)
- Interakcija permanentnog i induciranog dipola
- Interakcija induciranih dipola (disperzna, Londonova sila)

} van der Waalsove sile (interakcije)

Da bi molekula imala električni dipol

- Mora biti polarne simetrije.
- Mora imati pogodnu raspodjelu naboja – prisuće atomâ velikih razlika u elektronegativnosti.
  - Dipolni momenti obično reda veličine (10^{-30} – 10^{-29}) C m.
  - Pogodna jedinica

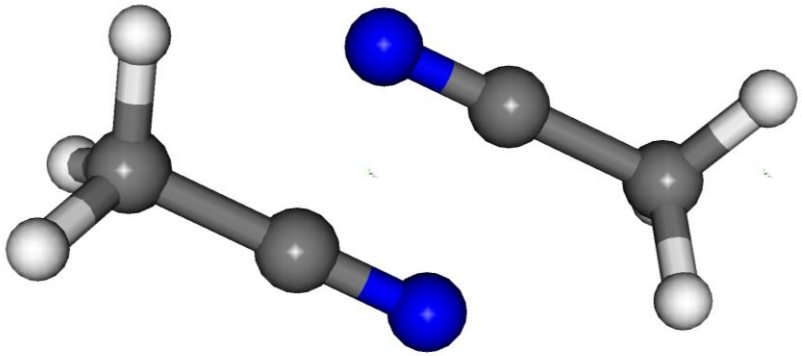
  D ≈ 3.33564×10^{-30} C·m

Molekula	μ/D
H_2O	1,8546(40)
HF	1,82618(6)
HCl	1,1086(3)
NH_3	1,14718
$CHCl_3$	1,04(2)
$(CH_3)_2CO$	2,88(3)
$(CH_3)_2SO$	3,96(4)
C_2H_5OH	1,69(3)
HCN	2,985188

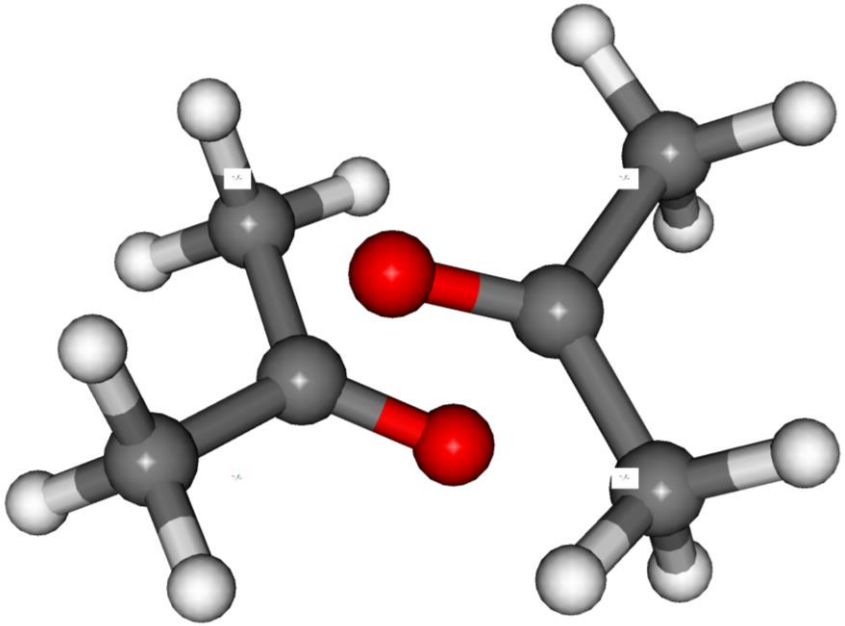
Određivanje dipolnog momenta molekule

- Mjerenjem dielektrične konstante (Clausius-Mosotti-Debyeova jednadžba).
- Iz rotacijskih spektara (Starkov učinak).
- Račun (*ab initio* ili semiempirijski) – nuždno poznavanje razmještaja atomâ u molekuli.

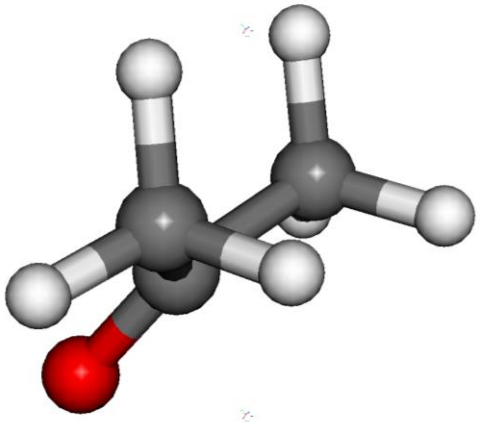
Energije dipolnih interakcija



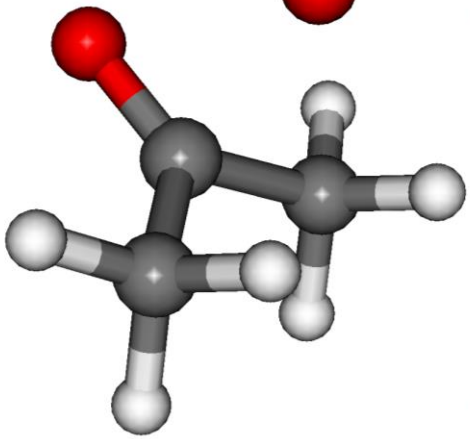
-16,0 kJ mol^{-1}



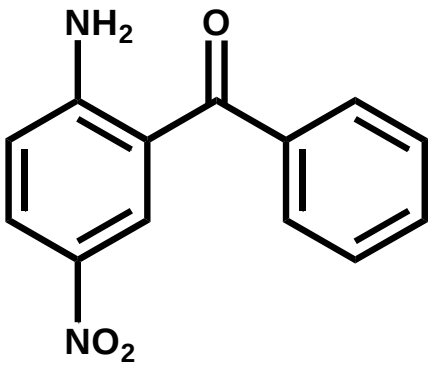
-22,3 kJ mol^{-1}

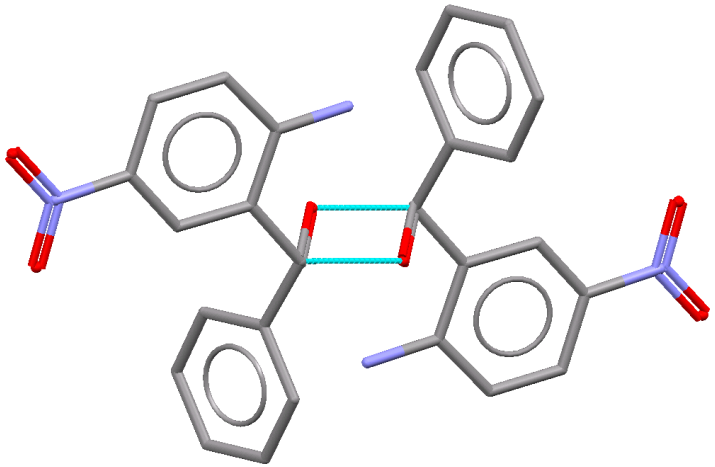


-7,6 kJ mol^{-1}



Približavanje karbonila – dipolna interakcija ili početak nukleofilne adicije?





Vodikova veza

An *A*–H···*B* interaction is called a hydrogen bond if 1) it constitutes a local bond, and 2) *A*–H acts as a proton donor to *B*.

***Interakcija* A–*H*···B *naziva se vodikovom vezom ako je 1) u pitanju lokalna veza, i 2)* A–*H djeluje kao proton-donor prema* B.**

T. Steiner, *Angew. Chem.*, **41** (2002), 41-76.

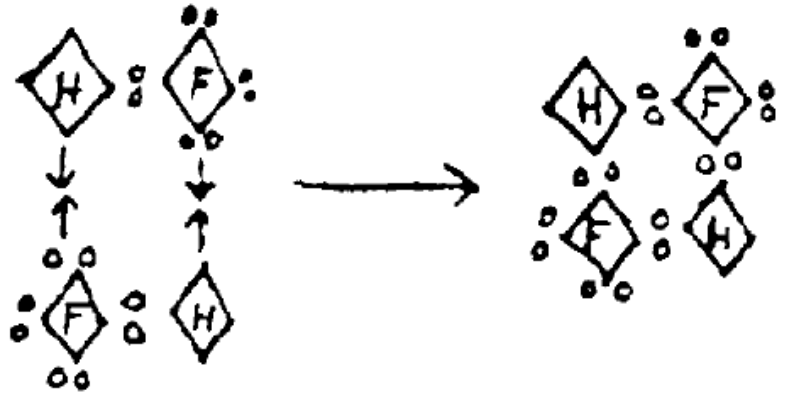
Podjela prema G. A. Jeffreyju (1997.)

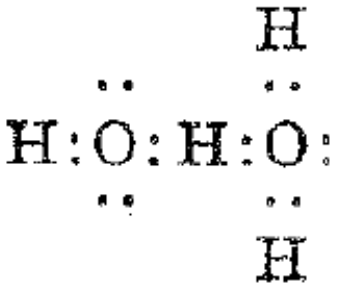
	jaka	srednja	slaba
vrsta interakcije	kovalentna	elektrostatska	elektrostatska / disperzijska
duljina veze H···*A* (Å)	1,2 – 1,5	1,5 – 2,2	> 2,2
produljenje veze *X*–H (Å)	0,08 – 0,25	0,02 – 0,08	< 0,02
omjer *X*–H/H···*A*	*X*–H ≈ H···*A*	*X*–H < H···*A*	*X*–H << H···*A*
X···*A* (Å)	2,2 – 2,5	2,5 – 3,2	> 3,2
usmjerenost	jaka	srednja	slaba
kut (°)	170 – 180	> 130	> 90
energija veze (kcal mol^{-1})	15 – 40	4 – 15	< 4
rel. pomak u IR spektru (cm^{-1})	25 %	10 – 25 %	< 10 %

Kovalentna?

G. N. Lewis, 1916.

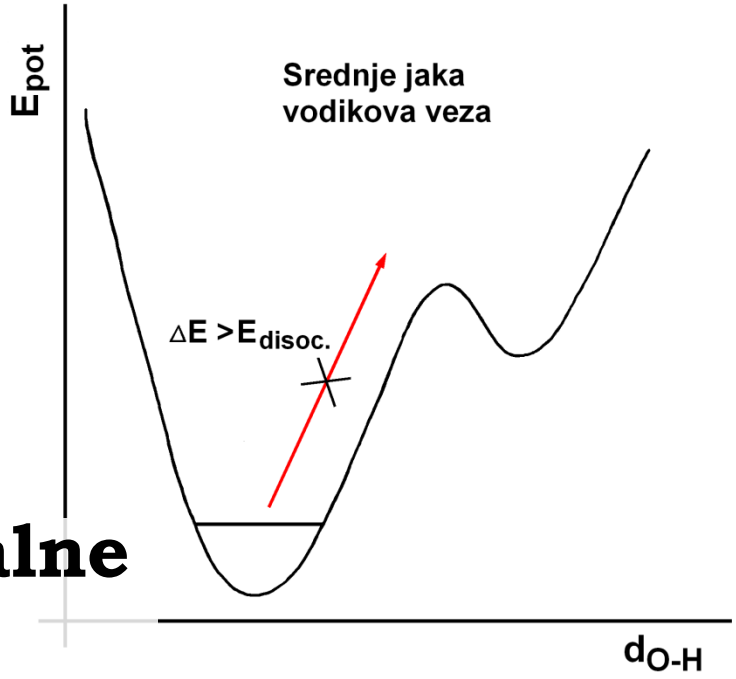
M. L. Huggins, 1919.





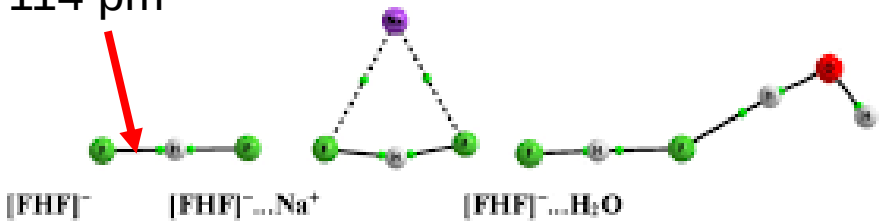
Latimer & Rodebush, 1920.

