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FROM: PROI (TI) (STINFO) 25 October 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-206**
Boatz, Jerry; Thompson, D. (OK State Univ), "Bond Dissociation Energies of Energetic Compounds: A Comparison of Theoretical Methods"

HEDM Contractors Conference (Park City, UT, 23-26 Oct 2000) (Statement A)
(Deadline: 20 Oct 2000 – PAST DUE)

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Bond Dissociation Energies of Energetic Compounds: A Comparison of Theoretical Methods

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AFOSR High Energy Density Matter Contractors' Conference
Park City, UT
24-26 Oct 00
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ABSTRACT

Due to their computational efficiency, density functional methods utilizing semiempirical hybrid functionals such as B3LYP are commonly used in calculating the molecular potential energy surfaces of a wide variety of molecules. In particular, potential energy surfaces of several energetic compounds such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 1,3,3-trinitroazetidine (TNAZ), 5-nitro-2,4-dihydro-3*H*-1,2,4-triazolone (NTO), and 1,1-diamino-2,2-dinitroethylene recently have been computed using density functional methods (B3LYP). These potential energy surfaces are used, for example, to predict the decomposition mechanisms and for constructing force fields for modeling and simulation of solid state phase transitions.

The accuracy of B3LYP relative energies and structures is generally observed to be comparable to that obtained using second order perturbation theory methods. However, an unresolved issue is the reliability of density functional based methods in cases where a significant degree of multiconfigurational character may be present in the compounds of interest, such as in the energetic molecules listed above.

The present study is a systematic comparison of several electronic structure methods in the prediction of bond dissociation energies of energetic molecules. In particular, the C-NO2 and C-NH2 bond dissociation energies of 1,1-diamino-2,2-dinitroethylene and its prototypes are used as a testbed for comparison of B3LYP with single configuration self-consistent field (SCF), second order perturbation theory (MP2), and coupled-cluster (CCSD(T)) calculations as well as multiconfigurational SCF (MCSCF) and quasi-dependent perturbation theory (MCQDPT) methods.

GOAL

Increase propellant specific impulse by 10-20%.

OBJECTIVES

Discover, characterize, and develop new high energy density chemical propellants.

TECHNICAL CHALLENGES

Energetic compounds are frequently unstable.

Synthetic routes are unknown.

Limited chemical tuition to guide choice of targets.

APPROACH

Predict energy content and kinetic stability characteristics using computational chemistry.

Determine which theoretical method(s) are best suited for prediction of reliable energetics.

OVERVIEW

One of the most widely used theoretical methods for computing properties of energetic molecules is density functional theory, due to its computational efficiency and the general accuracy of the results (comparable to second order perturbation theory).

DFT is generally benchmarked against other QC methods by comparing predicted properties of selected molecules with a modest amount of multiconfigurational character.

ISSUES

How accurate are DFT predictions (e.g., bond energies) for molecules with a high degree of multiconfigurational character?

How does one determine if a molecule has a high degree of multiconfigurational character?

- Large spin contamination for open-shell species
- Negative LUMO energy for neutral closed shells.
- Natural orbital occupation numbers > ~0.1 for “virtual” orbitals.
- CCSD(T) “T1” diagnostic.
- Non-physical NOONs[1].

