Diradicals in Oil Shale

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The name is Bond, Valence Bond !

Workshop on ab initio Valence Bond theory
Paris, 2012

UNIVERSITY OF RICHMOND

Parish Group @ U Richmond

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Raja Zope

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Emily Nelson ’12

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Nicki Smith ’13
Devin Sullivan ‘13
Jeff Schriber ’14
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Tabitha Yewer ’14
Alexis Achey ’14
Furong Bai ’14
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Lily Mawbry ‘15
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DOE-BES
NSF (RUI, REU, MRI)
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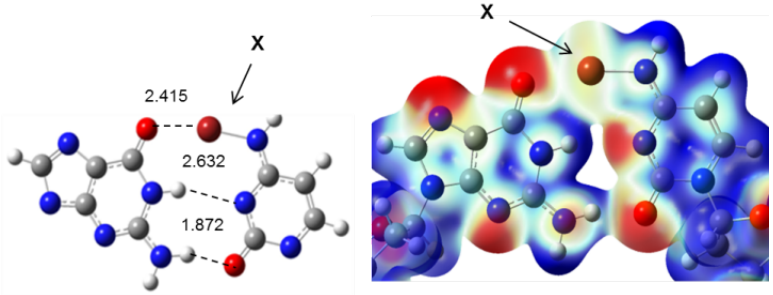
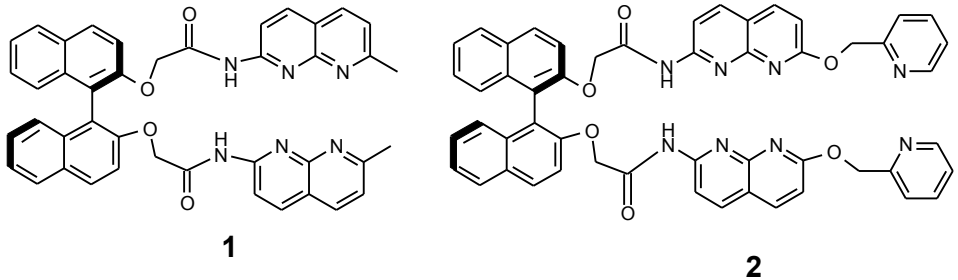
Dreyfus Foundation
Jeffress Foundation

Halogen Bonding in DNA Base Pairs



Parker, Stewart, Donald and Parish
JACS **2012** *134* 5165

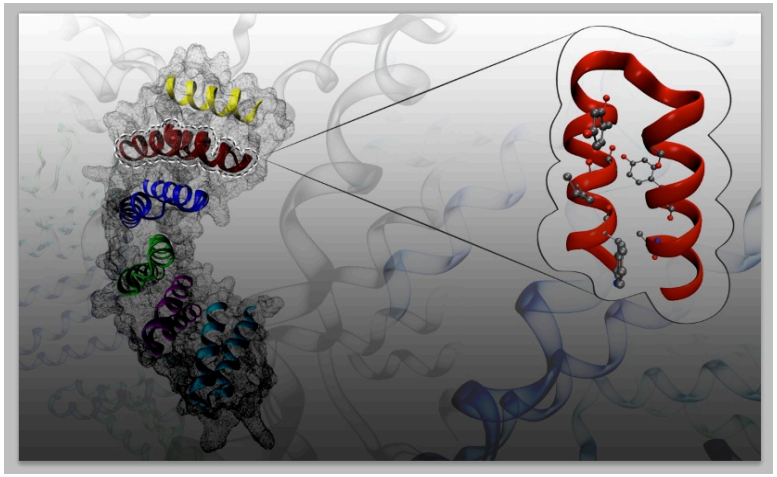
(rac)- 1,1′-Binaphthyl-based simple receptors designed for fluorometric discrimination of maleic and fumaric acids



1 **2**

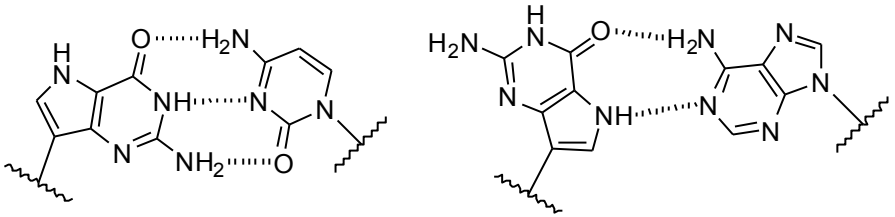
Ghosh, Sen, Patra, Mancini, Cook and Parish
JPC B, **2011**, *115*, 8597

Evidence that the Kinesin Light Chain Domain contains Tetratricopeptide Repeat Units



Fisher, Weck, Landers, Emrich, Middleton, Gentile and Parish
Journal Str. Biology **2012** *117,* 602

Oligonucleotide Incorporation and Base Pair Stability of 9-deaza-2'-deoxyguanosine



9-Deaza-dG(anti):dC **9-Deaza-dG(syn):dA**

Hamm, Parker, Carman, Steele, and Parish, *JOC* **2010**, *75*, 5661

Diradicals in Oil Shale

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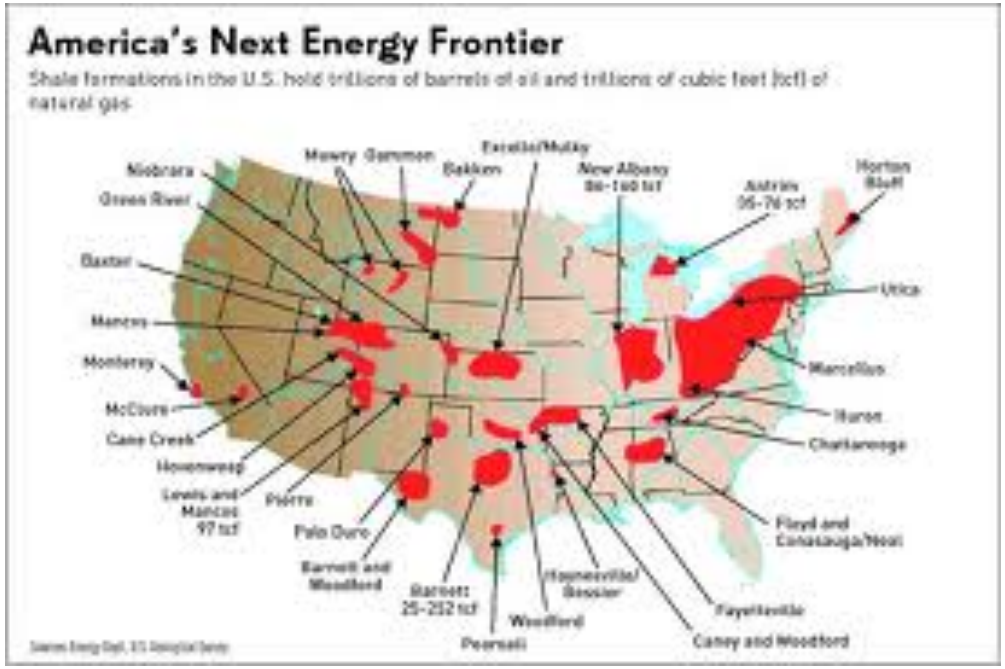
Oil Shale and Gas

- Global energy demands are high and increasing
- Longer term – develop renewable fuels
- Shorter term – better exploit alternative hydrocarbon resources
- Vast global oil shale resources
  - Athabasca Oil Sands in Alberta, Canada
  - Vaca Muerta, Argentina
  - Poland, Russia

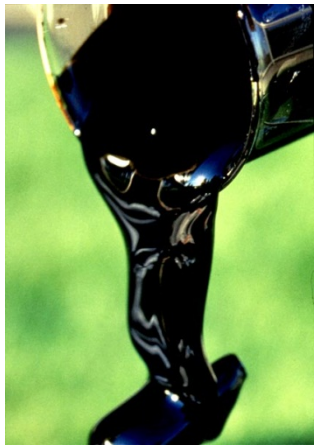
Oil Shale and Gas

- Vast global oil shale resources
  - Green River deposits in parts of Colorado, Utah and Wyoming; Texas
  - Marcellus Play in Northeast U.S.; 50 tcf
  - Israel - Shefla, Leviathan and Tamar; 250 bb



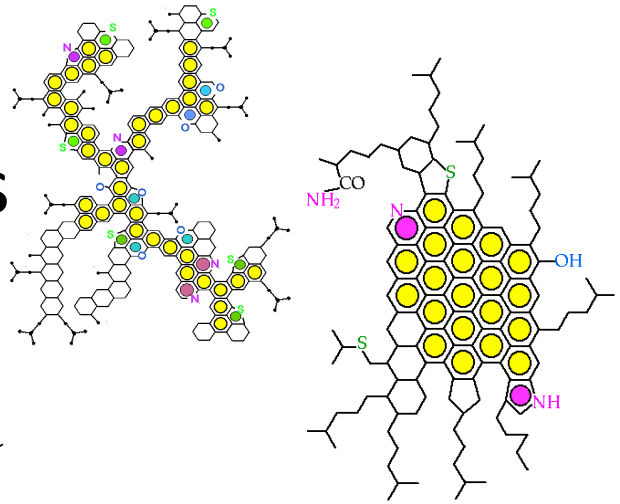
Oil Shale and Gas

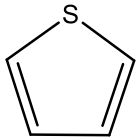
- Geological jargon
  - Oil shale/gas contains kerogen
  - Kerogen contains bitumen
  - Bitumen comprised of asphaltenes

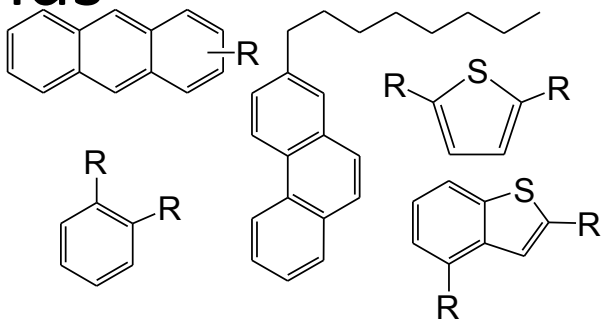


Asphaltenes

- Molecular constituents only recently discovered (Mullins, Zare, Kenttammaa)
- Contain hydrocarbon and polyaromatic cores with long alkyl chains
- Sulfur and nitrogen present
- Island or archipelago structures
- EPR evidence of radical nature
- Model compounds
- Thiophene

