DEI 2022 @ SRCE

Kvantno-kemijski programi na klasteru Isabella

Rješavanje kemijskih problema upotrebom optimalnih metoda

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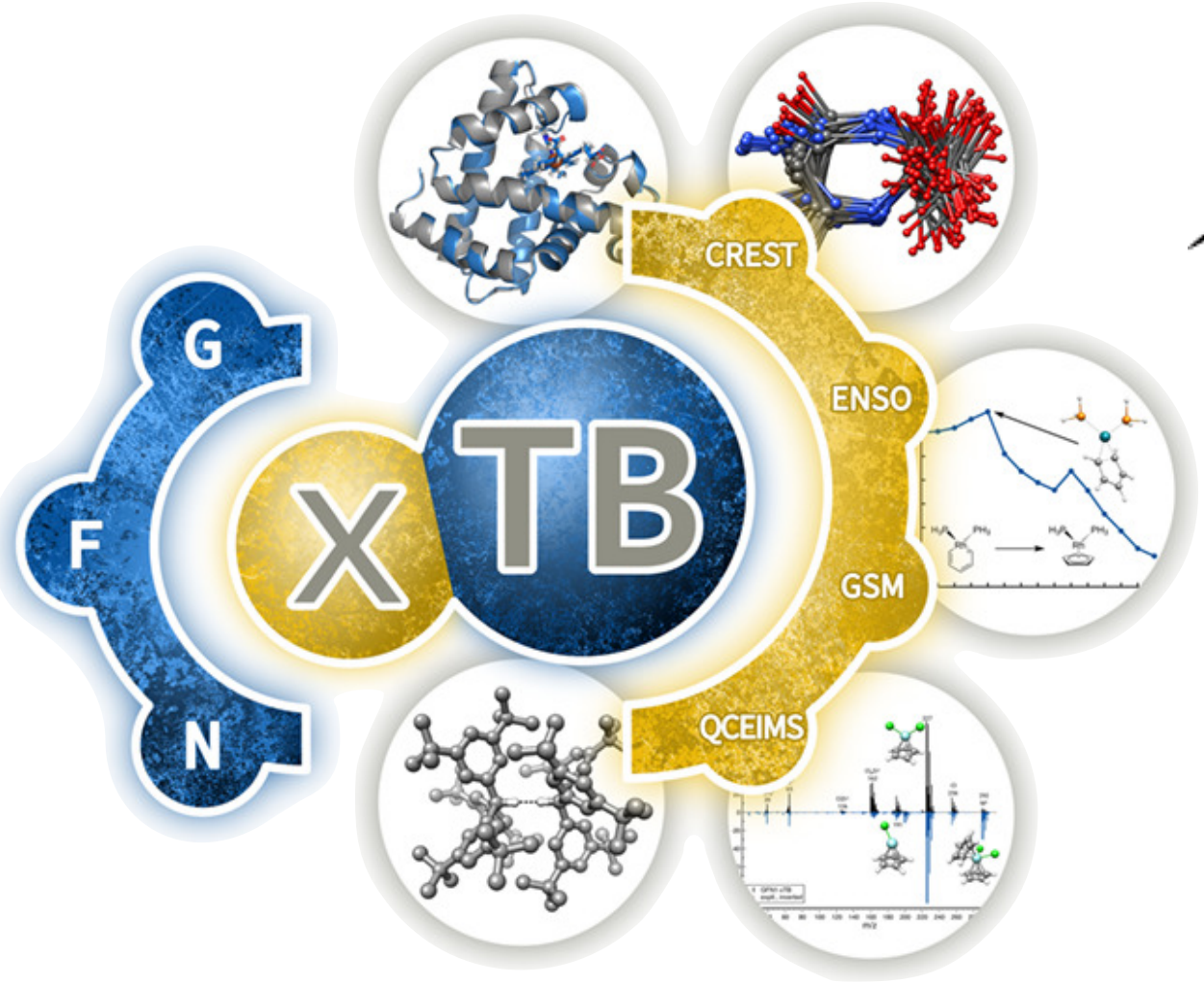
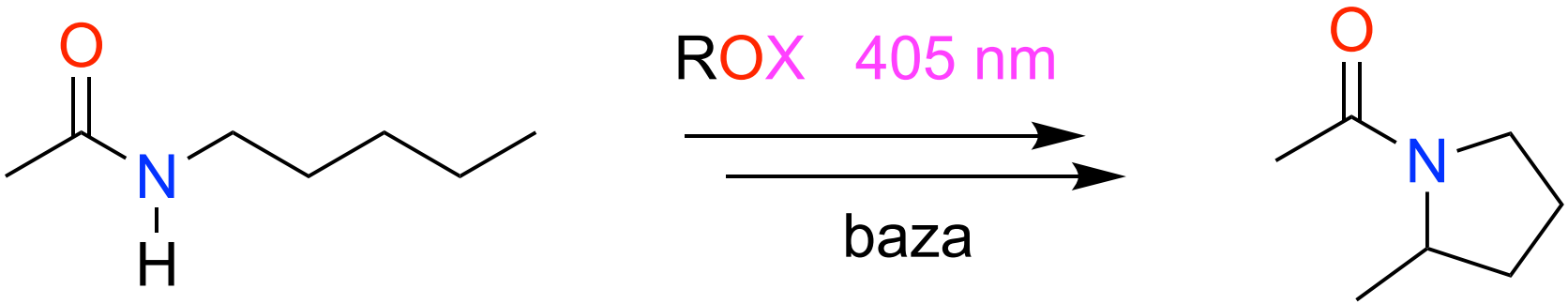
LIGHT RING



