MNDO-ESTIMATIONS OF THE STANDARD ENTHALPY OF FORMATION OF SOME BINARY SULFUR-NITROGEN COMPOUNDS AND THEIR DERIVATIVES

S. SENSARMA
A. G. TURNER
M. J. DELONG
L. P. DAVIS

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

PROJECT 2303

AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
82 02 19 055 319 12
This document was prepared by the Molecular Dynamics Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO. The research was conducted under Project Work Unit Number 2303-F4-03. Dr. Almon G. Turner was the project scientist.

When U. S. Government drawings, specifications or other data are used for any purpose other than a definitely related government procurement operation, the government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the government may have formulated, furnished or in any way supplied the said drawings, specifications or other data is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Inquiries concerning the technical content of this document should be addressed to the Frank J. Seiler Research Laboratory (AFSC), FJSRL/NC, USAF Academy, CO 80840. Phone AC 303 472-2655.

This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

ALMON G. TURNER, Ph.D. ARMAND A. FANNIN, JR., Lt Colonel, USAF
Project Scientist Director, Chemical Sciences

WILLIAM D. SIURU, JR., Colonel, USAF
Commander

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

Printed in the United States of America. Qualified requestors may obtain additional copies from the Defense Documentation Center. All others should apply to National Technical Information Service 6285 Port Royal Road Springfield, Virginia 22161
MNDO-ESTIMATIONS OF THE STANDARD ENTHALPY OF FORMATION OF SOME BINARY SULFUR-NITROGEN COMPOUNDS AND THEIR DERIVATIVES

By

S. Sensarma†
A. G. Turner†,*
M. J. DeLong
L. P. Davis

TECHNICAL REPORT FJSRL-TR-82-0001
February 1982

Approved for public release; distribution unlimited

Directorate of Chemical Sciences
Frank J. Seiler Research Laboratory
Air Force Systems Command
US Air Force Academy, Colorado 80840

† Permanent Address: Department of Chemistry, University of Detroit, Detroit, MI 48221

* University Resident Research Professor, 1981-82. To whom correspondence should be addressed.
UNCLASSIFIED

REPORT DOCUMENTATION PAGE

1. REPORT NUMBER
FJSRL-TR-82-0001

2. GOVT ACCESSION NO.
ADA111153

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
MNDO-Estimations of the Standard Enthalpy of Formation of Some Binary Sulfur-Nitrogen Compounds and Their Derivatives

5. TYPE OF REPORT & PERIOD COVERED

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(S)
S. Sensarma M. J. DeLong
A. G. Turner L. P. Davis

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
F. J. Seiler Research Laboratory (AFSC)
FJSRL/NC
USAF Academy, CO 80840

10. PROGRAM ELEMENT PROJECT, TASK AREA & WORK UNIT NUMBERS
61102F/2303/F4/03

11. CONTROLLING OFFICE NAME AND ADDRESS
F. J. Seiler Research Laboratory (AFSC)
FJSRL/NC
USAF Academy, CO 80840

12. REPORT DATE
February 1982

13. NUMBER OF PAGES

14. MONITORING AGENCY NAME & ADDRESS (IF different from Controlling Office)

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Standard Enthalpy of Formation
Cyclic Sulfur Nitrides
Sulfur Nitrides
Tetrasulfur tetranitride
MNDO molecular orbital calculations

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
A table of standard enthalpies of formation of all known binary compounds of sulfur and nitrogen has been compiled from a large number of MNDO type molecular orbital calculations.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>PREFACE</td>
<td>11</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>CALCULATIONS AND RESULTS</td>
<td>2</td>
</tr>
<tr>
<td>TABLE OF THERMODYNAMIC DATA FOR VARIOUS SULFUR-NITROGEN COMPOUNDS</td>
<td>4</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>6</td>
</tr>
</tbody>
</table>
PREFACE

The research as herein described was performed under Work Unit 2303-F4-03 (Molecular Orbital Calculations of Excited Species).
INTRODUCTION

The area of the chemistry of the binary molecules and ions formed from sulfur and nitrogen is of potential interest to the U. S. Air Force. Characterized by a dominance of highly endothermic compounds it offers a wide variety of materials for applications as primary solid state explosives and detonating agents. These materials are available in solid, liquid, and plastic forms. Representative compounds include tetrathion tetrasulfide, $S_4N_4$; tetrasulfur dinitride, $S_4N_2$ and the isomers thereof; and $S_2N_2$, disulfur dinitride. The latter compound can be readily converted into polymeric sulfur nitride, $(SN)_x$, which has been extensively studied for its electrical properties being a superconductor below 4K.

