

07-20

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-04-

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1. REPORT DATE (DD-MM-YYYY) 07/08/2004		2. REPORT TYPE FINAL		3. DATES COVERED (From - To) 04/01/02 - 03/31/04	
4. TITLE AND SUBTITLE GRANT TITLE: POLYNITROGEN FUELS: THE CONTRIBUTION OF PREDICTIVE THEORY DOCUMENT TITLE METASTABLE MOLECULES IN GROUND AND EXCITED STATES: MOLECULAR DESIGN WITH THEORY				5a. CONTRACT NUMBER F49620-02-1-0146	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
6. AUTHOR(S) RODNEY J BARTLETT					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITY OF FLORIDA DIVISION OF SPONSORED RESEARCH 219 GRINTER HALL GAINESVILLE FL 32611-5500				8. PERFORMING ORGANIZATION REPORT NUMBER FINAL-1	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT DOCUMENTS INTENDED FOR PUBLIC RELEASE					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT HIGHLIGHTS FROM FISCAL 04 INCLUDE: DETERMINED THE OPTIMUM STRUCTURE AND VIBRATIONAL FREQUENCIES FOR A POLYMERIC NITROGEN SPECIES; EXPLORED A VARIETY OF OXYGEN SUBSTITUTED NITROGEN MOLECULES WHERE COORDINATE COVALENT BONDS TO O ARE INTRODUCED; FINALIZED STUDIES OF AZACUBANES AND NITROZACUBANE; DID A STUDY OF THE NO DIMER IN ITS GROUND AND EXCITED STATES.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 75	19a. NAME OF RESPONSIBLE PERSON Antoinette Knight
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (Include area code) 352-392-7545

20040907 050

ACKNOWLEDGMENTS

DARPA--Art Morrish, Don Woodbury

Don Kimble, Doug Ladouceur, Gail Heim

AFOSR--Mike Berman

DARPA FINAL REVIEW

June 3, 2004

Arlington, VA

***Metastable Molecules in Ground and Excited States: Molecular Design
with Theory***



RODNEY J. BARTLETT

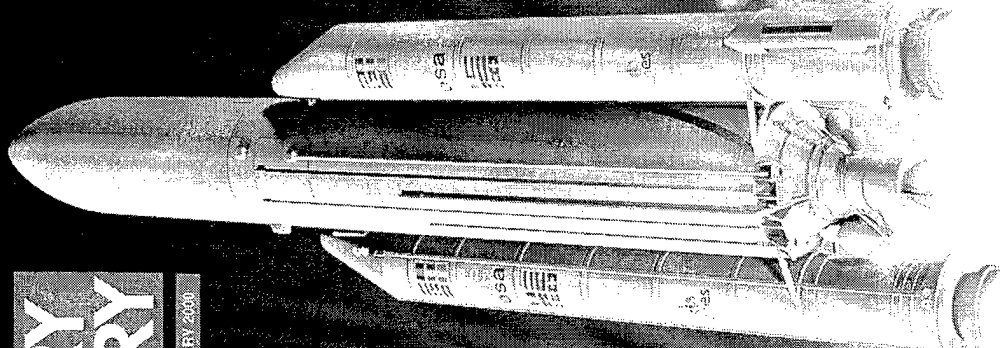
***Quantum Theory Project
Departments of Chemistry and Physics
University of Florida
Gainesville, Florida USA***

**Work supported by
DARPA**

CHEMISTRY & INDUSTRY

NUMBER 6 PAGES 121-160 21 FEBRUARY 2000

Rocket science: is nitrogen the fuel of the future?



Decoupling glycolate ♦ UK contaminated lead policy ♦ Pmt careers crisis

OUR CHARTER FROM HEDM (1989)...

PROPOSE NEW WAYS TO STORE ENERGY THAT WILL LEAD TO “REVOLUTIONARY” IMPROVEMENTS IN SPECIFIC IMPULSE

CHEMICAL STORAGE

- Electronic Metastability
Trapping Electrons in High Energy States ($\sim 1-10^3 \text{eV/g}$)
- Geometric Metastability
Unusual bonding patterns ($\sim 10-100 \text{kcal/g}$)
- Pure Nitrogen species, and beyond

Lauderdale, W.J., Myers, M.J., Bernholdt, D.E., Stanton, J.F., Bartlett, R.J. in
Proceedings of the High Energy Density Materials Contractors Conference, Feb. 1990, Long Beach, CA, pp 25-28,
AFOSR.

EXTENDED ABSTRACT:

POLYNITROGEN FUELS: THE ROLE OF THEORY

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University of Florida, Gainesville, FL. 32611-8435

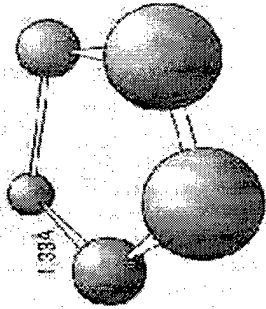
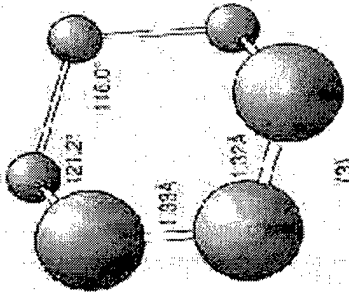
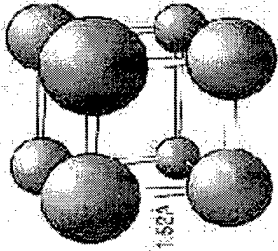
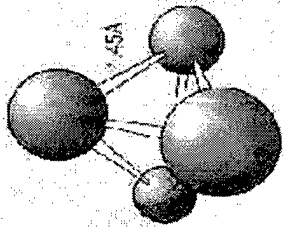
In 1989 we submitted a proposal to the AFOSR on the basic research topic of investigating 'metastability' in molecules, meaning states whose energies are far above the norm even for highly endothermic molecules. A consequence of such an investigation, might be ways to enhance the energy content of potential rocket fuels. The avowed objective of the initial HEDM program was to explore ways to make potentially revolutionary improvements in thrust to provide significant gains in payload. Metastability can occur due to long-lived excited states of a molecule, but no solution to trapping such states is apparent. The other alternative is what we termed 'geometric metastability' which means to put atoms together into a molecule in unusual ways, and depend upon the bonds formed to store the energy. An additional condition was that the perspective fuels had to be lightweight yet have more energy per mass unit than known bi-propellant species like $\text{LOX} + \text{H}_2$; or a molecule like hydrazine, as a mono-propellant. Since the molecules to be proposed are not known experimentally, and since synthesis and characterization of candidate systems would be very expensive and difficult; *only predictive quantum chemical methods makes it possible to assess the energy content and kinetic stability (barrier to dissociation) of such structures, to identify the best prospects for success prior to any synthetic effort.* Modern quantum chemistry also provides very accurate spectroscopic signatures to identify such energetic molecules when they are formed, frequently even in very small quantities.

In our proposal we focused on low-mass molecules which had the capacity to store very large amounts of energy per mass unit. The prototype for such molecules would be polynitrogen systems, and in particular, purely nitrogen molecules. Replacing CH groups in an organic molecule by nitrogen atoms can significantly increase its endothermicity since the standard state for N is N_2 , one of the stronger bonds known. This may also be viewed less quantitatively as increasing the N-N repulsions, since unlike CH_4 , N- carries a lone pair of electrons with it. As the perfect all nitrogen molecule would also 'burn' to just N_2 there would even be the bonus that it would be innocuous to the atmosphere and would leave no signature. Hence, in our proposal we suggested fascinating, speculative molecules like N_4 with the four atoms in a tetrahedral configuration, N_8 or the nitrogen analog of cubane, various pentazole species like NaN_5 , N_5-N_5 , and a wealth of others involving high nitrogen content together with heteroatoms. None were known experimentally, but according to high level, predictive quantum chemical calculations, all could be shown to store large amounts of energy and to have significant barriers to dissociation, suggesting their probable formation under appropriate (not usually easily obtained) conditions. Our first report showing these results is in the Proceedings of the High Energy Density Materials Conference, in Feb, 1990, [1]. We reported the I_{sp} of N_4 would exceed $LOX + H_2$ and that it has a barrier to dissociation exceeding that of TNT. N_8 would also be very effective, though its computed barrier is about half that of N_4 [2]. We made similar studies of pentazole derivatives [3].

Our suggestions were pursued in the AFOSR HEDM program, and then in this DARPA program, with the avowed intent to synthesize some of these pure nitrogen species. In the DARPA program there has been a potential observation of N_4 [4], using our predictions of the vibrational spectra and IR and Raman intensities for identification [5]. Also substantial success has been achieved with the synthesis of N_5^+ AsF_6^- , however, that molecule is still a long way from a pure nitrogen species or even a fuel, until we can replace the AsF_6^- [6] group with a light, suitable anion. If it were also composed of only nitrogen, we would meet our objective. Through this work we now have the N_5^+ unit as a potential partner in forming purely nitrogen species.

Some Energetic Considerations in Polynitrogen Chemistry

	ΔH_f (Kcal/mol)	Bond Energy
N	~120	0
-N-N-	~40	~40
-N $\ddot{\cdot}$ ·N-	~28	~100
-N=N-	~16	
N \equiv N	0	226

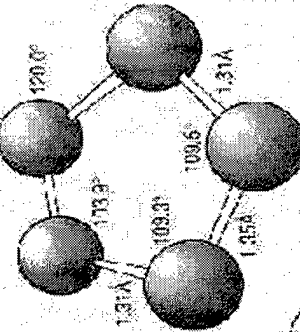
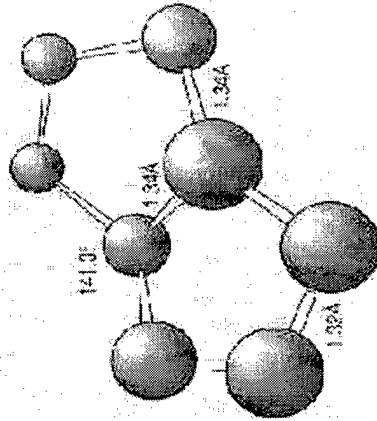
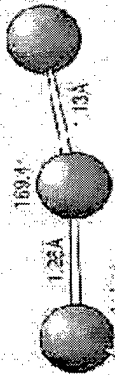
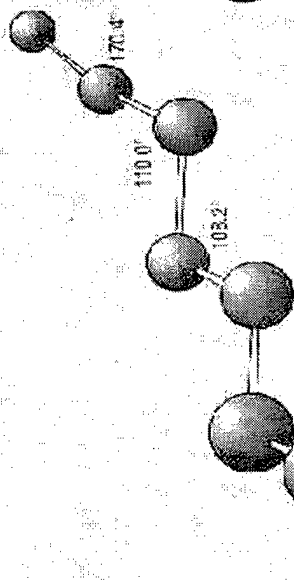


(1)

(2)

(3)

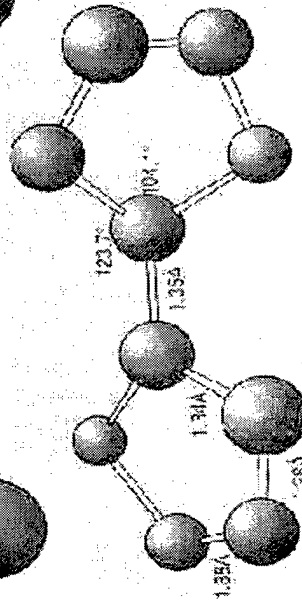
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(6a)

