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14. ABSTRACT
The High Energy Density Materials (HEDM) Program objectives are: Identifying and developing advanced chemical propellants for rocket propulsion applications; specific impulse (Isp) is the major metric of a propellant's performance; density can also be a significant contributor.

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Structural Isomers of bis(pentazolyl)iron(II): A Theoretical Study

AFOSR Molecular Dynamics Contractors Conference
May 22-24, 2005

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Isomers of bis(pentazolyl)iron(II)

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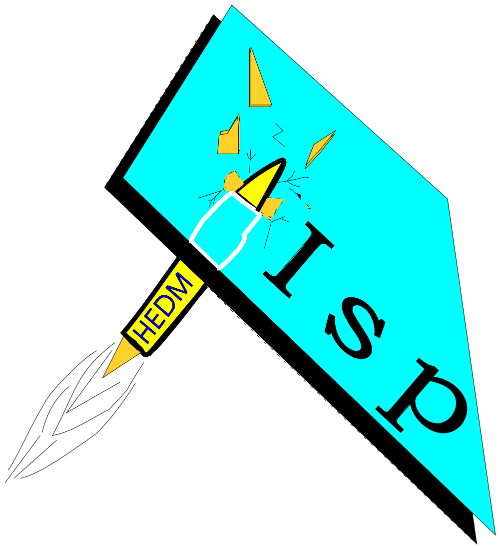
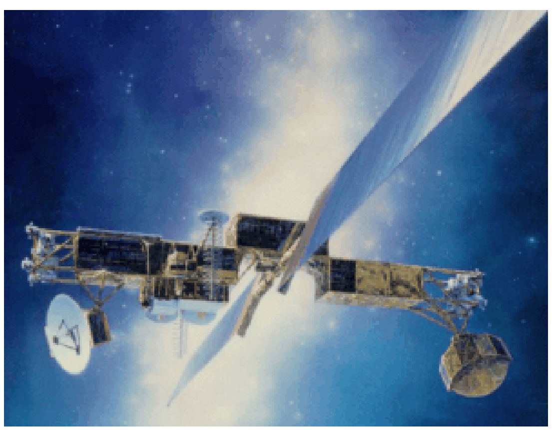
HEDM Program Objective

Identifying and developing advanced chemical propellants for rocket propulsion applications

