REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE October 10, 1996

3. REPORT TYPE AND DATES COVERED Final Report 9/1/93 - 8/31/96

4. TITLE AND SUBTITLE
Environmental Effects on High Energy Density Materials

5. FUNDING NUMBERS
61102F/2303/B3

6. AUTHOR(S)
Henry F. Schaefer III

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Georgia Univ Research Foundation Inc
Boyd Grad Studies Res Cntr
Athens, GA 30602

8. PERFORMING ORGANIZATION
AFOSR-TR-96
0511

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NCL
Building 410, Bolling AFB DC
20332-6448
Dr. Michael R. Berman.

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
F49620-93-1-0529

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The object of this research is to characterize, using ab initio quantum mechanical methods, the stabilizing or destabilizing effects of hydrogen and/or oxygen matrices on proposed high energy density molecular (HEDM) systems. In addition, the unimolecular fragmentation reactions of large HEDM species such as N_{20} will be studied via density functional methods.

19961028 006

14. SUBJECT TERMS
Ab initio, computational chemistry, quantum chemistry, theoretical chemistry, propellants.

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

Final Technical Report

Air Force Office of Scientific Research

Grant F49620-93-1-0529

"Environmental Effects on High Energy Density Materials"

Principal Investigator: Henry F. Schaefer III

Center for Computational Quantum Chemistry

University of Georgia

I. Summary

The development of efficient and safe conventional (i.e., nonnuclear) propellants and/or fuels is a goal of obvious technological significance. A desirable quality of such a propellant is clearly a high ratio of energy release to mass. The present hypothesis rests on a simple, but previously unrecognized, analogy between oxygen and sulfur. Preliminary studies showed that the oxygen ring systems are sufficiently promising to warrant the detailed, high-level theoretical research reported here.

Our idea begins with the observation that elemental sulfur exists as sulfur rings, S_n. The essence of our proposal is to make an analogy between sulfur rings and oxygen rings. Given the remarkable stability of sulfur rings, should it not be possible to prepare oxygen rings? Oxygen lies directly above sulfur in the Periodic Table, and the analogy is an appealing one.

Work completed includes our study of the prospective HEDM material $C_2H_2Li_2$. This molecule has been of sustained intellectual interest since 1976 when Paul Schleyer and John Pople suggested that the lowest triplet state of 1,1 -diliythioethylene might allow nearly free rotation about the supposed classical C=C "double bond". In 1985 Manceron

and Andrews intercepted dilithioethylene via matrix isolation infrared spectroscopy in the laboratory. Moreover, in 1987 Maercker, Graule, and Demuth used mercury precursors to characterize *cis* and *trans* 1,2-dilithioethylene as more conventional reaction products. So this species is by no means simply a figment of the theorist's imagination.

The work I describe was published in the *Journal of the American Chemical Society*, having been carried out jointly with the Proctor and Gamble Company. The bulk of the research was carried out by my graduate student Evan Bolton, supported by the AASERT program.

The potential energy surface (PES) for the singlet 1,2-dilithioethene and acetylenic $C_2H_2Li_2$ isomers was carefully surveyed using high level quantum mechanical methods. Three previously undiscovered minima (including, remarkably, the global minimum) were located: a planar monobridged *trans* 1,2 dilithioethene and two acetylenic structures. A total of seven minima and ten transition states for interconversion of minima were investigated, while seven transition states are located for the first time. Vibrational frequencies were evaluated for all structures through the coupled-cluster method including all single and double excitation with a double-ζ plus polarization basis set. A remarkable isomer, the C_s complex between lithioacetylene and LiH, is the global minimum on the $C_2H_2Li_2$ PES. This structure was 34 kcal/mol more stable than the two lowest lying singlet 1,2-dilithioethene structures, a *trans* planar C_{2h} form with acute CCLi angles and a *cis* doubly bridged C_{2v} structure . The other singlet 1,2-dilithioethene minima , *cis* planar monobridged C_s, *cis* planar dibridged C_{2v} , and *trans* planar monobridged C_s, are 4.3, 8.4, and 19.4 kcal/mol higher lying, respectively. The carbon-lithium bonding is ionic in character in all these species.

Another important study has been carried out by graduate student John Galbraith and published recently in the *Journal of the American Chemical Society.* Motivated by the recent isolation and spectroscopic characterization of nitrosyl azide (N_4O), we have undertaken an *ab initio* investigation of the originally reported structure as well as various structural isomers on the potential energy hypersurface. Geometries and harmonic vibrational frequencies have been predicted for the *trans*-chain isomer, along with the 6 π-electron potentially aromatic ring structure, with various levels of theory up through the triple-ζ plus double polarization single and double excitation coupled cluster (TZ2P CCSD) method and the multi-reference configuration interaction method (MRCISD). In addition, estimates are made for extension to higher levels of theory, arriving at final structural predictions for the *trans*-chain and ring isomers. Energy relationships, bond lengths, vibrational frequencies, Mulliken bond indices, and molecular orbital arguments are used to elucidate the nitrogen oxide bonding. While the ring isomer is predicted to be the most stable structure on the hypersurface, the barrier to dissociation is most likely between 1 and 2 kcal mol^{-1} (including zero point vibrational energy [ZPVE] the existence of any barrier becomes questionable), making isolation theoretically possible but experimentally difficult. This small barrier also detracts from the attractiveness of the N_4O ring structure as a high energy-density material. The *trans*-chain isomer, however, lies in an energy valley with higher sides, consistent with its experimental observation.

II. Publications Supported by F49620-93-J-0529

1. E. E. Bolton, H. F. Schaefer, W. D. Laidig, and P. R. Schleyer, "Singlet $C_2H_2Li_2$: Acetylenic and 1, 2 - Dilithioethene Isomers. A Remarkably Congested Potential Energy Hypersurface for a Simple Organometallic System", *J. Amer. Chem. Soc.*, **116**, 9602 (1994).
2. M. L. Leininger, C. D. Sherrill, and H. F. Schaefer, "N_8: A Structure Analogous to Pentalene and Other High Energy Density Minima," *J. Phys. Chem.* **99**, 2324 (1995).

3. P. R. Schreiner, H. F. Schaefer, and P. R. Schleyer "Can AlH_5 Exist?", *J. Chem. Phys.* **103**, 5565 (1995).
4. E. E. Bolton, W. D. Laidig, P. R. Schleyer, and H. F. Schaefer, "Does Singlet 1,1 Dilithioethene Really Prefer a Perpendicular Structure?" *J. Phys. Chem.* **99**, 17551 (1995).
5. J. M. Galbraith and H. F. Schaefer, "The Nitrosyl Azide (N_4O) Potential Energy Hypersurface: A High Energy-Density Boom or Bust?", *J. Amer. Chem. Soc.* **118**, 4860 (1996).
6. J. C. Stephens, E. E. Bolton, and H. F. Schaefer, "Quantum Mechanical Vibrational Frequencies and Matrix Isolation Assignments for Al_2H_2", *J. Chem. Phys.* submitted.
7. A. Tian, F. Ding, L. Zhang, Y. Xie, and H. F. Schaefer, "New Isomers of N_8 without Double Bonds", *J. Phys. Chem.* submitted.

III. List of Participating Professionals

A. Senior Research Personnel:

Professor Henry F. Schaefer III

B. Junior Research Personnel:

Mr. Evan E. Bolton

Mr. Matthew L. Leininger

Mr. John M. Galbraith

Mr. C. David Sherrill

Mr. Jeffrey C. Stephens