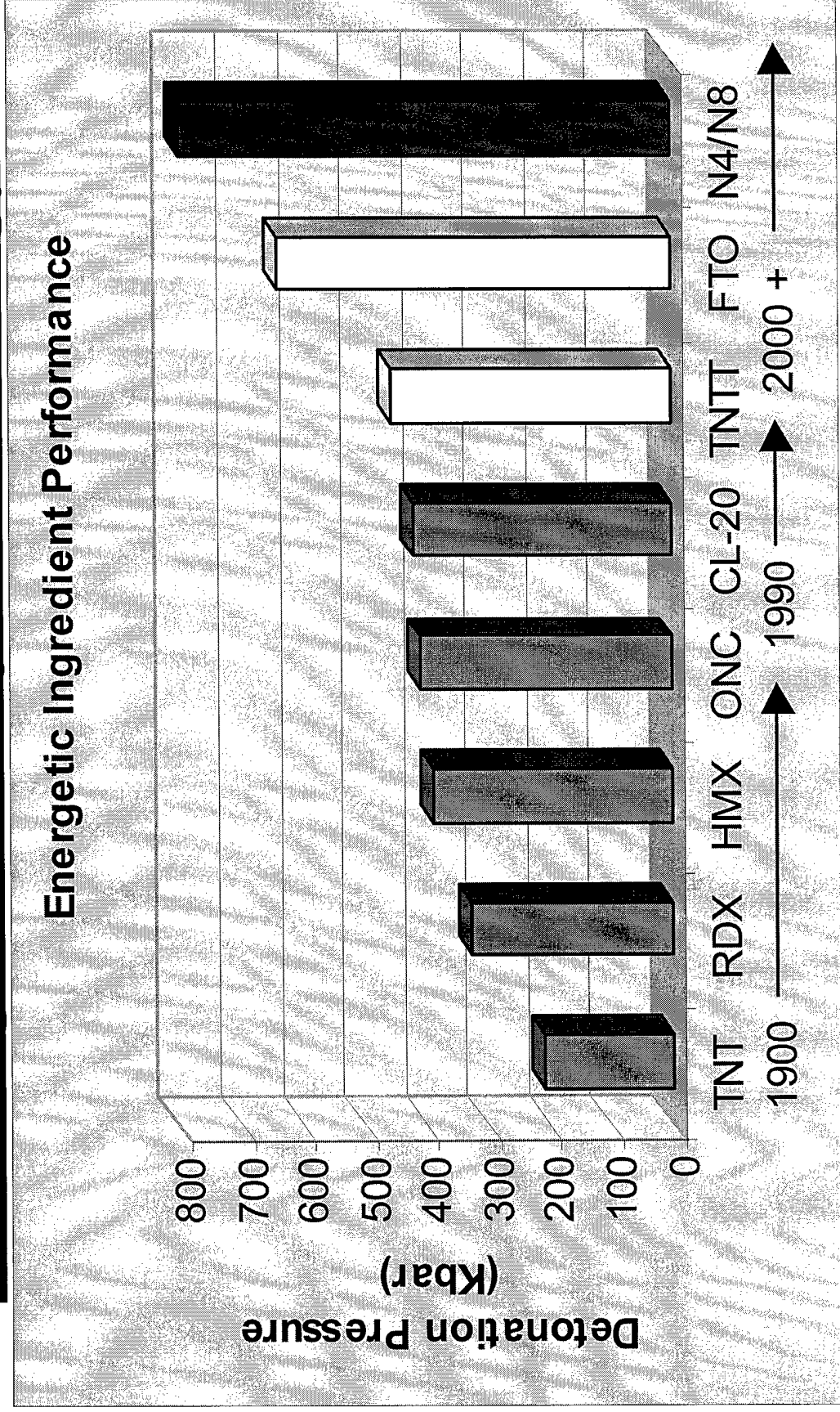
(6b)

(5)



(7)

Existing and Projected Energy Yields



Courtesy of Bill Koppes at NSWC-IH

TEAM MEMBERS

Stefan Fau, Postdoc

Ken Wilson, Received Ph. D.

Motoi Tobita, Received Ph. D.

Rafael Podeszwa, Postdoc, Polymers

Ajith Perera, Associate Scientist

ANNUAL FUNDING ~\$70K

SPECIFIC OBJECTIVES

- Explored the limits of metastability in molecules
- Proposed novel, high energy structures, like N₄, N₈, N₅⁻, N₆O₃, and many, many others
- Assessed prospects for their energetics and stability by applying the predictive, state-of-the-art Coupled-Cluster, quantum chemical methods we have introduced.
- Developed new methods as required to describe properties, like Raman intensities for identification and detection of unknown molecules.
- Provided theory support to the experimental effort.
- Attempted to bring some order into the generation of vast numbers of possible energetic molecules, by seeing them as dimers, trimers, etc of common units.

Some Highlights of Our DARPA Work

- Provided the reference theoretical results required in the identification of the transient N_4 Molecule [5].
- Developed new coupled-cluster methods for obtaining accurate Raman intensities, which are crucial to the identification of many polynitrogen species including N_4 [5].
- Showed that it is unlikely to be able to synthesize N_4 without one or two molecules excited [9]. (It would be better to have a cyclic N_3+N)
- Demonstrated that an ionic lattice composed of N_5^+ and N_3^- is not likely to exist [7].
- Proposed that the next target for the DARPA program should be to synthesize the pentazole anion, N_5^- , the 'inorganic benzene' [8].
- Predicted the properties of the pentazole anion using our high level couple-cluster methods, including its energetics, structure, vibrational frequencies, and IR and Raman intensities, and its UV-vis (electronic excited state) spectrum [5].

- Performed a large number of high level quantum chemical calculations to survey all stable purely nitrogen species, from N_2 to N_{10} and some larger species, their cations and anions. We provide the vibrational frequencies, IR and Raman intensities for all, and for selected molecules, excited and ionized state information. This information is collected into a Compendium that can be downloaded from my web page [11].
- Recommended that we seriously consider synthesis of the N_6O_3 molecule, which by virtue of its three coordinate covalent bonds to oxygen, permits the long sought N_6 pseudo-benzene ring to form. We report detailed studies of its activation barrier and properties in a recent paper [12].
- Made an extensive study of potential molecules that are generalizations of hydrazine, to assess structures, Heats of Formation, and vibrational frequencies. Also considered Li substitution for H. This information is collected into a second Compendium that can be downloaded from my webpage[14].

HIGHLIGHTS FROM FISCAL

04

- Determined the optimum structure and vibrational frequencies for a polymeric nitrogen species. Extensions to two and three dimensions need to be made to help to fully characterize potential high pressure forms of nitrogen. Similar studies of polymeric oxygen, and nitrogen oxygen combinations are likely to suggest some exciting, novel, energetic forms. Also studied polymeric form of CO. Found it to be barely stable[P1]
- Explored a variety of oxygen substituted nitrogen molecules where coordinate covalent bonds to O are introduced. These structures make it possible to form a perfect six nitrogen atom ring, or to form various $N_5O_x^-$ alternatives that offer almost the same ionization potential as N_5^- with better stability and oxygen balance. We also considered substituting CH- for a N atom in N_5^+ and N_5^- and P for N[P2].

(Cont)

- Finalized studies of azacubanes and nitroazacubane. Compared results of various methods, DFT, NDDO, MBPT2, to CC theory for Heats of Formation, finding that for such large molecules that DFT is not very accurate[P3].
- Did a study of the NO dimer in its ground and excited states. Demonstrated that the demands of its Van der Waals ground state and its highly degenerate valence excited states requires the whole set of quantum chemical tools we have developed recently, including DEA-STEOM, EOM-CCSDT, MR-AQCC, MR-BWCC, etc. Recommend this molecule as an essential test of any new method developed in quantum chemistry[P4].

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- P2. M. Tobita, S.A. Perera, M. Nooijen and R.J. Bartlett, "A critical comparison of single- and multi-reference coupled cluster methods: Geometry, harmonic frequencies, and excitation energies of (NO)₂, *J. Chem. Phys.* 119, 10713-10723 (2003).
- P3. S. Fau, R.J. Bartlett, "Changing the Properties of N₅⁺ and N₅⁻ by Substitution" *Advances in Energetic Materials*, (P.Politzer editor), 2004.
- P4. K. Wilson, A. Perera, J. S. Stanton, S. Beck & R. J. Bartlett, "Azacubanes and Nitroazacubanes", *J. Phys. Chem.*, submitted.

**SPECIFIC PRODUCTS
PRODUCED**

Structure and Stability of Polynitrogen Molecules and Their Spectroscopic Characteristics

Rodney J. Bartlett



Stefan Eric
Mordechai Tobin
Ken Wilson
Ajith Perera

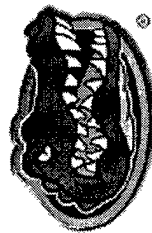
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This work is supported by AFOSR-DARPA (F49620-98-1-0477)

To be published

Predicted Structures and Spectroscopic
Characteristics of Hydrazine, Lithium-substituted
Hydrazine and Their Higher Derivatives

Rodney J. Bartlett



Coworker:
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This work is supported by AFOSR-DARPA (F49620-98-1-0477)

ACES II

UNIQUE QUANTUM CHEMICAL METHODS

- CCD, CCSD, and CCSD(T) [and QCISD, QCISD(T)] analytical gradients for open-and closed-shell systems, using RHF, UHF and ROHF references
- Full CCSDT for open and closed shells
- CCSDTQ and CCSDTQP for closed shells
- CCSDT(Qf) and CCSD(TQf)
- RHF, UHF MBPT(4) analytical gradients
- ROHF-MBPT(2), MBPT(3) and MBPT(4) energies, and gradients
- CC/MBPT analytical gradients using general contractions (atomic natural orbitals).
- Quasi-restricted Hartree Fock (QRHF-CC) methods and associated analytical gradients
- Analytical first-order property evaluation at the CC/MBPT levels using the “Relaxed Density”
- Ab Initio DFT

- EE-EOM-CCSD methods for excited states
- EA-EOM-CCSD for electron attachment
- Any order TDHF for frequency dependent hyperpolarizabilities
- Analytical EOM-CC NMR spin-spin coupling constants and other second-order properties
- Multiplicity monitoring for UHF based correlated calculation
- IP-EOM-CCSD for ionization process
- TD-CCSD open-shell singlets and analytical gradients
- EE-EOM-CCSD(T), EE-EOM-CCSDT-3, and EE-EOM-CCSDT
- STEOM – CC for excited states
- IP-EOM-CCSDT for ionization processes.
- UHF and ROHF analytical MBPT(2) Hessians

**ADVANCES IN THE STATE-
OF-THE ART IN ENERGETIC
MATERIALS RESEARCH**

**THIS PROGRAM, AND THE AFOSR
HEDM EFFORT, HAS CHANGED THE WAY
WE THINK ABOUT MAKING NEW
ENERGETIC MATERIALS.**

IT HAS GREATLY BROADENED PERSPECTIVE!

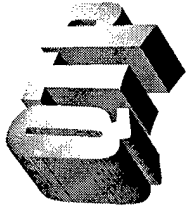
OUTLINE

- Why Theoretical Design of Energetic Molecules?
- The Pentazole Anion, an example where predictions were verified by experiment.
- Variations on a theme, using N-O bonds.
 - A. with CH replacing N.
 - B. with P replacing N.
- Generalizations of Hydrazine
- Azacubanes and their nitro derivatives.

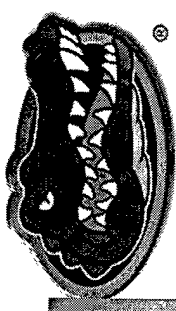
- **Rational Quantum Chemical Design**

Role of Theory

- **Relative Energetics**
 - Molecular Structure
 - ΔH_f and ΔH_{rxn}
 - Activation Barriers (E^\ddagger)
 - Potential for Excited State Decomposition Paths
- **Spectroscopic Detection**
 - Vibrational Frequencies
 - Infrared Intensities
 - Raman Intensities
 - Ultraviolet-Visible Spectra
 - NMR and ESR Spectra
 - Photoelectron Spectra
- **Potential Synthetic Routes and Excited State Paths**



A quote...



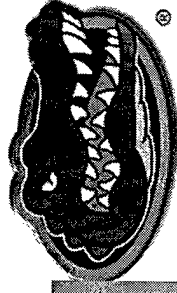
“Ab initio quantum chemistry is an emerging computational area that is fifty years ahead of lattice gauge theory...and a rich source of new ideas and new approaches to the computation of many fermion systems.”

Ken Wilson,

Ab initio quantum chemistry: A source of ideas for lattice gauge theorists, Nuclear Physics B - Proceedings Supplements, Volume pgs. 82-92
September 1990 (1989).