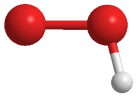


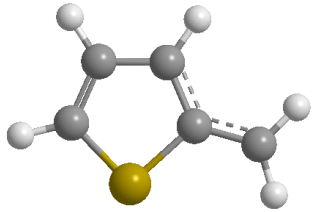




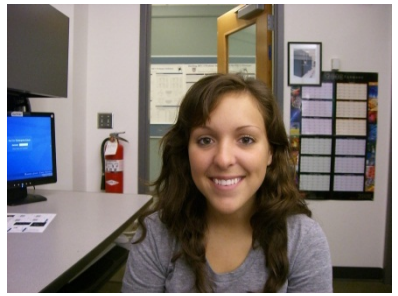
Our results to date

Xinli Song





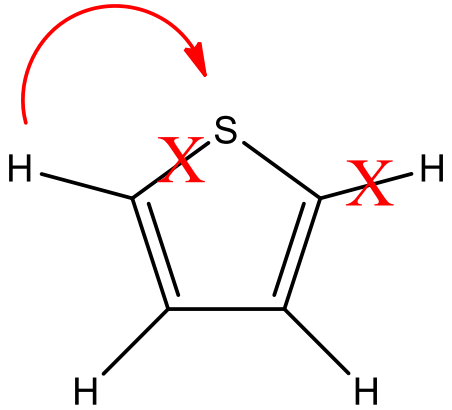
- Decomposition mechanisms of thiophene and methyl thiophene
- Reactions between HO_2 and 2-thienyl methyl radicals
- Mechanisms for reaction between singlet and triplet O_2 and thiophene/ methyl thiophene
- MR-CISD/MR-AQCC analysis of 2,5 didehydrothiophene



Anna Parker
Pines Lab, Berkeley

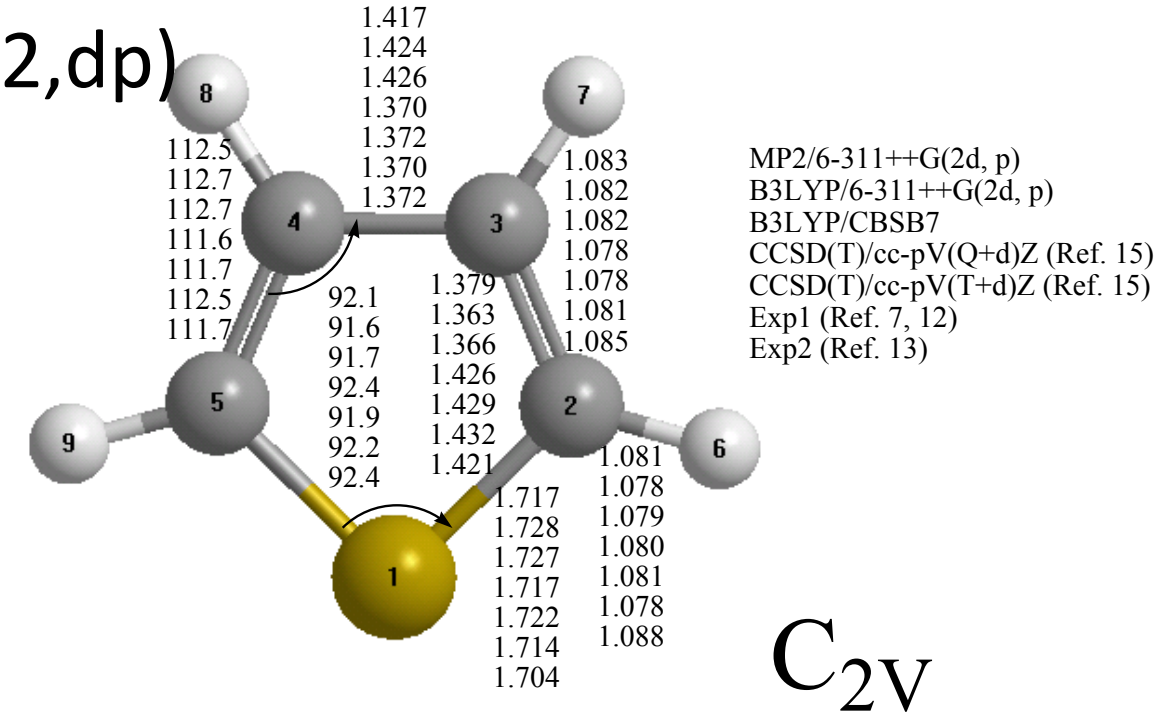
Decomposition of Thiophene – Previous work by others

- Memon, 2598-2022K, shock tube, initiated by C-S fission, major products = acetylene
- Winkler, 773-1373K, continuous flow, initiated by C-H fission; H_2S increases significantly above 1123K.
- Hore, laser pyrolysis, 1-2 H transfer = most probable initiation step; requires about 300 kJ/mol
- Chong, B3LYP/6-31G*, initiated by C-S fission
- Wang, PW91/DND, initiated by α-H migration to S



Methods

- B3LYP/6-311++G(2d,p) geometry optimization
- G3MP2B3 energy refinement
- B3LYP/CBSB7 geometry optimization
- CBS-QB3 refinement of energies
- MP2/6-311++G(2,dp)



C_{2V}

Heats of Reaction (kcal/mol)

	MP2/6-311+ +G(2d,p)	B3LYP/6-311+ +G(2d,p)	CBS-QB3	G3MP2B3	Exp[a]
C_2H_2+CH_2CS (R1)	68.88	60.37	75.27	78.23	73.10[b]
CS+CH_3CCH (R2)	79.56	75.30	84.96	85.46	83.05
CS+CH_2CCH_2 (R3)	83.83	72.79	85.73	89.61	84.49
CS+CH_2CHCH(S) (R4)	147.01	132.82	147.29	155.65	
CS+CH_2CHCH(T) (R4)	141.30	121.77	138.61	145.27	
H_2S+HCCCCH (R5)	67.11	61.08	79.0	84.69	76.88
CH_2C+CH_2CS (R6)	116.81	99.42	116.69	127.08	
HCS+CH_2CCH (R7)	138.14	104.24	125.20	146.99	119.10
HS + C_4H_3 (R8)	147.09	117.01	138.45	154.53	
H +2-C_4H_3S (R9)	124.21	108.47	118.39	126.20	
H + 3-C_4H_3S (R10)	121.69	105.53	115.93	123.99	
SCHCHCHCH (R11)	107.42	75.43	89.55		
CHCHSCHCH (R12)	149.55	120.36	133.67		
IM4	50.47	48.05	53.27		
IM8	44.27	39.34	48.00		

[a] Heats of reaction determined using the enthalpies of formation found in Goos, Burcat, Ruscic, *Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion*

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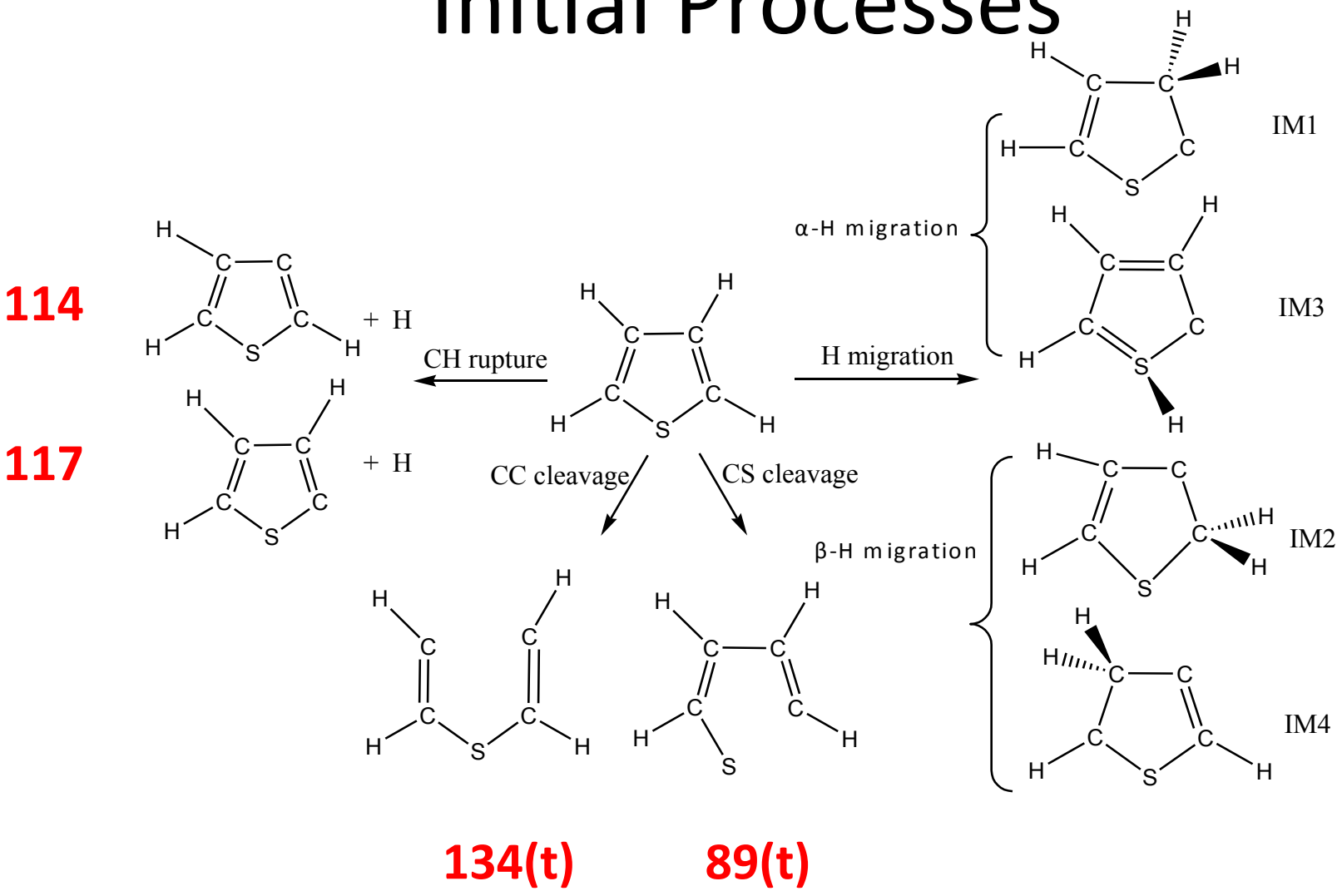
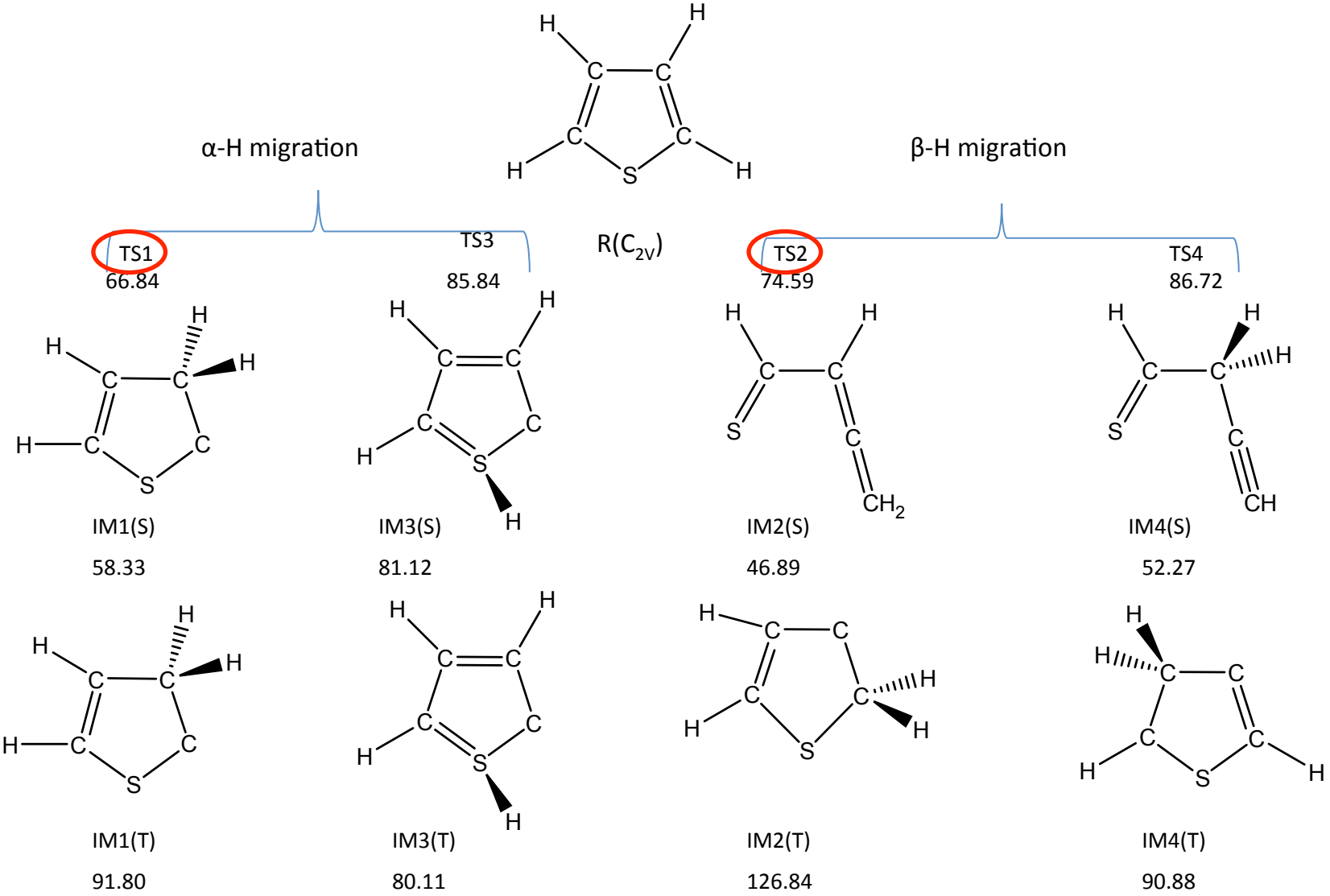
Initial Processes