Potencijalne jame

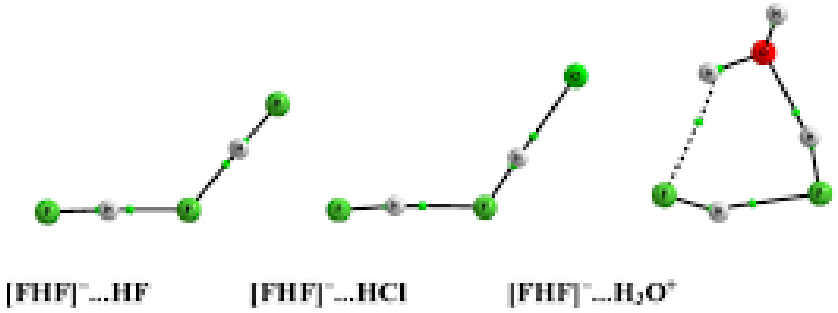


Jaka vodikova veza: hidrogendifluoridni anion (HF_2^-)

114 pm

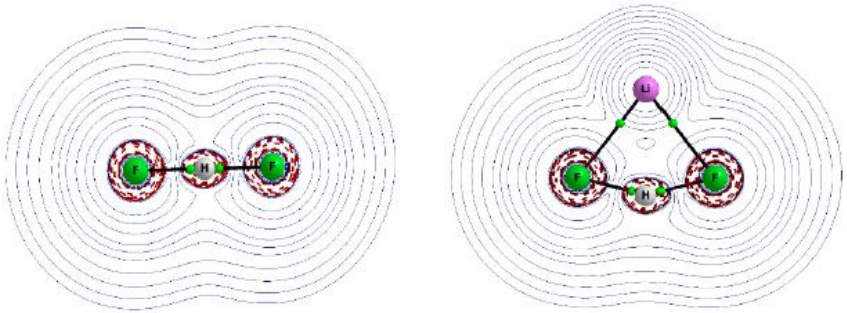


[FHF]⁻ [FHF]⁻...Na⁺ [FHF]⁻...H₂O

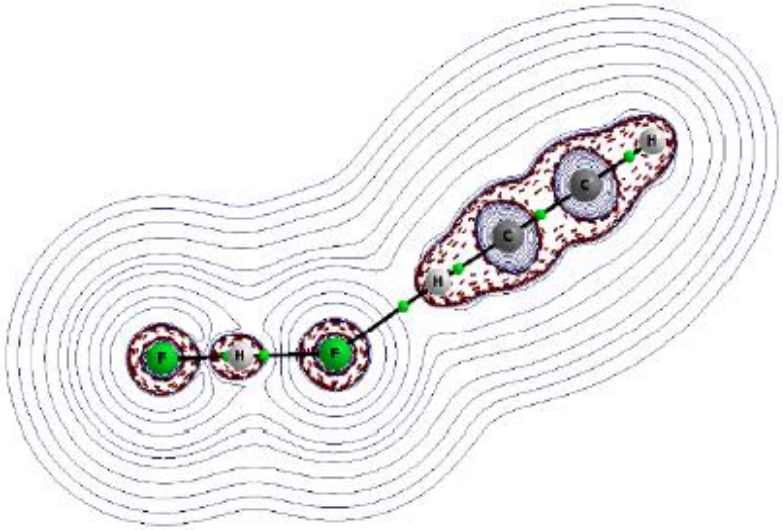


[FHF]⁻...HF [FHF]⁻...HCl [FHF]⁻...H₃O⁺

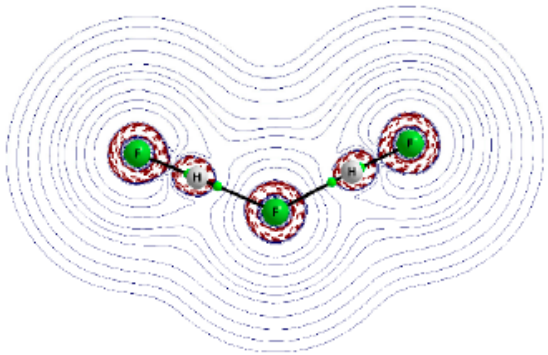
Energija veze > 155 kJ/mol. (energija veze u molekuli HF 565 kJ/mol, a u molekuli F_2 = 155 kJ/mol).



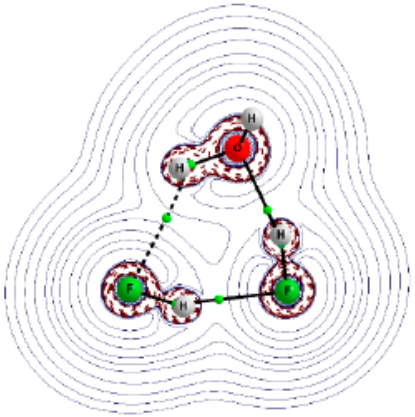
[FHF]⁻ [FHF]⁻...Li⁺



[FHF]⁻…HCCH

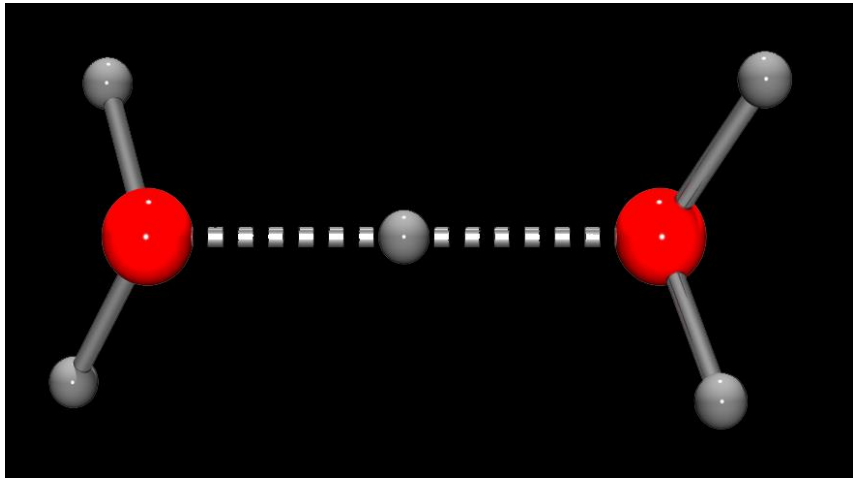


[FHF]⁻…HF

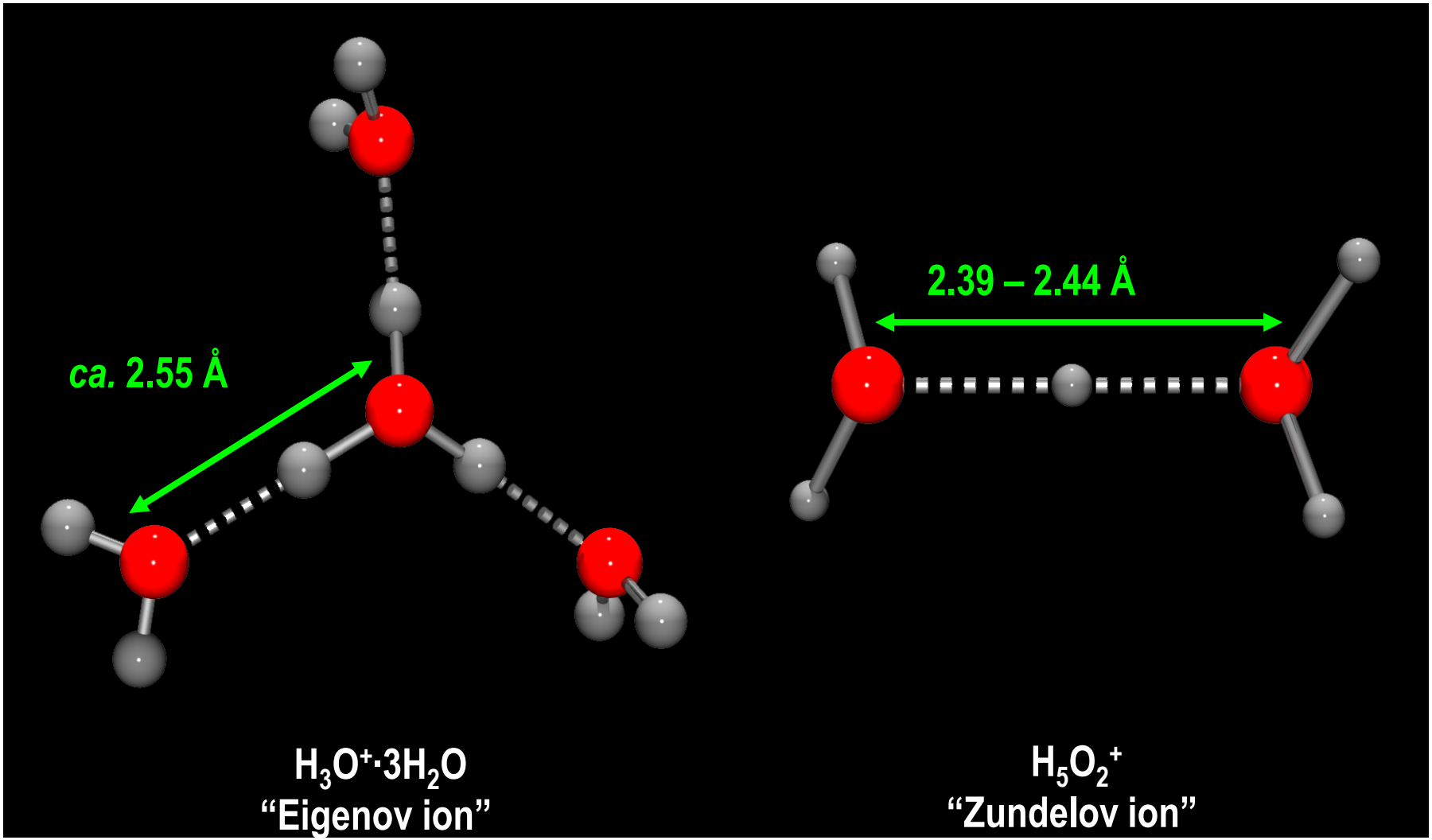


[FHF]⁻…H_3O^+

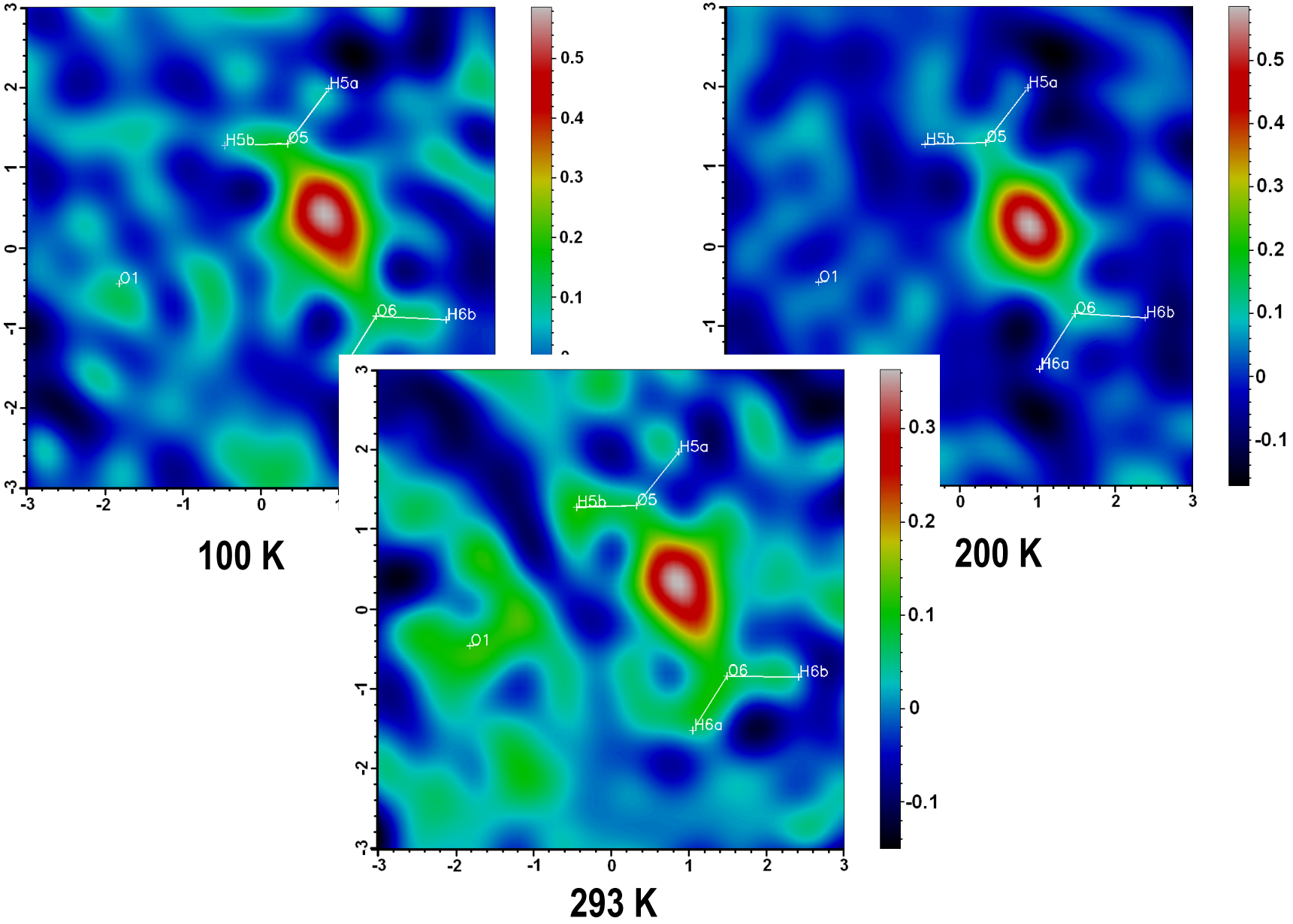
Jaka vodikova veza: Zundelov ion ($H_5O_2^+$)