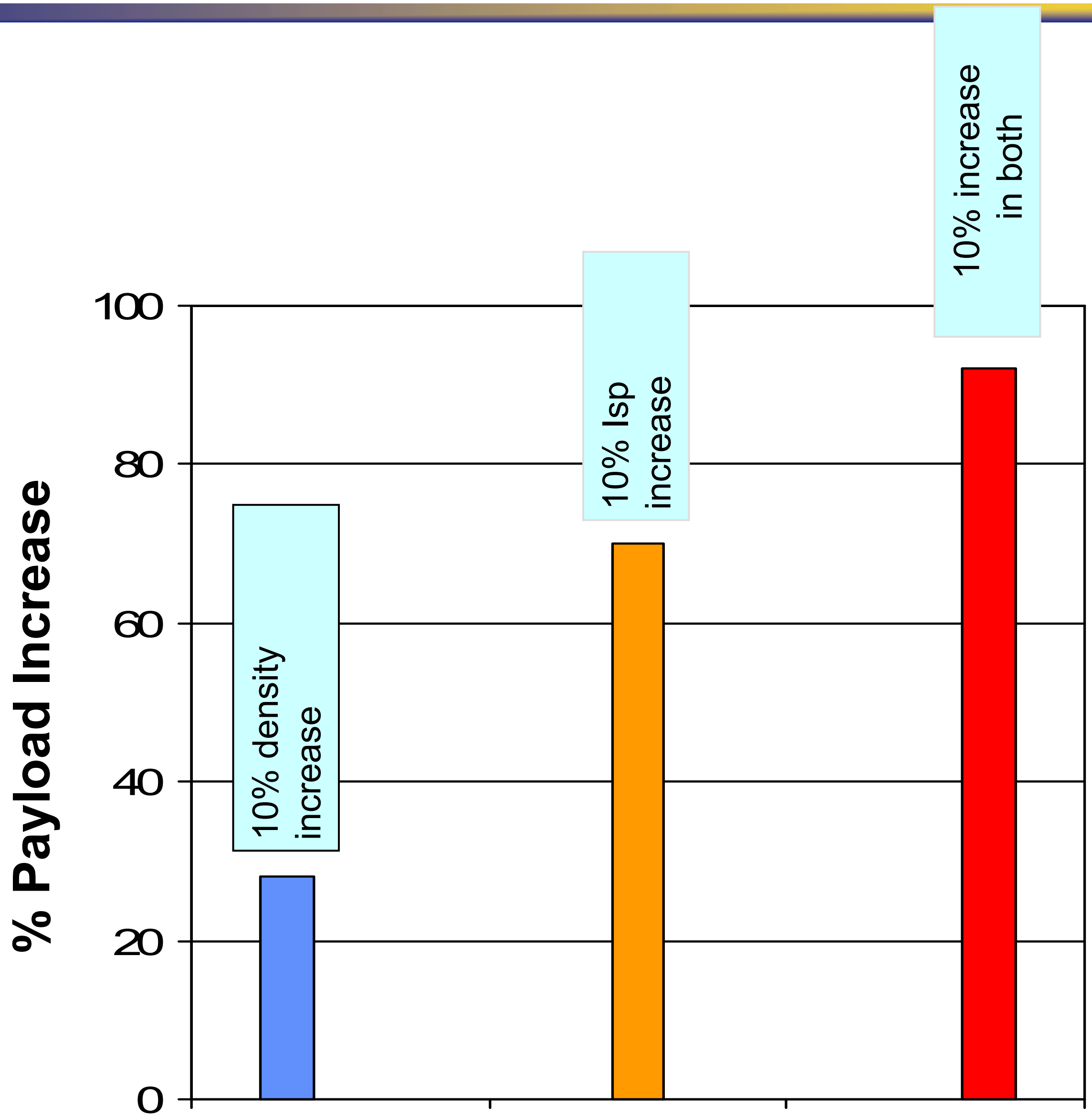


Breaking the performance barrier

- **Isp is the major metric of a propellant's performance**
- **Density can also be a significant contributor**

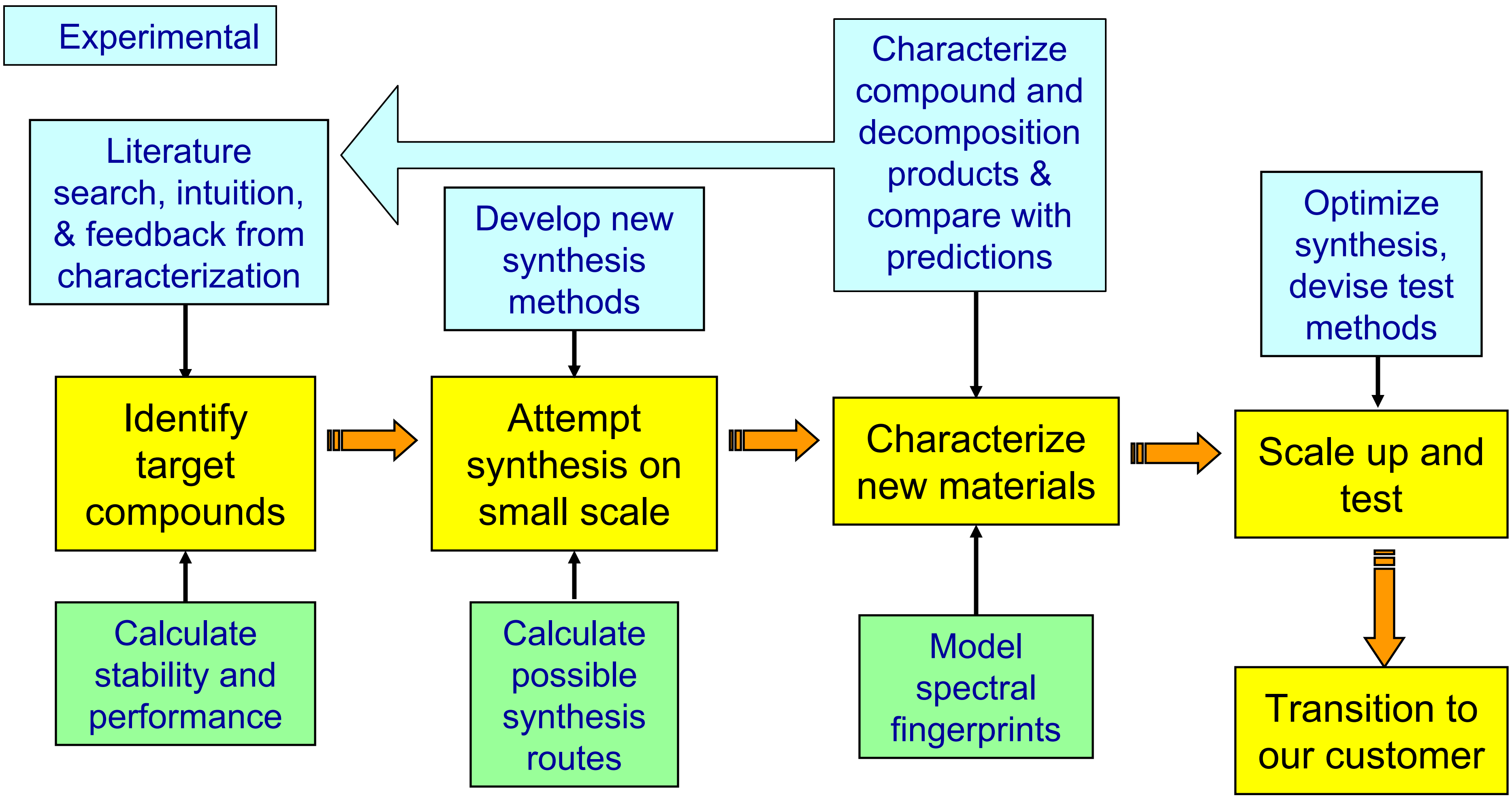


Why We Are Doing It



Propellants Program General Approach

Employ a synergic blend of experimental (synthesis and physical) and computational techniques derived from the disciplines of chemistry and physics