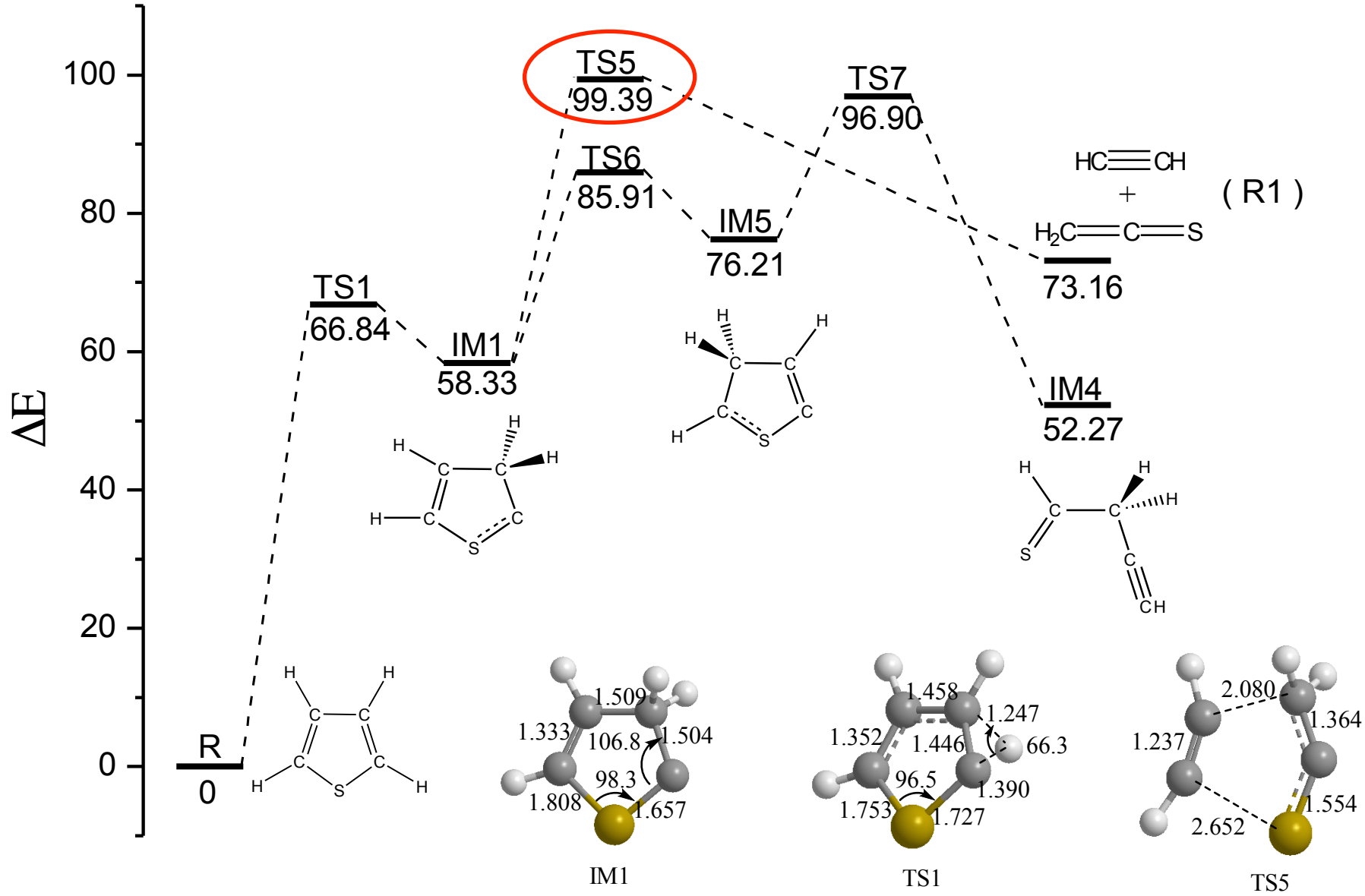


Hydrogen Migration



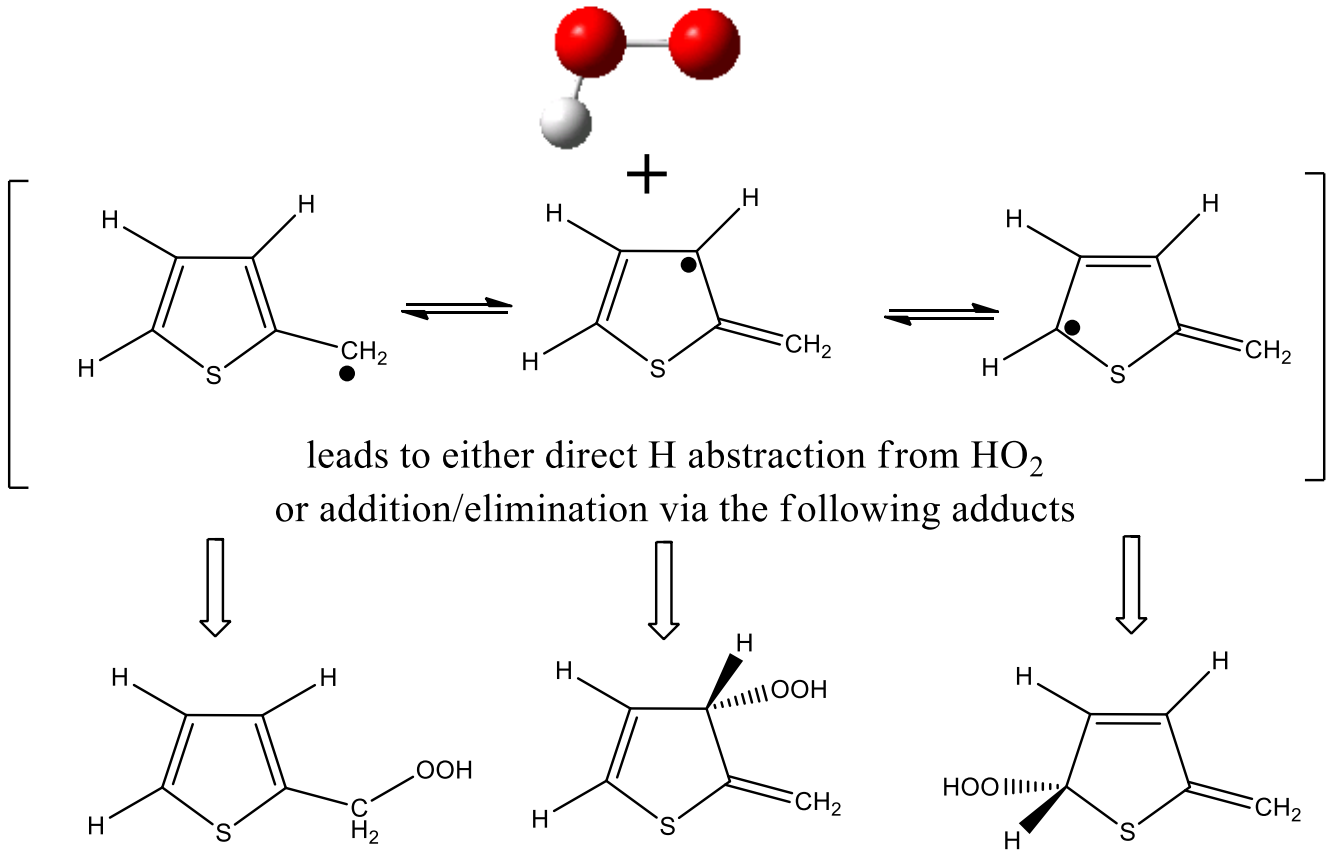
Song and Parish, *JPCA*, **2011**, *115*, 2882-2891

