(2) The optimized geometries of disilene with correlated wave functions became strongly trans-bent $C_{2h}$ structures.

(3) The basis set dependencies of the optimized geometries of disilene are proven to be artificial in the RHF treatment in all previous work that did not involve a contribution from the diradical structures.

On the basis of these results, we feel that the full potential surface of the $Si_2H_4$ system as well as that of the other silicon double bonded systems should also be reconsidered.

**Note Added in Proof.** After finishing this manuscript, the work by Olbrich appeared.[23] His optimized structure of disilene at CPF level is consistent with the present work.

**Acknowledgment.** The author thanks Prof. Shigeru Nagase of Yokohama National University and Prof. Shigeki Kato of the University of Tokyo for stimulating discussions and suggestions.

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# An ab Initio MO Study of Isomers of $HNS_2$ and $HNO_2$

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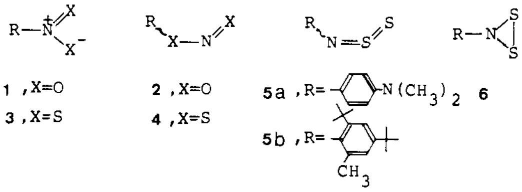
**Abstract:** A systematic comparison of the geometry and stability of many possible isomers of $HNO_2$ and $HNS_2$ has been carried out. The geometry optimization at the HF/4-31G* level and the energetics at the MP3/6-31G** level show for $HNS_2$ that, although *N*-thiosulfinylamine, H—N═S═S, is the most stable, several other isomers may exist within a reasonable energy range. This suggests a wider variety of chemistry of $RNS_2$ than is known, in which only *N*-thiosulfinylamines are established. For $HNO_2$, only the nitrous acid H—O—N═O and the nitro compound H—N($\overset{\cdots}{—}$O)$_2$ are reasonably considered as thermodynamically stable. This difference of sulfur compounds compared with the oxygen analogues has been attributed to the availability of sulfur d orbitals for facile hypervalency. The preferred stability of *Z* isomers relative to *E* isomers and the barrier for *E* → *Z* isomerization have been discussed. An assignment of vibrational spectra has been proposed for some isomers.

## I. Introduction

Although nitro compounds **1** and nitrites **2** are among the most important classes of nitrogen-containing compounds and have been extensively studied,[1] the corresponding sulfur analogues **3** and **4** have been yet unknown. Some years ago Barton[2] and some of the present authors[3] reported that attempted syntheses of dithionitro compounds **3** resulted in the formation of *N*-thiosulfinylamines **5**, a new type of S(IV) thiocumulene.[4]



In a series of studies on *N*-thiosulfinylamines, we reported the photoreaction of **5b** leading to the formation of sulfur diimide (R—N═S═N—R) and proposed the reaction mechanism involving a thionitroso intermediate (R—N═S) which is most likely to be formed from dithionitro compound **3** or dithiaziridine **6**, both isomeric to **5**.[3b] Our recent studies on the detailed mechanism of the photoreaction of **5b** have also revealed the initial photoisomerization of (*Z*)-**5b** to (*E*)-**5b** and thermal reversion of (*E*)-**5b** to (*Z*)-**5b**.[5]

However, the detailed nature of these reactions is far from determined. Indeed, the relative stabilities or geometrical structures of the various possible isomers of the compounds $RNS_2$ are not known. Especially the fact that *N*-thiosulfinylamine **5** so far is the only stable compound known to exist among possible $RNS_2$ isomers is of great interest in view of the well-known facts that both nitro compounds **1** and nitrites **2** are stable chemical species in the case of oxygen analogues.

In order to give an insight to the chemistry of $RNS_2$ (R = H as a model) in connection with the experimental studies which have been already done and will be done in the future about this new series of compounds, we carried out an ab initio MO study. We tried to explain the structure, vibrational frequencies, hypervalency of the sulfur atoms as well as the isomerization between *Z* and *E* isomers. In order to compare sulfur and oxygen compounds, we also carried out calculations for various isomers of $HNO_2$.

## II. Computational Details

All calculations were carried out for closed-shell singlets. Geometries were fully optimized at the Hartree-Fock (HF) level with the split valence + polarization 4-31G*[6] basis set by using the analytical energy gradient method.[6] The harmonic vibrational frequencies were calculated