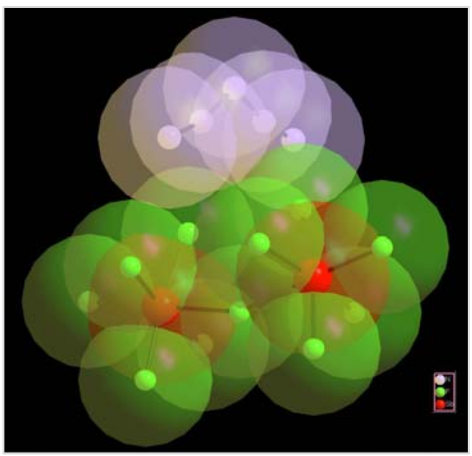


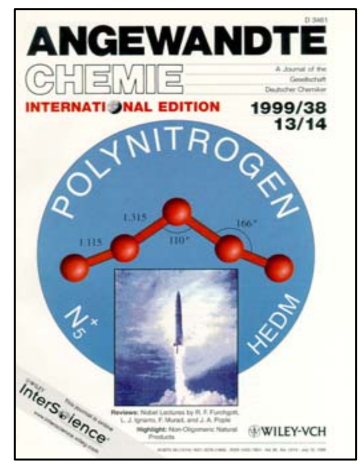
Polynitrogen Project

Discover, synthesize, characterize, and scale-up novel, highly energetic polynitrogen allotropes

Modeling and simulation guides the experimental program:

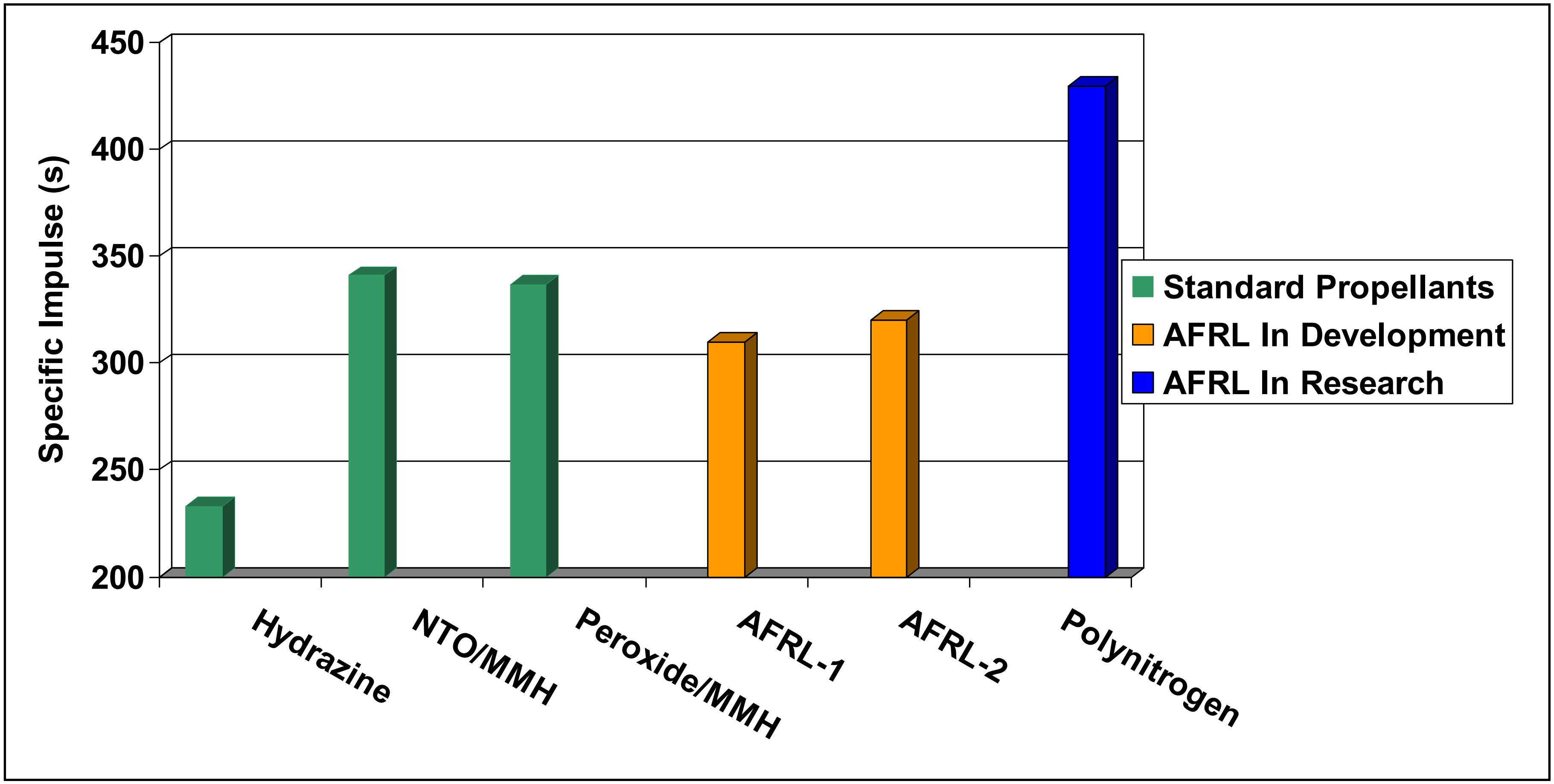
- **Determines which molecules should exist and how energetic they are**
- **Gives information on how to synthesize promising molecules**
- **Provides critical data for identification and characterization of new molecules**