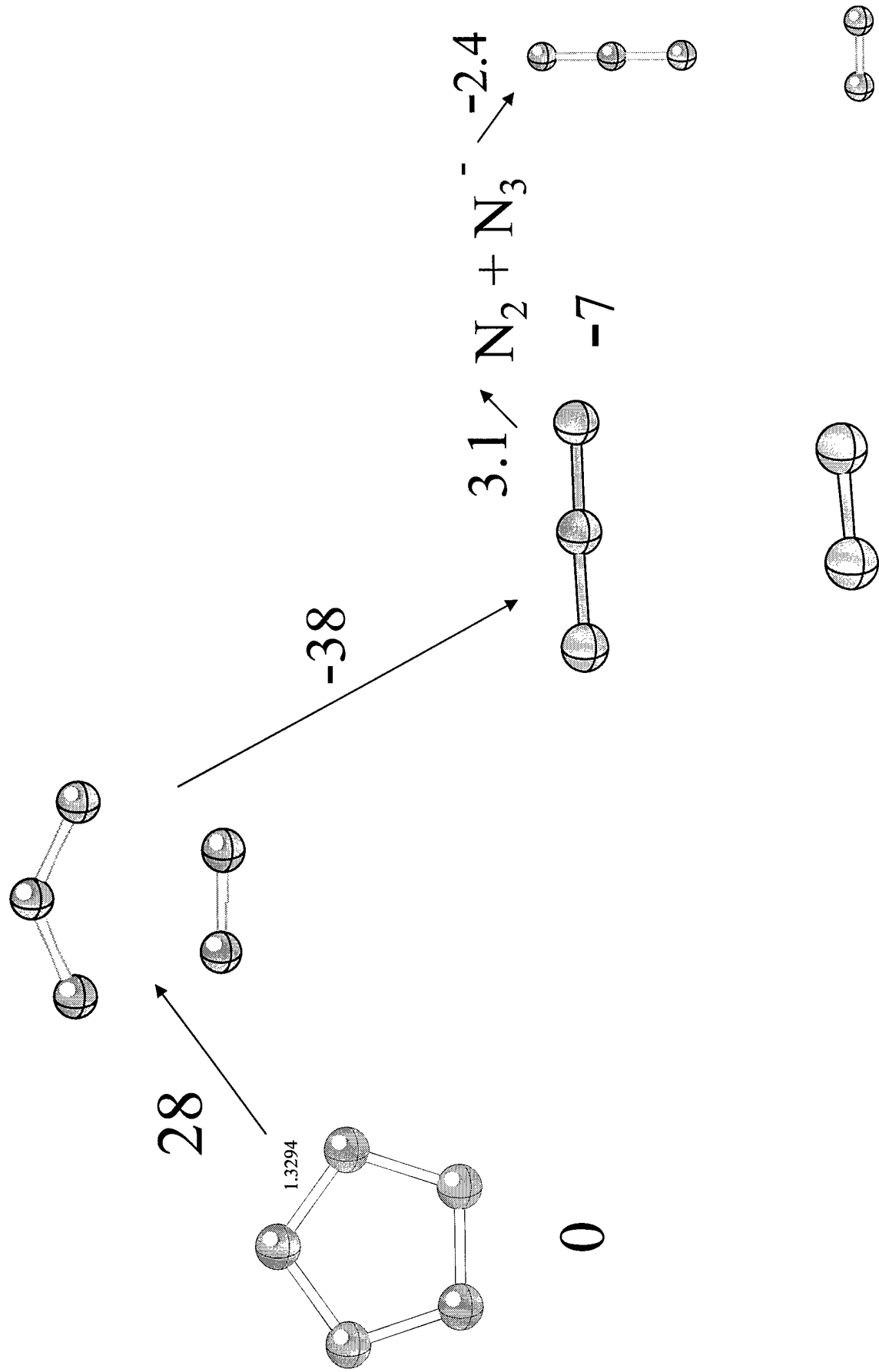


And more from Ken Wilson

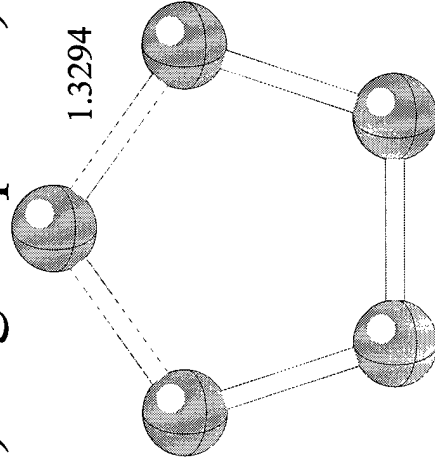


“There are roughly 10^6 classified chemical compounds at the present time. Each individual molecule has many properties to compute and/or measure: binding energies, electron density, atomic structure, spectra (vibrational, rotational, and electronic), reaction rates, electron and molecular scattering cross sections. However, the spectacular opportunity for the future lies in compounds not yet synthesized or classified... $92^{(10^{23})}$.. These unexplored forms of matter contain innumerable surprises...”

Dissociation of N_5^- : Energy differences in kcal/mol



N_5^- D_{5h} $^1A_1'$ (CCSD(T)/aug-cc-pVTZ) Structure



Vibrational frequencies

Symm.	Frequency	IR Intensity	Raman Intensity	Depolarization Ratio
1	E_2''	754.6	0.0	0.75
2	E_2'	1075.1	0.0	0.75
3	E_2'	1113.3	0.0	0.75
4	A_1'	1207.8	0.0	0.04
5	E_1'	1276.7	13.6	0.57

**$N_5^- D_{5h} \ ^1A_1'$ (EOM-CCSD/PBS//B3LYP/aug-cc-pVDZ) Vertical
Excitation Energies by EE-STEOM**

Mult.	Symmetry	Excitation energy (eV)	Osc. Strength
Singlet	E_1''	6.65	0
Singlet	E_2'	6.68	0
Singlet	E_1'	6.74	0
Singlet	E_2'	6.96	0.156
Singlet	E_2''	7.02	0
Singlet	A_2''	7.47	0.081
Singlet	A_1''	7.48	0
Singlet	E_2'	7.49	0
Triplet	E_1'	5.63	0
Triplet	E_1''	5.77	0
Triplet	E_2'	5.95	0
Triplet	A_2''	6.10	0
Triplet	E_2''	6.28	0
Triplet	E_1'	6.87	0
Triplet	E_1''	6.97	0
Triplet	E_2'	7.19	0
Triplet	A_1''	7.33	0

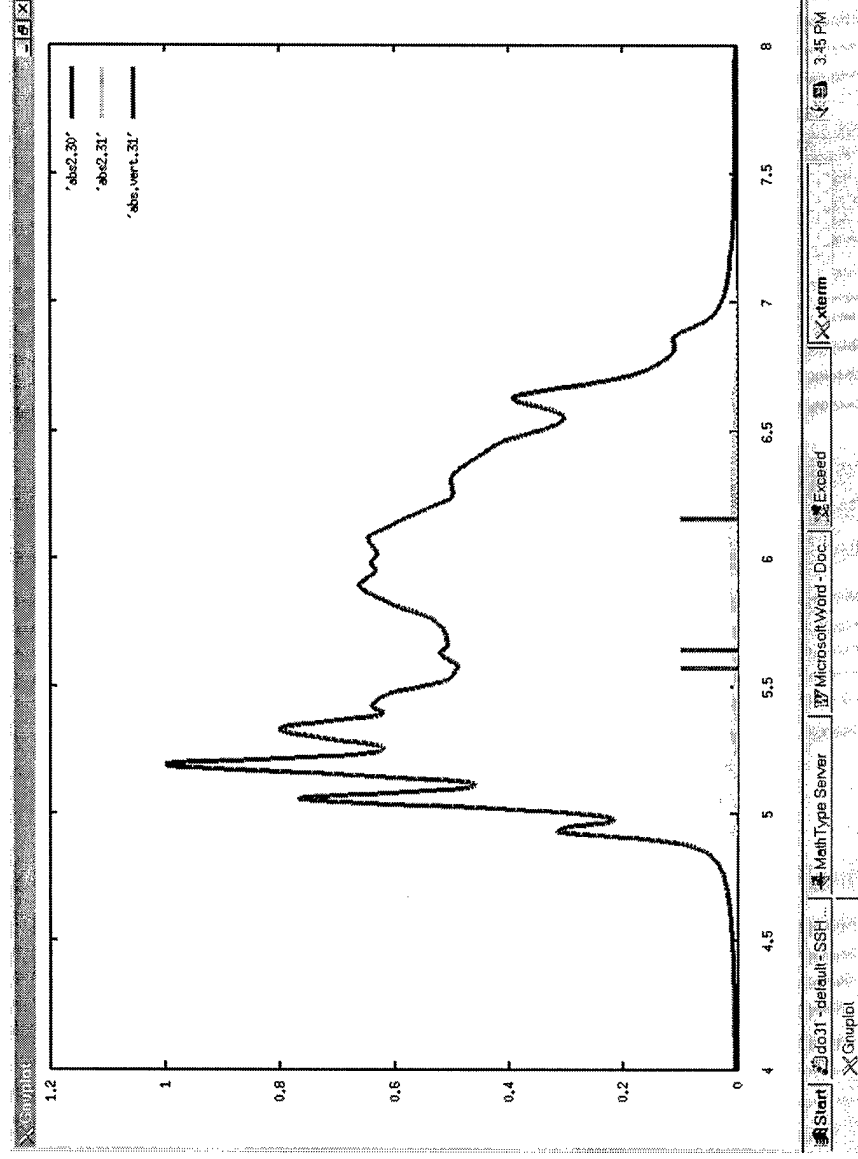
**Vertical Electron Detachment Energies
(Ionization Potentials) of N_5^- by IP-EOM**

Mult.	Symmetry	IP (eV)
Doublet	E_1'	5.58
Doublet	E_1''	5.65
Doublet	E_2'	6.14
Doublet	A_1'	9.98
Doublet	A_2''	10.58

Vertical Electron Affinities by of N_5^- by EA-EOM

Mult.	Symmetry	EA (eV)
Doublet	A_1'	5.36
Doublet	E_1'	5.95
Doublet	E_2'	6.53
Doublet	A_2''	7.72
Doublet	E_2''	7.84

Simulated Photoelectron Spectrum



Two lowest vertical transitions at 5.57 (E1') and 5.64 (E1'') eV in PBS basis set and IP-EOMCC calculations (order is reversed in SCF). The third state lies at 6.15 eV and has E2' symmetry.

As seen vibronic coupling and complicated JT distortions shift the origin of the peak by about 0.8 eV! Marcel Nooijen. Princeton

A word about 'adiabatic' transitions...

NOTE THE VALUE FOR THE ORIGIN OF THE BAND IN THIS SPECTRUM, I.E. THE ADIABATIC TRANSITION, IS NOT THE SAME VALUE AS THE HEAT OF REACTION,



Despite the fact that $[N_5]$ is not a minimum on the energy surface the structure is changed from the original anion due to vibronic effects, and the spectra samples that.

EXPERIMENTS

Ostmark reported observing
the pentazole anion in mass spec

Vij, Christie, et al mass spec

Ostmark, et al further observation

Butler in solution, identified by NMR

Super nitrogen structures

Allotropes of carbon are a girl's best friend. Or so they say. New research indicates that allotropes of nitrogen may be a scientist's best friend. A collaborative team of scientists from Galway University, Ireland, and Rutgers University in Camden, New Jersey, US, has isolated the pentazole anion – a five-membered nitrogen ring and one of nitrogen's rare allotropes – for the first time in solution (*Chem. Commun.*, 2003, 8, 1016).

The Irish scientists' search for pentazole was prompted by a discovery in the early 1990s of a new

nitrogen oxide, N_4O , which formed a stable solid at -110°C . Team leader Dick Butler, and his colleague at Galway University, Anthony Fox, predicted that replacing the oxygen atom in N_4O with a nitrogen atom attached to an aryl group would result in an aryl diazide species ($\text{Ar}-\text{N}=\text{N}-\text{N}_3$) – a suspected intermediate in aryl pentazole formation.

The Galway group then set about isolating pentazole from aryl pentazoles. The problem the researchers faced was how to cleave the strong aryl–nitrogen bond – a

hetero-bond that is notoriously difficult to break – without breaking up the fragile pentazole ring. Butler's clue came from a reported quinone synthesis that used ceric ammonium nitrate ($\text{HgCeN}_8\text{O}_{18}$) to cleave an aryl–oxygen bond. Using this method, the team successfully isolated pentazole from *N-p*-methoxyphenyl pentazole.

Luke Burke, Butler's co-worker from Rutgers, identified Zn^{2+} as the most suitable cation to hold the highly acidic N_5^- ion in solution. He also determined the theoretical ^{15}N NMR shift for the molecule, allowing the scientists to confirm that their molecule was the long sought-after pentazole.

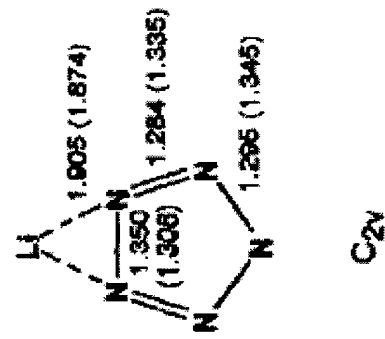
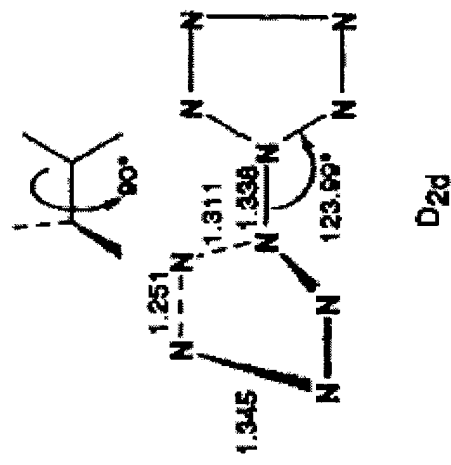
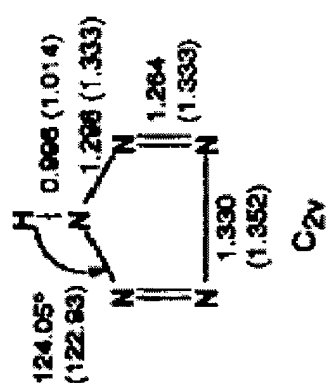
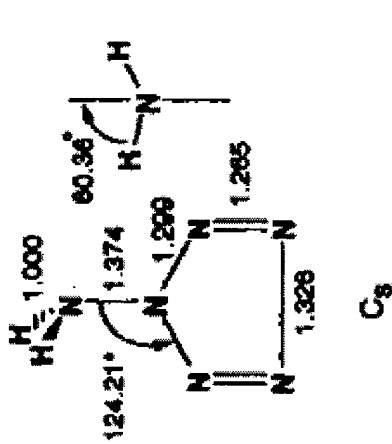
CHEMISTRY IN BRITAIN, MAY, 2003

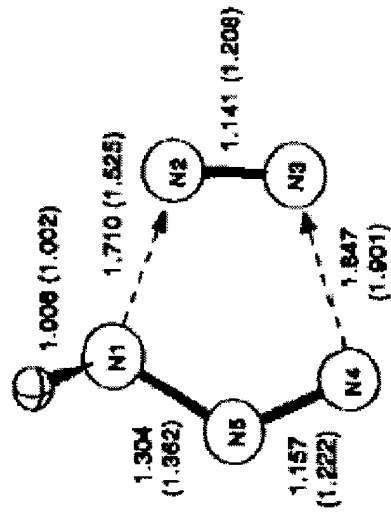
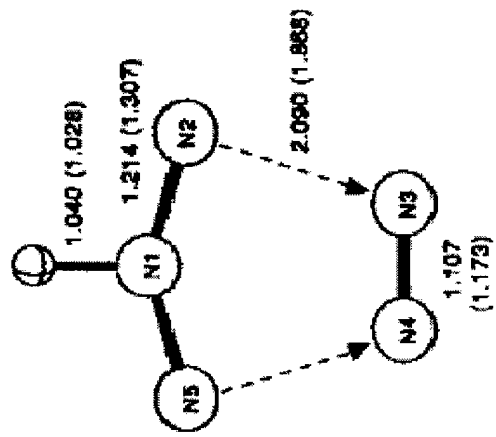
Pentazole derivatives...