ORCA

Hofmann–Löffler–Freytag reakcija



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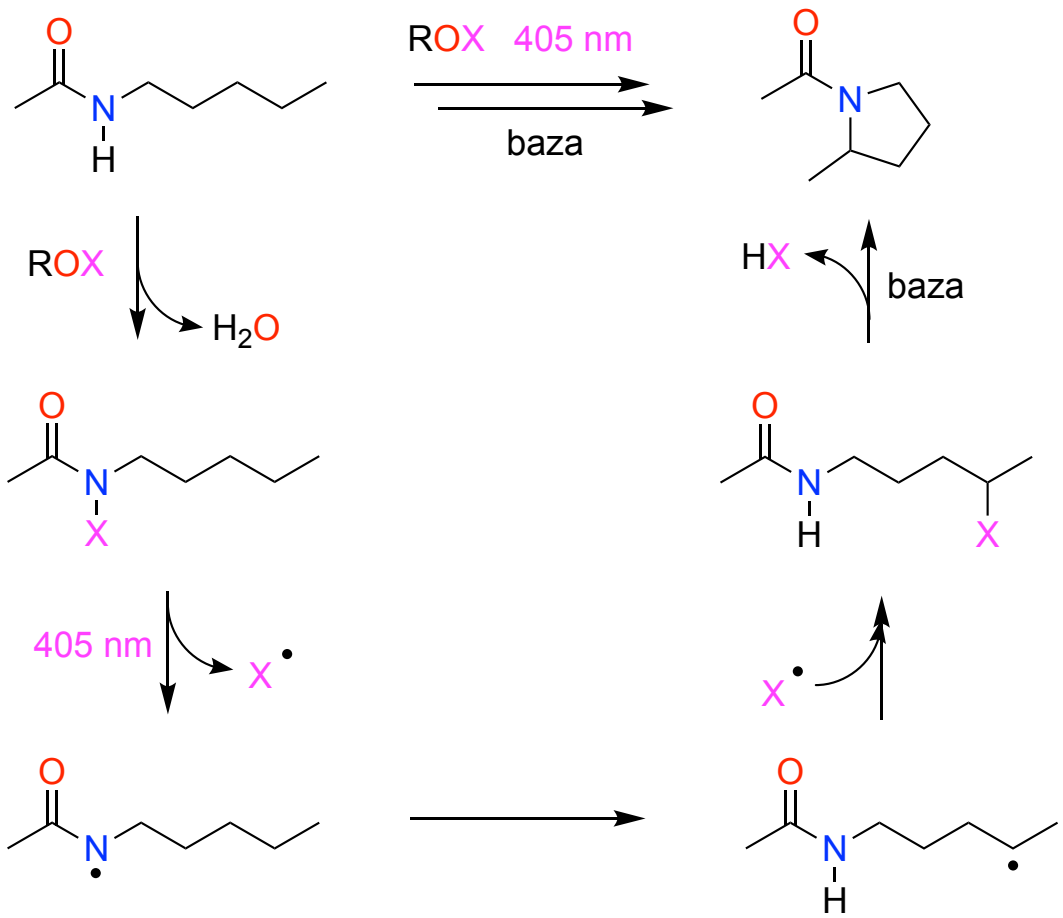
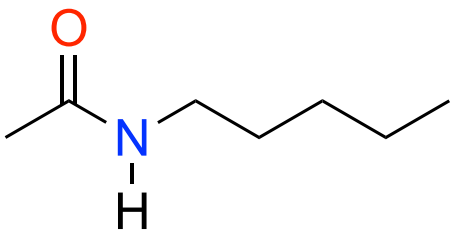
Hofmann–Löffler–Freytag reakcija