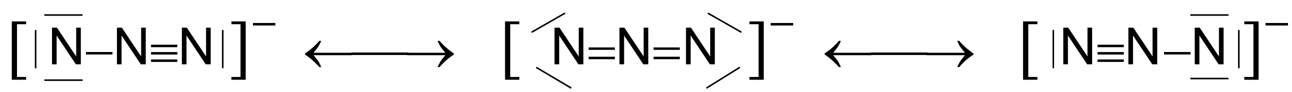
Performance of Polynitrogen Monopropellants

The performance of polynitrogens as monopropellants would dwarf that of hydrazine, and would greatly exceed even bipropellants



The Search for New Polynitrogens

- All polynitrogens are unstable with respect to N_2 molecules
- Their activation energy for N_2 elimination is largely determined by the weakest bond in the compound
- Their metastability is enhanced if suitable resonance structures exist:

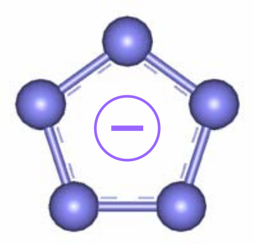


- The double-bond character of the N—N bonds in the azide anion explains its exceptional stability
- How can this stabilization effect be used to our advantage in preparing new compounds?

Pentazolate (N_5^-)?

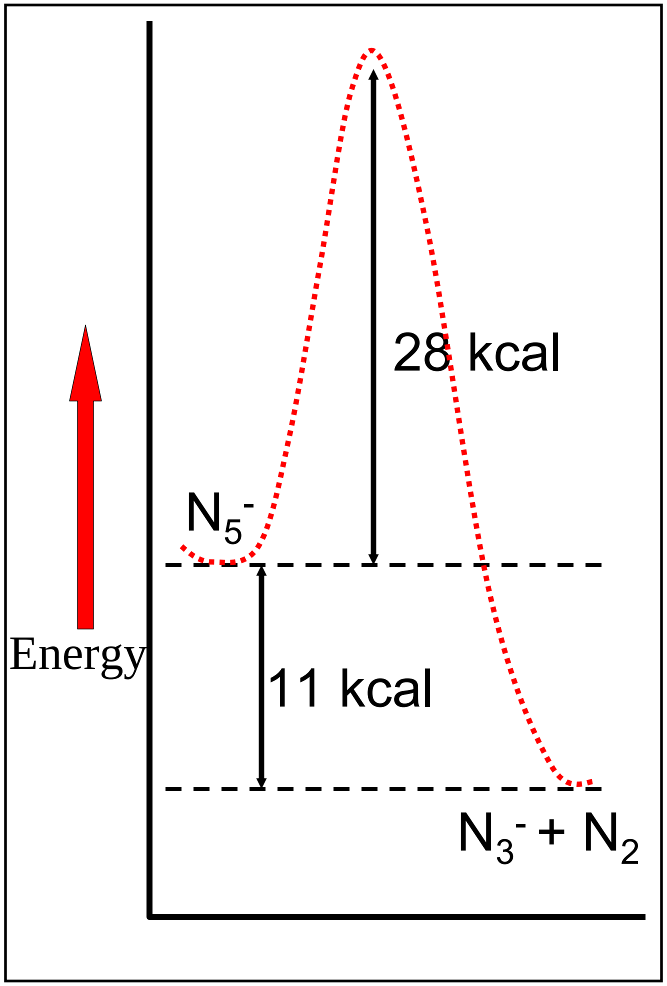
- Substituted pentazoles R-N_5 have been known for decades (R=aryl)
- Cyclic N_5^- is aromatic
- Conversion of the diazonium salt, RN_2^+, to the substituted pentazole ring R-N_5 by the reaction with azide ion, N_3^-, has been demonstrated many years ago by Ugi and Huisgen.
- N_5^- has been recently detected in the gas phase for the first time, using collisional fragmentation (electrospray ion mass spectroscopy).
- Can a chemical route to N_5^- be found?