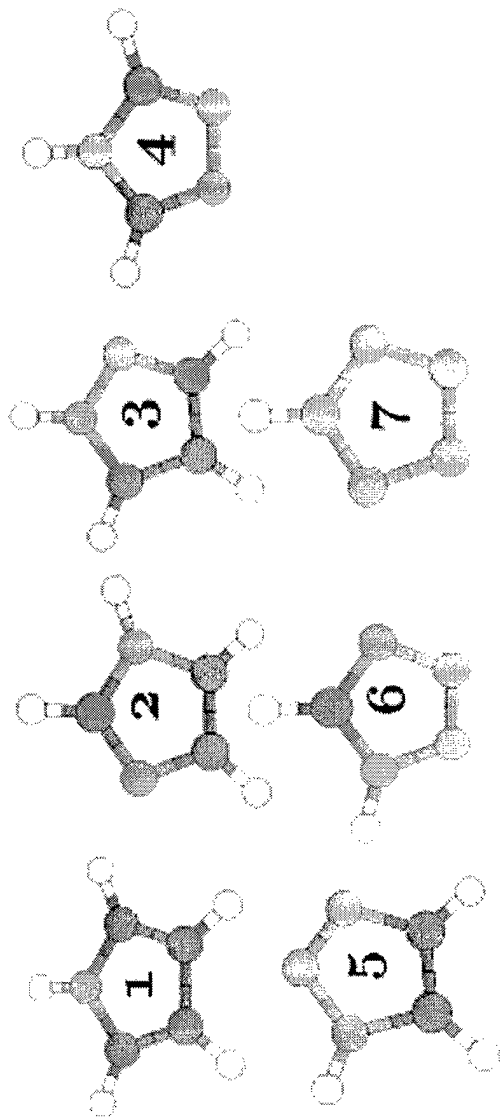
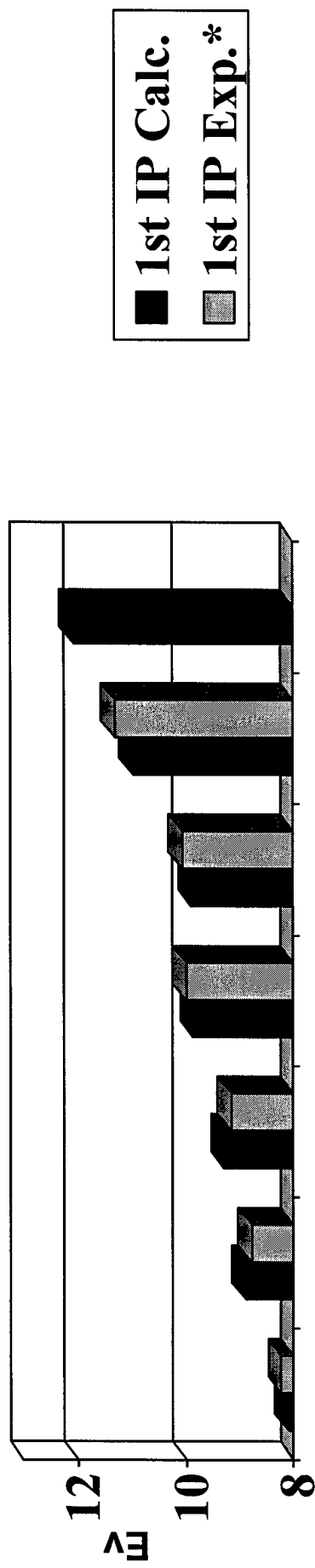
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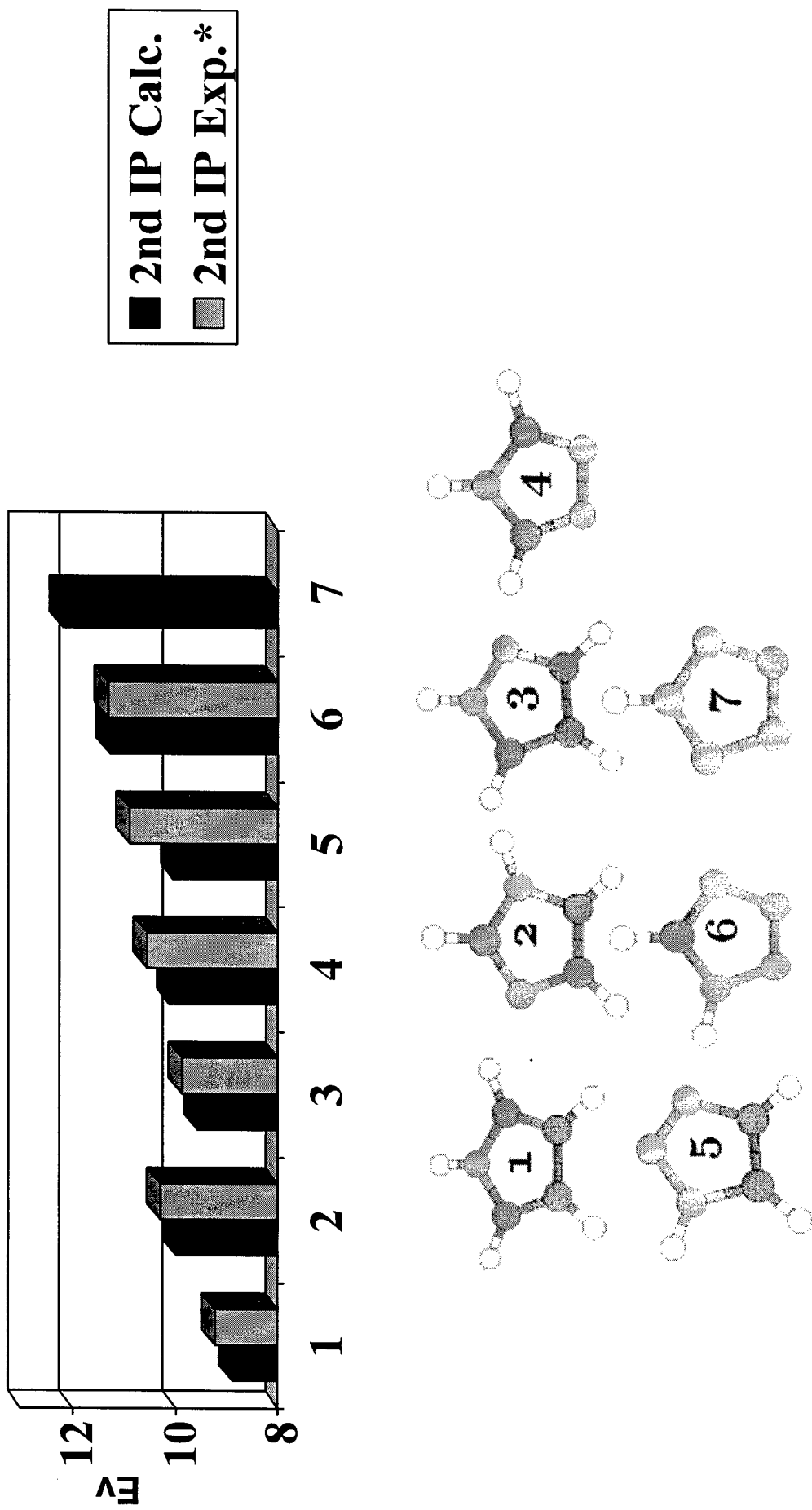


Azoles: IPs from IP-EOM CCSD



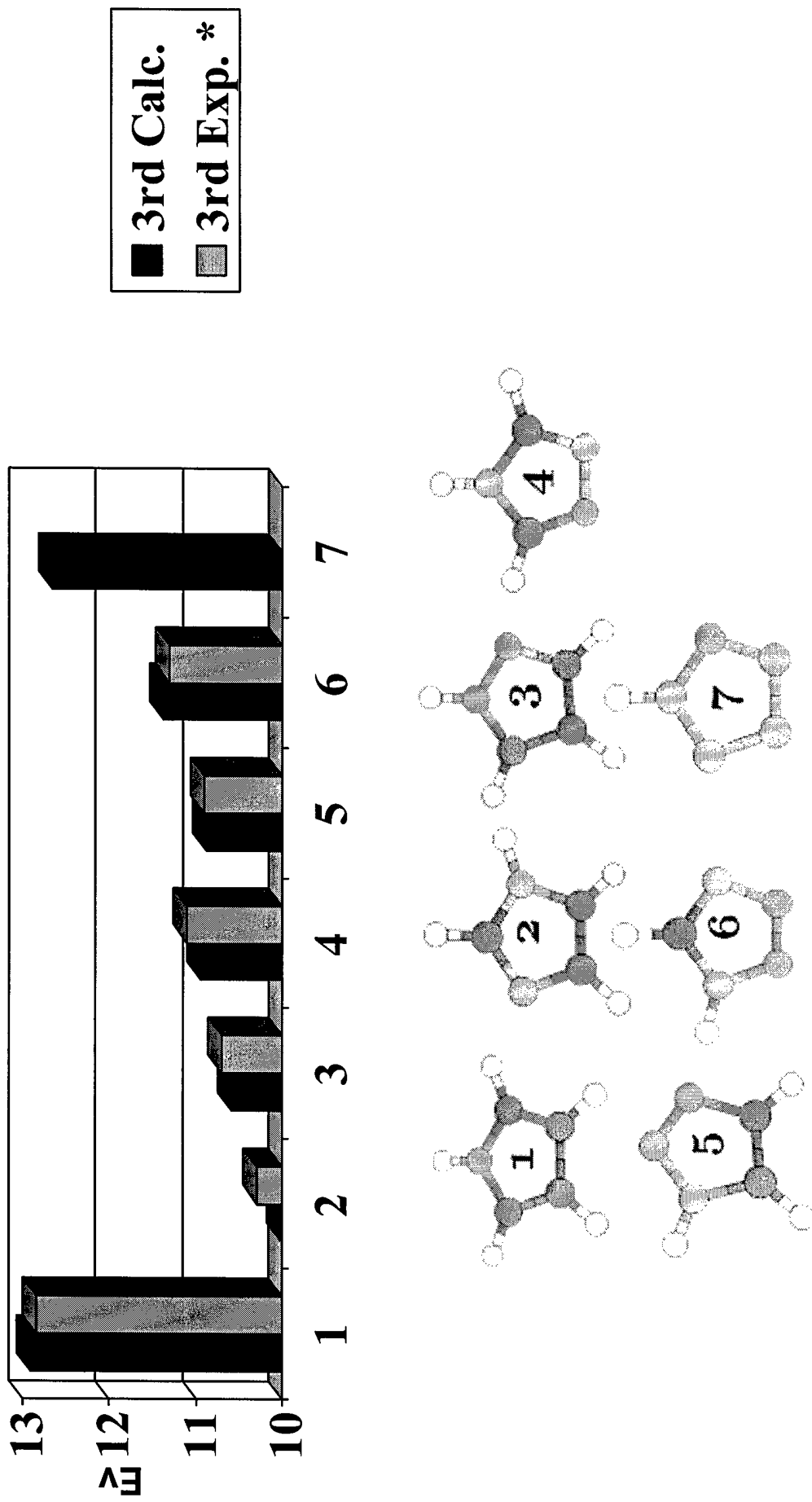
* S. Cradock, R. H. Findlay and M. H. Palmer, *Tetrahedron* 25 1173 (1973)