Reaktant



CRTANJE!

- konformacijska analiza reaktanata
- Boltzmannova raspodjela
- tautomerne forme i ravnoteža
- utjecaj otapala - implicitno, eksplicitno, kombinirano
  - prva solvatacijska ljuska
  - ostale ljuske
- odabir odgovarajuće teorijske razine

CRTANJE

Avogadro

- besplatan
- interface s drugim programima
- uključeni FF optimizator
- vizualizacija orbitala/frekvencija
- konformacijska analiza

IQmol

besplatan

uključen FF optimizator

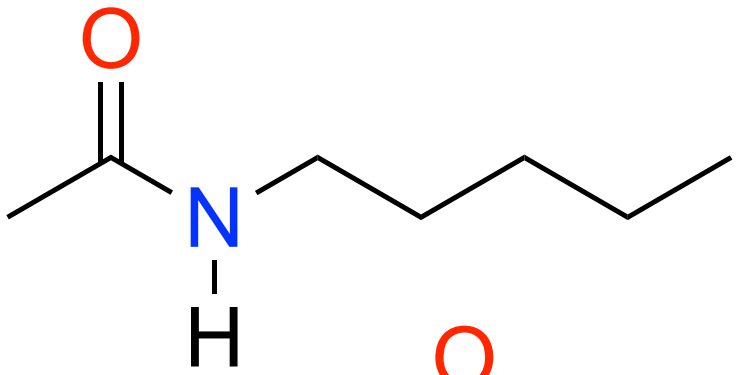
direktno pokretanje računa QChem

.xyz format

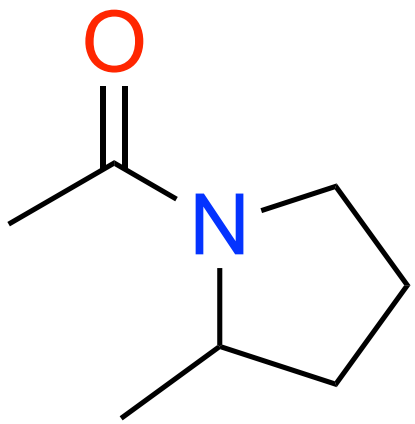
GAUSSVIEW

Crtanje molekula

N-pentilacetamid



2-metilpiridinilacetamid



Formati

.xyz

Broj atoma

Naslov/prazni red

Element x y z

Položaji u angs

```
24

N        2.47853     0.21632     0.04817
C        1.80729    -1.02331     0.41525
C        0.27138    -0.90081     0.40757
C       -0.40452    -0.19974     1.60585
C       -0.13598     1.30206     1.75733
C       -1.00658     1.90240     2.85924
C        3.24995     0.34913    -1.06774
O        3.41030    -0.58626    -1.83902
C        3.91446     1.66084    -1.36366
H        2.39153     1.03499     0.65793
H        2.16405    -1.38063     1.40468
H        2.05733    -1.81560    -0.32309
H       -0.11720    -1.94312     0.43902
H       -0.06444    -0.45524    -0.55404
H       -0.12845    -0.72263     2.54777
H       -1.49951    -0.32829     1.45423
H       -0.36186     1.82318     0.80187
H        0.91291     1.48012     2.05031
H       -2.08304     1.77534     2.61589
H       -0.79182     2.98780     2.95432
H       -0.79246     1.41114     3.83255
H        3.14369     2.45228    -1.47318
H        4.50268     1.60209    -2.30450
H        4.59809     1.92887    -0.53112
```