1-2 α-H Migration – Dominant Mechanism



Reaction of 2-thienylmethyl + HO_2 radicals

17 product channels were characterized



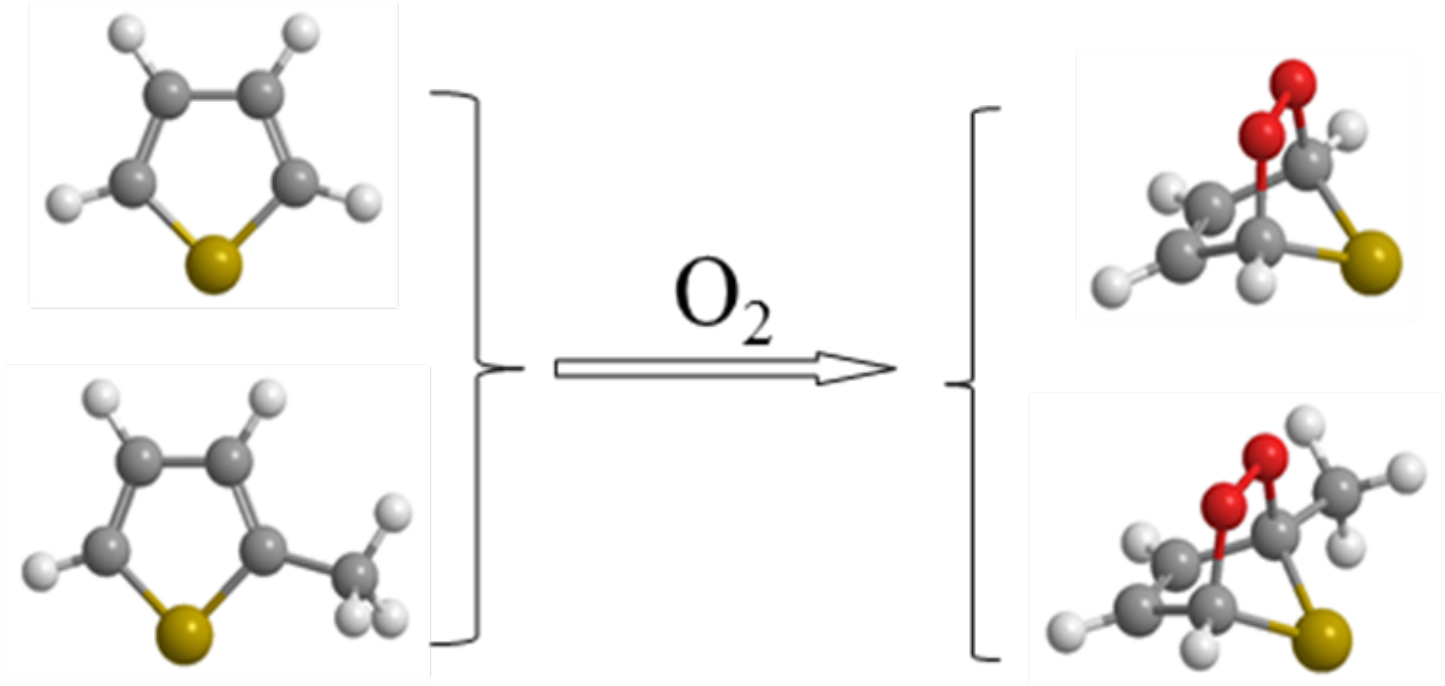
Addition – barrierless, exothermic 37-55 kcal/mol
H abstraction – barriers < 10 kcal/mol

Song and Parish, *JPCA*, **2011**, *115*, 14546

Reaction of thiophene with singlet and triplet oxygen

MP2/6-311++G(d,p)//G4MP2

- Direct hydrogen abstraction from thiophene
- Addition/elimination



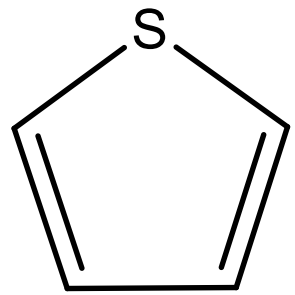
Justin Cook
Princeton

Matt Fanelli
Penn State

- Barriers on triplet surface are > 30 kcal/mol
- Most favorable singlet reaction – (2+4) cycloaddition leading to endoperoxides (barrier 8 kcal/mol; exothermic 18 kcal/mol)

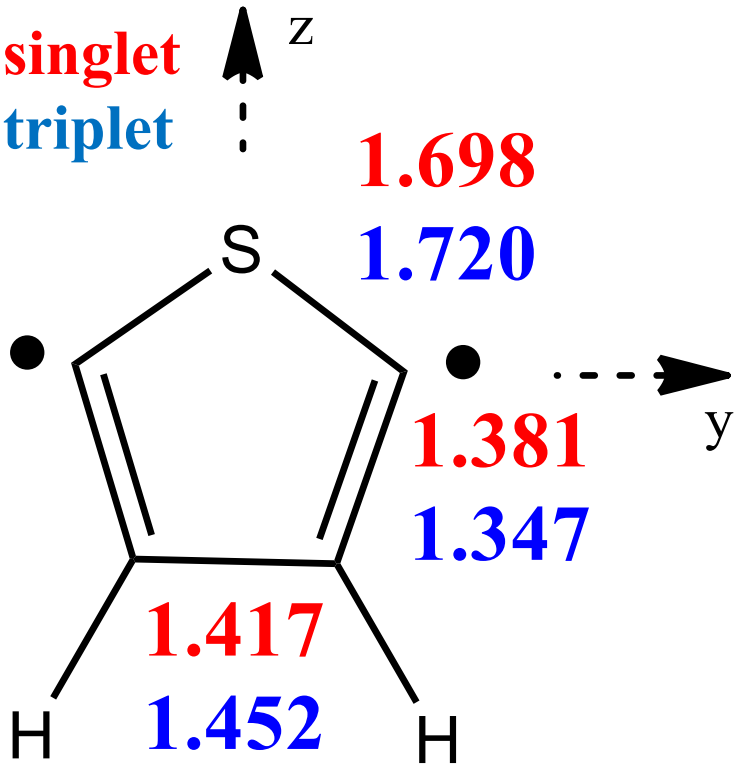
Song, Fanelli, Cook, Bai and Parish, *JPCA*, **2012**, *ASAP*

Multireference characterization of thiophene 2,5 diradical



- 2-electrons in 2 orbitals – 4 states: under C_{2v} symmetry: $^1A_1$, $^3B_2$, $^1B_2$ and a second $^1A_1$
- CAS(8,8) including π ($2b_1$, $3b_1$, $1a_2$), π^* ($4b_1$, $5b_1$, $2a_2$), σ ($11a_1$) and σ^* ($6b_2$)
- MCSCF orbitals used for MR-CISD, MR-CISD+Q and MR-AQCC with cc-pvDZ and cc-pvTZ
- Geometry optimized lowest singlet and triplet states

Multireference characterization of thiophene 2,5 diradical



MR-AQCC/TZ

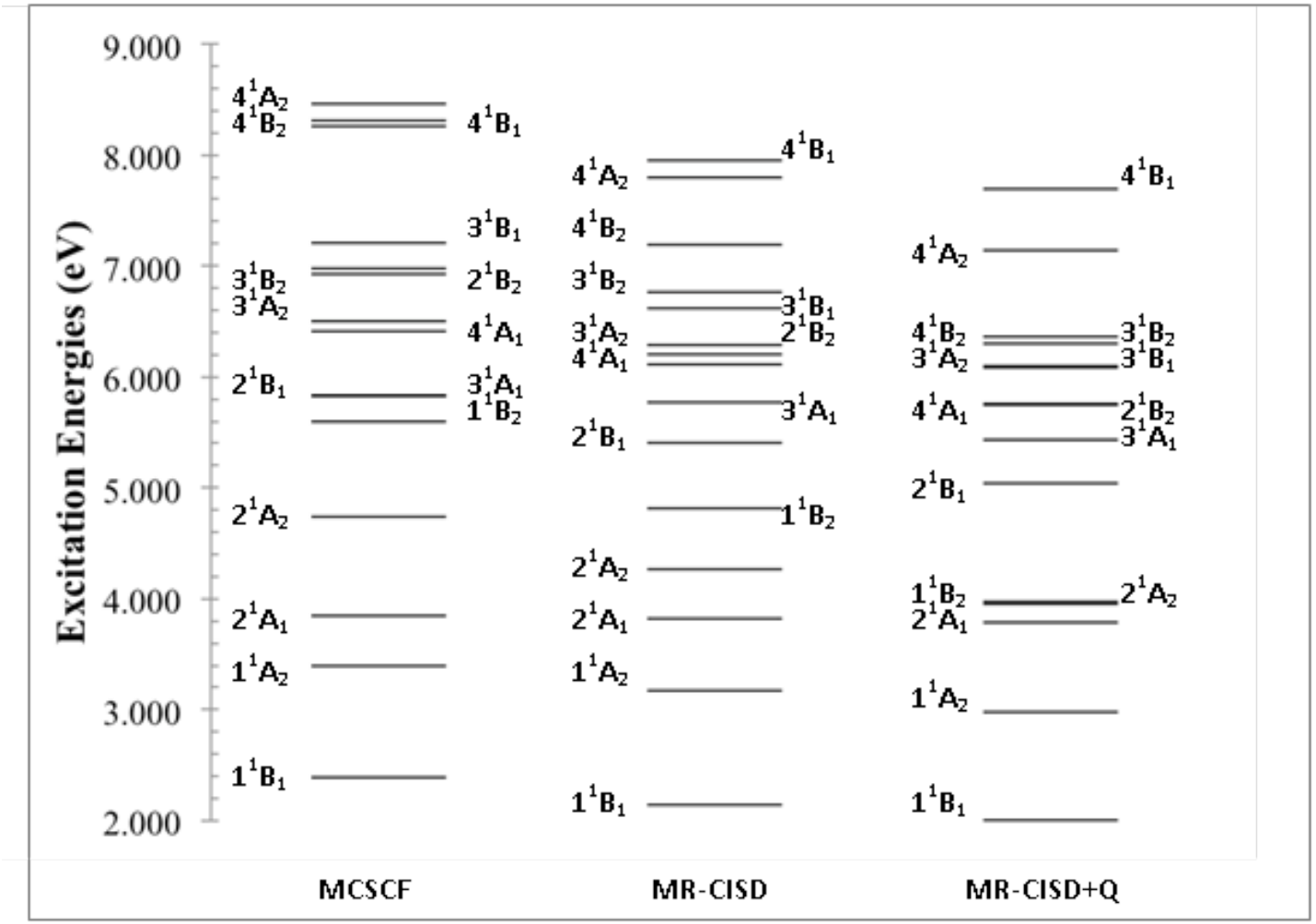
Splitting energies (kcal/mol) between the singlet A1 and triplet B2 states:

	cc-pVDZ	cc-pVTZ
adiabatic		
MCSCF	14.243	14.919
MR-CISD	15.181	16.587
MR-CISD+Q	14.738	16.470
MR-AQCC	14.108	15.848
vertical		
MCSCF	18.186	19.915
MR-CISD	18.786	20.924
MR-CISD+Q	18.860	21.447
MR-AQCC	17.929	20.437