New Polynitrogen Anions



Pentazole anion (N_5^-)

- *Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to N_3^- and N_2 is only 11 kcal/mol exothermic*
- *Aryl substituted pentazoles can be isolated as stable compounds only if stored at low temperatures. In methanol, these compounds rapidly decompose at room temperature to form aryl azides and N_2 gas*



Transition Metal Complexes of $[N_5]^-$?

$[N_5]^-$ is isoelectronic with cylcopentadienyl anion $[C_5H_5]^-$ (cp)

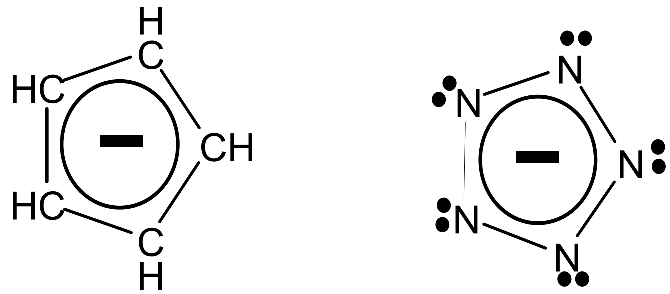
cp ligands readily bind to many transition & main group metals to form "sandwich" complexes

Ferrocene (cp-Fe-cp) – first observed in 1951 (T.J. Kealy, P.L. Pauson *Nature*, **168**, 1039(1951); S.A. Miller, J.A. Tebboth, J.F. Tremaine *J. Chem. Soc*. 632 (1952).)

Chemistry of metallocenes has been thoroughly studied

Insights into possible reaction pathways for isoelectronic N_5-TM-N_5 compounds?

$[N_5]^-$ versus $[C_5H_5]^-$



$[N_5]^-$ is isoelectronic with aromatic cylcopentadienyl anion $[C_5H_5]^-$

cp ligands can coordinate to metal center via π electrons only (η^5)

$[N_5]^-$ can, in principle, coordinate via π electrons or σ lone pairs

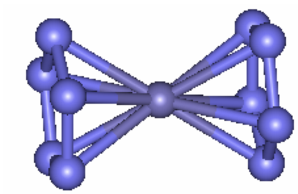
π coordination: η^5

σ coordination: η^1 or η^2

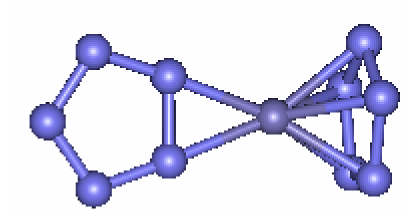
Quantum Chemical calculations of N_5-Fe-N_5

Determine possible bonding modes and their relative energies

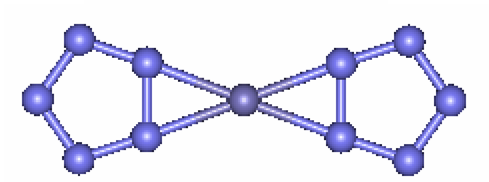
η^5-Fe-η^5



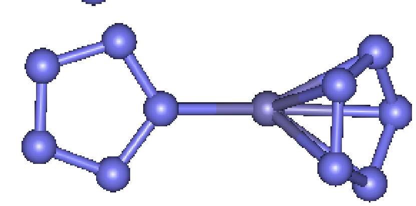
η^2-Fe-η^5



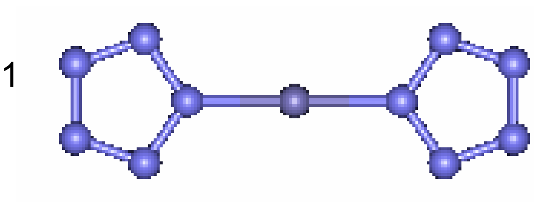
η^2-Fe-η^2



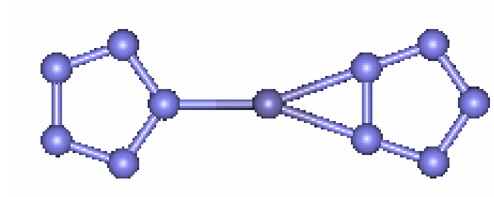
η^1-Fe-η^5



η^1-Fe-η^1



η^1-Fe-η^2



Determine possible spin states and their relative energies

Singlet, triplet, quintet electronic states.