.pdb

.sdf

.com

.mol

Brza optimizacija i konformacijska analiza

- semi-empirijske metode
- AM1, PM3, PM6
- GFN-1, GFN-2
- CREST, MD, MTD
- GFN-FF
- ENSO, CENSO, QCxMS

```
ime.xyz
xtb ime.xyz -opt --chrg 0 --uhf 0 --namespace ime
ime.xtbopt.xyz
xtb ime.xtbopt.xyz -hess --chrg 0 --uhf 0 --namespace ime.xtbopt
ime.xtbopt.g98.out
crest ime.xtbopt.xyz -T 4 --v4 --gfn2 --chrg 0 --uhf 0
crest_conformers.xyz
```

https://xtb-docs.readthedocs.io/en/latest/contents.html

Optimizacija

G16 i ORCA input

ime.com

```
%nproc=4
%mem=8gb
%chk=ime.chk
# opt freq b3lyp/SVP

naslov

0 1
A x.x y.y z.z
```

ime.script

```
#!/bin/sh
#$ -N ime
#$ -l memory=4
#$ -cwd
#$ -pe mpi 2
#$ -o ime.out
#$ -e ime.err
export PATH=…
dog16 ime
```

ime.inp

```
! B3LYP SV(P) OPT FREQ
%pal nprocs 4 end
%maxcore 8000
* XYZ 0 1
A x.x y.y z.z
*
```

ime.script

```
#!/bin/sh
#$ -N ime
#$ -o ime.err
#$ -j Y
#$ -l memory=8
#$ -pe mpi 4
#$ -cwd
module load orca/5.0.3
run-orca-isabella.sh ime.inp > ime.out
```

```
qsub ime.script
```

Odabir metoda i baznih skupova

Basis Set	Applies to	Polarization Functions	Diffuse Functions
3-21G	H-Xe		+
6-21G	H-Cl	* or **	
4-31G	H-Ne	* or **	
6-31G	H-Kr	*through* (3df,3pd)	+,++
6-311G	H-Kr	*through* (3df,3pd)	+,++
D95	H-Cl *except Na and Mg*	*through* (3df,3pd)	+,++
D95V	H-Ne	(d) *or* (d,p)	+,++
SHC	H-Cl	*	
CEP-4G	H-Rn	* *(Li-Ar only)*	
CEP-31G	H-Rn	* *(Li-Ar only)*	
CEP-121G	H-Rn	* *(Li-Ar only)*	
LanL2MB	H-La, Hf-Bi		
LanL2DZ	H, Li-La, Hf-Bi		
SDD, SDDAll	*all but Fr and Ra*		
cc-pVDZ	H-Ar, Ca-Kr	*included in definition*	
cc-pVTZ	H-Ar, Ca-Kr	*included in definition*	
cc-pVQZ	H-Ar, Ca-Kr	*included in definition*	
cc-pV5Z	H-Ar, Ca-Kr	*included in definition*	
cc-pV6Z	H, B-Ne	*included in definition*	
SV	H-Kr		
SVP	H-Kr	*included in definition*	
TZV and TZVP	H-Kr	*included in definition*	
QZVPand Def2	H-La, Hf-Rn	*included in definition*	
MidiX	H, C-F, S-Cl, I, Br	*included in definition*	
EPR-II, EPR-III	H, B, C, N, O, F	*included in definition*	
UGBS	H-Lr	UGBS(1,2,3)P	
MTSmall	H-Ar		
DGDZVP	H-Xe		

Local and gradient

HFS
LDA or LSD
VWN or VWN5
VWN3
PWLDA
BP86 or BP
BLYP
OLYP
GLYP
XLYP
PW91
mPWPW
mPWLYP
PBE
RPBE
REVPBE
RPW86PBE
PWP

Hybrid functionals

B1LYP
B3LYP and B3LYP/G
O3LYP
X3LYP
B1P
B3P
B3PW
PW1PW
mPW1PW
mPW1LYP
PBE0
REVPBE0
REVPBE38
BHANDHLYP

TPSS
TPSSh
TPSS0
M06L
M06
M062X
PW6B95
B97M-V
B97M-D3BJ
B97M-D4
SCANfunc

wB97
wB97X
wB97X-D3
wB97X-D4
wB97X-V
wB97X-D3BJ
wB97M-V
wB97M-D3BJ
wB97M-D4
CAM-B3LYP
LC-BLYP
LC-PBE

B2PLYP
mPW2PLYP
B2GP-PLYP
B2K-PLYP
B2T-PLYP
PWPB95
PBE-QIDH
PBE0-DH

Traženje prijelaznog stanja - iz nacrtane strukture

G16 i ORCA input

ime.com

```
%nproc=4
%mem=8gb
%chk=ime.chk
# opt=(calcfc,ts,noeigentest)
freq b3lyp/SVP

naslov

0 1
A x.x y.y z.z
```

