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

By

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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.

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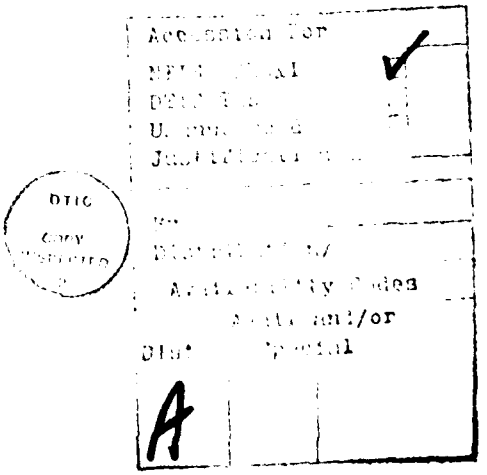

## PREFACE

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 tetranitrogen 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[1]. 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[3], we have put together in tabular form estimates of the standard enthalpy of formation, $\Delta H^\circ_f$ 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[4].

CALCULATION AND RESULTS

The enthalpies of formation have been calculated by the MNDO method of Dewar et.al.[5] using the Restricted Hartree-Fock approximation. Open shell systems have been calculated using an Unrestricted Hartree-Fock wave function[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, $S_4N_4$[8], the pentasulfur pentanitrogen cation, $S_5N_5^{+}$[9], and the $S_3N_3^{-}$, the trisulfur trinitrogen cation[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 determinent SCF calculations[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 $\Delta H^\circ_f$'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 sulfric 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

| Compound | $\Delta H°_f$ (Kcal/mol) | I.P.(ev) | $\Delta H°_f$/relative[†] | Dipole Moment[††] |
|---|---|---|---|---|
| SNN | 47.6 | 10.4 | 0.237 | 1.57 |
| NSN | 212 | 10.6 | 1.05 | 1.69 |
| $S_2N_2$ | 118 | 10.9 | 0.587 | 0.01 |
| $S_2N_2$ chain | 147* | - | 0.731 | 2.74 |
| | 142** | - | 0.706 | 2.48 |
| $S_2N_2^{2+}$ | 771 | 25.1 | 3.84 | - |
| $S_2N_2^{2-}$ | 174 | - 4.6 | 0.866 | - |
| $S_2N_3^{1+}$ | 300 | 18.2 | 1.49 | - |
| $S_3N_2^{1+}$ | 309 | 12.0 | 1.54 | - |
| $S_3N_2^{2+}$ | 661 | 23.4 | 3.29 | - |
| $S_3N_3^{1-}$ | 89.7 | 3.3 | 0.446 | - |
| $S_3N_3^{1+}$ | 373 | 15.3 | 1.85 | - |
| $S_4N^{1-}$ | 10.1 | 4.32 | 0.0502 | - |
| 1,2 $S_4N_2$ | 43.7 | 10.8 | 0.217 | 1.67 |
| 1,3 $S_4N_2$ | 104 | 9.9 | 0.517 | 2.04 |
| 1,4 $S_4N_2$ | 113 | 9.8 | 0.562 | 1.62 |
| $S_4N_3^{1+}$ | 351 | 14.6 | 1.75 | - |
| $S_4N_4$ | 201 | 9.4 | 1.00 | 5.52 |
| $S_4N_4$ chain | 236* | 9.56 | 1.17 | 0.81 |
| | 240** | 5.30 | 1.19 | 1.42 |
| $S_4N_4H_4$ | 66.5 | 10.1 | 0.331 | 1.54 |

TABLE 1 (Continued)

| Compound | $\Delta H°_f$(Kcal/mol) | I.P.(ev) | $\Delta H°_f$/relative[‡] | Dipole Moment[††] |
|---|---|---|---|---|
| $S_4N_4^{2+}$ | 674 | 19.8 | 3.35 | - |
| $S_4N_4^{2-}$ | 190 | - 1.6 | 0.945 | - |
| $S_4N_5^{1+}$ | 389 | 14.5 | 1.93 | - |
| $S_4N_5^{1-}$ | 219 | 4.8 | 1.09 | - |
| $S_5N_5^{1+}$ | 434 | 12.9 | 2.16 | - |
| $S_5N_5^{1+}$ (heart) | 434 | 12.9 | 2.16 | - |
| $S_5N_5^{1+}$ (azulene) | 434 | 12.9 | 2.16 | - |

‡ The standard enthalpy of formation relative to $\Delta H°_f$ for $S_4N_4$

†† units - Debyes

* (singlet state)

** (triplet state)

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