Quantum Chemical calculations of N_5-Fe-N_5

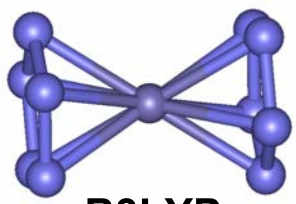
Results of initial, modest-level calculations (B3LYP/SBK+(d) and MP2/SBK+(d))
Singlet electronic states, relative energies in kcal/mol

	B3LYP	MP2
η^5-η^5	21.5 (D_{5d})	3.6 (D_{5h})
η^2-η^2	10.1 (D_{2d})	10.0(D_{2d})
	4.6 (D_{2h})	0.5(D_{2h})
	0.0 (C_2)	**0.0 (C_2)**
η^1-η^1	9.2 (C_{2v})	n/a
η^1-η^2	n/a	5.8 (C_s)
η^1-η^5	n/a	n/a
η^2-η^5	13.2 (C_s)	9.5 (C_s)

015

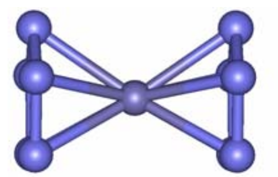
Quantum Chemical calculations of N_5-Fe-N_5

η⁵-η⁵



B3LYP

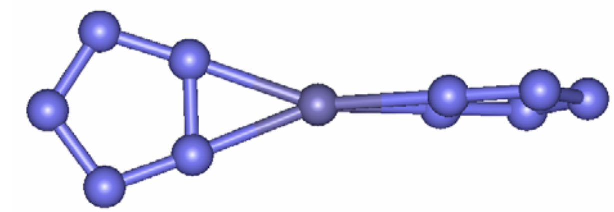
21.5 (D_{5d})



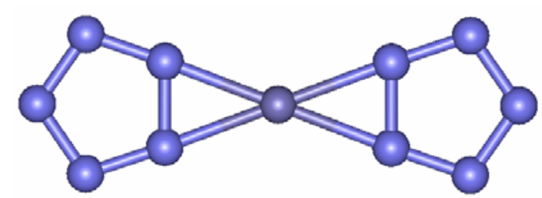
MP2

3.6 (D_{5h})

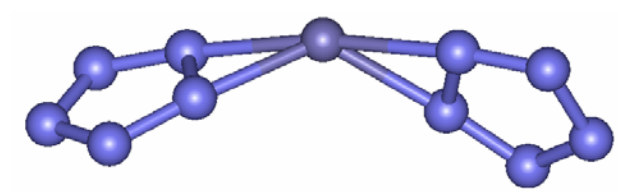
η²-η²



B3LYP	MP2
10.1 (D_{2d})	10.0 (D_{2d})

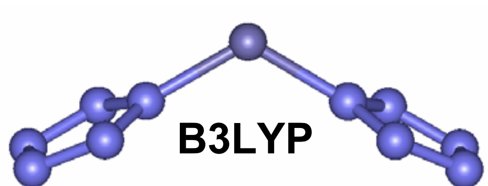


B3LYP	MP2
4.6 (D_{2h})	0.5(D_{2h})



B3LYP	MP2
0.0 (C_2)	0.0 (C_2)

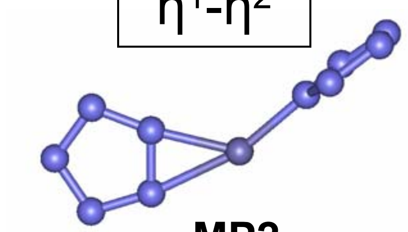
η¹-η¹



B3LYP

9.2 (C_{2v})

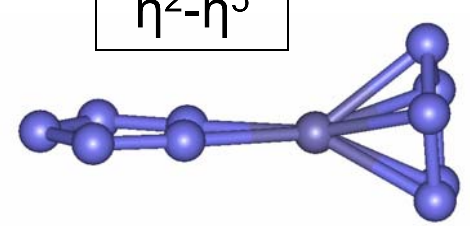
η¹-η²



MP2

5.8 (C_s)

η²-η⁵

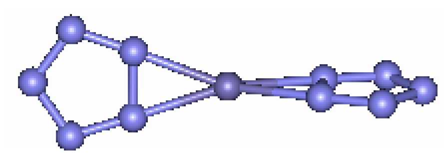


B3LYP	MP2
13.2 (C_s)	9.5 (C_s)

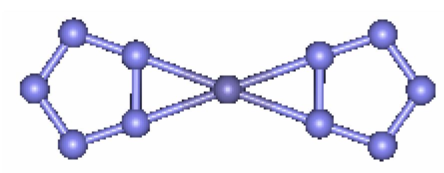
Quantum Chemical calculations of N_5-Fe-N_5

B3LYP, triplet electronic states, relative energies in kcal/mol

η^2-η^2

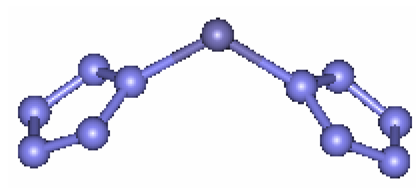


9.4 (D_{2d})

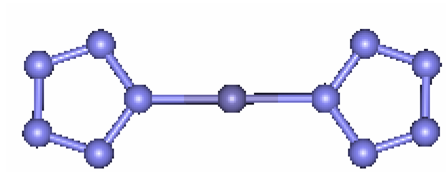


-29.3 (D_{2h})
-31.2 (D_{2h})