ime.inp

```
! B3LYP SV(P) OPTTS FREQ
%pal nprocs 4 end
%maxcore 8000
* XYZ 0 1
A x.x y.y z.z
*
```

ime.script

```
qsub ime.script
```

Traženje prijelaznog stanja - iz reaktanata/produkata

G16 i ORCA input

ime.com

```
%nproc=4
%mem=8gb
%chk=ime.chk
# opt=(qst2) freq b3lyp/SVP

reaktant

0 1
A x.x y.y z.z

produkt

0 1
A x.x y.y z.z
```

ime.script

```
%nproc=4
%mem=8gb
%chk=ime.chk
# opt=(qst3) freq b3lyp/SVP

reaktant

0 1
A x.x y.y z.z

produkt

0 1
A x.x y.y z.z

TS

0 1
A x.x y.y z.z
```

ime.inp

```
! B3LYP SV(P) NEB-TS FREQ
%pal nprocs 4 end
%maxcore 8000
%NEB NEB_END_XYZFILE "produkt.xyz"
END
* XYZfile 0 1 reaktant.xyz
```

ime.script

```
! B3LYP SV(P) NEB-TS FREQ
%pal nprocs 4 end
%maxcore 8000
%NEB NEB_END_XYZFILE “produkt.xyz"
NEB_TS_XYZFILE "mislimTS.xyz" END
* XYZfile 0 1 reaktant.xyz
```

U skripti obavezno navesti koji podaci i gdje se prebacuju

Traženje prijelaznog stanja - pretraživanje PES-a

G16 i ORCA input

ime.com

```
%nproc=4
%mem=8gb
%chk=ime.chk
# opt=(modredundant) b3lyp/SVP

naslov

0 1
A x.x y.y z.z

B 1 2 S 15 -0.01
```

ime.script

Brojanje atoma u ORCA-i ide od 0!

ime.inp

```
! B3LYP SV(P)
! ScanTS
%geom
scan B 1 0 = 2.0, 1.0, 10 end
end
%pal nprocs 4 end
%maxcore 8000
* XYZ 0 1
A x.x y.y z.z
*
```

Više o skriptiranju
https://tldp.org/LDP/abs/html/

Traženje prijelaznog stanja:

cis/trans amid

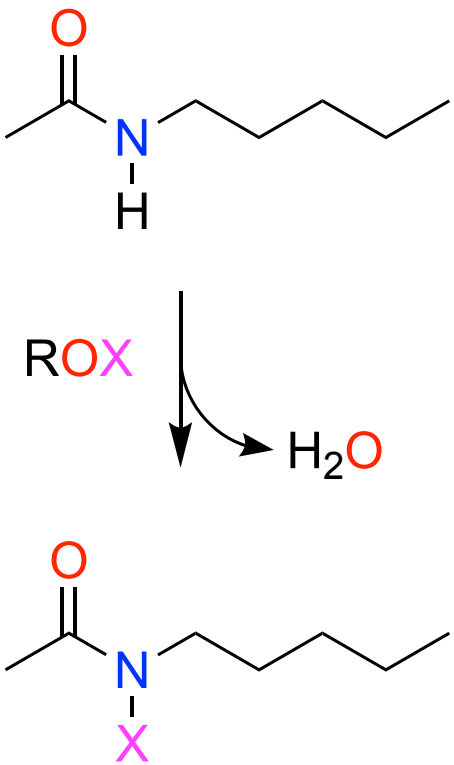
amid/imid

Karakterizacija minimuma

Energijski račun na zahtjevnijim metodama

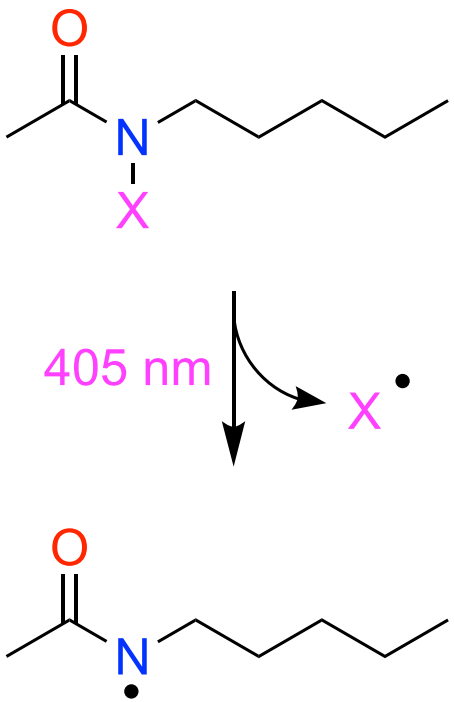
```
# G3B3

! DLPNO-CCSD(T) DEF2-TZVPP DEF2-TZVPP/C
```

Halogeniranje



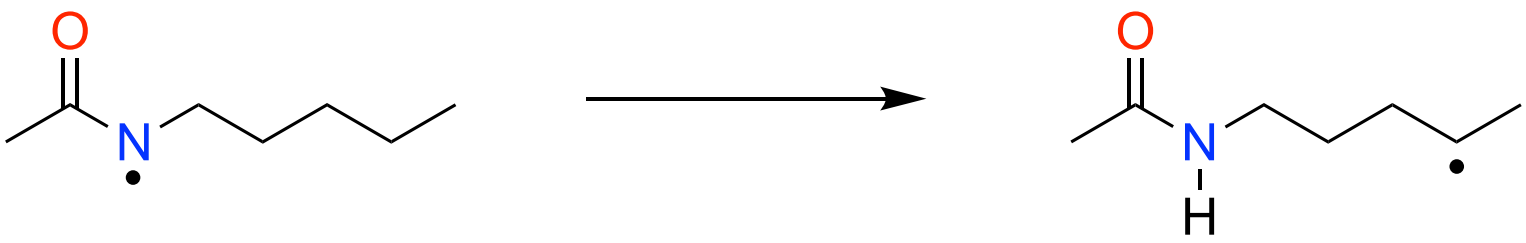
- određivanje reakcijskih parametara za HOCl
- prijelazno stanje kloriranja za amido i imido formu
- IRC računi
- globalni, lokalni minimumi
- termodinamika i kinetika reakcije
- promjena halogena
- promjena R-supstituenta (npr. AcOX)

Homolitičko cijepanje N-halogen veze



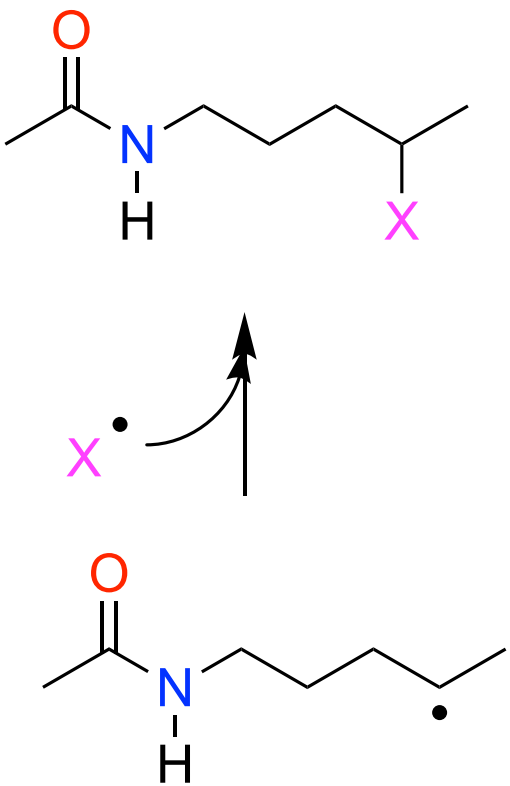
- skeniranje reakcijske koordinate
- plohe potencijalne energije
- singlet vs triplet
- elektronski prijelazi
- promjena redosljeda popunjavanja orbitala

Prijenos atoma vodika (HAT)