Azoles: IPs from IP-EOM CCSD



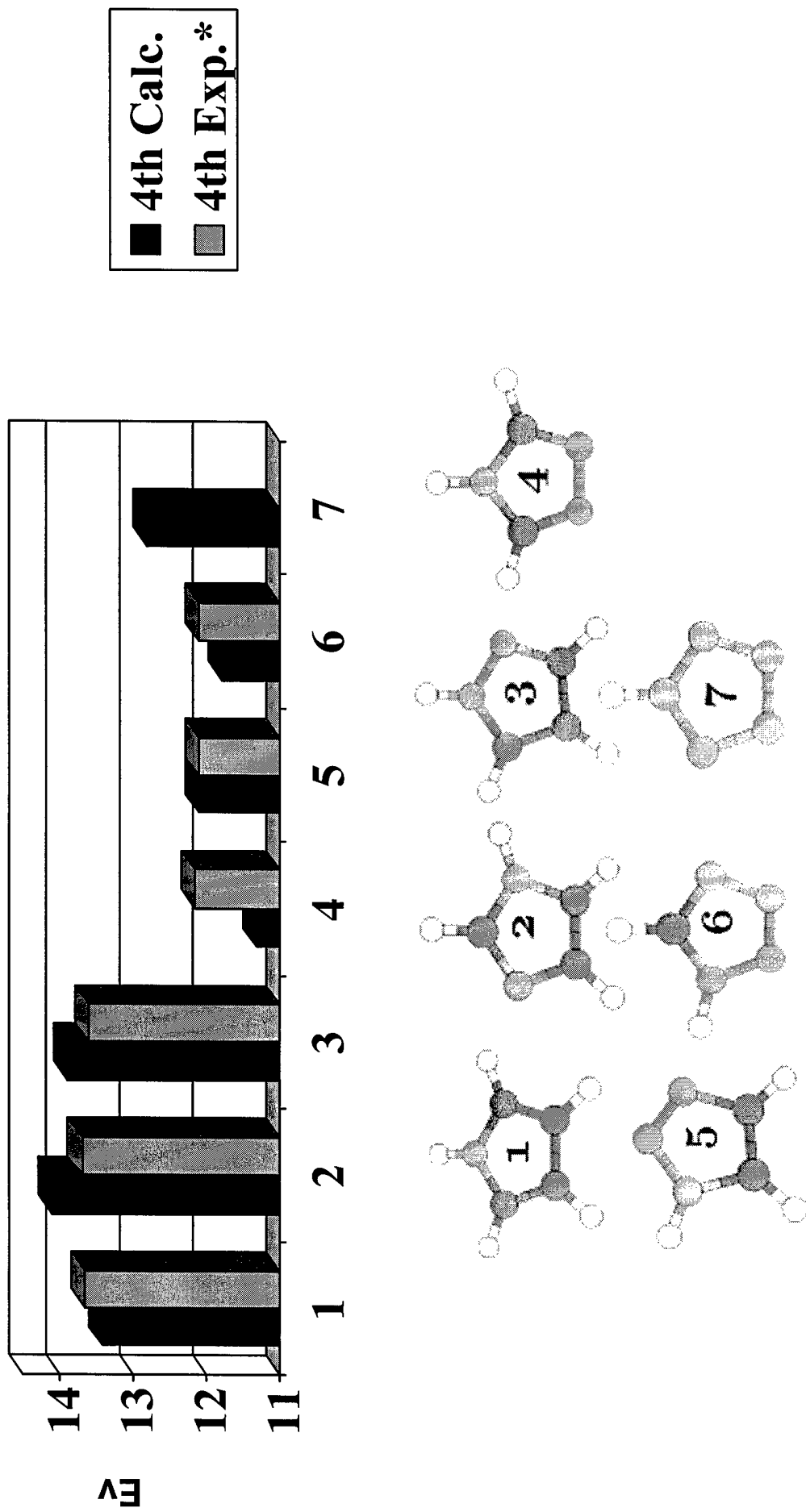
* S. Cradock, R. H. Findlay and M. H. Palmer, *Tetrahedron* 25 3173 (1973)

Azoles: IPs from IP-EOM CCSD



* S. Craddock, R. H. Findlay and M. H. Palmer, *Tetrahedron* 25 2173 (1973)

Azoles: IPs from IP-EOM CCSD



* S. Cradock, R. H. Findlay and M. H. Palmer, *Tetrahedron* 25: 1175 (1973)

Organization of Energetic Molecules

SOME ENERGETIC UNITS OF INTEREST

NH, NH₂

NNO

O₂N -CN

O₂N-NC

O₂N-CC-H

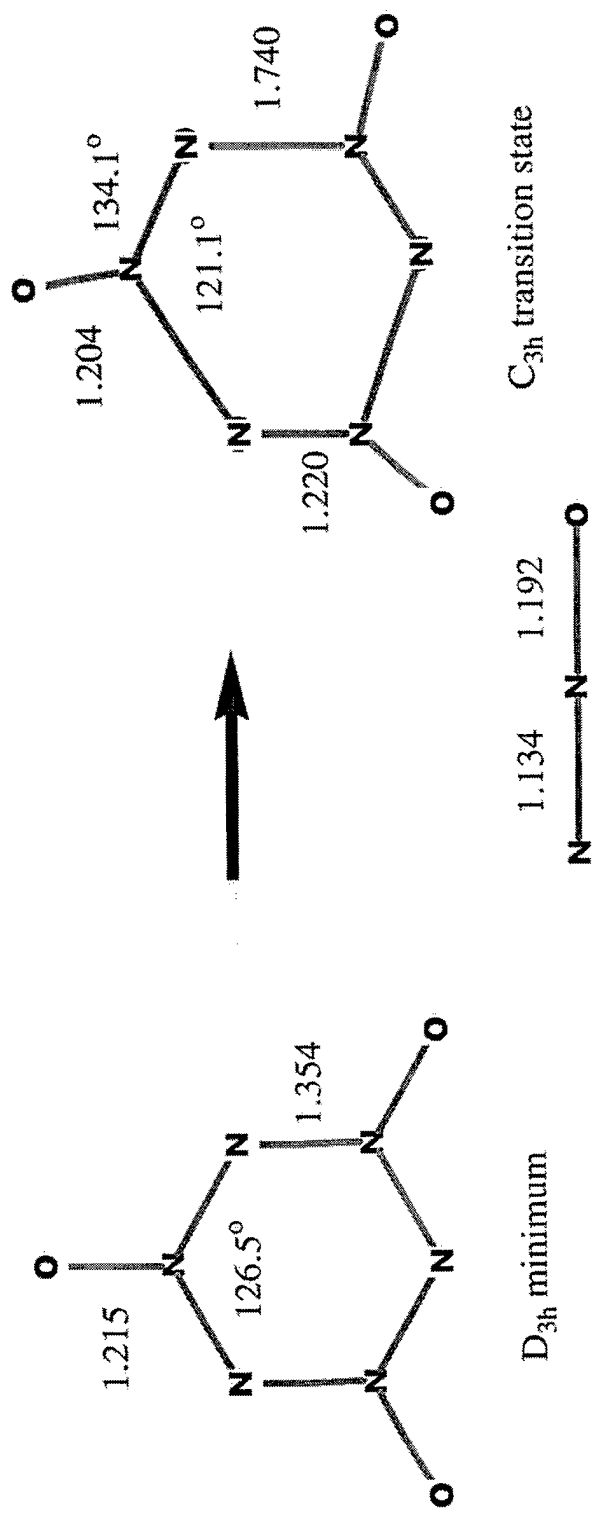
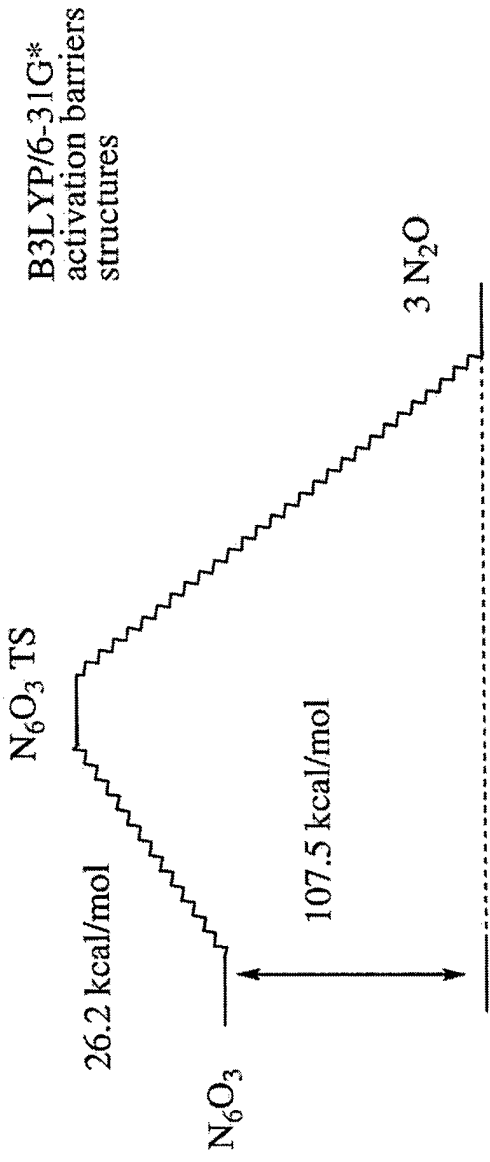
OCN-CC-H

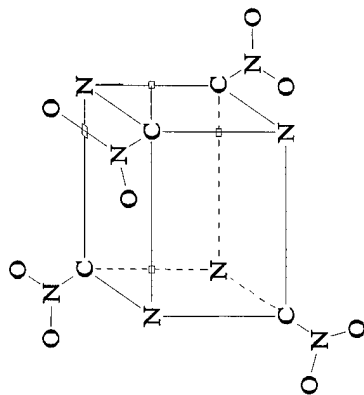
ONC-CC-H

O₂N-CC-NO₂

...

Form monomers,
dimers, trimers, etc.
of pure and mixed
units.





FURTHER DESIGN VIA QUANTUM CHEMISTRY...

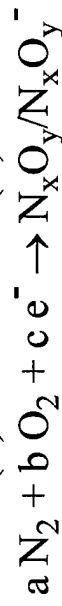
**Consider the role of the N-O bond in alleviating some
of the instability of pure nitrogen systems;**

Or replace N by CH;

Or substitute P for N.

Heats of Formation (298.15 K, 1 bar) with different basis sets

CCSD(T)-fc/X//CCSD(T)-fc/6-31G* using the reaction



	6-31G*	cc-pVDZ	cc-pVTZ	CBS2(XZ)	exp.
N_3^-	69.3	72.4	57.0	48.1	48.5±2.3
N_2O	24.8	23.7	21.1	19.5	19.61
NO^\cdot	21.7	20.4	21.5	22.1	21.58
RMS dev.	12.4	14.0	5.0	0.4	

CBS2: A two-point extrapolation derived from the three-point extrapolation given by Peterson, Woon & Dunning.

$$A_X = A_\infty + \text{Be}^{-(X-1)} \left[+ \text{Ce}^{-(X-1)^2} \right]$$

The two-point formula for X=D, T is:

$$A_\infty = A_D + \frac{e^{-1}}{e^{-1} - e^{-2}} (A_T - A_D) = A_D + 1.5820(A_T - A_D)$$

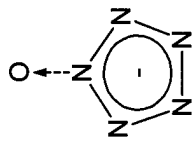
Heats of Formation at CCSD(T)-fc/CBS2(cc-pVDZ,cc-pVTZ)//CCSD(T)-fc/6-31G*

N_5^- : 61.4

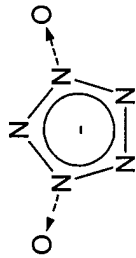
$N_imag = 1,$

out of plane $\rightarrow C_2$

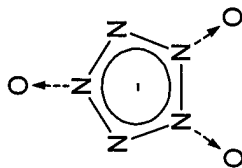
56.1



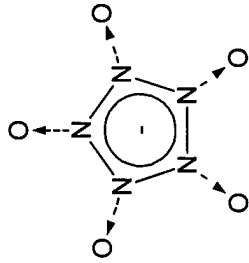
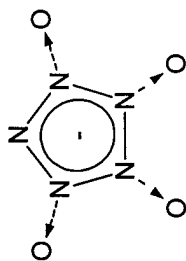
52.8