η^1-η^1

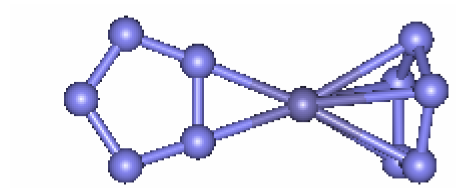


-8.7(C_{2v})



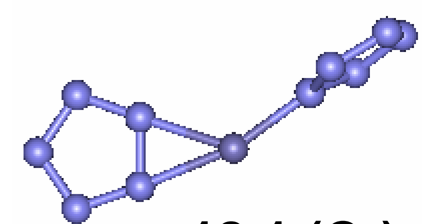
-12.9 (D_{2h})

η^2-η^5



-7.1 (C_1)

η^1-η^2



-12.1 (C_s)

Total (au) and Relative (kcal/mol) Energies of N5-Fe-N5 stationary points

	B3LYP(5)	MP2	CCSD(T)//MP2	T1
<u>η5-η5</u>				
D5h	-221.897766[1](21.5)	-220.722672[0](3.6)	-220.817543(12.2)	0.0435
D5d	.897778[0](21.5)	.721345[1](4.4)	-220.818049(11.9)	0.0432
<u>η2-η2</u>				
D2h	-221.914555[1](10.9)	-220.711445[1](10.6)	-220.833418(2.2)	0.0253
C2h	.924379[1](4.8)	.721884[1](4.1)	n/a	n/a
D2h*	.924679[0](4.6)	.727578[0](0.5)	-220.831820(3.2)	0.0218
D2d	.915901[0](10.1)	.712431[0](10.0)	.833717(2.0)	0.0254
C2	.931975[0](0.0)	.728409[0](0.0)	.836247(0.4)	0.0296
D2d(triplet)	.916963[0](9.4)			
D2h(triplet)	.978715[0](-29.3)			
D2h*(triplet)	.981686[0](-31.2)			
<u>η1-η1</u>				
D2h	-221.869702[2](39.1)	-220.676205[2](32.8)	-220.788778(30.2)	0.0277
D2h*	.906936[1](15.7)	.701173[1](17.1)	-220.812963(15.1)	0.0257
D2h**	.896858[2](22.0)	.707632[1](13.0)	-220.809089(17.5)	0.0188
D2d	.847741[2](52.9)	.643839[2](53.1)	-220.789710(29.7)	0.0228
C2v	.917363[0](9.2)	.711637[1](10.5)	-220.817459(12.2)	0.0246
Cs	n/a	.692082[1](22.8)	n/a	n/a
D2h(triplet)	.952592[0](-12.9)			
c2V(triplet)	.945762[0](-8.7)			

Total (au) and Relative (kcal/mol) Energies of N5-Fe-N5 stationary points

	B3LYP(5)	MP2	CCSD(T)//MP2	T1
η1-η2				
C2v	-221.898673[2](20.9)	-220.702113[2](16.5)	-220.807136(18.7)	0.0223
C2v'	.914327[1](11.1)	.713738[1](9.2)	-220.820661(10.2)	0.0230
Cs	.919090[1](8.1)	.719127[0](5.8)	-220.823692(8.3)	0.0236
Cs(triplet)	.951282[0](-12.1)			
η1-η5				
Cs	n/a	-220.688408[1](25.1)	-220.801039(22.5)	0.0402
η2-η5				
Cs	-221.910857[1](13.3)	-220.713209[0](9.5)	-220.836962(0.0)	0.0451
Cs‘	.910869[0](13.2)			
C1(triplet)	.943231[0](-7.1)			

Occupation Restricted Multiple Active Space (ORMAS)

ORMAS: flexible CAS method for reducing size of full CI step, similar to generalized CASSCF.

Active space is product of three sub-spaces:

(6e,5o) $[N_5]^-$ π+ π* (left)

(6e,6o) $[Fe]^{2+}$ 3d+4s (middle)

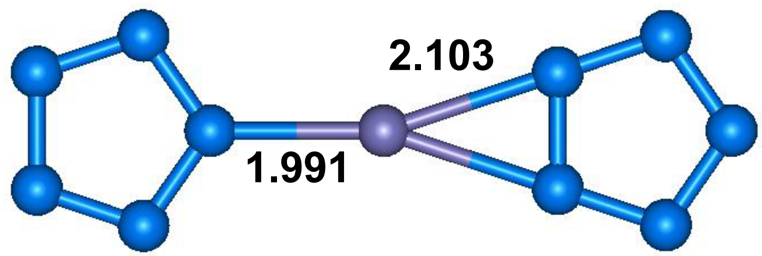
(6e,5o) $[N_5]$- π+ π* (right)

SBK+(d) effective core potential and valence-only basis set used throughout.

