

## An *Ab Initio* Study of Isomerization in the *Cis* Thionylimide, HNSO-*Cis* Thiazyl-S-hydroxide, HOSN System

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*The relative stabilities of HOSN and HNSO as studied as a function of basis set using ab initio restricted Hartree-Fock-SCF molecular orbital methods. The relative energies are shown to be very sensitive to the choice of basis set employed. The imide is shown to be the most stable form for the system for all basis sets of quality 3-21G\* or better.*

### Introduction

The chemical system of empirical formula HOSN has been known for many years. Readily synthesized by the gas phase reaction of thionyl chloride and ammonia [1, 2], the reaction product has been characterized as the *cis* form of thionylimide, HNSO. The infrared spectrum of this material has been extensively studied [3–6]. The same materials react in condensed medium to yield a material which has been suggested to be thiazyl-S-hydroxide, HOSN, and also characterized as thionylimide [7]. The situation is further complicated by the presence of additional reactions which result in polymeric reaction products such as a tetrameric molecule (OSNH)<sub>4</sub> of unknown structure [8]. Since this laboratory has an interest in the study of these later polymerization reactions, it was of interest to study first the basic monomeric materials which might be present in the system. There have been a few previous theoretical studies of the imide form, the most recent *ab initio* study being the force field study of Raghavachari [9]. No studies have been carried out on the hydroxide form. Slightly over one year ago this laboratory studied the isomerization reaction on a semi-empirical basis and concluded that the

thiazyl-S-hydroxide was the more stable form [10]. The present study will show this conclusion to be in error.

### Calculations

Raghavachari has recently demonstrated the importance of the use of the proper basis set in dealing with sulfur–nitrogen containing molecules [9]. The hypervalent nature of the sulfur atom in HOSN and HNSO require the use of polarization type functions in the basis. A simple split level valence set does not suffice to establish correct geometries. Extended sets such as 4-31G\*, 6-31G\*, 6-311G\*, are known to yield results which provide accurate bond distances and bond angles. In these two molecules, a fully extended basis set such as the 6-311G\* is necessary to obtain a completely correct geometry. Accordingly calculations were carried out at the restricted Hartree-Fock level using the following basis sets: STO-3G [10], 3-21G [11], 3-21G\* [12], 6-31G\* [13], and 6-311G\* [14] for both thionyl imide, HNSO and thiazyl-S-hydroxide, HOSN. The geometries were fully optimized at all levels. A gradient based method was utilized for the geometry optimizations.

### Results and Discussion

The calculated energies and geometries for the *cis* forms of thionyl imide and thiazyl-S-hydroxide are shown in Table I. The results for HNSO agree with those calculated previously by Raghavachari for all basis sets except 6-31G\* where the difference is attributable to the fact that he employed d type functions on S, N and O whereas this work entailed the use of d functions on sulfur only. The calculated differences in geometry between the 6-31G\* and 3-21G\* sets are primarily traceable to

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TABLE I. Geometries and Energies Calculated for Various Basis Sets.

	Basis Set				
	STO-3G	3-21G	3-21G*	6-31G* <sup>b</sup>	6-311G*
<b>HNSO</b>					
Energy <sup>a</sup>	-521.11359	-524.54982	-524.75976	-527.18306	-527.35050
d <sub>N-S</sub>	1.602	1.578	1.480	1.475	1.487
d <sub>S-O</sub>	1.585	1.564	1.440	1.448	1.431
d <sub>N-H</sub>	1.504	1.020	1.010	1.062	1.010
NSO angle	106.6	114.3	119.9	119.6	119.0
HNS angle	105.7	116.2	125.7	132.5	117.3
<b>HOSN</b>					
Energy <sup>a</sup>	-521.19585	-524.57432	-524.74556	-527.17512	-527.33534
d <sub>N-S</sub>	1.604	1.583	1.451	1.459	1.443
d <sub>S-O</sub>	1.711	1.718	1.638	1.617	1.631
d <sub>O-H</sub>	0.996	0.975	0.973	1.013	0.950
NSO angle	101.7	108.3	114.7	114.6	114.6
HOS angle	103.1	111.8	116.7	125.4	112.4

<sup>a</sup>Units: energy in Hartrees; distances in Angstroms; angles in degrees. <sup>b</sup>See ref. [13].

TABLE II. Isomerization Energy.<sup>a</sup>

Basis Set	$\Delta E$ (Kcal/mol)
STO-3G	51.59
3-21G	15.36
3-21G*	-8.91
6-31G* <sup>b</sup>	-4.98
6-311G*	-9.51

<sup>a</sup> $E_{\text{HOSN}} - E_{\text{HNSO}}$ . <sup>b</sup>See Ref [13].

the improvement in the inner shell orbitals of the constituent atoms. The effect of polarization functions is apparent from a comparison of the 6-31G\* and 6-311G\* results. The geometries are fairly well determined at the 6-31G\* level except for the bond angles which involve the hydrogen atom. A proper description of this angle is not attained until sufficient basis functions are employed for the hydrogen atom. This in turn seems to occur in the range of the 6-31G\* to 6-311G\* level where we have two and six functions respectively centered on hydrogen.