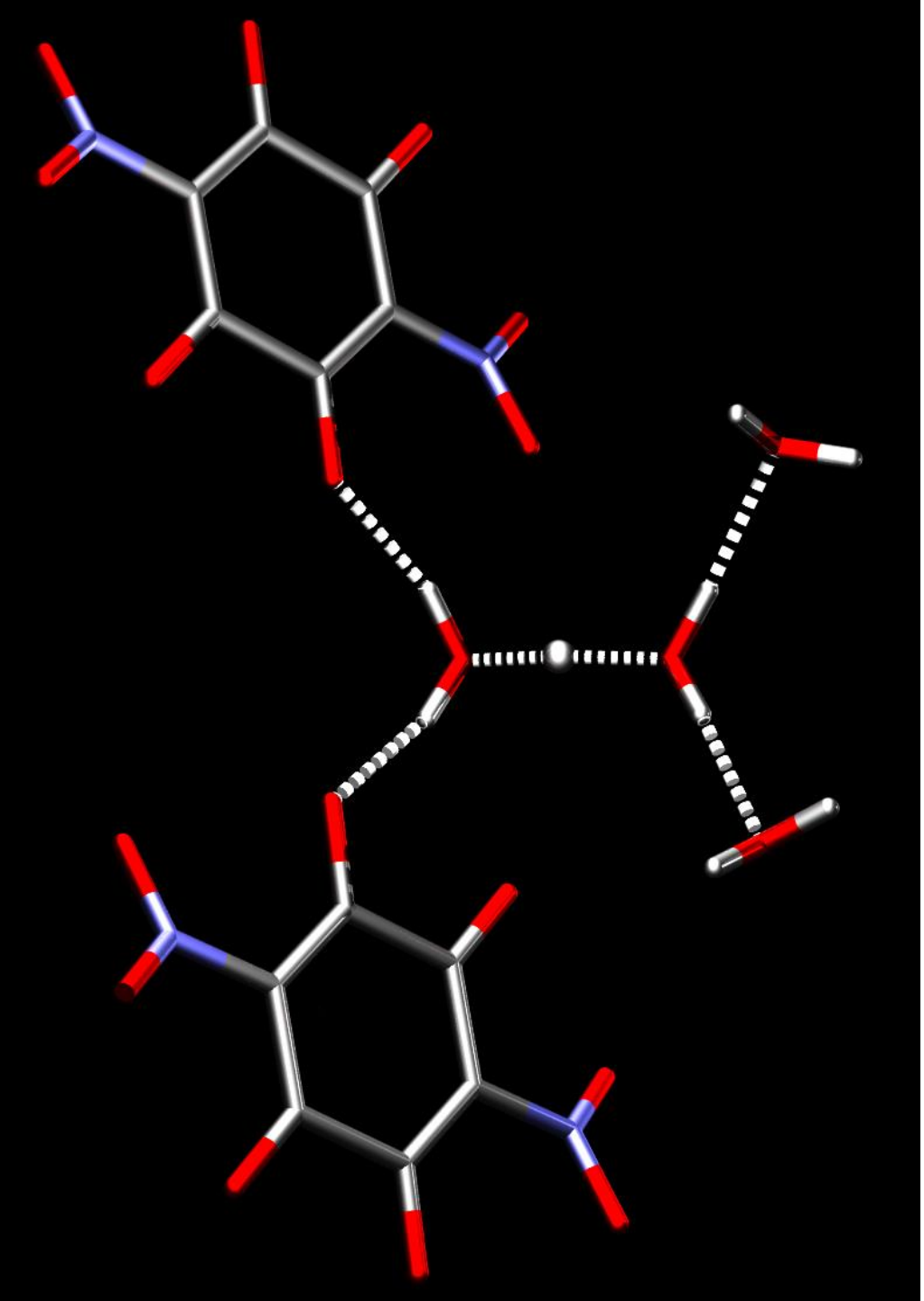


Hidronijevi ioni: koji je stabilniji?



Gdje je proton?

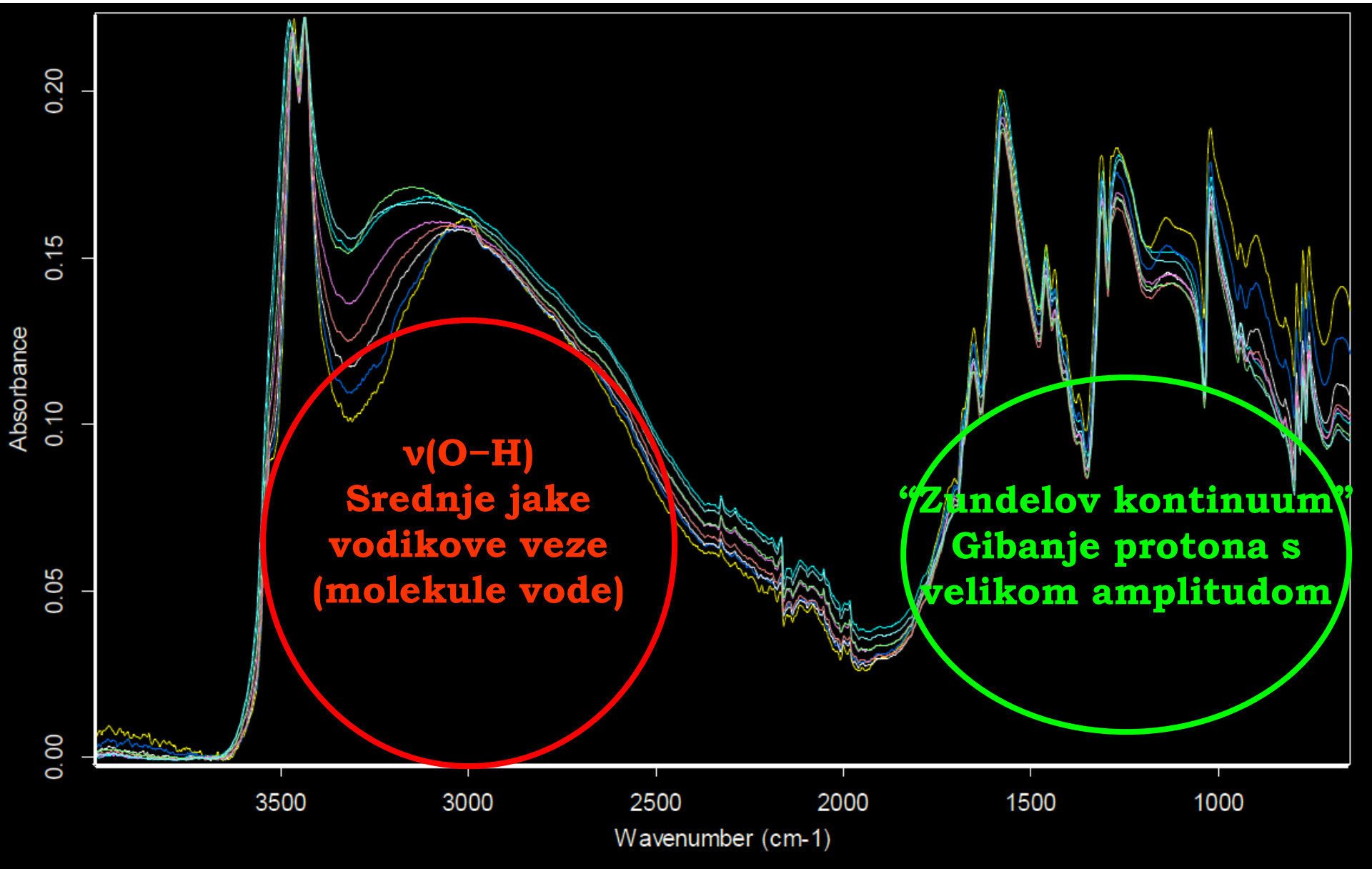




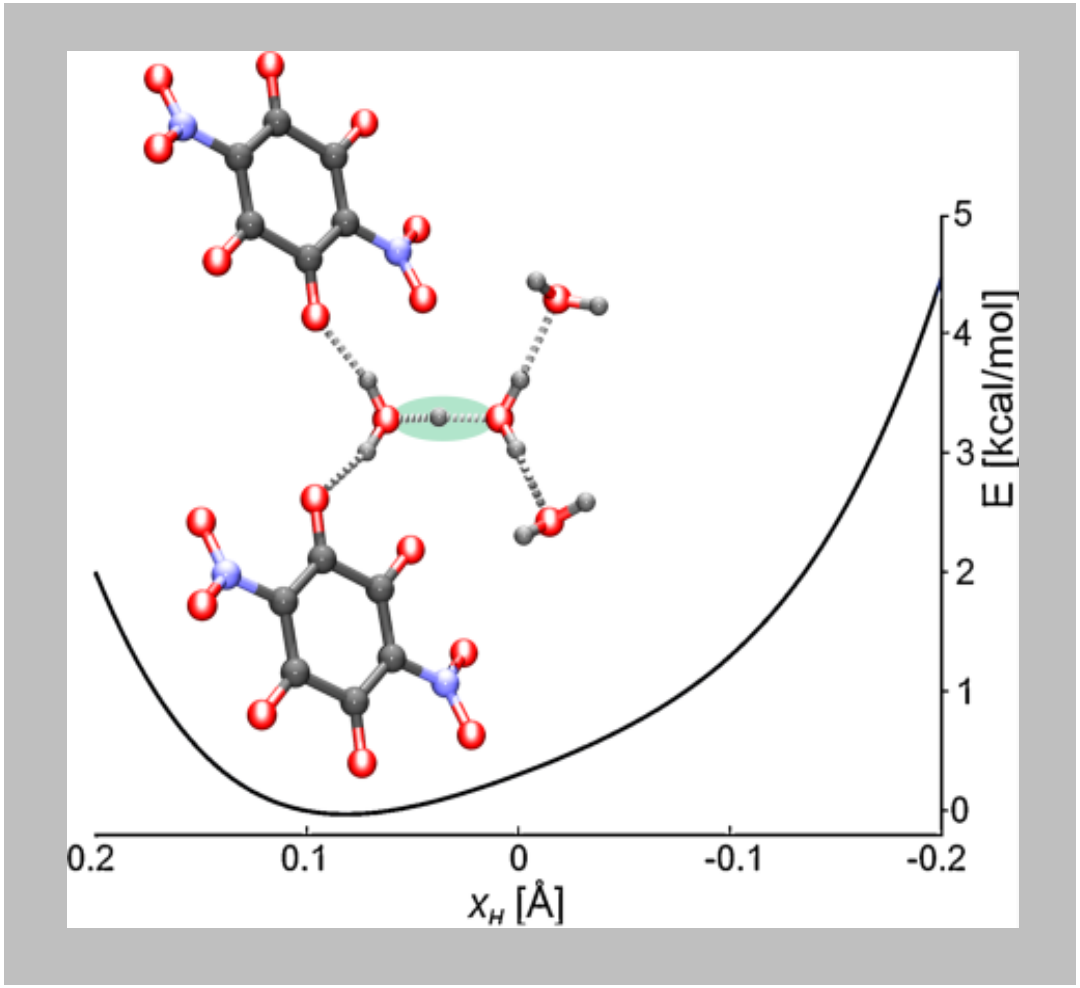
Duljina veze
O···H···O:

100 K	**2.433(2)**
150 K	**2.433(2)**
200 K	**2.433(2)**
250 K	**2.436(2)**
293 K	**2.438(2)**

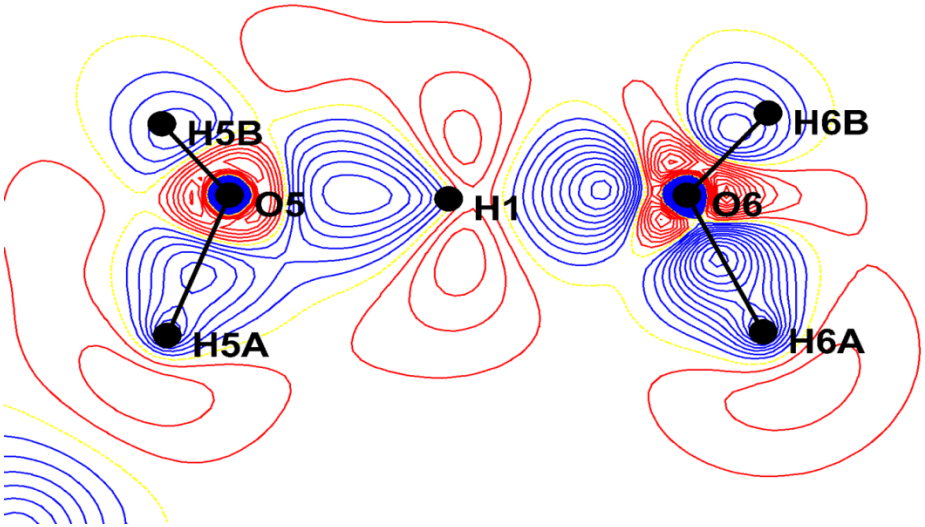
IR spektri


Absorbance
0.00
0.05
0.10
0.15
0.20
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
ν(O–H)
Srednje jake
vodikove veze
(molekule vode)
“Zundelov kontinuum”
Gibanje protona s
velikom amplitudom