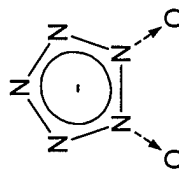
59.2



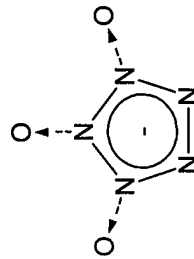
73.5



59.8



65.0

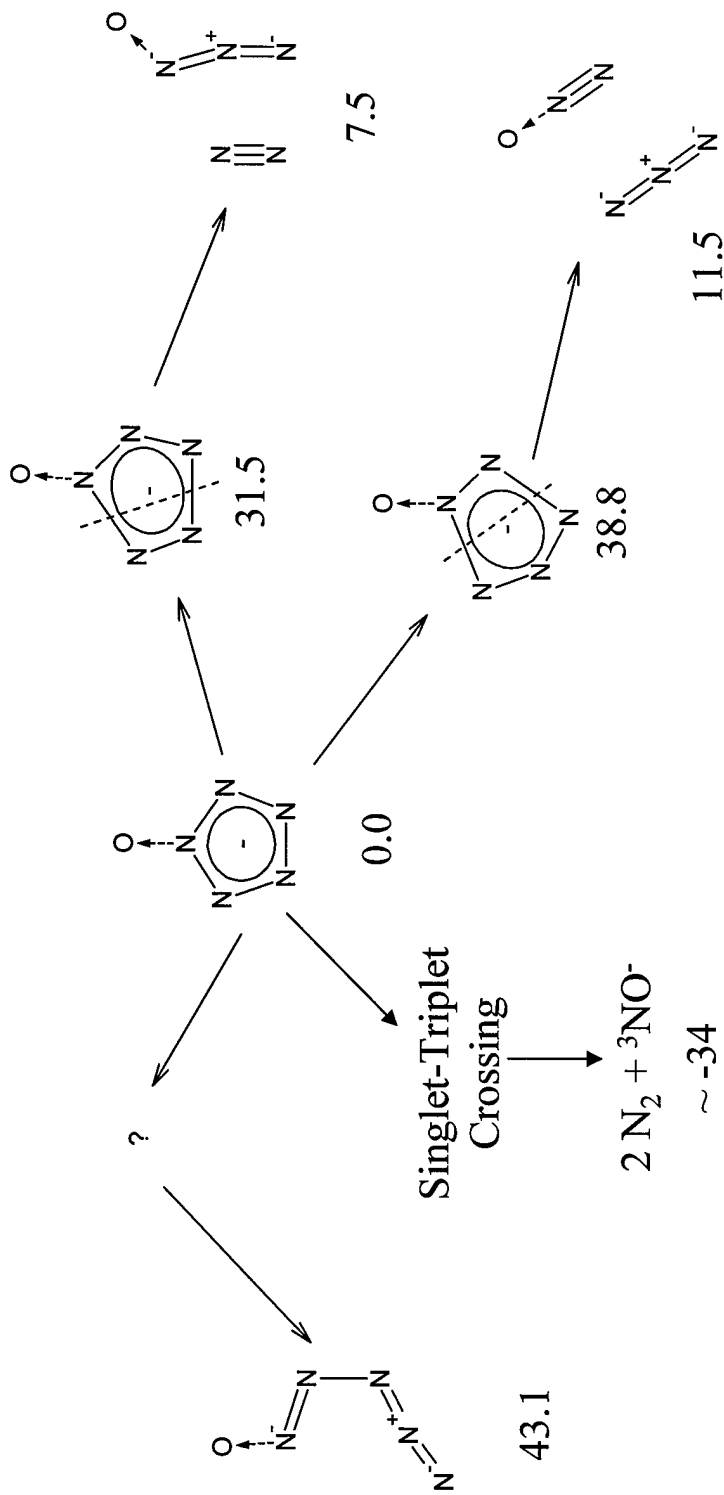


Bond Lengths:

NN: 1.33 - 1.39Å

NO: 1.26 - 1.28Å

Possible Dissociation Reactions and Relative Enthalpies (CBS2)



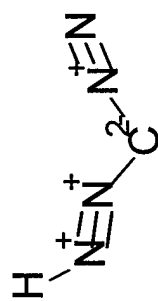
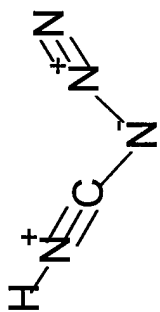
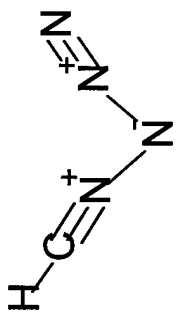
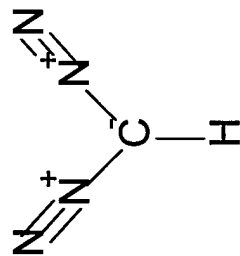
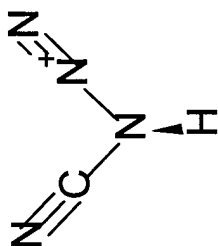
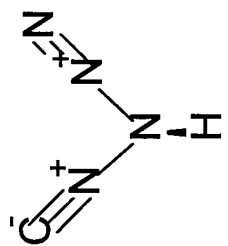
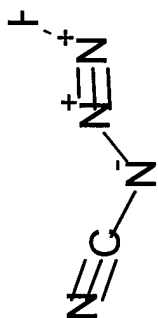
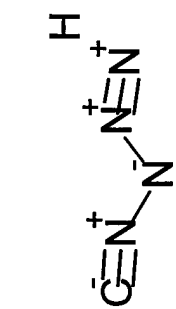
Geometries, Frequencies: CCSD(T)-fc/6-31G*

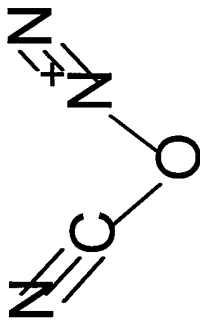
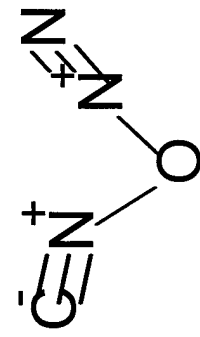
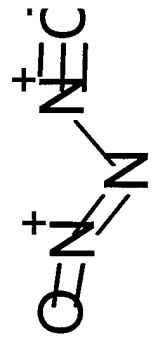
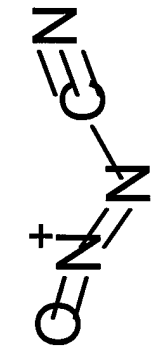
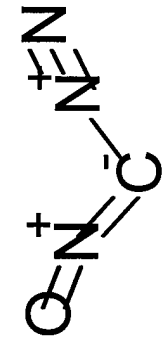
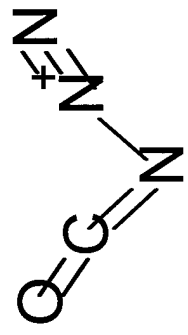
Energies: Extrapolation of CCSD(T)-fc/cc-pVDZ and cc-pVTZ single points

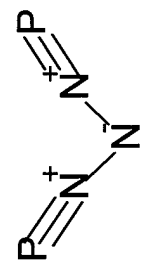
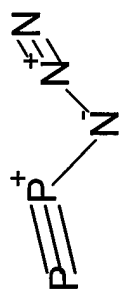
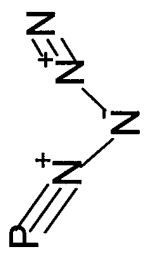
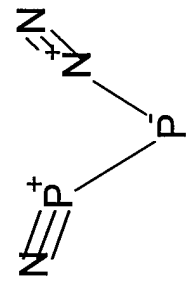
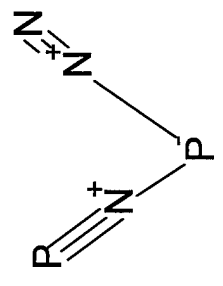
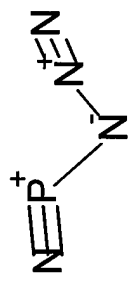
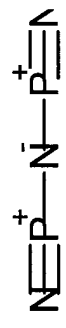
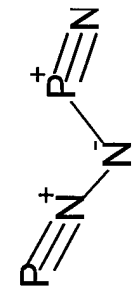
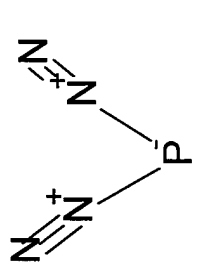
Accuracy for NO, N3, and N3- better than 0.5 kcal/mol

Vertical Ionization Potentials and Electron Affinities from EOM-CCSD/PBS

	EOM-CCSD	exp.
N_5^-	5.4	
N_5O^-	3.9	
$1,3\text{-N}_5\text{O}_2^-$	3.9	
$1,2\text{-N}_5\text{O}_2^-$	3.8	
$1,2,4\text{-N}_5\text{O}_3^-$	3.8	
$1,2,3\text{-N}_5\text{O}_3^-$	4.3	
N_5O_4^-	4.1	
N_5O_5^-	4.4	
CH_3NH_3^+		4.3
NH_4^+	4.5	4.73±0.06







N_5^+ Derivatives with One or Two Phosphorus Atoms

Geometries and frequencies of all derivatives at CCSD(T)-fc/6-31G*

Electron affinities (in eV) by EA-EOM-CCSD/PBS single point calculations

N_5^+	6.1				
1- N_4P^+	6.4				
2- N_4P^+	8.8				
3- N_4P^+	6.2				
1,2- $N_3P_2^+$	7.7				
1,3- $N_3P_2^+$	7.6				
1,4- $N_3P_2^+$	7.8				
1,5-$N_3P_2^+$	5.9				
2,3- $N_3P_2^+$	7.7				
2,4- $N_3P_2^+$	8.0				
					$\Delta_f H = 345$ kcal/mol
					$\Delta_f H = 264$ kcal/mol

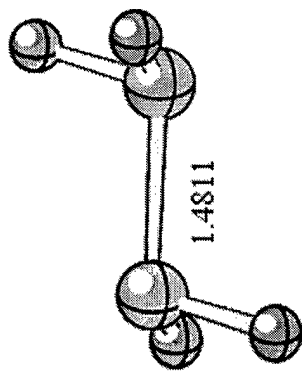
EXTENSIONS OF HYDRAZINE

Investigation of HEDM molecules.

Propellants which are currently in use.

N_2H_4 , Hydrazine (1)

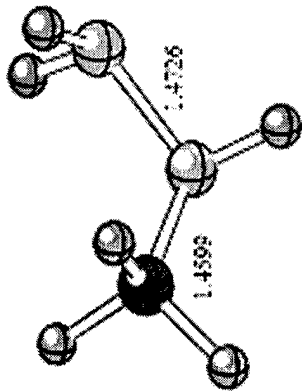
C_{2h} , 1A_g , $H_f=15.7$ kcal/mol, $L_{sp}=185.7$ sec.



No.	Symm.	Frequency	IR Intensity	Raman Intensity	Depolarisation Ratio
1	Au	-25.8	110.3	0.0	0.65
2	Ag	945.9	0.0	13.7	0.29
3	Bu	1034.4	160.8	0.0	0.61
4	Au	1104.7	1.1	0.0	0.61
5	Ag	1214.5	0.0	4.0	0.06
6	Bg	1475.7	0.0	3.1	0.75
7	Bu	1609.5	37.3	0.0	0.41
8	Ag	1671.4	0.0	6.1	0.64
9	Ag	3428.7	0.0	254.8	0.10
10	Bu	3446.2	2.6	0.0	0.51
11	Bg	3499.6	0.0	104.3	0.75
12	Au	3518.3	2.2	0.0	0.70

2. Dissociation into $2NH_3$.

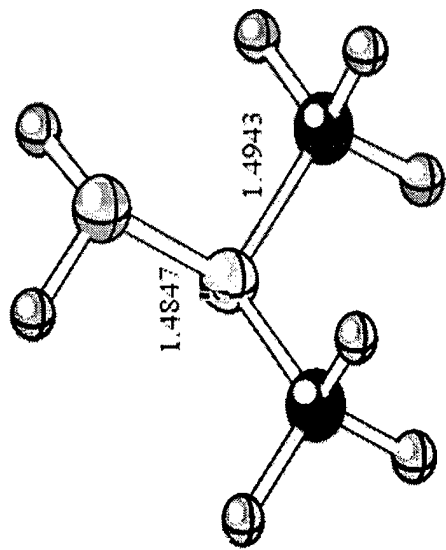
C_2H_6 , Monomethylhydrazine (MMH)
 C_p , A , $H_p = 15.70$ kcal/mol, $I_p = 154.7$ sec



No.	Order	Frequency	Irreducibility	Parity	Intensity	Depolarization Ratio
1	A	263.8	3.0		0.3	0.63
2	A	343.0	24.5		0.9	0.37
3	A	421.4	6.5		1.5	0.25
4	A	780.4	99.3		2.3	0.50
5	A	911.2	64.5		0.3	0.66
6	A	980.3	26.5		6.6	0.27
7	A	1124.9	6.7		1.6	0.46
8	A	1138.2	9.8		3.3	0.70
9	A	1215.2	4.1		3.3	0.20
10	A	1304.7	6.4		1.2	0.66
11	A	1423.0	0.3		2.1	0.75
12	A	1454.6	9.4		6.0	0.75
13	A	1470.2	3.0		3.7	0.71
14	A	1506.3	3.7		3.3	0.73
15	A	1559.5	13.0		5.2	0.63
16	A	2936.0	90.0		170.7	0.11
17	A	3056.7	37.4		116.1	0.23
18	A	3103.1	27.1		83.9	0.64
19	A	3379.6	18.6		156.9	0.11
20	A	3515.6	1.8		136.4	0.26
21	A	3532.3	0.0		29.3	0.75

S.Distribution into C_{2H_5} , $-NH_2$ or $CH_3 + NH_2$.