METHODOLOGY

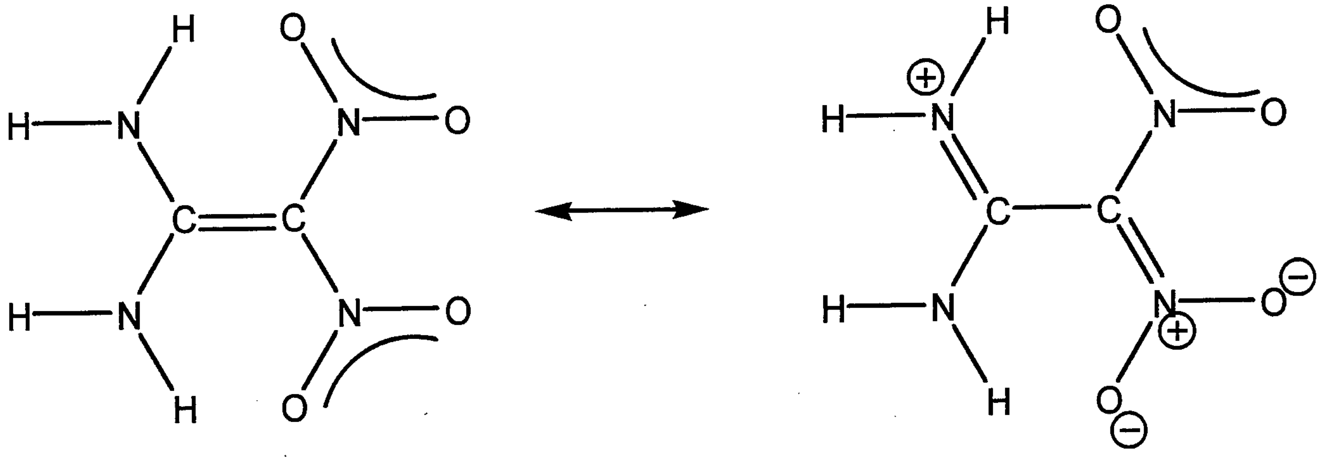
Use MBPT, CCSD(T) non-physical (i.e., > 2 or < 0) natural orbital occupation numbers[1] (NOON) as diagnostic for multiconfigurational character.

Use predicted C-NH2 and C-NO2 bond dissociation energies of 1,1-diamino-2,2-dinitroethylene ("FOX-7") and its simpler prototypes as testbed.

Compare DFT with other single reference methods (MBPT2, CCSD(T), G2) and with multireference methods (MCSCF, MCQDPT).

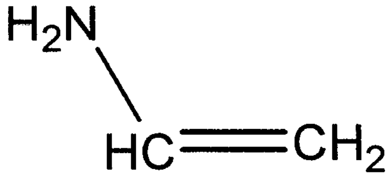
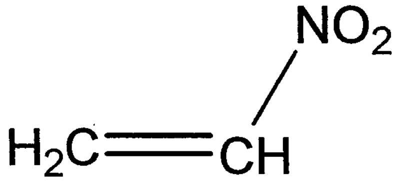
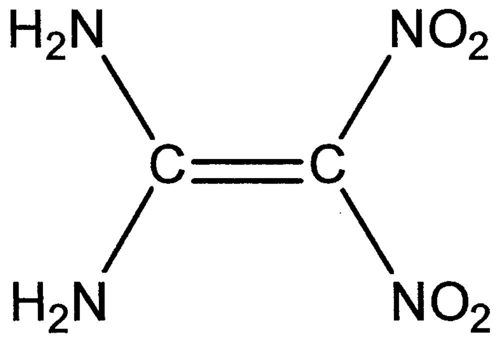
1. M.S. Gordon, M.W. Schmidt, G.M. Chaban, K. R. Glaesemann, W.J. Stevens, and C. Gonzalez, "A Natural Orbital Diagnostic for Multiconfigurational Character in Correlated Wavefunctions", J. Chem. Phys., 110, 4199 (1999).

FOX-7: a “Push-Pull” Ethylene



Multiple Lewis valence structures suggest that FOX-7 may require multiconfigurational methods.

DFT Geometries

	C=C	C-NH$_2$	C-NO$_2$
$H_2C{=}CH_2$	**1.331*** **1.327*****		
	**1.340*** **1.336*****	**1.386*** **1.392*****	
	**1.326*** **1.322*****		**1.459*** **1.473*****
	**1.426*** **1.428**** **1.421***** **(1.456)**	**1.339*** **1.345**** **1.345***** **(1.319, 1.325)**	**1.424*** **1.432**** **1.438***** **(1.399, 1.426)**