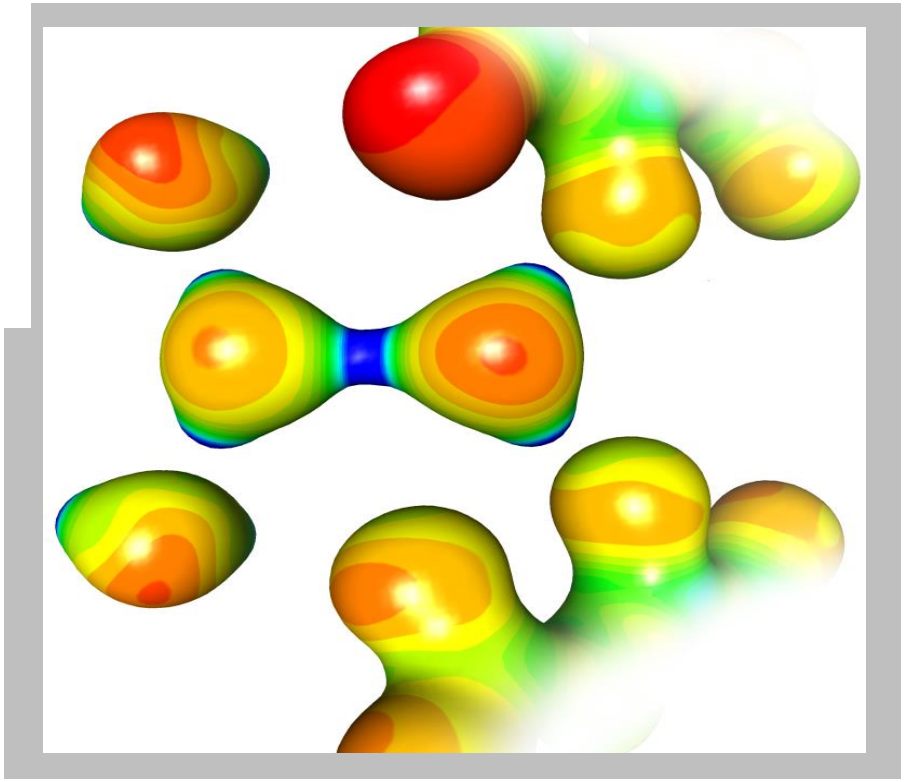
Iz kvantno-kemijskih računa:



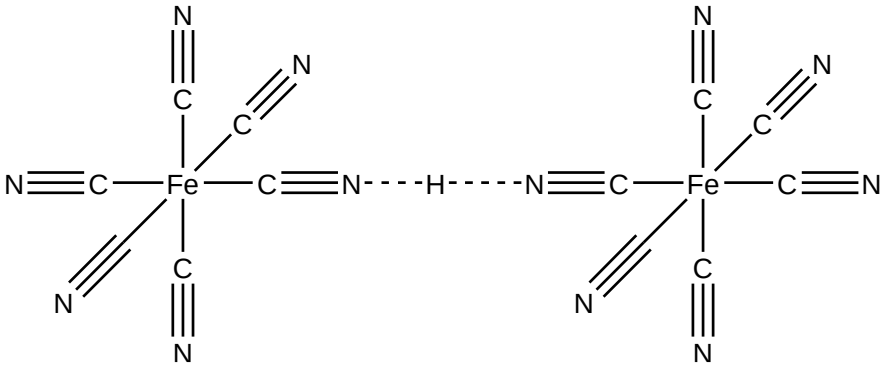
Gustća naboja na Zundelovom ionu

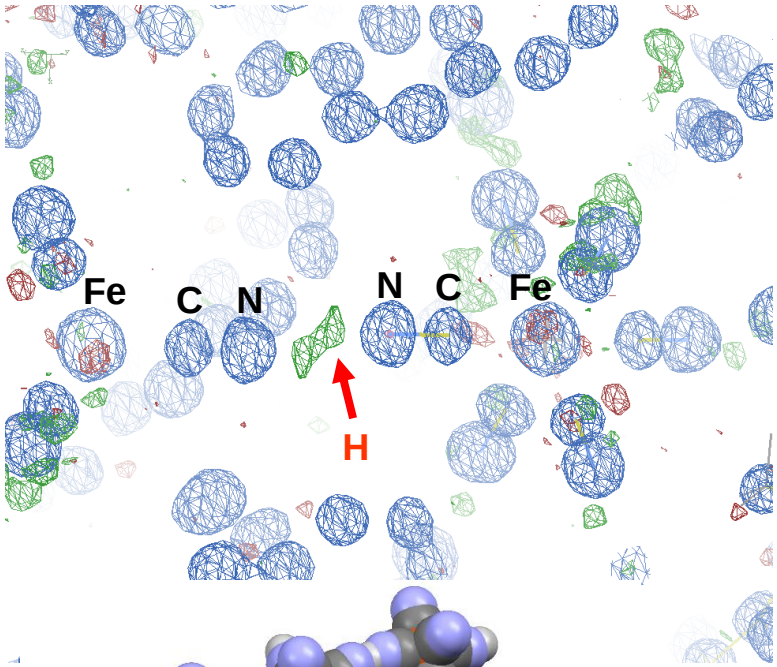


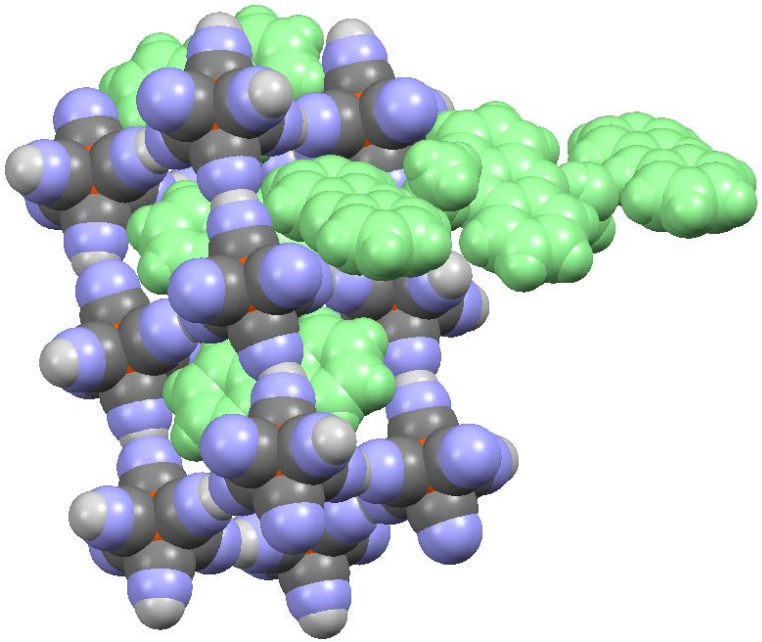
Površina: 0,5 e Å-3

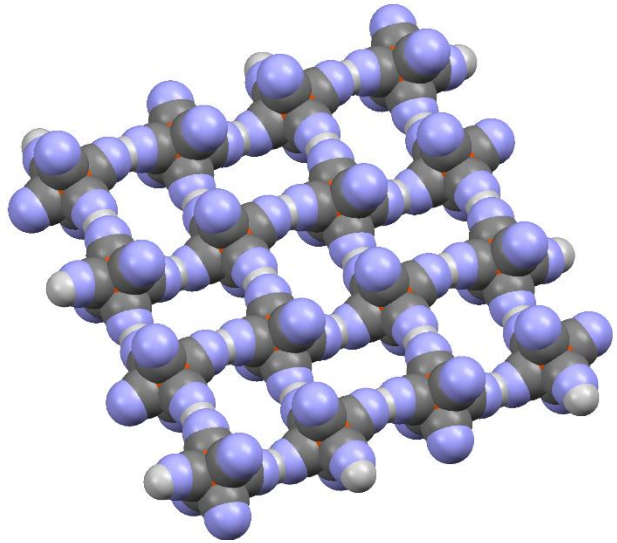


Jaka vodikova veza: protonirani heksacijanoferati





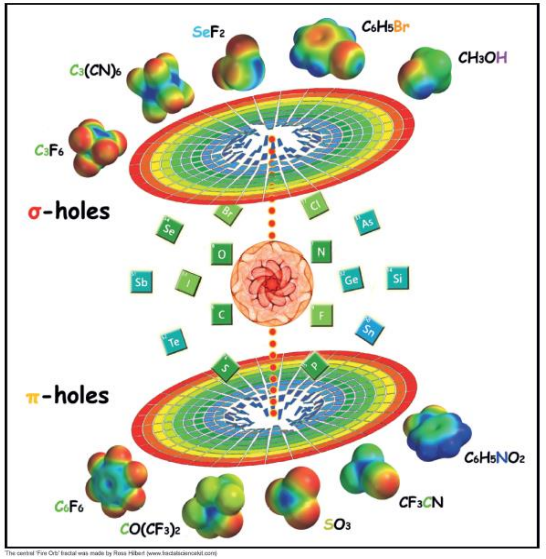




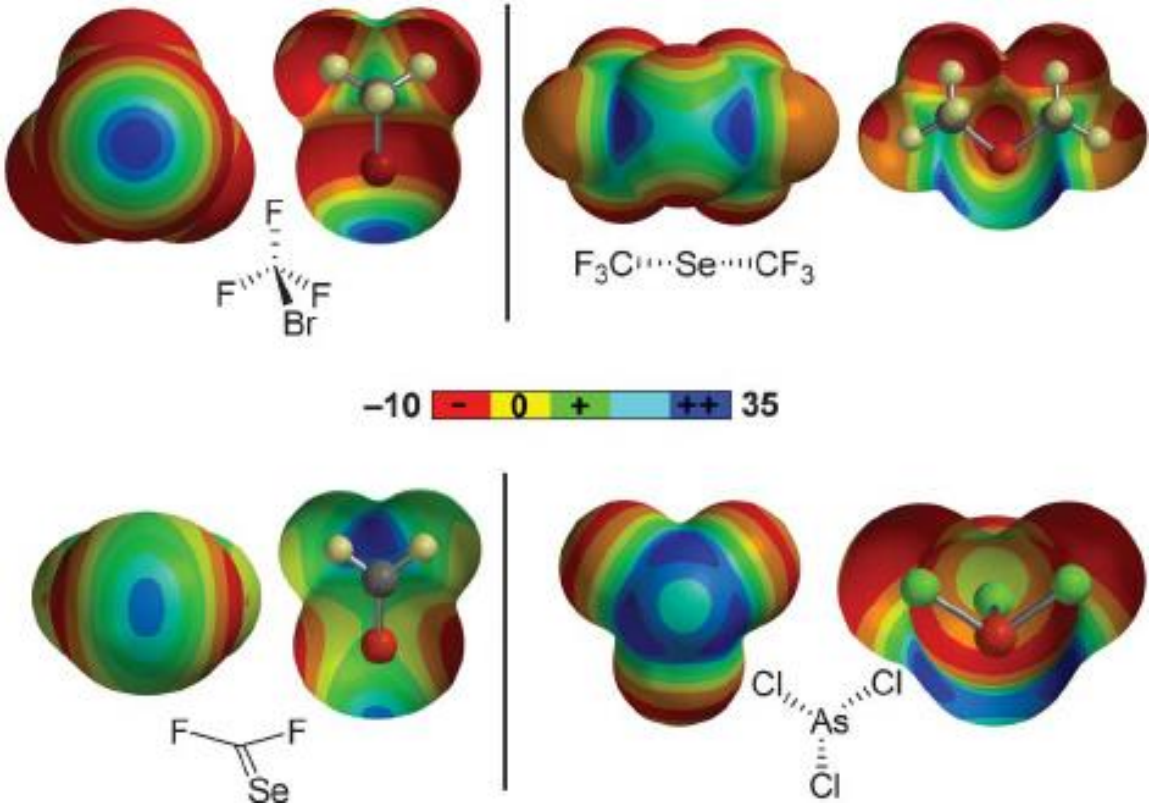
Interakcije σ-šupljine

Svi teški atomi su polarizabilni – nasuprot kovalentne veze imaju manjak elektrionske gustoće – Lewisove kiseline (elektrofili)

Halogenska veza
Halkogenska veza
Pnikogenska veza
Tetrelna veza
Trielna veza
Aerogenska veza