16 State Averaged Singlet Vertical Excitations (eV), TZ

State	Dominant configuration in **MRCI**	MCSCF E_{exc}	MR-CISD E_{exc}	MR-CISD+Q E_{exc}	MR-AQCC E_{exc}
$1\ ^1A_1$[a]	64% $\sigma^2\pi_1^2\pi_2^2\pi_3^2$ + 12% $(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^2$	**0.000**	**0.000**	**0.000**	**0.000**
$1\ ^1B_1$	76% $\sigma^2(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^1$	**2.391**	**2.144**	**2.005**	**2.007**
$1\ ^1A_2$	69% $\sigma^2(\sigma^*)^1\pi_1^2\pi_2^1\pi_3^2$	**3.395**	**3.174**	**2.978**	**2.967**
$2\ ^1A_1$	70% $\sigma^2(\sigma^*)^2\pi_1^2\pi_2^2$	**3.845**	**3.818**	**3.787**	**3.818**
$2\ ^1A_2$	59% $\sigma^1(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^1$ + 14% $\sigma^2(\sigma^*)^1\pi_1^1\pi_2^2\pi_3^2$	**4.740**	**4.267**	**3.954**	**3.836**
$1\ ^1B_2$	45% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^2$ + 29% $\sigma^2\pi_1^2\pi_2^2\pi_3^1(\pi_4^*)^1$	**5.597**	**4.810**	**3.975**	**-6.366**
$2\ ^1B_1$	62% $\sigma^1(\sigma^*)^2\pi_1^2\pi_2^1\pi_3^2$	**5.826**	**5.403**	**5.036**	**5.027**
$3\ ^1A_1$	46% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^1(\pi_4^*)^1$	**5.828**	**5.767**	**5.433**	**5.871**
$4\ ^1A_1$	25% $\sigma^2\pi_1^2\pi_2^1\pi_3^2(\pi_4^*)^1$ + 14% $(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^2$ + 13% $\sigma^2\pi_1^2\pi_2^2\pi_3^1(\pi_5^*)^1$	**6.408**	**6.112**	**5.748**	**b**
$2\ ^1B_2$	71% $\sigma^2(\sigma^*)^2\pi_1^2\pi_2^1\pi_3^1$	**6.925**	**6.203**	**5.757**	**6.795**
$3\ ^1A_2$	42% $\sigma^2(\sigma^*)^1\pi_1^2\pi_2^2(\pi_4^*)^1$ + 24% $\sigma^2(\sigma^*)^1\pi_1^1\pi_2^2\pi_3^2$	**6.502**	**6.287**	**6.094**	**5.992**
$3\ ^1B_1$	71% $\sigma^1\pi_1^2\pi_2^2\pi_3^2(\pi_4^*)^1$	**7.207**	**6.619**	**6.080**	**5.707**
$3\ ^1B_2$	33% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^1\pi_3^2(\pi_4^*)^1$ + 11% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^1(\pi_5^*)^1$ + 11% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^1\pi_3^2(\pi_4^*)^1$	**6.976**	**6.764**	**6.362**	**5.686**
$4\ ^1B_2$	25% $\sigma^2\pi_1^2\pi_2^2\pi_3^1(\pi_4^*)^1$ + 16% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^1\pi_3^2(\pi_4^*)^1$ + 13% $(\sigma^*)^2\pi_1^2\pi_2^2\pi_3^1(\pi_4^*)^1$ + 13% $\sigma^1(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^2$	**8.309**	**7.186**	**6.300**	**b**
$4\ ^1A_2$	25% $\sigma^1\pi_1^2\pi_2^2\pi_3^2(\pi_5^*)^1$ + 24% $(\sigma^*)^1\pi_1^2\pi_2^2\pi_3^2(\pi_4^*)^1$	**8.460**	**7.797**	**7.135**	**b**
$4\ ^1B_1$	27% $\sigma^2(\sigma^*)^1\pi_1^2\pi_2^2(\pi_5^*)^1$ + 16% $\sigma^1(\sigma^*)^2\pi_1^1\pi_2^2\pi_3^2$ + 13% $\sigma^1(\sigma^*)^2\pi_1^2\pi_2^2(\pi_4^*)^1$	**8.259**	**7.951**	**7.693**	**b**

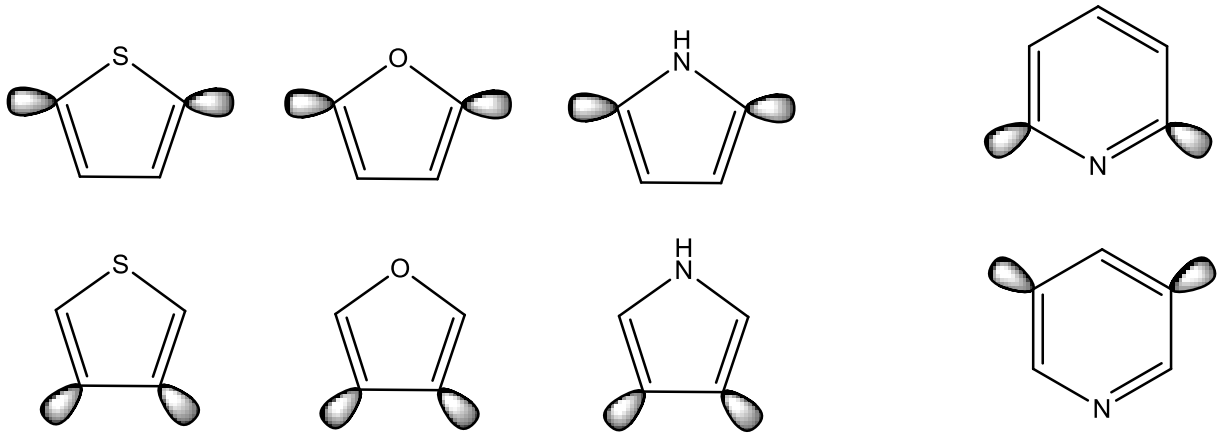
Multireference characterization of thiophene 2,5 diradical



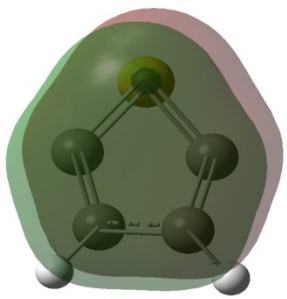
- 2,5 didehydrothiophene is a stable diradical
- Likely forms under high temperature pyrolysis reactions within 5 eV
- adiabatic ΔE_{ST} = 16 kcal/mol; vertical ΔE_{ST} = 20 kcal/mol
- ground state singlet is multiconfigurational
- high density of multiconfigurational excited states

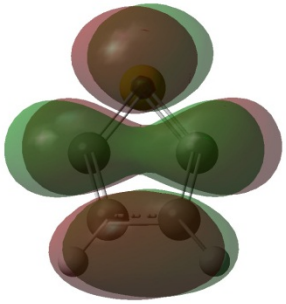
- Other heteroaromatic diradicals

  - CAS(8,8) MCSCF/MRCI based calculations underway
  - Would like to apply VB
    - Will these systems be well described with fewer VB structures than (8,8) active orbitals necessary using MCSCF?
    - Sigma versus pi bonding
    - Measures of aromaticity (covalent/ionic mixing)
    - Through bond coupling