$C_3N_2H_8$, 1,1-Dimethyl hydrazine (UDMH)
 C_2 , $^1A'$, $H_f=20.16$ kcal/mol, $L_{fp}=153.5$ sec

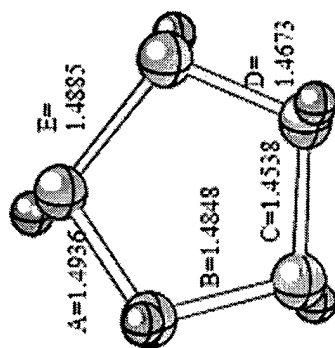


1	A"	154.5	35.0	0.2	0.75
2	A"	260.5	8.8	0.0	0.75
3	A'	277.9	0.1	0.9	0.72
4	A'	412.7	4.4	1.6	0.34
5	A"	438.4	1.6	1.3	0.75
6	A'	441.5	18.1	1.9	0.23
7	A'	818.6	15.0	13.1	0.37
8	A'	983.6	20.2	9.5	0.35
9	A"	1035.4	11.9	1.5	0.75
10	A"	1092.5	1.0	0.9	0.75
11	A'	1100.5	46.2	3.7	0.16
12	A"	1127.5	10.9	2.6	0.75
13	A'	1193.8	3.7	8.4	0.32
14	A'	1247.3	0.2	2.1	0.66
15	A"	1389.9	3.8	0.0	0.75
16	A"	1408.2	1.2	2.1	0.75
17	A'	1435.2	3.6	2.6	0.62
18	A"	1451.6	9.5	5.6	0.75
19	A'	1462.3	8.3	8.5	0.72
20	A"	1471.5	1.2	5.2	0.75
21	A'	1485.3	14.0	3.5	0.75
22	A'	1632.8	35.7	3.5	0.75
23	A"	2947.8	50.7	24.1	0.75
24	A'	2956.4	103.7	281.6	0.06
25	A"	3066.2	35.6	52.7	0.75
26	A'	3068.6	31.8	143.9	0.21
27	A"	3113.5	7.4	20.2	0.75
28	A'	3118.7	39.3	106.0	0.66
29	A'	3422.3	2.0	149.6	0.12
30	A"	3502.4	0.1	66.6	0.75

7. Dissociation into $NH_3 + C_2NH_4$

N_5H_5 , Cyclopentazane

Ci, $A, E_f=103.16$ kcal/mol, $I_p=310.6$ sec.



No.	Dyns.	Freq.	Intensity	IR Intensity	Remain	Depolarization
					Intensity	Ratio
1	A	155.7	2.3		0.1	0.75
2	A	459.4	0.1		1.2	0.57
3	A	707.8	9.7		7.4	0.34
4	A	778.7	12.1		2.9	0.75
5	A	823.2	28.1		8.7	0.09
6	A	861.4	71.7		0.1	0.74
7	A	887.5	54.8		0.4	0.27
8	A	890.7	12.9		8.3	0.09
9	A	921.5	16.6		0.1	0.75
10	A	1035.8	15.5		1.0	0.67
11	A	1038.7	27.0		3.0	0.75
12	A	1079.8	98.6		2.6	0.41
13	A	1213.4	61.5		0.5	0.75
14	A	1259.5	26.7		15.4	0.04
15	A	1368.4	6.8		0.6	0.75
16	A	1426.0	2.9		5.1	0.08
17	A	1463.4	4.4		4.8	0.75
18	A	1528.5	0.5		1.9	0.75
19	A	1532.2	0.1		7.6	0.71
20	A	3410.9	0.2		20.8	0.75
21	A	3441.5	0.7		296.5	0.14
22	A	3457.9	0.2		57.0	0.40
23	A	3482.3	0.8		24.5	0.75
24	A	3490.4	6.0		24.9	0.36

3. Open ring at D.

4. Open ring at E.

5. Dissociation into $NH + N_2H_4$ (two bonds breaking at D and E).

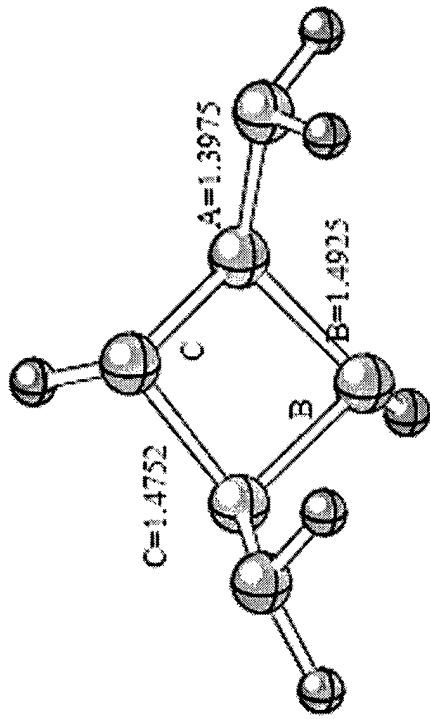
6. Open ring at A or C.

7. Open ring at B or E.

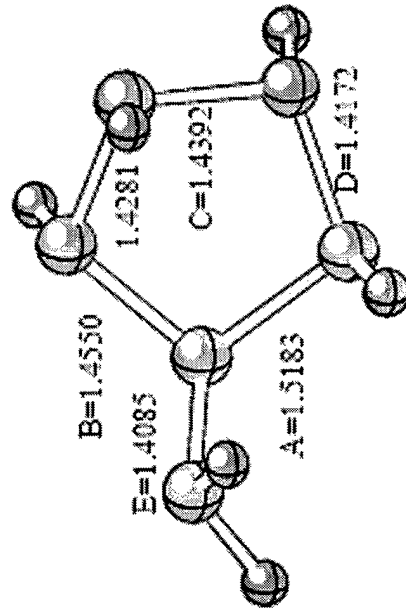
8. Open ring at A or C.

9. Dissociation into $N_2H_2 + N_2H_3$ (two bonds breaking at A and C).

N_6H_6 , Paradiaminocyclohexane
 C_1 , 3A , $E_f=135.86$ kcal/mol, $I_{sp}=325.4$ sec.



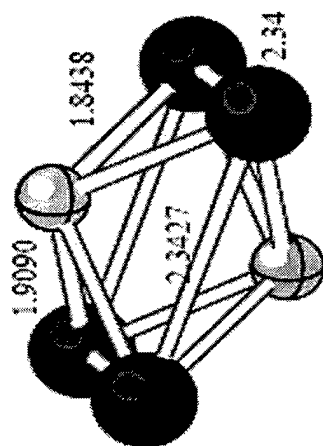
N_6H_6 , Aminocyclopentazane
 C_1 , 3A , $E_f=121.65$ kcal/mol, $I_{sp}=307.9$ sec.



Lithium substituted hydrazine derivatives: N_2Li_2 molecules.

N_2Li_2

C_{2h} , 1A , $H_f=79.83$ kcal/mol, $I_p=317.03$ sec.



Initial geometry for geometry optimization was hydrazine type structure.

No.	Sym.	Frequency	IR Intensity	Raman Intensity	Dissociation Ratio
1	Σ_u	219.1	0.0	0.0	0.41
2	Σ_u	375.3	40.7	0.0	0.46
3	Σ_u	376.0	40.8	0.0	0.75
4	Σ_g	472.8	0.0	973.4	0.00
5	Σ_g	484.5	0.0	196.0	0.75
6	Σ_g	485.3	0.0	149.2	0.75
7	Σ_g	486.3	0.0	58.0	0.73
8	Σ_u	514.5	299.0	0.0	0.75
9	Σ_g	597.6	0.0	143.9	0.75
10	Σ_u	727.6	214.8	0.0	0.04
11	Σ_u	728.0	214.9	0.0	0.52
12	Σ_g	735.1	0.0	325.9	0.03

2.Li-Li-Li ring opening.

3.Li-Li-Li-Li ring opening.

7. Li ring rupture (two bonds breaking).

10. Li-N bond breaking (two bonds breaking).

11. Li-N bond breaking (four bonds breaking).

12. Dissociation into $2Li + N_2$.

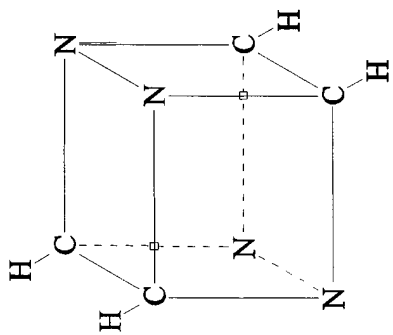
Conclusions.

1. Currently used propellants have calculated I_{sp} less than 200 sec, and the lowest dissociation mode vibrational frequency at more than 800 cm^{-1} .
2. Hydrazine derivatives, especially ring compounds, have I_{sp} about 300 to 360 sec, thus have potential as HEDM molecules. The lowest dissociation mode vibrational frequency is at the similar range as the currently used molecules. Also, as ring compounds must involve two bond breaking for dissociation into two fragments, the activation barrier is expected to be higher than linear molecules of similar kind.
3. Lithium substitution on hydrogen position further increases I_{sp} without lowering of the lowest dissociation frequency. For example, $I_{sp}=440$ sec for N3Li3 .

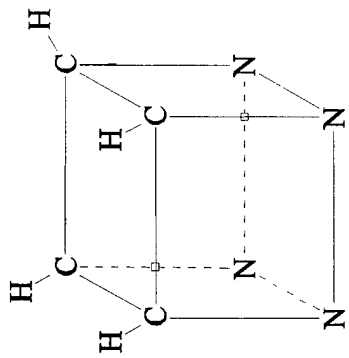
Acknowledgements

This work was supported by the DARPA-AFOSR under grant number F49620-98-1-0477.