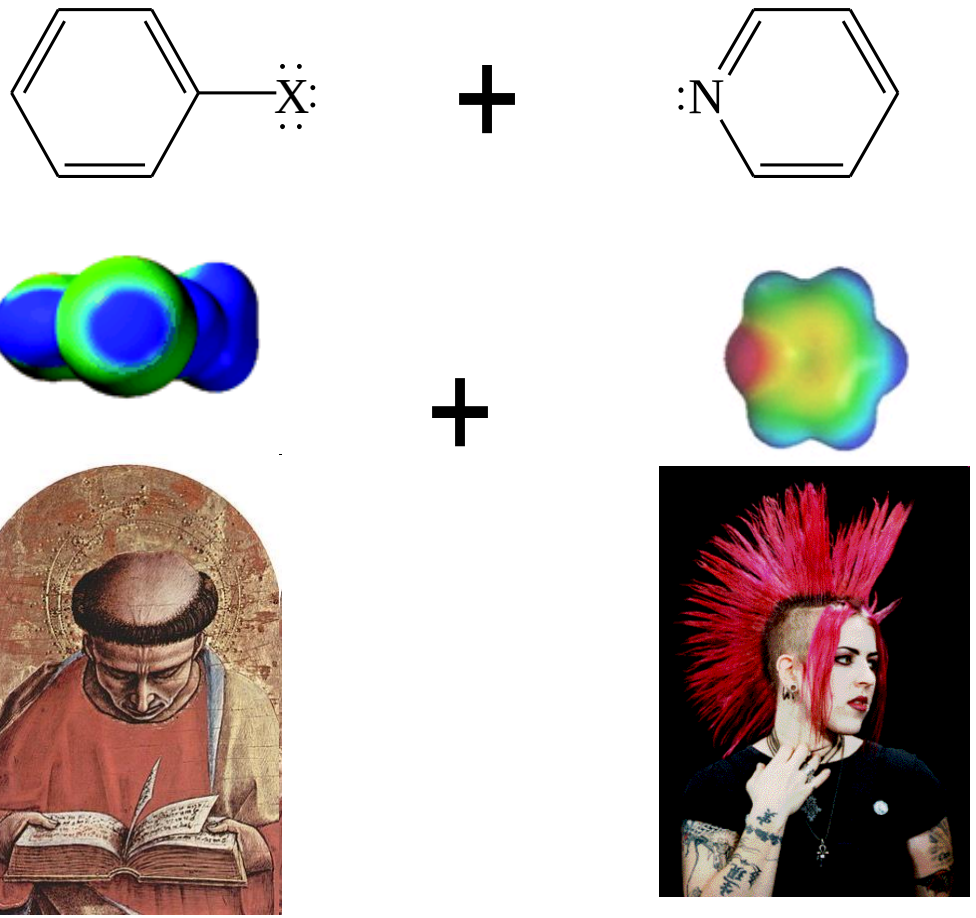
A. Bauza, T.J. Mooibroek, A. Frontera, The Bright Future of Unconventional σ/π-Hole Interactions, *ChemPhysChem.*, 2016, 16, 2496.



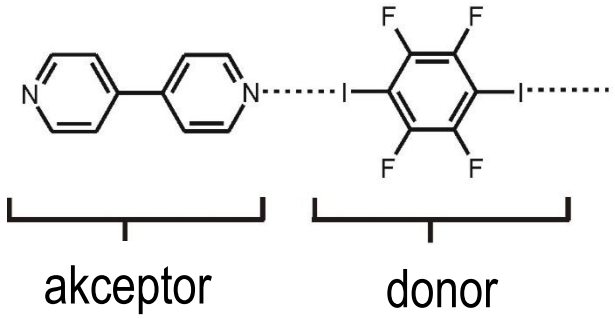
Halogenska veza

•A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.

Pure Appl. Chem., 2013, 85, 1711.



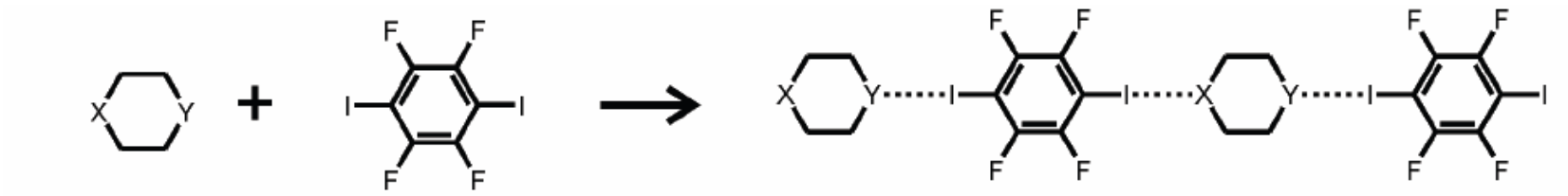
Halogenska veza

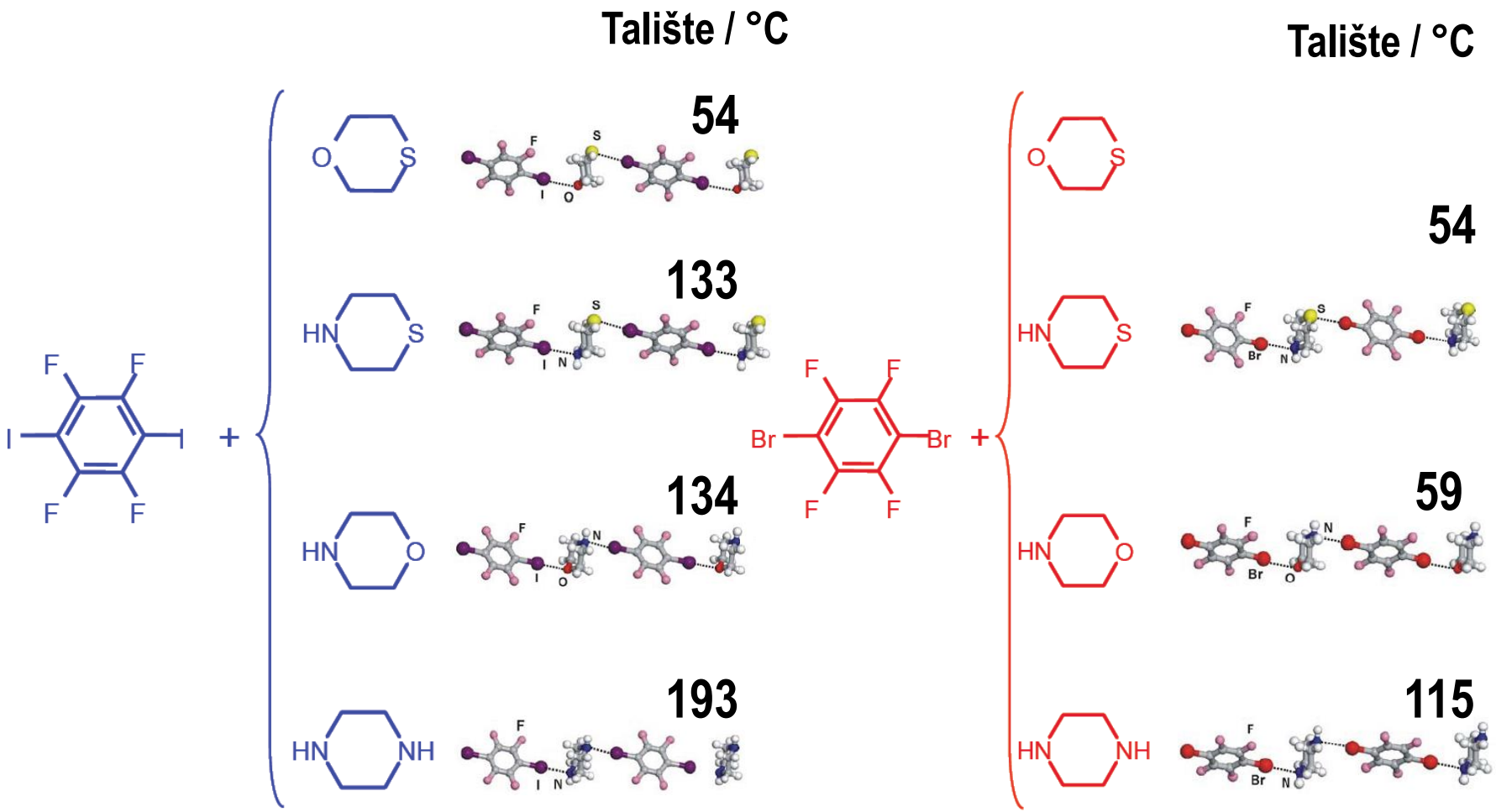


A··· X–Y

- Donor – polarizabilni (& polarizirani) atom halogena (I>Br>Cl>>F)
- Akceptor – Lewisove baze (N>O>S)
- Linearne (kut Y-X···A blizu 180°) i jake (neutralne 10–90 kJ mol^{-1} ionske > 150 kJ mol^{-1})

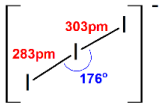
Heteroatomni derivati cikloheksana i *p*-dihalogentetrafluorbenzeni



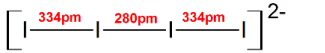


D. Cinčić, T. Friščić, W. Jones, *Chem. Eur. J.* 14 (2008) 747–753.

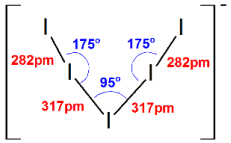
Jaka halogenska veza: polihalogenidni anioni



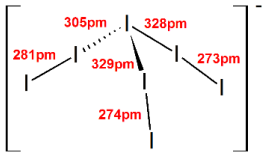
$[I_3]^-$ in $Cs^+[I_3]^-$



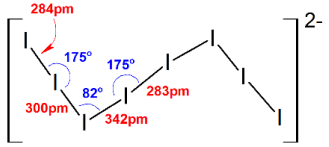
The linear $[I_4]^{2-}$ ion in $[Cu(NH_3)_4]^{2+}[I_4]^{2-}$