Table II shows the isomerization energy ( $E_{\text{HOSN}} - E_{\text{HNSO}}$ ) for the various levels of calculation. Minimal basis set calculation predicts that thiazyl-S-hydroxide is the lower energy form in accord with previous semi-empirical results [10]. However as the basis set is extended this result changes drastically. Introduction of a split level valence set leads to the

TABLE III. Population Analysis-Atomic Charges.

	Basis Set				
	STO-3G	3-21G	3-21G*	6-31G* <sup>a</sup>	6-311G*
<b>HOSN</b>					
q <sub>N</sub>	-0.272	-0.524	-0.401	-0.332	-0.445
q <sub>S</sub>	0.434	0.885	0.732	0.643	0.744
q <sub>O</sub>	-0.341	-0.761	-0.743	-1.002	-0.604
q <sub>H</sub>	0.178	0.400	0.412	0.693	0.306
P <sub>N-S</sub>	0.530	0.530	1.042	1.016	1.103
P <sub>S-O</sub>	0.308	0.168	0.188	-0.098	-0.056
P <sub>H-O</sub>	0.282	0.490	0.492	0.334	0.614
<b>HNSO</b>					
q <sub>N</sub>	-0.402	-0.802	-0.699	-0.894	-0.556
q <sub>S</sub>	0.644	1.173	0.920	0.776	0.874
q <sub>O</sub>	-0.385	-0.727	-0.573	-0.509	-0.570
q <sub>H</sub>	0.144	0.356	0.350	0.727	0.253
P <sub>N-S</sub>	0.539	0.282	0.668	0.568	0.600
P <sub>S-O</sub>	0.366	0.468	0.782	0.624	0.654
P <sub>N-H</sub>	0.584	0.572	0.600	0.472	0.704

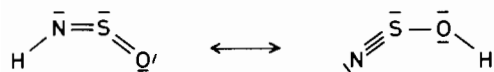
<sup>a</sup>See Ref. [13].

conclusion that the imide form is lowest in energy. The calculated isomerization energy is 9.51 Kcal/mol at the 6-311G\* level. The calculation of relative energies is one of the more difficult tasks in theoretical chemistry [13, 14]. Significant energy lowering is obtained by the addition of polarization

functions to the basis set. From the basis sets employed above one can be certain that the qualitative order of energies *i.e.*  $E_{\text{HOSN}} > E_{\text{HNSO}}$  is correct. The actual energy barrier is probably correct to within 0.01 Hartree *i.e.* 5 Kcal/mol.

The population analysis for the two molecules is given in Table III.

The calculated bond order reflects the advantage of using the split-valence level basis set with polarization. Only at this level does one obtain a population analysis which provides a reasonable picture of the bonding in the system.



The nitrogen–sulfur triple bond shows a bond order of 1.0, the double bonds orders of about 0.55–0.6, and the single bond about 0.4–0.5. The calculated charges in the molecule are relatively large, particularly for the oxygen atom, but are in accord with the chemical notion provided by electronegativity considerations.

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#### References

- 1 P. W. Schenk, *Ber.*, 75, 94 (1942).
- 2 T. Hata and S. Kinumaki, *Nature*, 203, 1379 (1964).
- 3 H. Richert, *Z. Anorg. Allgem. Chem.*, 309, 171 (1961).
- 4 H. H. Eysel, *J. Mol. Struct.*, 5, 275 (1970).
- 5 M. Carlotti, G. DiLionardo, G. Galloni and A. Trombetti, *J. Mol. Spectroscopy*, 84, 155 (1980).
- 6 E. B. Wilson, Jr., *Pure Appl. Chem.*, 7, 23 (1963).
- 7 M. Becke-Goehring, R. Schwarz and W. Spicss, *Z. Anorg. Allgem. Chem.*, 293, 294 (1957).
- 8 E. Fluck and M. Becke-Goehring, *Z. Anorg. Allgem. Chem.*, 292, 229 (1957).
- 9 K. Raghavachari, *J. Chem. Phys.*, 76, 3668 (1982).
- 10 W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969).
- 11 W. J. Hehre, R. Ditchfield, R. F. Stewart and J. A. Pople, *ibid.*, 52, 2769 (1970).
- 12 J. B. Collins, P. V. R. Schleyer, J. S. Binkley and J. A. Pople, *ibid.*, 64, 5142 (1976).
- 13 J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.*, 102, 939 (1980).
- 14 M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro and W. J. Hehre, *ibid.*, 104, 2797 (1982).
- 15 W. J. Pietro, M. M. Franel, W. J. Hehre, D. J. DeFrees, J. A. Pople and J. S. Binkley, *ibid.*, 104, 5039 (1982).
- 16 M. M. Franel, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 77, 3654 (1982). The basis at denoted 6-31G\* herein is not the usual 6-31G\* set referenced above, but rather the 6-31G set with polarization function added only to the sulfur atom.
- 17 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 72, 650 (1980).