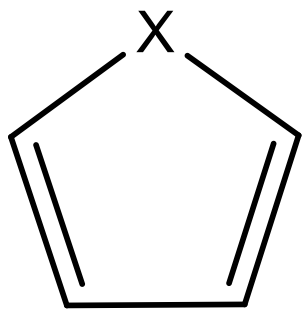


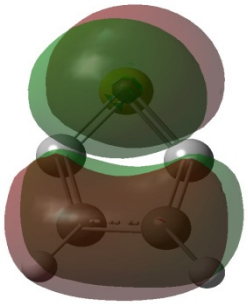
Aromatic diradical pi and pi* orbitals

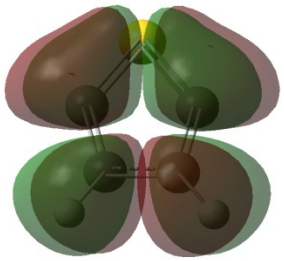
$2b_1$ 

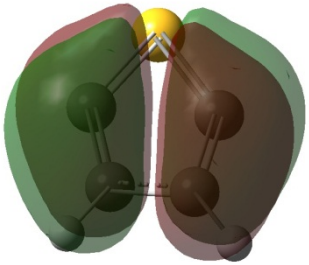
 $4b_1$

X = O, S, NH



$3b_1$ 

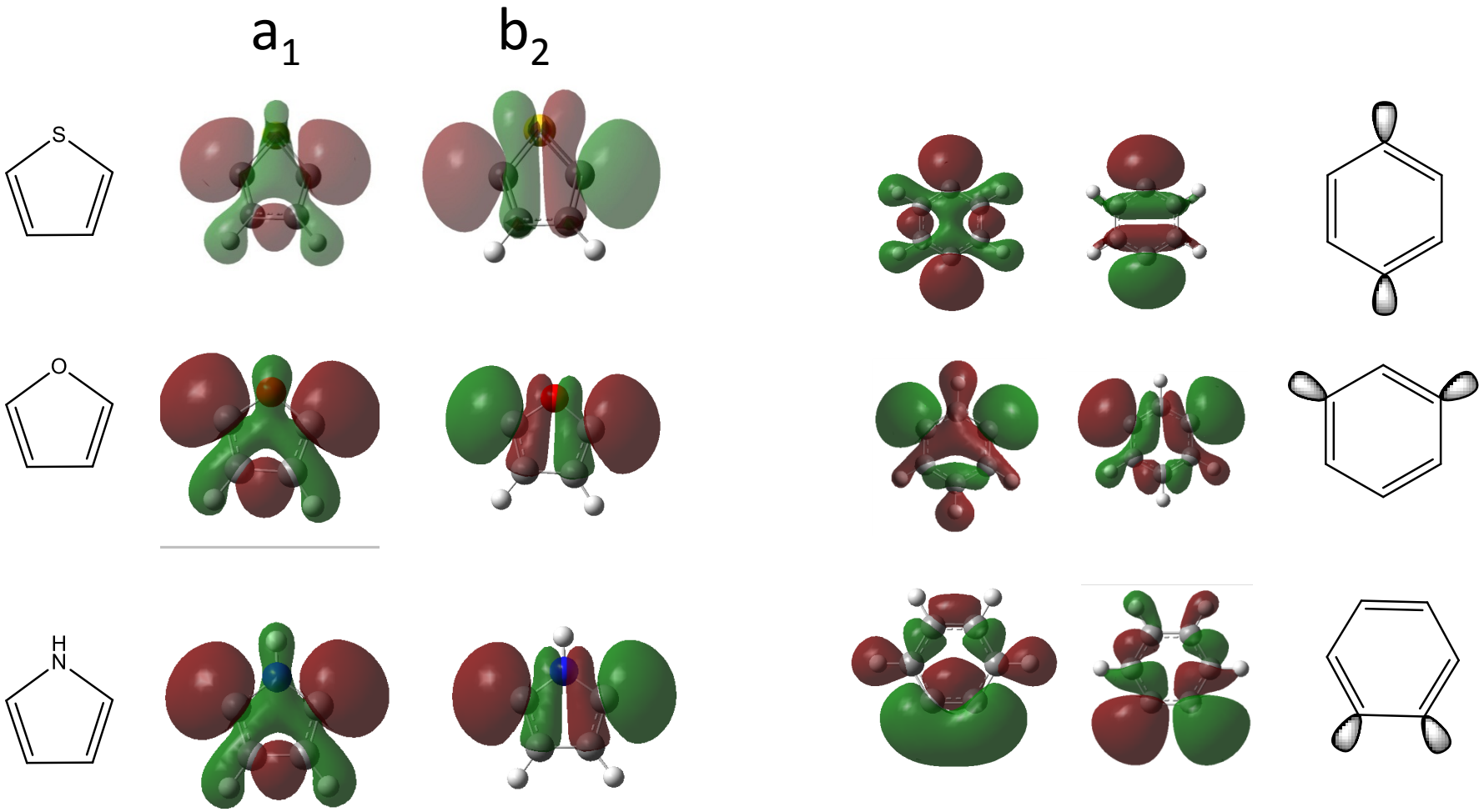
 $2a_2$

$1a_2$ 

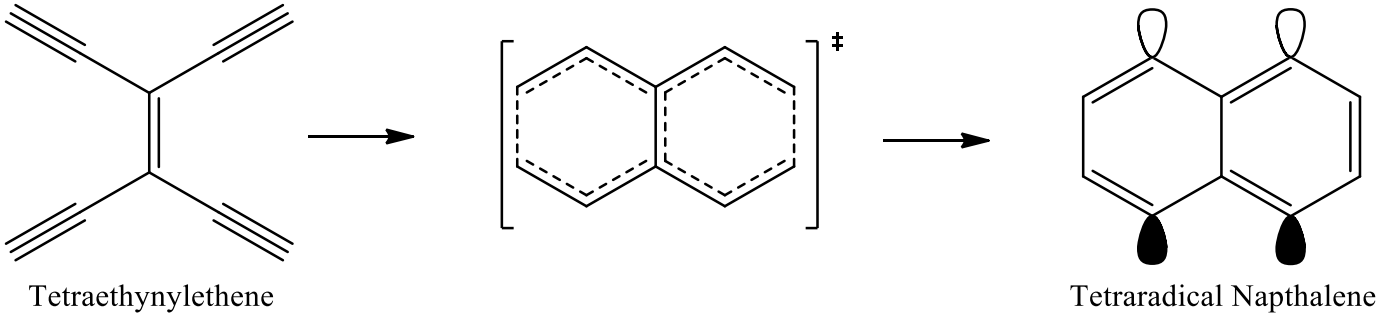
 $5b_1$

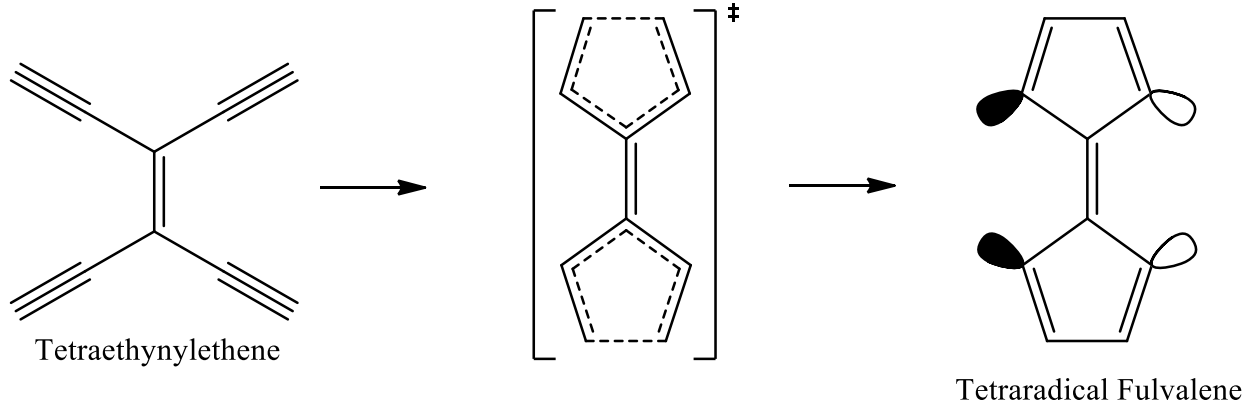
C_{2v}

Aromatic diradical σ and σ* orbitals

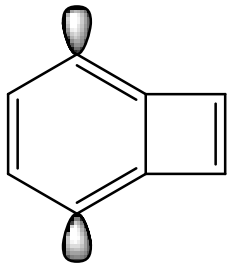


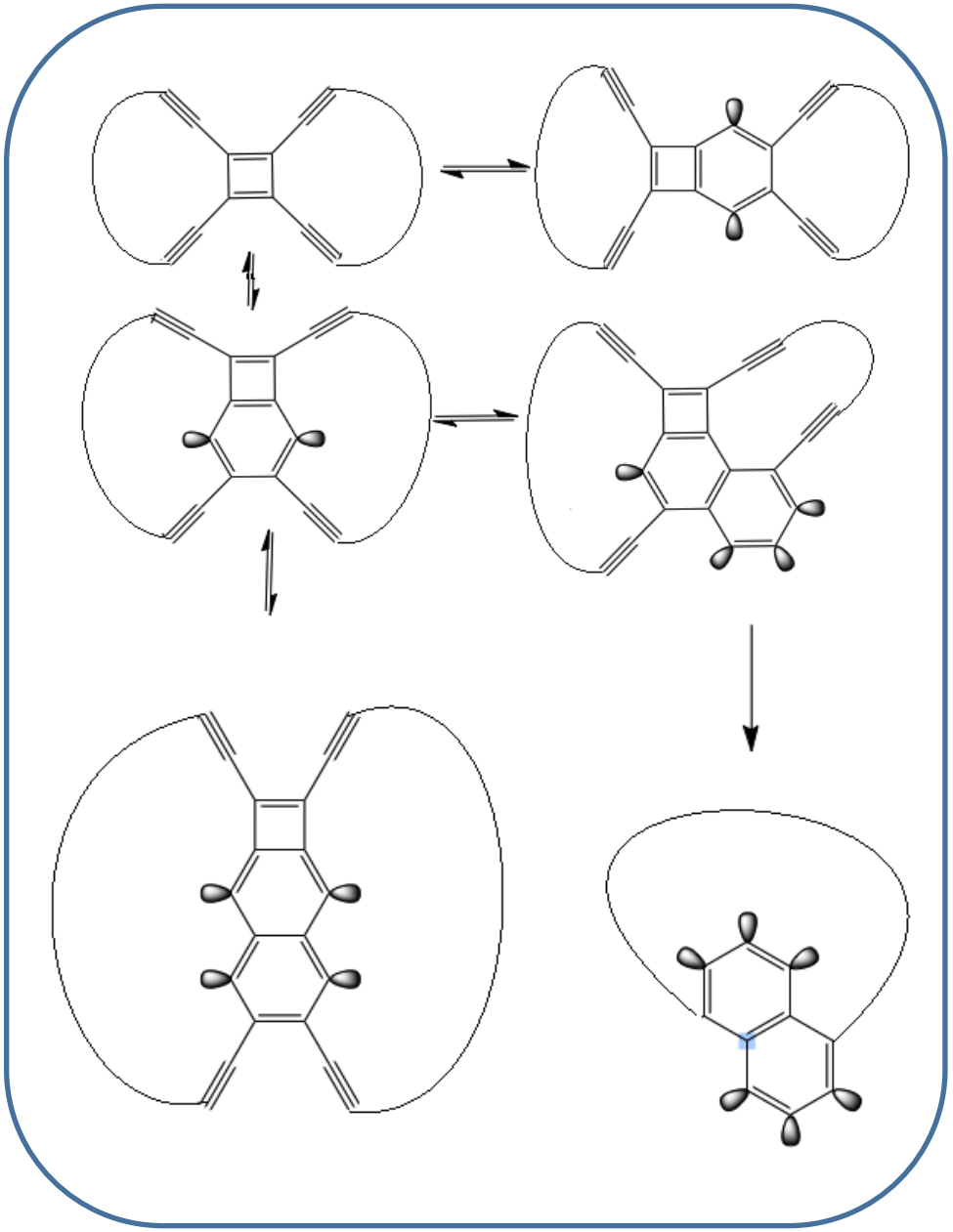
- Other heteroaromatic diradicals
  - B3LYP/TZ surface characterization and MCSCF/MRCI calculations currently underway
  - Would like to apply VB to measure
    - Sigma versus pi bonding, number of VB structures
    - Through bond coupling
    - Mechanism of electrocyclizations, nature of TSs





- Fullerene formation mechanism proposed by Hunter et al. *JPC 1994 98 1810*
  - B3LYP/TZ surface characterization
  - MCSCF/MRCI calculations of smallest system currently underway





Parish Group

CURRENT RESEARCH GROUP:

Post-Docs:

Xinli Song
Raja Zope

Post-Bacs:

Steve Holmes – MD iGluR
Kendra Cunningham ’11
Tyler Steele ‘10
Justin Cook ’12 – QM Ring Expansion Thiophene
Sally Fisher ’11
Emily Nelson ’12 – QM benzynes

Undergrads:

Alex Hahn ’13
Nicki Smith ’13
Devin Sullivan ‘13
Jeff Schriber ’14 – QM radical cyclizations
Idil Cazimoglu ’14 – ladder oligomers
Tabitha Yewer ’14
Alexis Achey ’14 – QM mechanism for C60 formation
Furong Bai ’14
Brian Doherty ’14
Josh Zeldin UNC ‘14
David Stevens ’15 – MD HIV Flap Dynamics
Lily Mawbry ‘15
J’nay Mikell ‘15

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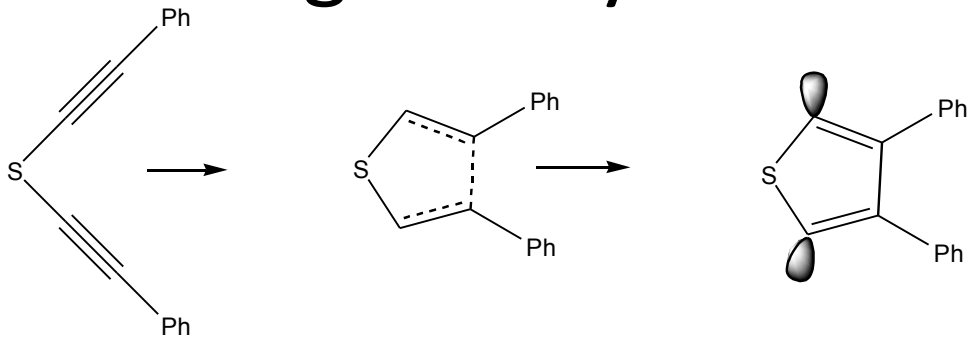
DOE-BES
NSF (RUI, REU, MRI)
ACS-PRF (GB, UFS, B, UR)
Dreyfus Foundation
Jeffress Foundation

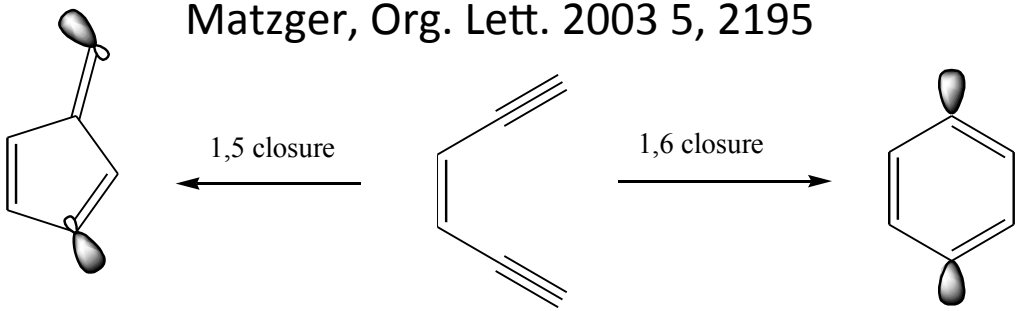
Post-Doc Opening

- **A postdoctoral position in theoretical chemistry is available at the University of Richmond.** Highly motivated candidates with a strong background in theoretical chemistry, chemical physics or related fields are encouraged to apply. The candidate should have experience in *ab initio* electronic structure methods and/or molecular dynamics. The postdoctoral fellow may be involved in more than one project depending on his/her interests and background.