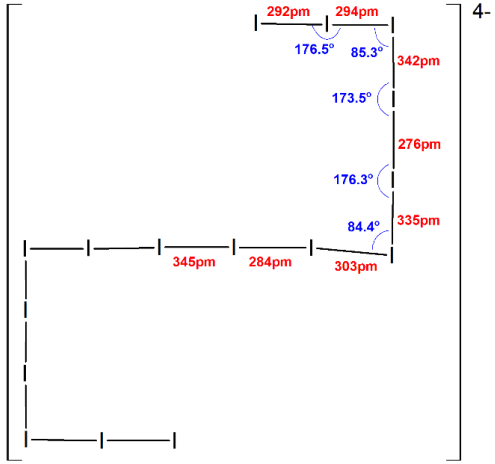
$[I_5]^-$ in $[Me_4N]^+[I_5]^-$



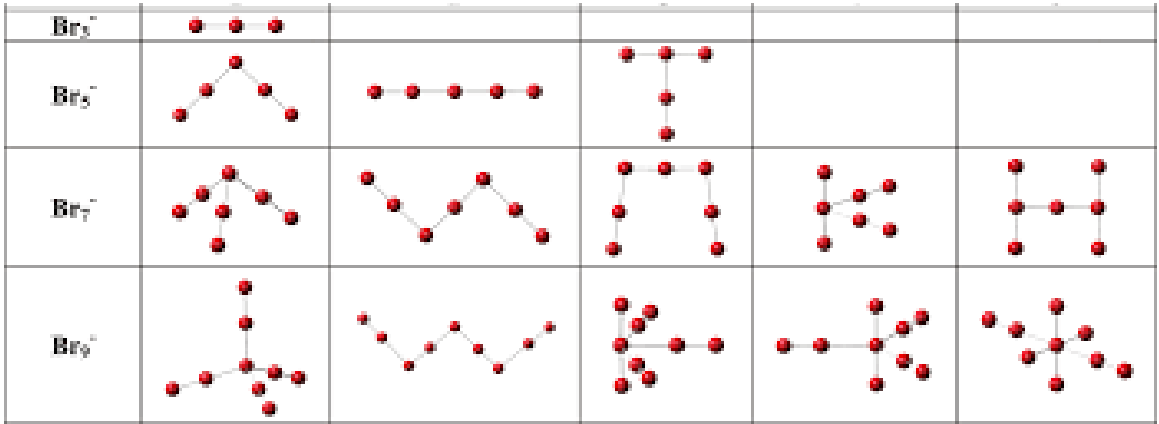
$[I_7]^-$ in $[Ph_4P]^+[I_7]^-$



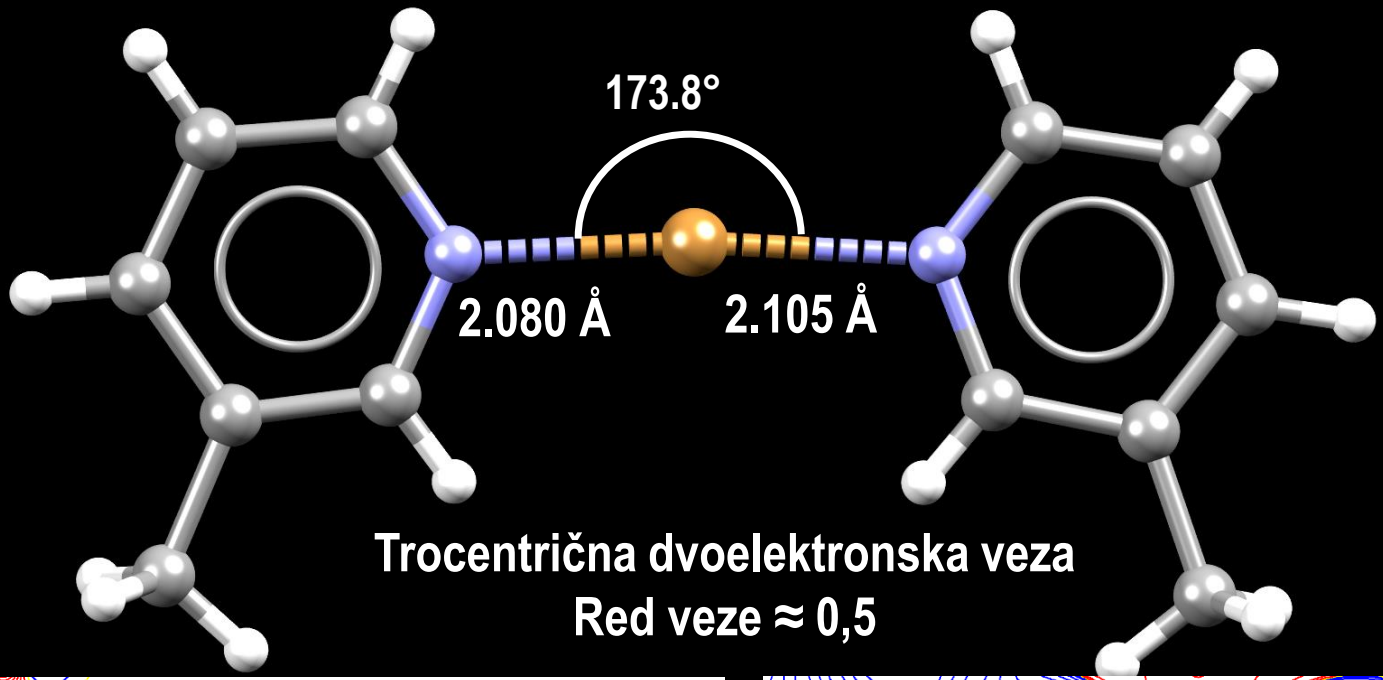
The centrosymmetric $[I_8]^{2-}$ ion in $Cs_2[I_8]$



The centrosymmetric $[I_{16}]^{4-}$ ion in $[C_7H_9N_4O_2]_4[I_{16}]$, $[C_7H_9N_4O_2]^+$ is the protonated theobromine ion

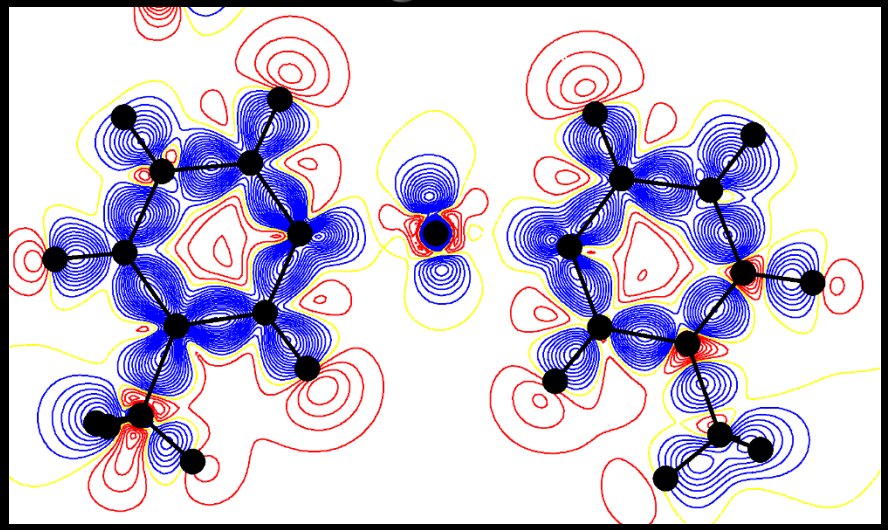


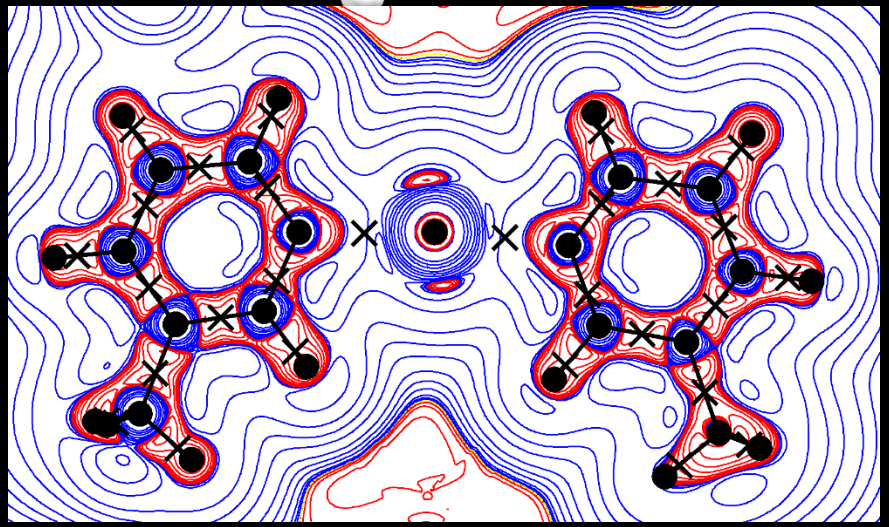
Kovalentna? Halonijevi ioni



Trocentrična dvoelektronska veza

Red veze ≈ 0,5

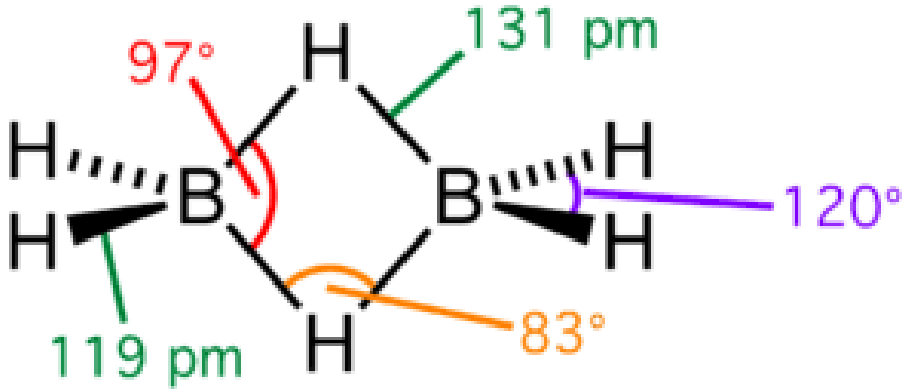


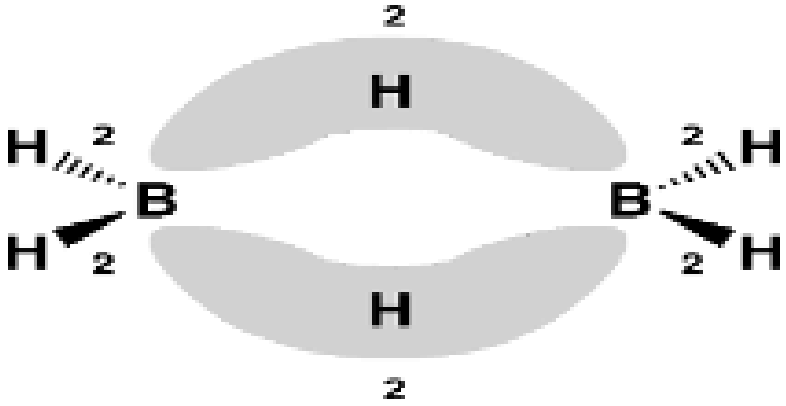


Banane i palačinke

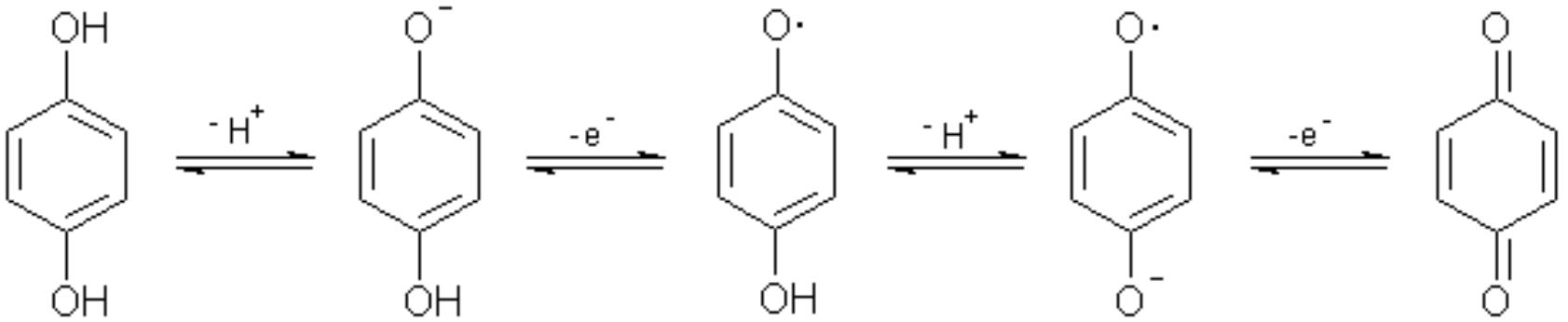
Kratak pogled u svijet policentričnih veza

3c, 2e – '*Banana Bond*'



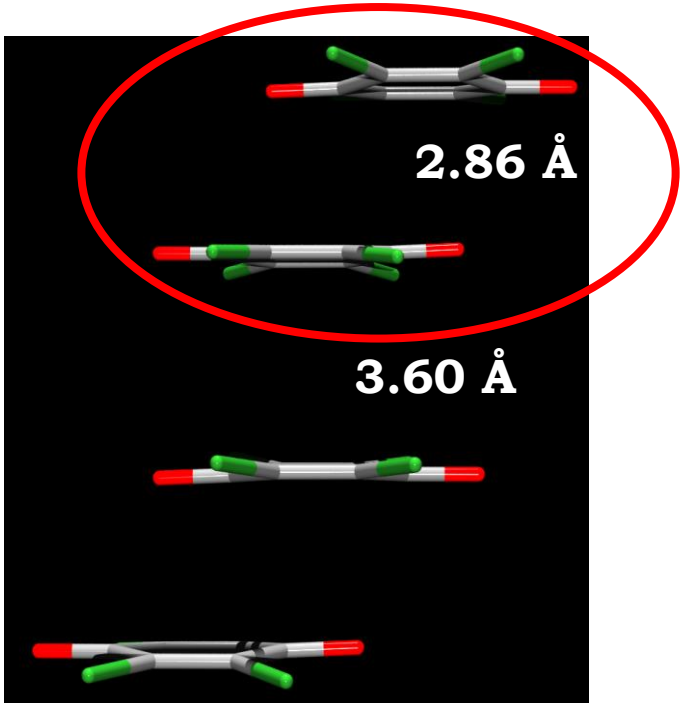


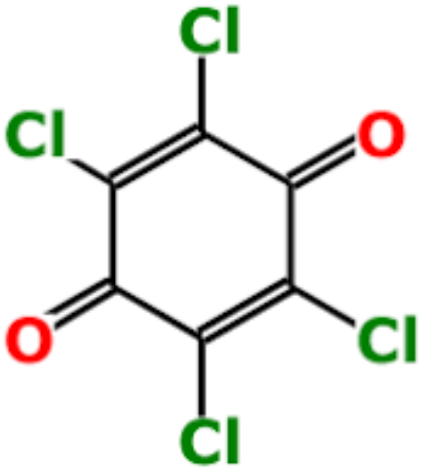
Višecentrične veze? semikinonski radikal-anioni



hidrokinon — fenoksidni anion — fenoksilni radikal — semikinonski radikal-anion — kinon

24c, 2e – '*Pancake Bond*'