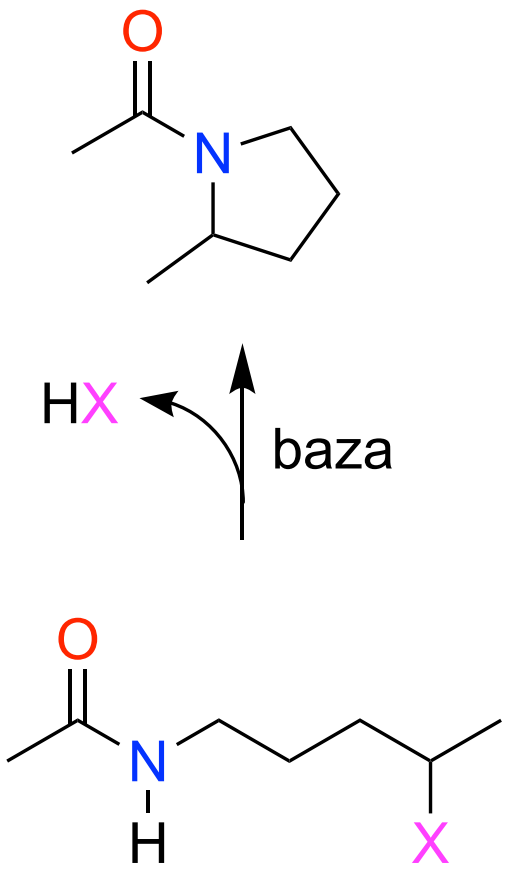
- stabilnost N- i C- radikala (termodinamika)
- određivanje kompeticijskih reakcija
  - 1,2-HAT, 1,3-HAT, 1,4-HAT i 1,5-HAT
- intra- vs inter-HAT (dodatni modelni sustavi)

Stvaranje C-halogen veze



- skeniranje reakcijske koordinate
- plohe potencijalne energije
- singlet vs triplet
- elektronski prijelazi
- računanje spektara
  - IR, NMR/EPR, UV/Vis
  - obavezno standard

Zatvaranje peteročlanog prstena

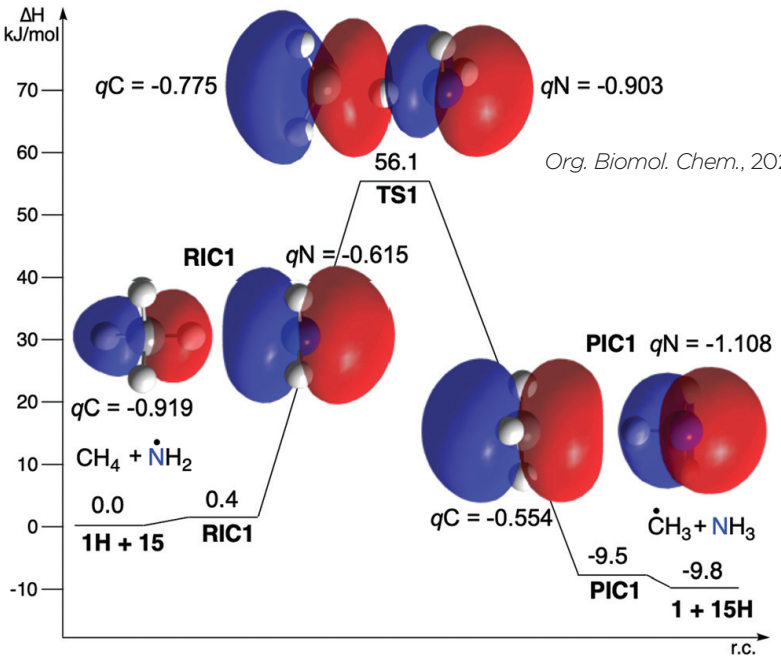


- S_N2 reakcija
- uloga baze
- uloga otapala
- stabilnost produkata
- teorijska razina
- provjera u odnosu na eksperimentalne podatke