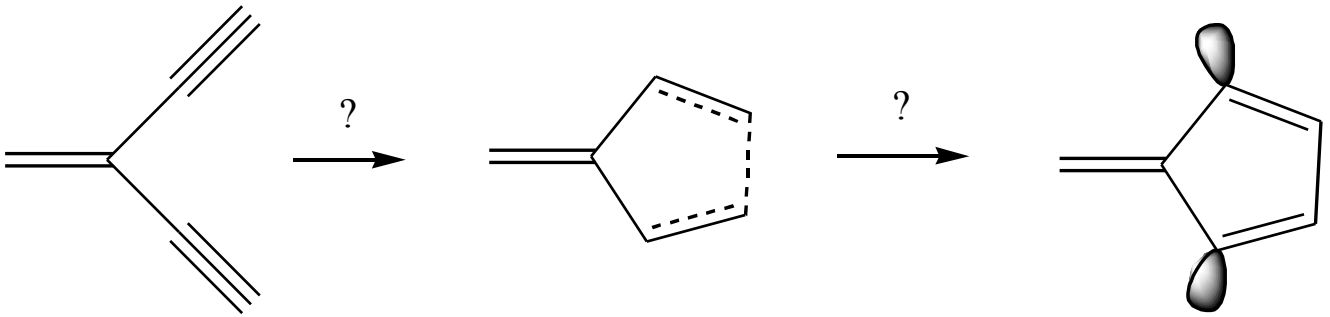
A Search for Interesting Alternatives to the Bergman Cyclization