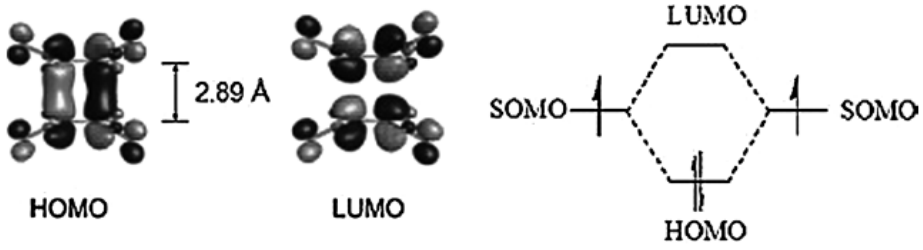
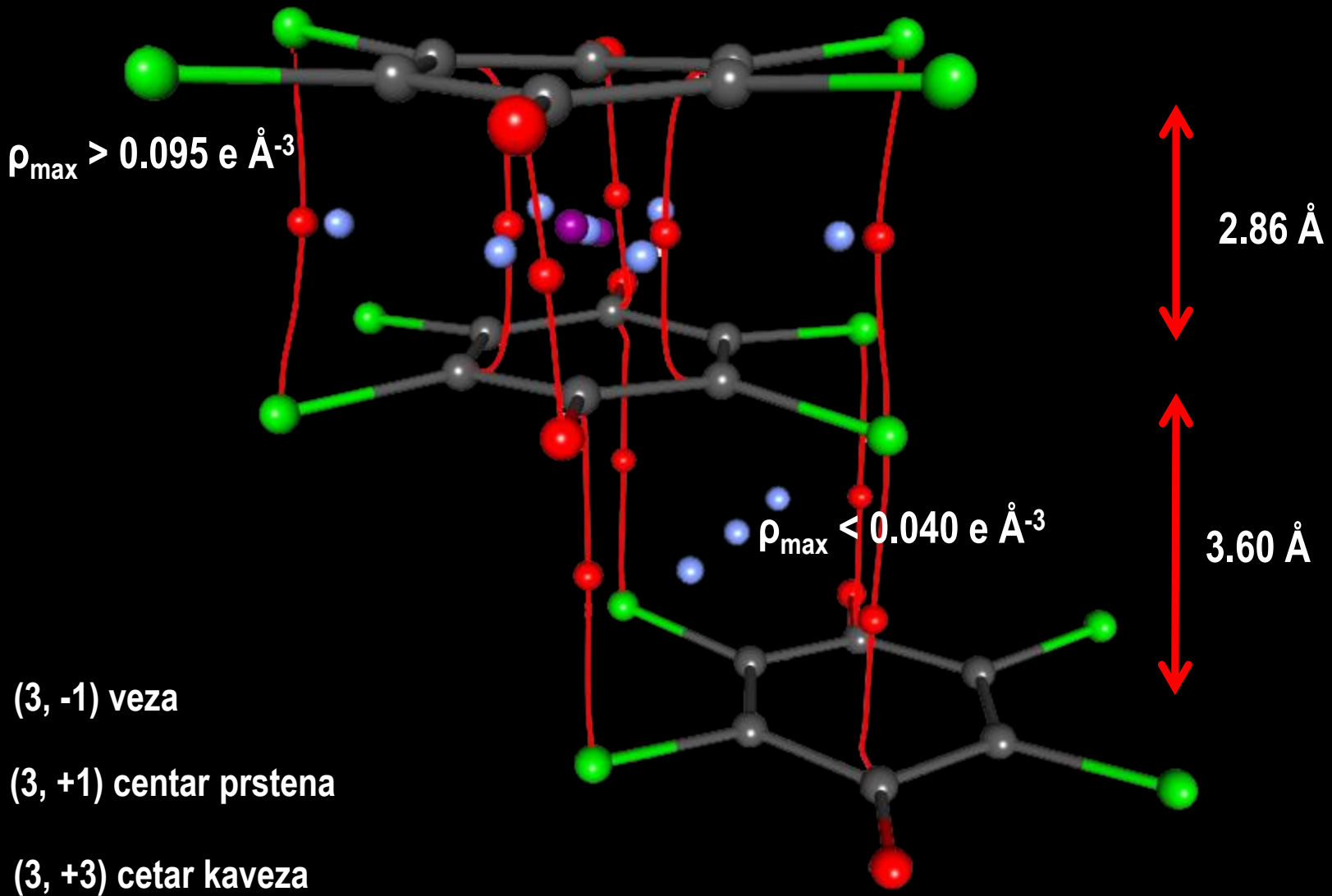
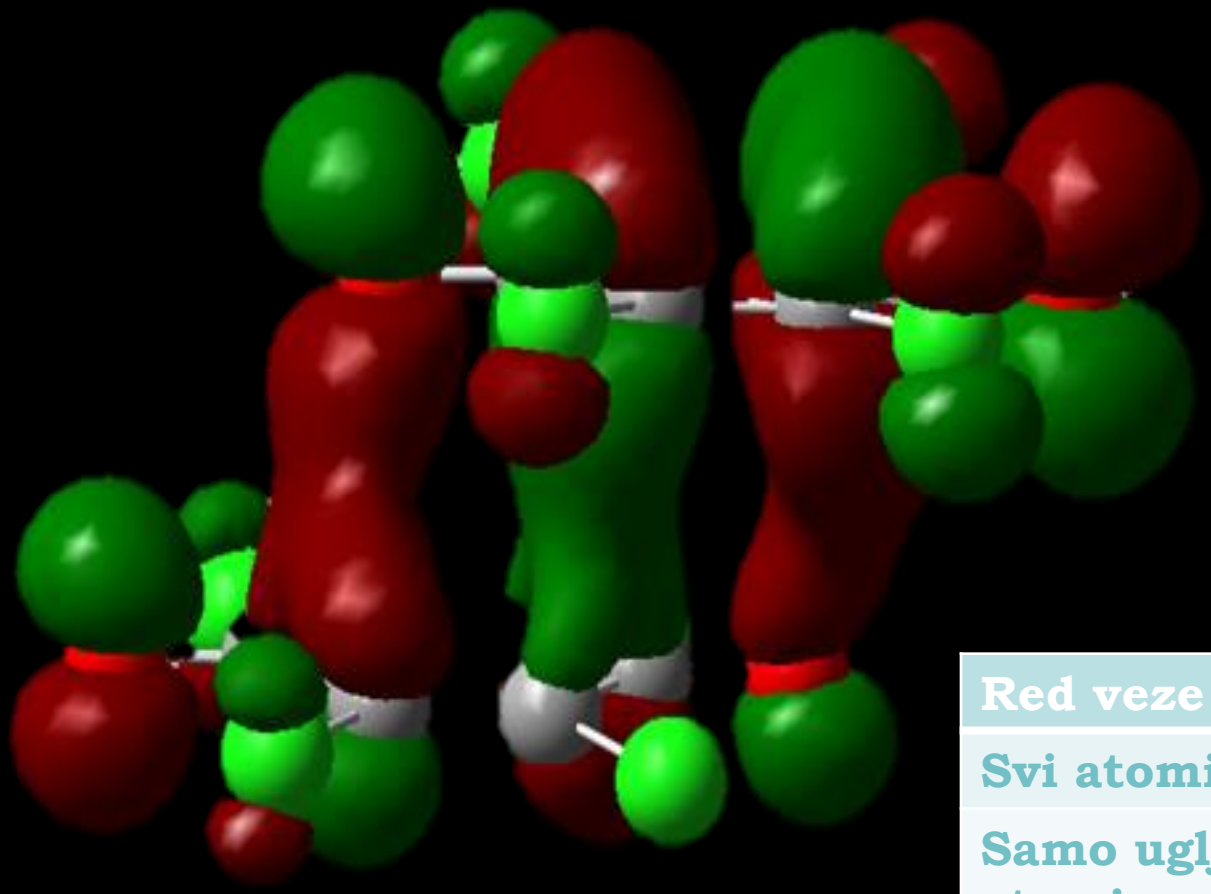


Figure 1. Illustration of the bonding (b_{3u}) and antibonding (b_{2g}) combinations of the two SOMOs in $TCNE_2^{2-}$ as obtained by using Hartree–Fock (HF) calculations. The energy level diagram is on the right.

Topologija elektronske gustoće u dimerima



HOMO orbitala dimera

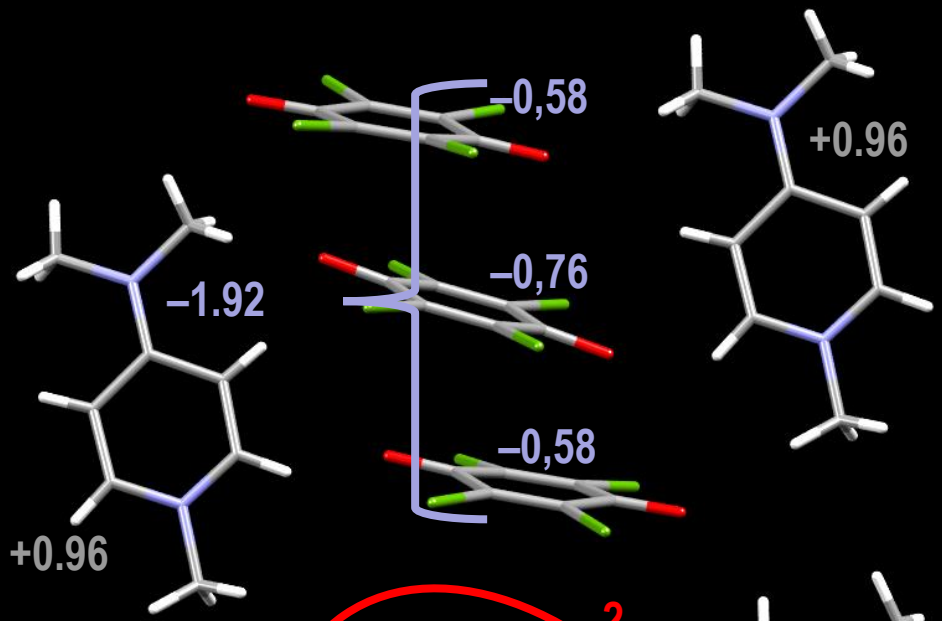


Red veze	
Svi atomi	0.80
Samo ugljikovi atomi	0.27

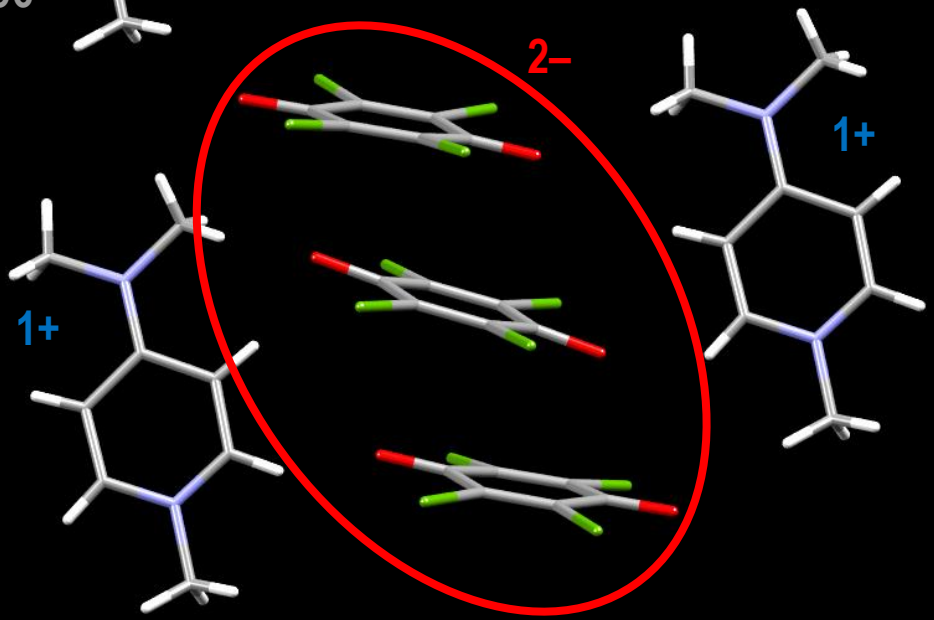
Energija veze (kovalentni doprinos): –39.4 kJ mol^{-1}