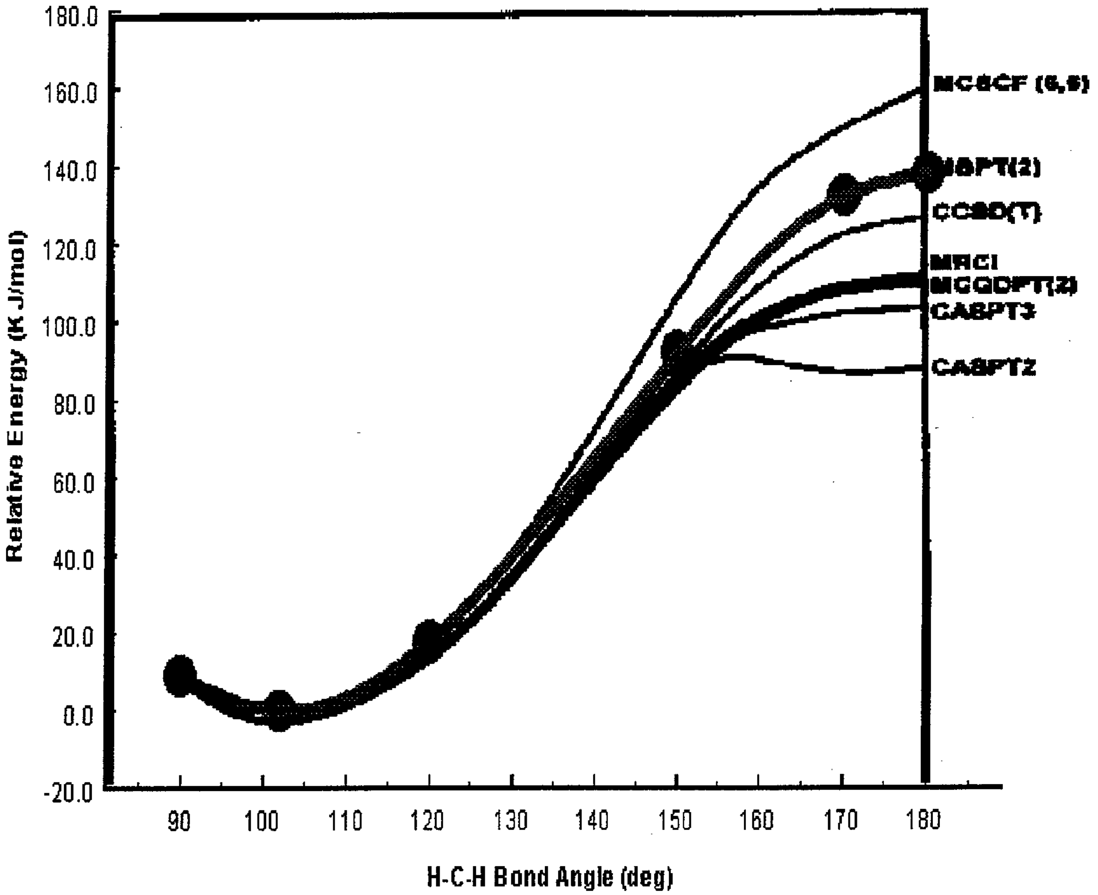
* P.Politzer, M.C.Concha, M.E.Grice, J.S.Murray, P.Lane, and D.Habibollazadeh Theochem, 452, 75(1998)

** A.Gindulyte, L.Massa, L.Huang, and J.Karl, J. Phys. Chem. A, 103, 11045(1999)

*** This work (B3LYP/6-311G(d,p)

( ) U. Bemm and H. Östmark, Acta Cryst. C54, 1997(1998).