ORMAS Results

C_{2v}

η^1-η^2 ($^5A_1$)



-219.351299

(0.0 kcal/mol)

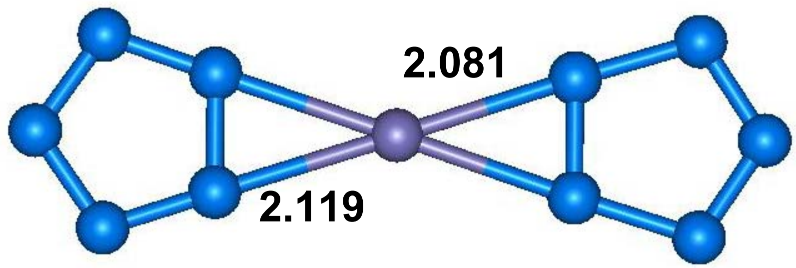
Natural Orbital Occupation Numbers

N_5 (left)	Fe	N_5 (right)
π 1.983	3d 1.993	π 1.976
π 1.938	3d 1.000	π 1.935
π 1.916	3d 1.000	π 1.930
π* 0.086	3d 1.000	π* 0.083
π* 0.077	3d 1.000	π* 0.077
	4s 0.007	

ORMAS Results

C_{2v}

η^2-η^2 ($^7A_1$)



-219.182241

(+106 kcal/mol)

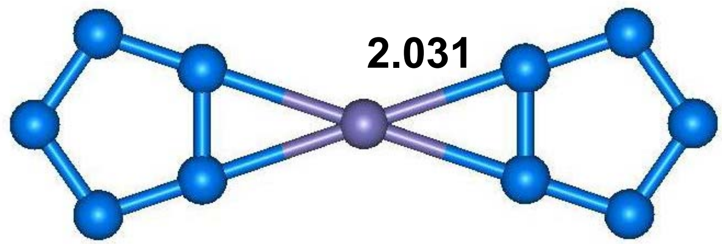
Natural Orbital Occupation Numbers

N_5 (left)	Fe	N_5 (right)
π 1.976	3d 1.989	π 1.996
π 1.936	3d 1.000	π 1.855
π 1.931	3d 1.000	π 1.027
π* 0.082	3d 1.000	π* 0.974
π* 0.076	3d 1.000	π* 0.148
	4s 0.011	

ORMAS Results

D_{2h}

η^2-η^2 ($^3B_{2g}$)



-219.260755

(+57 kcal/mol)

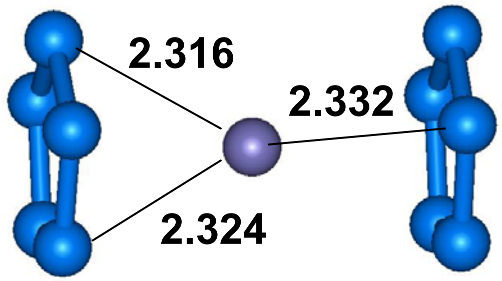
Natural Orbital Occupation Numbers

N_5 (left)	Fe	N_5 (right)
π 1.977	3d 1.963	π 1.977
π 1.935	3d 1.931	π 1.935
π 1.930	3d 1.035	π 1.930
π* 0.082	3d 0.982	π* 0.082
π* 0.077	3d 0.084	π* 0.077
	4s 0.006	

ORMAS Results

C_s

η^5-η^5 ($^3A''$)



-219.163546

(+118 kcal/mol)

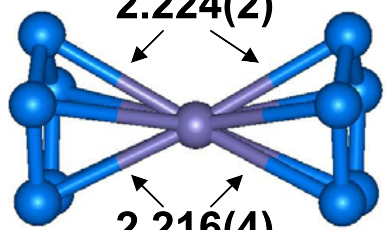
Natural Orbital Occupation Numbers

N_5 (left)	Fe	N_5 (right)
π 1.972	3d 1.972	π 1.972
π 1.951	3d 1.900	π 1.951
π 1.949	3d 1.024	π 1.949
π* 0.066	3d 0.985	π* 0.066
π* 0.064	3d 0.114	π* 0.064
	4s 0.005	

ORMAS Results

C_s

η^5-η^5 ($^1A'$)



-219.127764(?)

(+140 kcal/mol)

Natural Orbital Occupation Numbers

N_5 (left)	Fe	N_5 (right)
π 1.972	3d 1.996	π 1.972
π 1.945	3d 1.834	π 1.945
π 1.945	3d 1.824	π 1.945
π* 0.070	3d 0.171	π* 0.070
π* 0.068	3d 0.171	π* 0.068
	4s 0.004	

Conclusions

- At the B3LYP and MP2 levels of theory, there are six distinct stable singlet structures. The most stable structure is a twisted η^2-η^2 isomer with C_2 symmetry.

- At the B3LYP level, there are seven distinct stable triplet structures. The most stable structure is a planar η^2-η^2 isomer with D_{2h} symmetry.

- At the B3LYP level, all but one of triplet minima are more stable than the lowest energy singlet structure. The most stable triplet is a planar η^2-η^2 isomer with D_{2h} symmetry.

- ORMAS results indicate significant multiconfigurational character in N_5-Fe-N_5 complexes – B3LYP and MP2 results may not be reliable.

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