36c, 2e – [*N*-Me-4-$(Me)_2$NPy]$_2$$(Cl_4Q)_3$

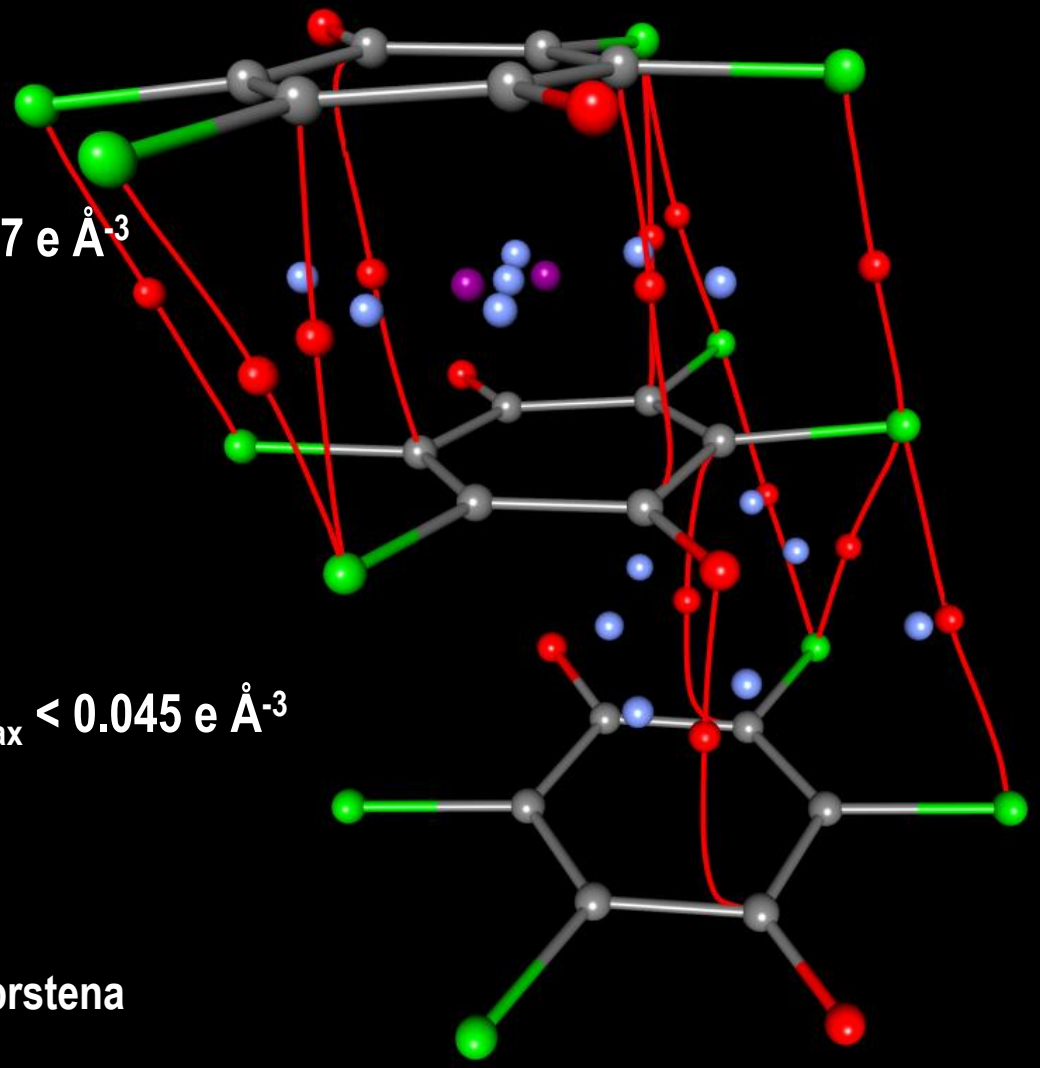
Naboji iz elektronske gustoće:



Naboji po kemijskom smislu:



Topologija elektronske gustoće u trimerima



$\rho_{max} > 0.077$ e Å^{-3}

$\rho_{max} < 0.045$ e Å^{-3}

2.84 Å

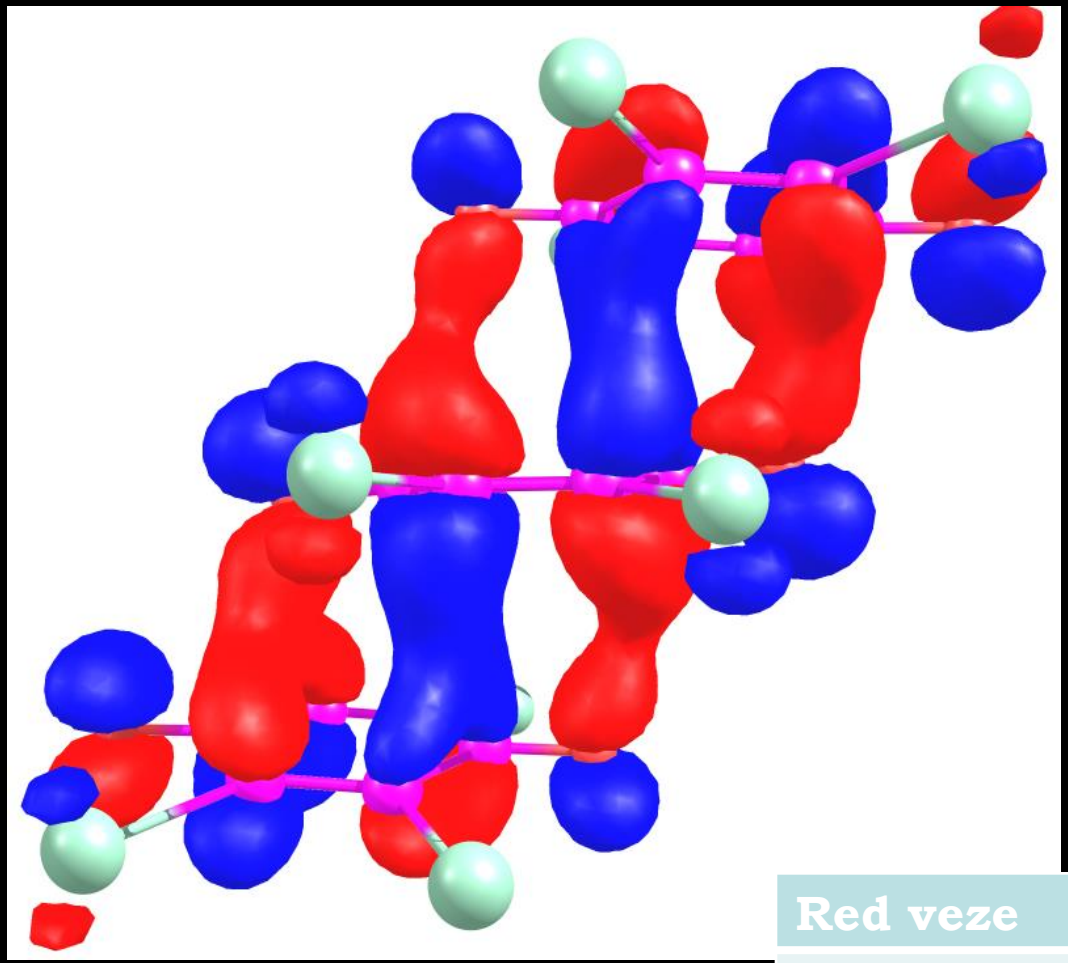
3.59 Å

(3, -1) veza

(3, +1) centar prstena

(3, +3) cetar kaveza

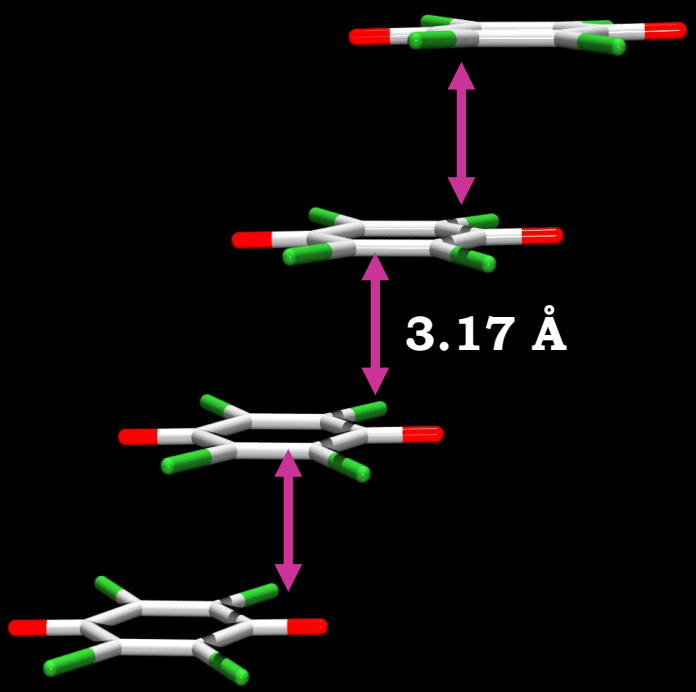
HOMO orbitala trimera

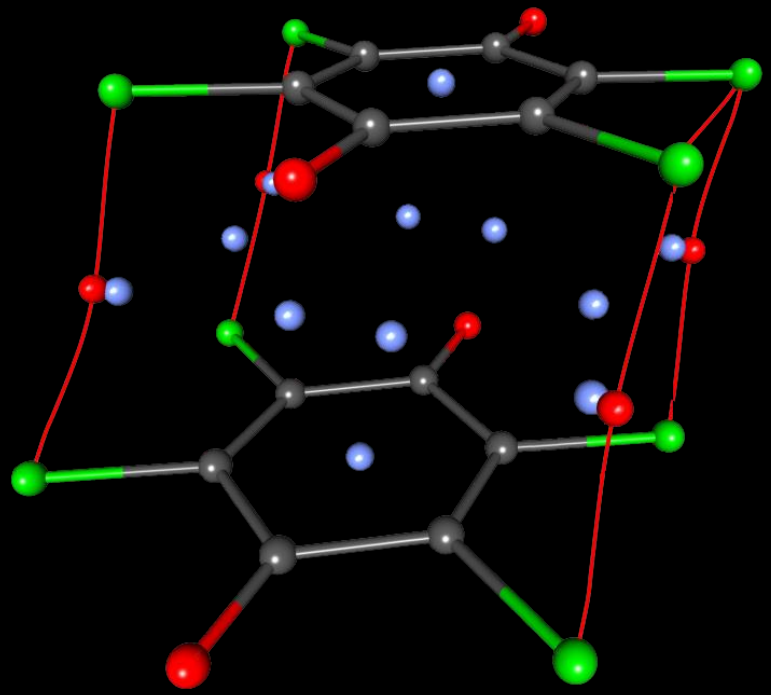


Red veze	
Svi atomi	< 0,71
(vjerojatno oko	0,5

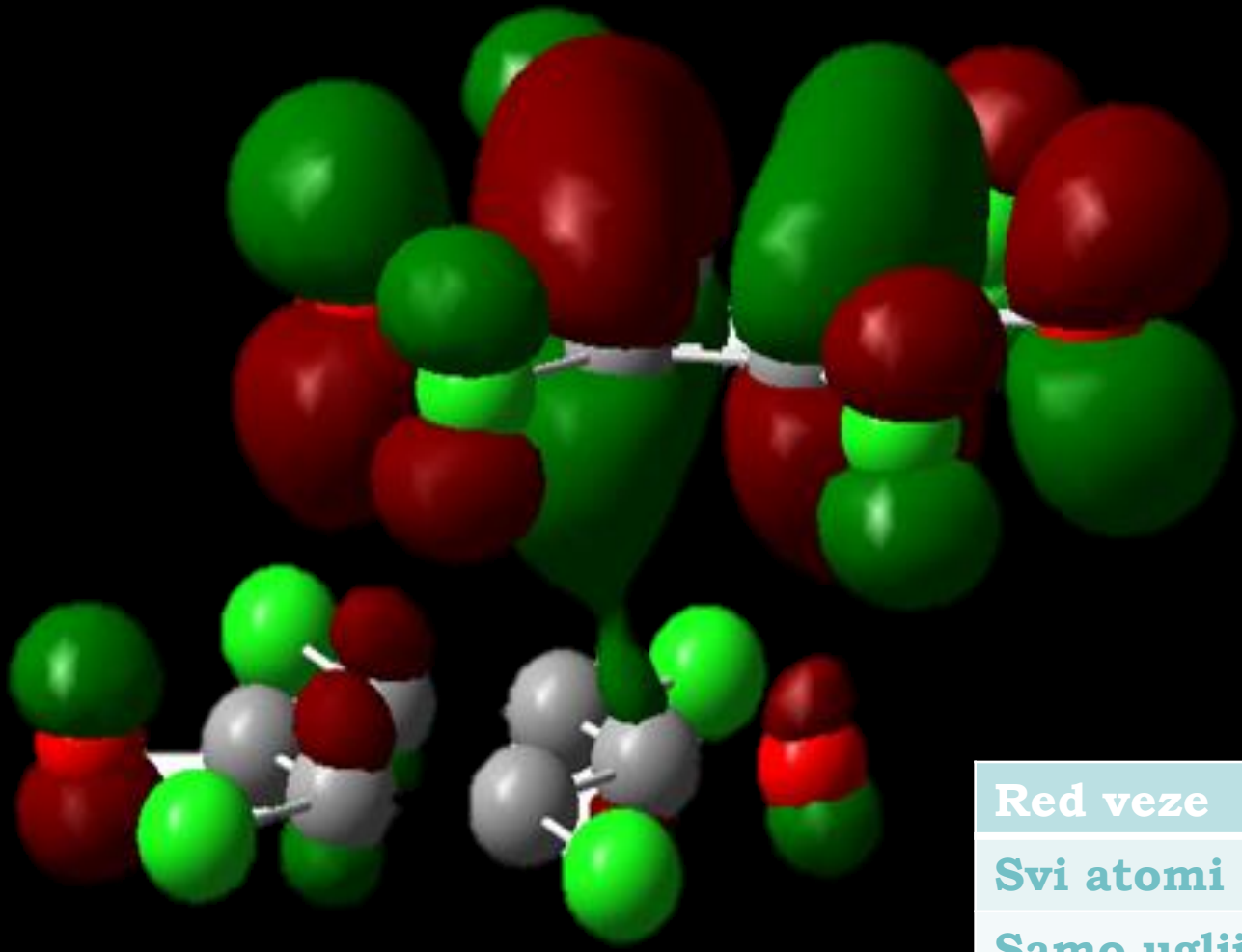
Energija veze (kovalentni doprinos): –17,2 kJ mol^{-1}

12*n* cc, *n* e – polimer





HOMO orbitala polimera



Energija veze (kovalentni doprinos): –12,4 kJ mol^{-1}

Red veze	
Svi atomi	0.26
Samo ugljikovi atomi	0.09