In addition to the above, the area of the binary compounds of sulfur and nitrogen contains a large number of polyhedral anions and cations. Representative members of this group include ions such as the tetrasulfur tetranitride dication, $S_4N_4^{2+}$; tetrasulfur pentanitride anion, $S_4N_5^{-1}$; tetrasulfur trinitride cation, $S_4N_3^{1+}$; and trisulfur trinitride anion, $S_3N_3^-$. These anions and cations have potential application in the area of battery development as possible candidates for components of supporting electrolytes.

The area of the chemistry of binary compounds composed of sulfur and nitrogen has become a very active field of research in the last two decades. Despite a wide range of research activities virtually no thermodynamic data are available for this class of materials, the exception being a single report of a value for the standard heat of formation of tetrasulfur tetrasulfur tetranitride $^2$, Since our laboratory has been concerned with theoretical studies of these materials for a number of
years\textsuperscript{3}, we have put together in tabular form estimates of the standard enthalpy of formation, $\Delta H_f^\circ$, for most of the known compounds of this class. We have included a few materials which are presently unknown, (e.g., $N_2S$, $S_4N_4^{2-}$, and $S_2N_2$ open chain) but whose existence may be considered probable, as reflected by the known chemistry of these materials\textsuperscript{4}.

**CALCULATION AND RESULTS**

The enthalpies of formation have been calculated by the MNDO method of Dewar et al.\textsuperscript{5} using the Restricted Hartree-Fock approximation. Open shell systems have been calculated using an Unrestricted Hartree-Fock wave function\textsuperscript{6}. The results are given in the Table.