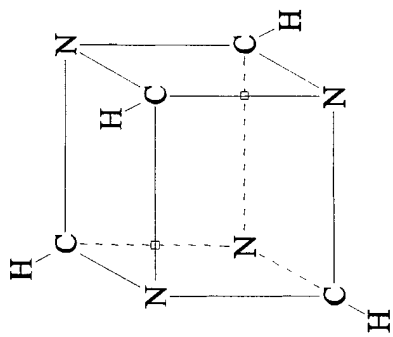
AZACUBANES



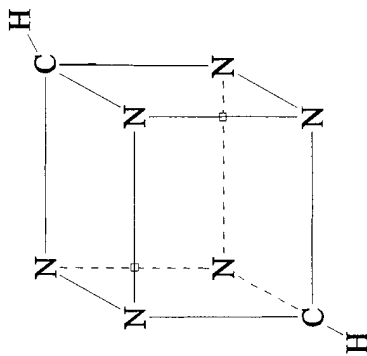
D_{2h}



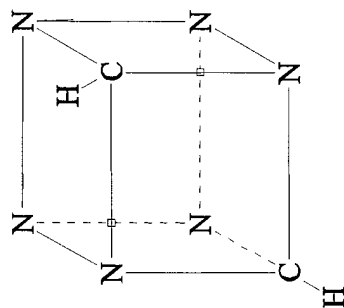
C_{2v}



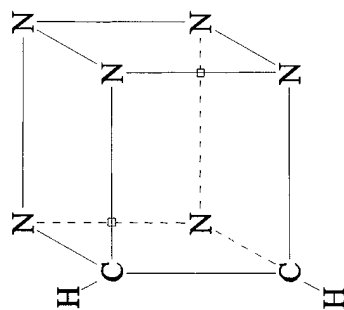
T_d



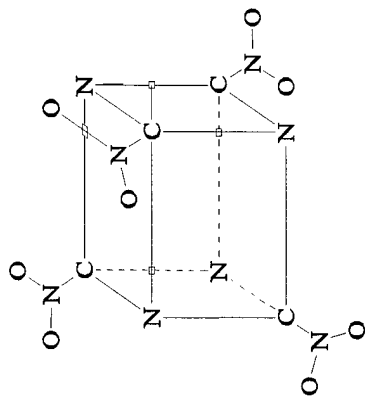
opp



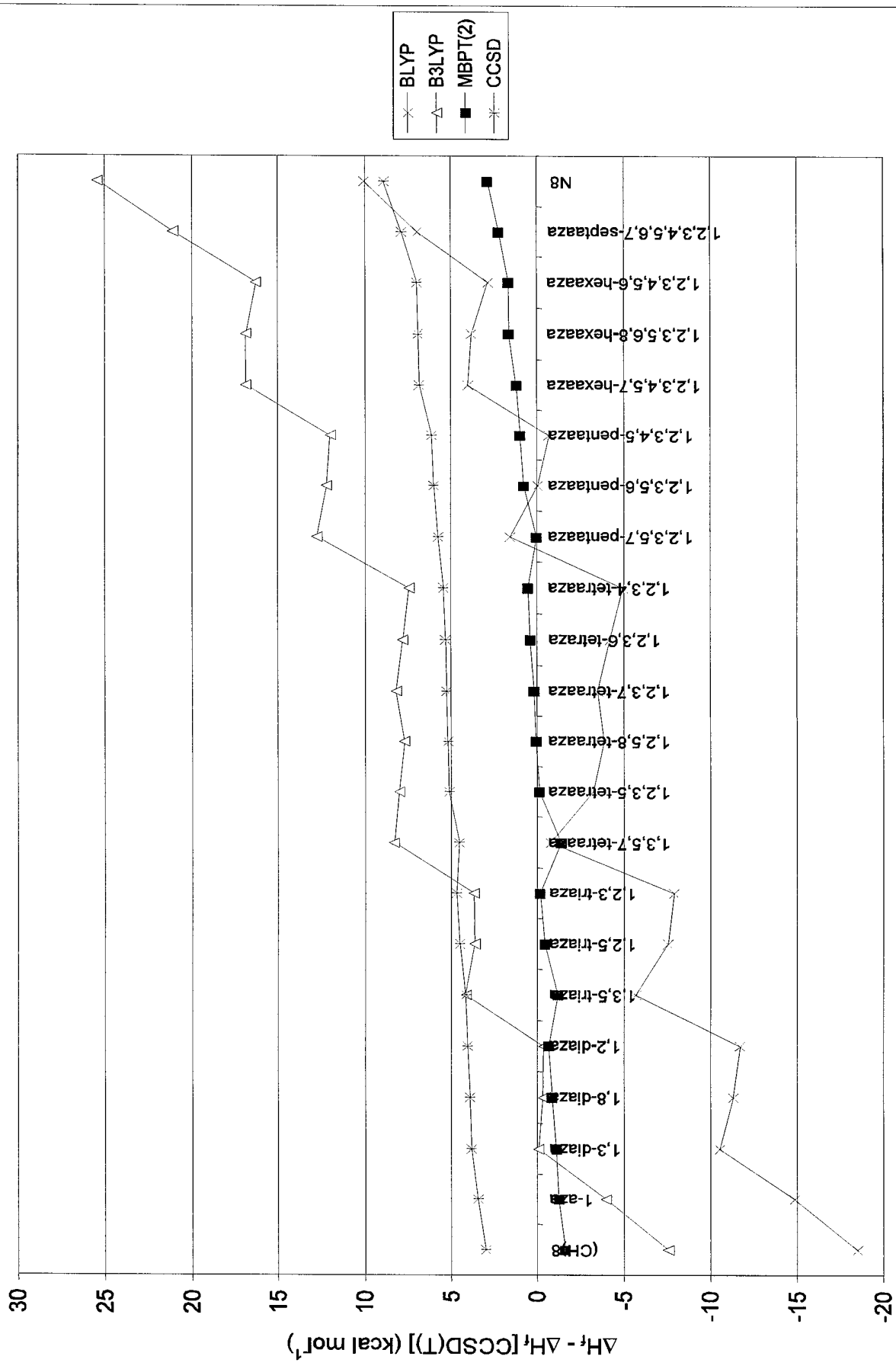
trans



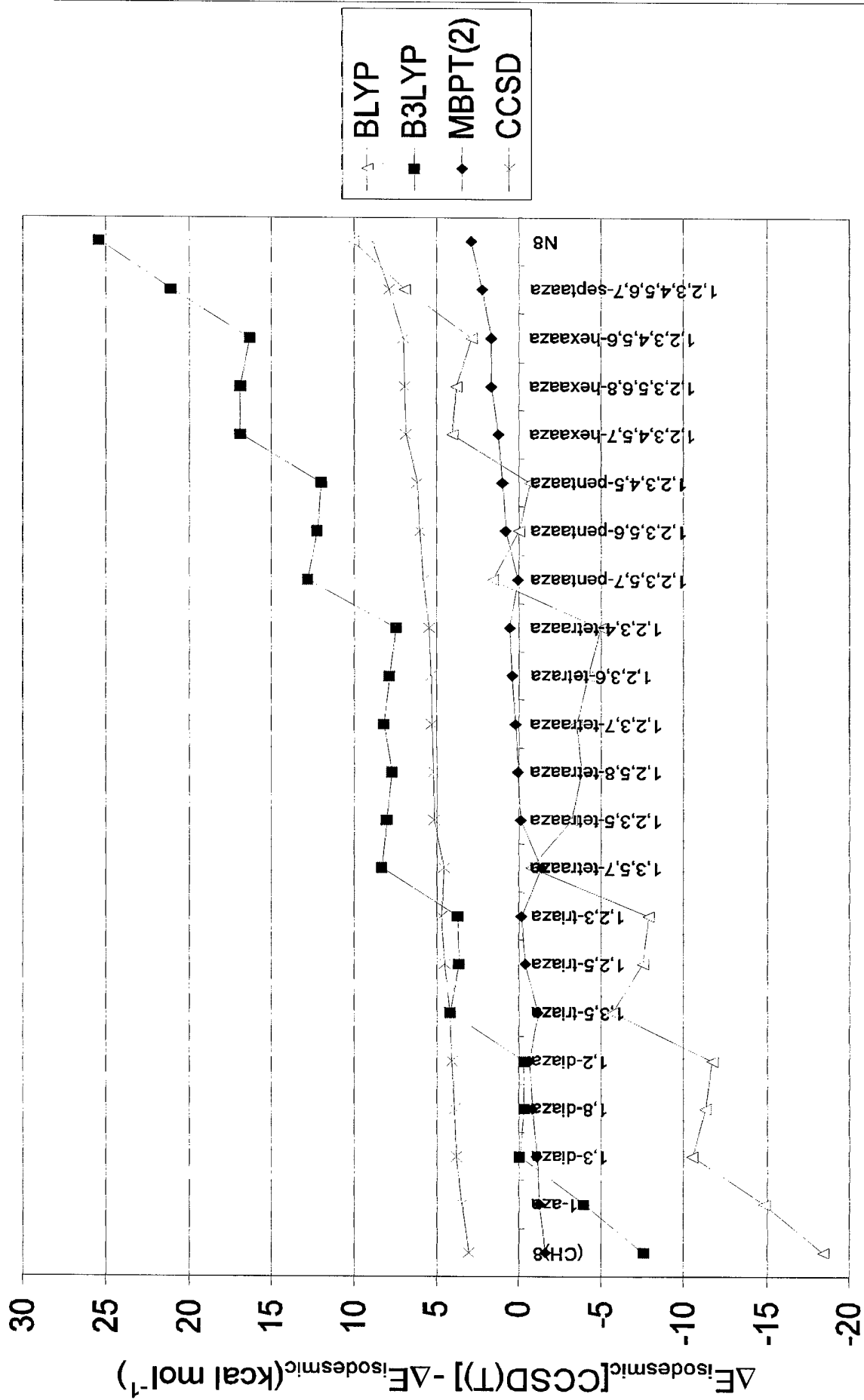
cis



ΔH_f relative to CCSD(T) for the azacubanes



$\Delta E_{\text{isodesmic}}$ relative to CCSD(T) for the azacubanes



HEATS OF FORMATION FOR LARGE AZA SUBSTITUTED CUBANES, AND THEIR -NO₂ DERIVATIVES

VARIOUS LEVELS OF THEORY HAVE BEEN APPLIED: CCSD(T), MBPT(2), DFT-BLYP, DFT-B3LYP AND SEMI-EMPIRICAL THEORY, AM1 AND PM3.

WE ALSO REPORT RESULTS FOR -NO₂ SUBSTITUTED FORMS, RANGING FROM OCTANITROCUBANE TO TETRANITROTETRAAZACUBANE.

THE MOST RELIABLE RESULTS RELATIVE TO CCSD(T) ARE GIVEN BY MBPT(2) AND CCSD. USING ISODESMIC REACTIONS SHOWS SOME IMPROVEMENT.

THE DFT METHODS, BLYP AND B3LYP ARE NOT RELIABLE THOUGH THEY ARE IMPROVED WITH ISODESMIC REACTIONS.

THOUGH VERY CHEAP, THE SEMI-EMPIRICAL METHODS ARE THE LEAST RELIABLE EVEN FAILING TO GET THE TRENDS.

Polymeric Nitrogen

So Hirata and Rodney J. Bartlett
Quantum Theory Project, University of Florida, Gainesville, FL 32611-8435, USA

Table I. Optimized geometry of polymeric nitrogen.

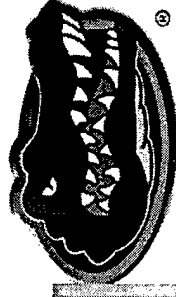
Theory	E / hartree	$\Delta E / \text{kJ mol}^{-1}$	$r(\text{N}=\text{N}) / \text{\AA}$	$r(\text{N}-\text{N}) / \text{\AA}$	$\angle(\text{N}-\text{N}-\text{N}) / \text{degree}$
HF/STO-3G	-107.423046	203.8	1.2772	1.4924	105.09
HF/6-31G	-108.744147	325.2	1.2186	1.4159	109.63
HF/6-31G(d)	-108.823186	317.1	1.2104	1.3985	107.94
HF/6-311G(d)	-108.849632	323.0	1.2058	1.3971	108.10
B3LYP/STO-3G	-107.951812	136.4	1.3411	1.5734	101.41
B3LYP/6-31G	-109.320803	257.5	1.2504	1.5176	106.26
B3LYP/6-31G(d)	-109.379129	243.7	1.2491	1.4324	106.05
B3LYP/6-311G(d)	-109.407887	255.1	1.2413	1.4333	106.38

Table II. Normal frequencies of polymeric nitrogen.

Theory	N=N stretch / cm^{-1}	N-N stretch / cm^{-1}
HF/STO 3G	1833	1334
HF/6-31G	1840	1264
HF/6-31G(d)	1902	1309
B3LYP/STO-3G	1453	922
B3LYP/6-31G	1468	785
B3LYP/6-31G(d)	1570	948
B3LYP/6-311G(d)	1566	942



Remember Ken Wilson's Quote



“There are roughly 10^6 classified chemical compounds at the present time. Each individual molecule has many properties to compute and/or measure: binding energies, electron density, atomic structure, spectra (vibrational, rotational, and electronic), reaction rates, electron and molecular scattering cross sections. **However, the spectacular opportunity for the future lies in compounds not yet synthesized or classified... $92(10^{23})$...These unexplored forms of matter contain innumerable surprises...**”

TECHNOLOGY TRANSITION/ MATURATION?

Rational Design of Energetic Materials

Involves the Following:

- Analyze an astronomical number of possibilities
- Generate all combinations of energetic units on a computer.
- Apply a battery of theoretical tools to obtain
 - a. Structural and energy/mass determination
 - b. Decomposition barriers/ estimate of weakest link in molecule.
 - c. Density and solid state characteristics.
 - d. Electrostatic potential maps.
- Assess synthetic prospects.
- Archive.

Organization of Energetic Molecules

SOME ENERGETIC UNITS OF INTEREST

NH, NH₂

NNO

O₂N -CN

O₂N-NC

O₂N-CC-H

OCN-CC-H

ONC-CC-H

O₂N-CC-NO₂

...

Form monomers,
dimers, trimers, etc.
of pure and mixed
units.

THE RATIONAL DESIGN OF ENERGETIC MATERIALS

- The overwhelming number of energetic molecules that could be hypothesized, some known, but vastly more unknown; requires a new approach that can organize the array of molecules into a workable framework for assessment and targeted synthesis.
- Because of the excessive number of possible structures, the only viable way to accomplish this objective is a computer-aided strategy.
- Elements in the procedure would include the unambiguous generation of possible molecular structures using a combinatorial schema based upon energetic units, or maybe synthons.
- This would be followed by the rapid evaluation of the prospects for a particular structure by using a battery of quantum chemical tools to specify the structures, including conformations and isomers; the heats of formation and reaction, and the energy density.

- Once the transition is made to the condensed phase, we need to predict the densities and crystalline stability..
- Other characterization tools would include electrostatic potential maps, bond orders, atomic charges, etc. Molecular sensitivity could be assessed to the degree that that can be discerned from electronic structure.
- Subsequent characterization for synthetic prospects would be added, by developing a series of criteria suggested by synthetic chemists.
- A final screening should include appropriateness for different applications like explosives, rocket fuels, or gun propellants.
- Genetic algorithms should enable a search of the data-base of screened possibilities to further identify an optimum subset of properties subject to a wide range of different criteria.
- Underlying all the above is the necessity of a convenient archiving procedure for the computer accessibility of all structures and their critical characteristics that, on command, can be readily further characterized with higher level quantum chemical tools as appropriate; and to offer input to further modeling as illustrated by a program like, CHEETAH, eg.