Matzger, Org. Lett. 2003 5, 2195

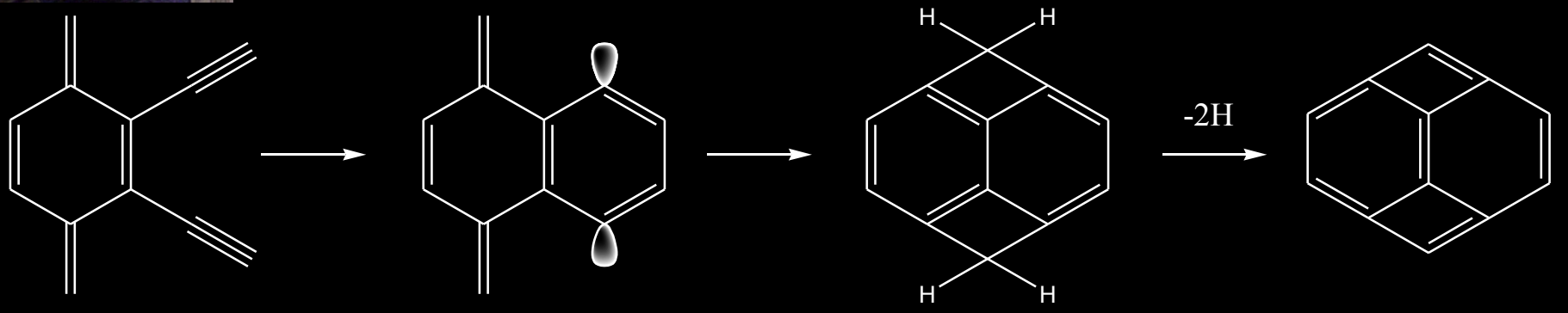


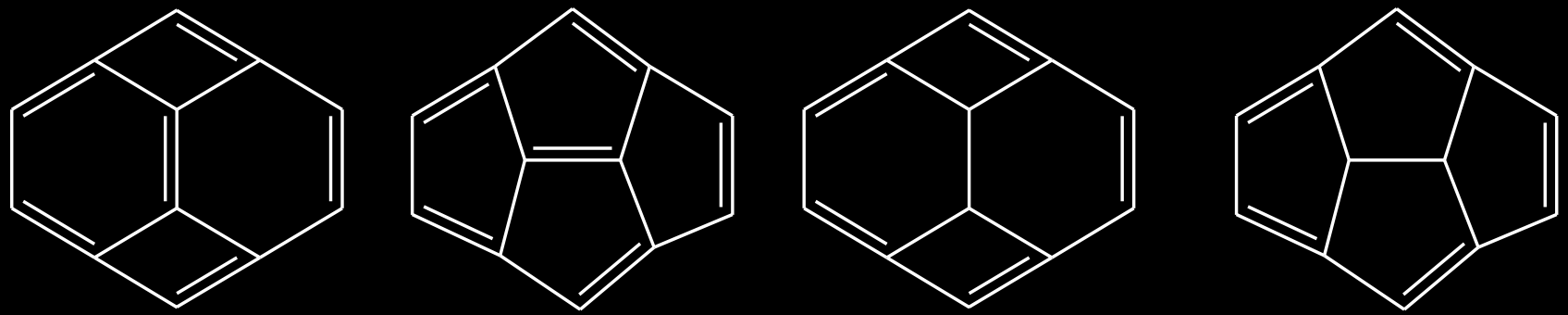
Schreiner, Angew. Chem. 2003 42, 5757



Search for Interesting Alternatives to the Bergman Cyclization

Max Macaluso '06

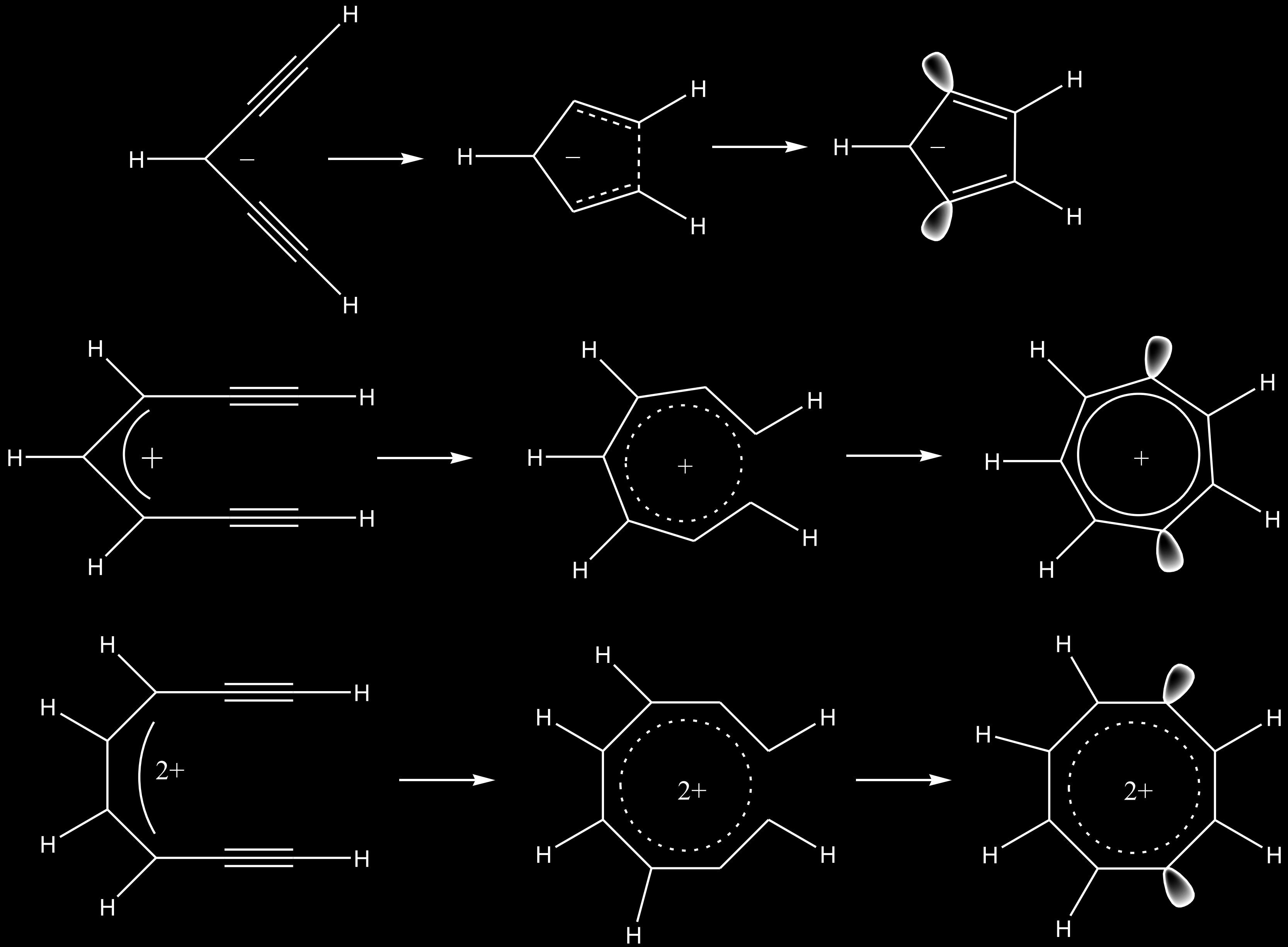




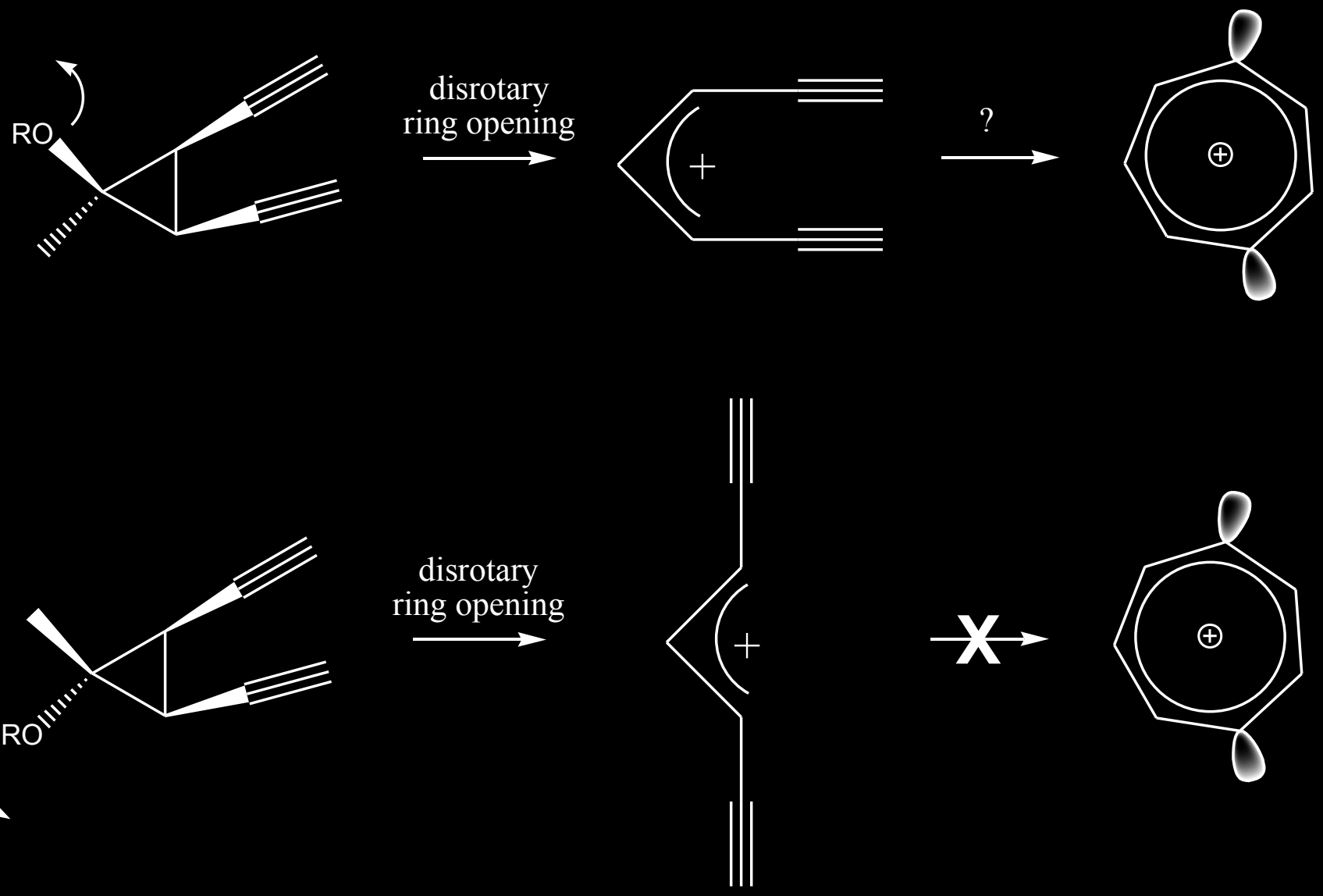
1 **2** **3** **4**

Macaluso, Parish, Hoffmann and Scott, J. Org. Chem. **2004**, *69* 8093

Electrocyclization of penta- hepta- and octadiynes



Triggering the Bergman Cyclization



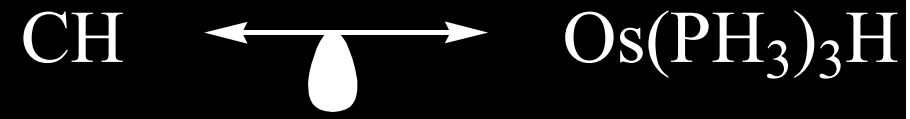
Energetics of hepta- are similar to the Bergman cyclization

Reactant	$\Delta E^{\neq}$(kcal/mol)	ΔE_r(kcal/mol)	r_{TS}(Å)*
(Z)-hexa-3-ene-1,5-diyne	25-34	8.0	2.1
penta-1,4-diyne anion	66.8 – 71.1	23.2 – 36.1	1.96
hepta-1,6-diyne cation	23.1 – 30.8	-4.2 - 8.8	1.93
octa-1,7-diyne dication	14.6 – 17.4	27.5**	2.28

* BLYP/6-311++G** geometry

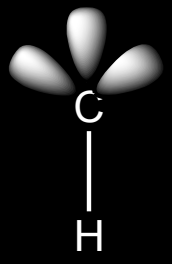
** BLYP/6-311++G** only method to find minima

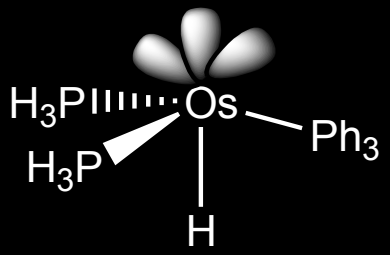
A Search for Alternatives to the Bergman Cyclization

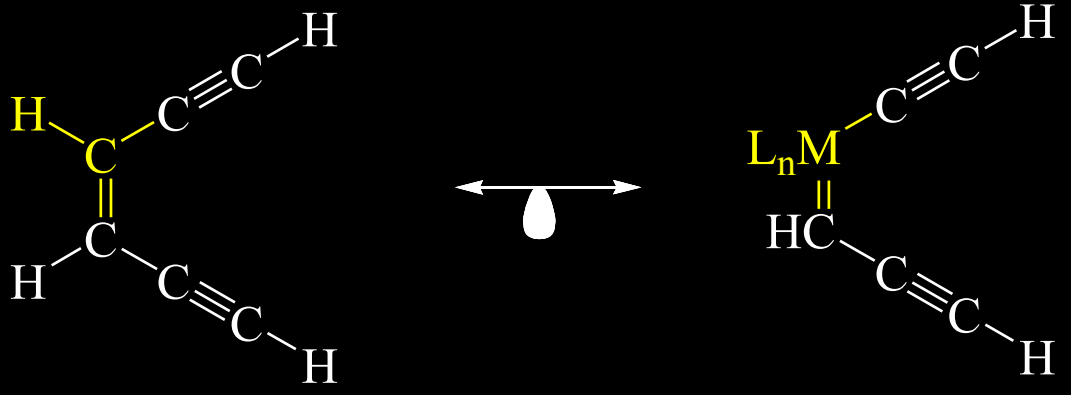


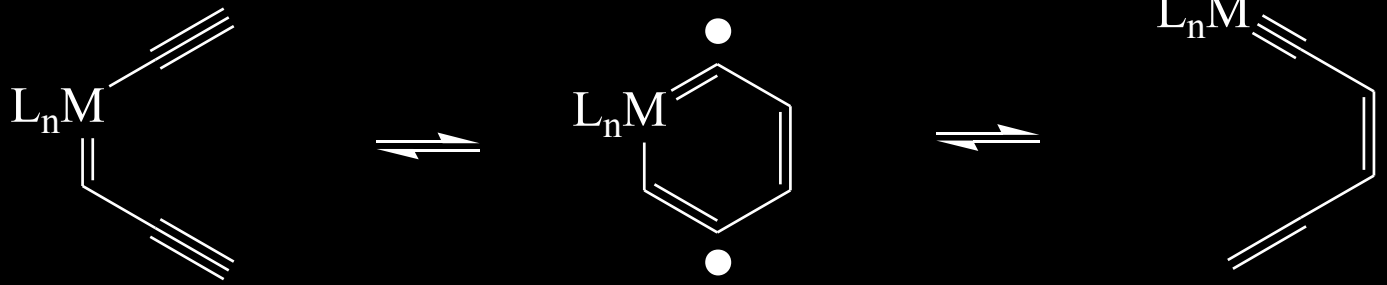
$Os(PH_3)_3H$ is isolobal with CH

Can the isolobal analogy be used to form metallabenzyne diradicals similar to p-benzyne?







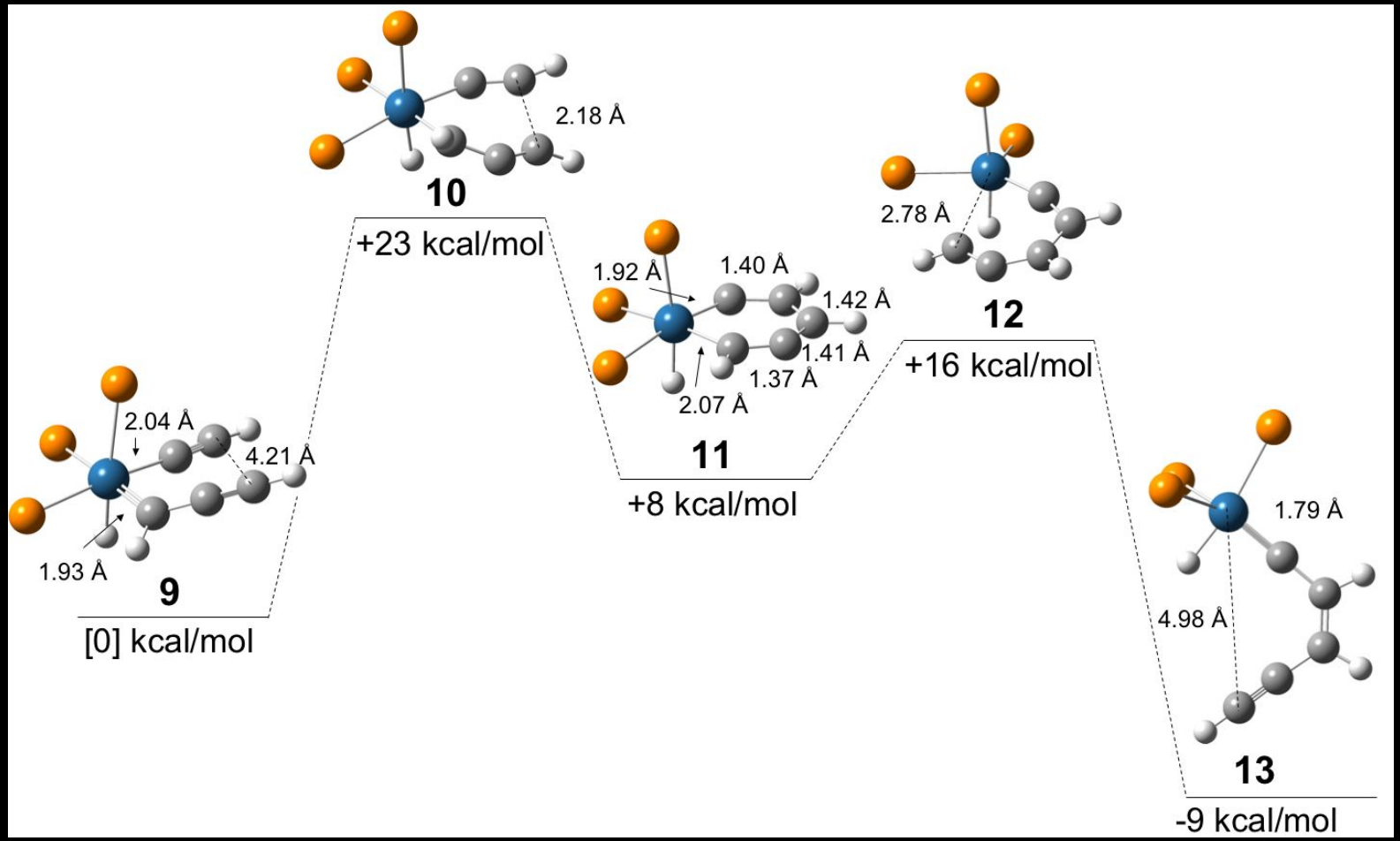


Brzostowska, Hoffmann and Parish, JACS **2007**, *129* 4401

ML_n: $Os(PH_3)_3H$
$Rh(PH_3)_3$

M = osmium, L = $(PH_3)_3H$ - B3LYP/SDD

Edyta Brzostowska



Brzostowska, Hoffmann and Parish, JACS **2007**, *129* 4401