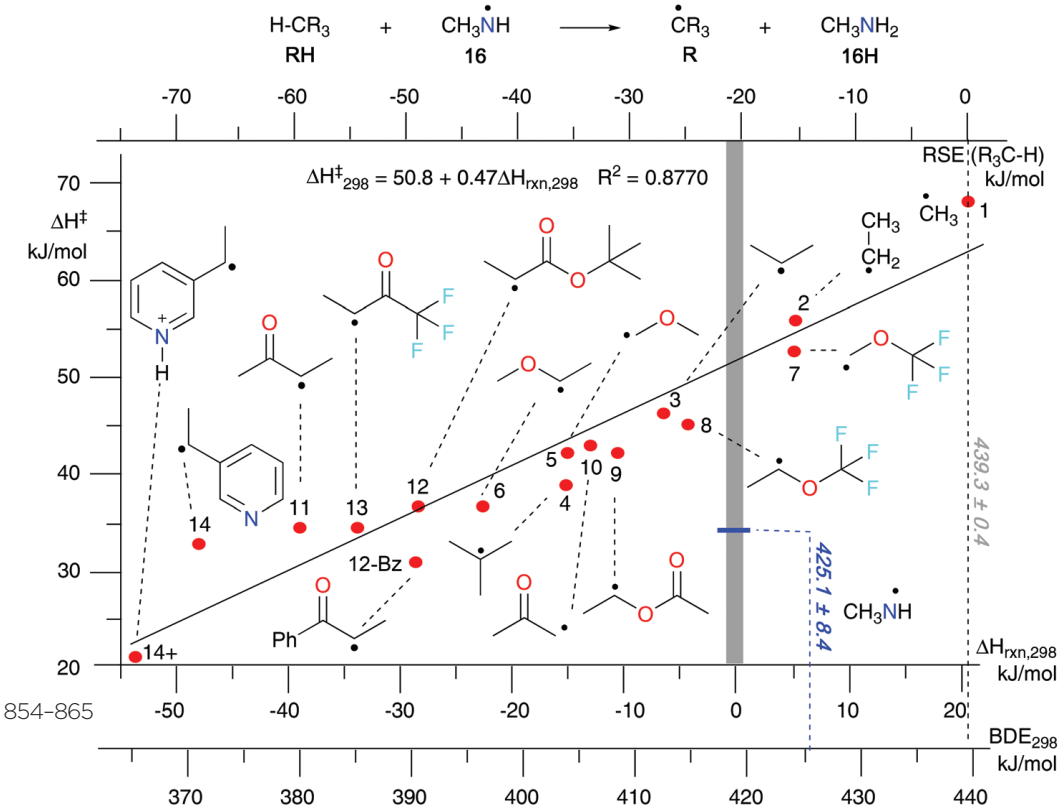
Prikaz rezultata

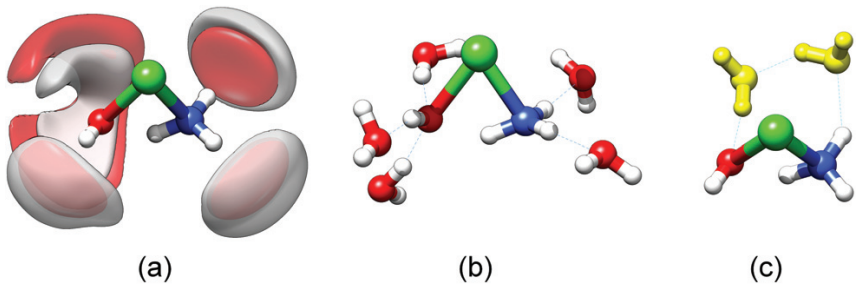
Table 3 RSE, $\Delta H_{rxn,298}$, and $\Delta H^{\ddagger}_{298}$ values for all systems shown in Chart 3

Species	RSE (*N*-rad)	RSE (*C*-rad)	BDE $(N–H)_{calc.}$	BDE $(C–H)_{calc.}$	$\Delta H_{rxn,298}$	$\Delta H^{\ddagger}_{298}$
L1	−33.8	−71.0	416.3	368.3	−47.9	45.7
L1+	−40.5	−89.4	409.6	349.9	−59.6	46.0
L2	−58.4	−71.1	391.7	368.3	−23.4	54.2
L2+	−71.7	−89.0	378.4	350.3	−28.0	54.0
L3	−26.1	−66.7	424.0	372.7	−43.0	30.1
L4	−2.0	−63.5	448.1	375.8	−82.9	18.5
L5	2.0	−75.2	452.0	364.1	−87.2	16.2
L6	15.4	−73.7	465.5	365.6	−99.3	4.8



Org. Biomol. Chem., 2021, **19**, 854–865





Org. Biomol. Chem., 2015, **13**, 11740–11752

HRZZ
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LIGHT RING

isabella CLUSTER

Hvala

SW.PHARMA.HR

PART OF FARMINOVA PROJECT

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