The MNDO method when applied to sulfur-nitrogen compounds has been shown to predict molecular geometries that agree with the experimental structures in the cases of disulfur dinitride, $S_2N_2(D_{2h}$ ground state)$^7$, tetrasulfur tetranitride, $S_4N_4$\textsuperscript{8}, the pentasulfur penta nitrogen cation, $S_5N_5^{+9}$, and the $S_3N_3^-$, the trisulfur trinitrogen cation\textsuperscript{3}. In general, the MNDO calculated enthalpies of formation tend to be somewhat more negative than the corresponding experimental values for carbon containing compounds and the same is probably true for sulfur-nitrogen compounds as well. Nevertheless, in an absolute sense the values calculated are comparable in accuracy to those obtainable from minimal basis set, single determinant SCF calculations\textsuperscript{10}. More importantly the values calculated relative to each other are probably reliable. Thus in the Table we indicate the enthalpy of formation of the materials listed relative to the enthalpy of formation of $S_4N_4$. It is somewhat difficult to assign absolute error estimates for the calculated heats of formation, but we estimate the values to be accurate to about 10\%.
The unstable nature of these materials (note all the calculated $\Delta H_f$'s are positive) makes the experimental calorimetric measurement of heats of reaction for these materials difficult. The lack of knowledge of heat capacity data additionally complicates the experimental problem. Simple combustion calorimetry is complicated by the formation of gaseous products, i.e., SO$_3$ and NO$_2$, and should probably be carried out in the presence of water to enable the formation of nitric and sulfuric acids. Until these problems are resolved it is hoped that these MNDO estimates of the standard enthalpies of formation will serve some useful purpose.
TABLE 1. Thermodynamic Data for Various Sulfur Nitrogen Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_f$ (Kcal/mol)</th>
<th>I.P. (ev)</th>
<th>$\Delta H_f$/relative$^+$</th>
<th>Dipole Moment$^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNN</td>
<td>47.6</td>
<td>10.4</td>
<td>0.237</td>
<td>1.57</td>
</tr>
<tr>
<td>NSN</td>
<td>212</td>
<td>10.6</td>
<td>1.05</td>
<td>1.69</td>
</tr>
<tr>
<td>$S_2N_2$</td>
<td>118</td>
<td>10.9</td>
<td>0.587</td>
<td>0.01</td>
</tr>
<tr>
<td>$S_2N_2$ chain</td>
<td>147*</td>
<td>-</td>
<td>0.731</td>
<td>2.74</td>
</tr>
<tr>
<td></td>
<td>142**</td>
<td>-</td>
<td>0.706</td>
<td>2.48</td>
</tr>
<tr>
<td>$S_2N_2^{2+}$</td>
<td>771</td>
<td>25.1</td>
<td>3.84</td>
<td>-</td>
</tr>
<tr>
<td>$S_2N_2^{-}$</td>
<td>174</td>
<td>- 4.6</td>
<td>0.866</td>
<td>-</td>
</tr>
<tr>
<td>$S_2N_2^{1+}$</td>
<td>300</td>
<td>18.2</td>
<td>1.49</td>
<td>-</td>
</tr>
<tr>
<td>$S_3N_2^{1+}$</td>
<td>309</td>
<td>12.0</td>
<td>1.54</td>
<td>-</td>
</tr>
<tr>
<td>$S_3N_2^{2+}$</td>
<td>661</td>
<td>23.4</td>
<td>3.29</td>
<td>-</td>
</tr>
<tr>
<td>$S_3N_2^{-}$</td>
<td>89.7</td>
<td>3.3</td>
<td>0.446</td>
<td>-</td>
</tr>
<tr>
<td>$S_3N_2^{1+}$</td>
<td>373</td>
<td>15.3</td>
<td>1.85</td>
<td>-</td>
</tr>
<tr>
<td>$S_4N_1^{1-}$</td>
<td>10.1</td>
<td>4.32</td>
<td>0.0502</td>
<td>-</td>
</tr>
<tr>
<td>$1,2S_4N_2$</td>
<td>43.7</td>
<td>10.8</td>
<td>0.217</td>
<td>1.67</td>
</tr>
<tr>
<td>$1,3S_4N_2$</td>
<td>104</td>
<td>9.9</td>
<td>0.517</td>
<td>2.04</td>
</tr>
<tr>
<td>$1,4S_4N_2$</td>
<td>113</td>
<td>9.8</td>
<td>0.562</td>
<td>1.62</td>
</tr>
<tr>
<td>$S_4N_3^{1+}$</td>
<td>351</td>
<td>14.6</td>
<td>1.75</td>
<td>-</td>
</tr>
<tr>
<td>$S_4N_4$</td>
<td>201</td>
<td>9.4</td>
<td>1.00</td>
<td>5.52</td>
</tr>
<tr>
<td>$S_4N_4$ chain</td>
<td>236*</td>
<td>9.56</td>
<td>1.17</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>240**</td>
<td>5.30</td>
<td>1.19</td>
<td>1.42</td>
</tr>
<tr>
<td>$S_4N_4H_4$</td>
<td>66.5</td>
<td>10.1</td>
<td>0.331</td>
<td>1.54</td>
</tr>
</tbody>
</table>
TABLE 1 (Continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_f^\circ$ (Kcal/mol)</th>
<th>I.P. (ev)</th>
<th>$\Delta H_f^\circ$/relative $^+$</th>
<th>Dipole Moment $^{\dagger\dagger}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_4N_4^{2+}$</td>
<td>674</td>
<td>19.8</td>
<td>3.35</td>
<td>-</td>
</tr>
<tr>
<td>$S_4N_4^{2-}$</td>
<td>190</td>
<td>-1.6</td>
<td>0.945</td>
<td>-</td>
</tr>
<tr>
<td>$S_4N_5^{1+}$</td>
<td>389</td>
<td>14.5</td>
<td>1.93</td>
<td>-</td>
</tr>
<tr>
<td>$S_4N_5^{1-}$</td>
<td>219</td>
<td>4.8</td>
<td>1.09</td>
<td>-</td>
</tr>
<tr>
<td>$S_5N_5^{1+}$</td>
<td>434</td>
<td>12.9</td>
<td>2.16</td>
<td>-</td>
</tr>
<tr>
<td>(heart) $S_5N_5^{1+}$</td>
<td>434</td>
<td>12.9</td>
<td>2.16</td>
<td>-</td>
</tr>
<tr>
<td>(azulene) $S_5N_5^{1+}$</td>
<td>434</td>
<td>12.9</td>
<td>2.16</td>
<td>-</td>
</tr>
</tbody>
</table>

$^+$ The standard enthalpy of formation relative to $\Delta H_f^\circ$ for $S_4N_4$

$^{\dagger\dagger}$ units - Debyes

*(singlet state)*

**(triplet state)**
REFERENCES


8. The structure calculated for $S_4N_4$ in formation of the Table is in reasonable agreement with the x-ray studies. $d_{N-S} = 1.60$; (exptl = 1.61), NSN angle = 108°, (exptl 104°), SNN angle = 120°, (exptl = 113°).