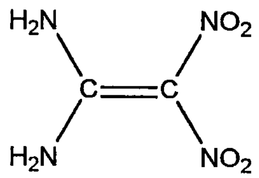
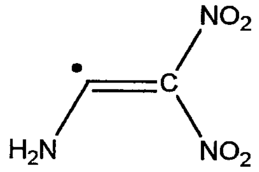
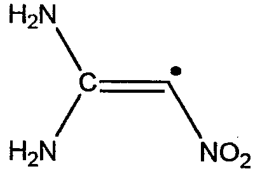
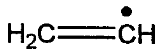
A Preliminary test: the CH2 Bend potential



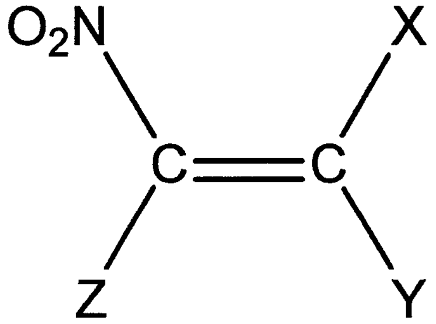
Circles: B3LYP/aug-cc-pVTZ

Curves: aug-cc-pVTZ basis used for all methods; taken from M.S. Gordon, M.W. Schmidt, G.M. Chaban, K. R. Glaesemann, W.J. Stevens, and C. Gonzalez, “A Natural Orbital Diagnostic for Multiconfigurational Character in Correlated Wavefunctions”, J. Chem. Phys., 110, 4199 (1999).

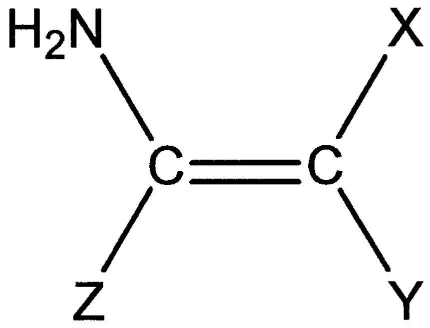
Non-physical Natural Orbital Occupation Numbers

	MBPT(2)	CCSD(T)
	-0.0001 (2)	
	-0.00014	
	2.296, 2.12, 2.00001 -0.99092, -0.xxxx	
 $H_2C{=}\dot{C}H$	2.07575 -0.09409	
$\bullet NO_2$	2.00001	

C-NO_2 Bond Dissociation Energies (kcal/mol)

	X=H Y=H Z=H	X=NH_2 Y=H Z=H	X=NH_2 Y=NH_2 Z=H	X=NH_2 Y=NH_2 Z=NO_2
DFT	68.8	81.4		67.4
MBPT(2)	77.7			
MCSCF				
G2(MP2)				
CCSD(T)//MBPT2				
MCQDPT(2)//MCSCF				

C-NH_2 Bond Dissociation Energies (kcal/mol)



	$X=H$ $Y=H$ $Z=H$	$X=NO_2$ $Y=H$ $Z=H$	$X=NO_2$ $Y=NO_2$ $Z=H$	$X=NO_2$ $Y=NO_2$ $Z=NH_2$
DFT	105.2			
MBPT(2)	115.6			
MCSCF				
G2(MP2)				
CCSD(T)//MBPT2				
MCQDPT(2)//MCSCF				

SUMMARY

1. The bend potential of $^1A_1$ CH_2 has been computed using DFT (B3LYP) and compared against earlier MBPT(2), MCQDPT(2), CCSD(T), and MRCI calculations.

2. The B3LYP C-NO_2 and C-NH_2 bond dissociation energies of FOX-7 and its prototypes have been benchmarked against correlated single-configuration (MBPT(2), CCSD(T)) and multiconfigurational methods (MCSCF, MCQDPT).

CONCLUSIONS

1. The B3LYP $^1A_1$ CH_2 bend potential is in good agreement with MRCI, CCSD(T), and MCQDPT(2) predictions. It is in nearly exact agreement with MBPT(2).

2. B3LYP gives C-NH2 bond dissociation energies in FOX-7 within ~5 kcal/mol of G2(MP2), CCSD(T), and MCQDPT(2).

3. B3LYP apparently "captures" a reasonable amount of non-dynamical correlation energy (e.g., works well for 2-configuration problems.)

4. B3LYP performance for C-NO2 BDEs: TBD.

FUTURE DIRECTIONS

1. Examine effects of more flexible basis sets (e.g., cc-pvtz).

2. Benchmark DFT methods using other highly multiconfigurational molecules (e.g., FOOF).

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