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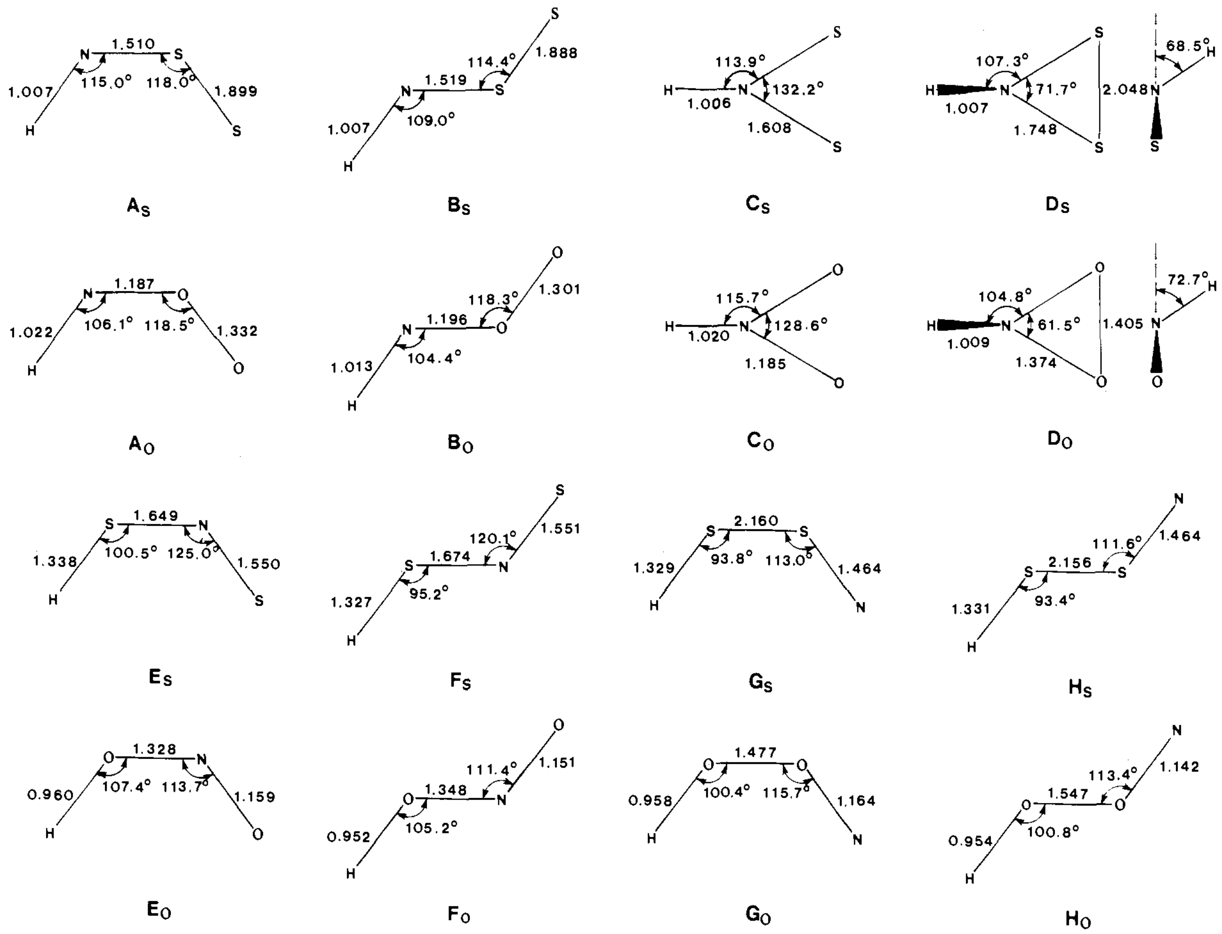

**Figure 1.** Geometrical parameters (in Å and deg) optimized at the HF/4-31G* level for isomers of $HNS_2$ and $HNO_2$.

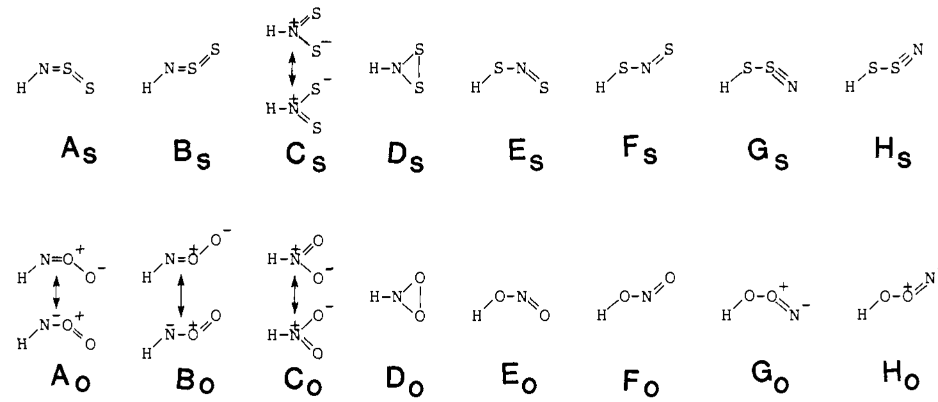

**Figure 2.** Electronic structure representation of isomers of $HNS_2$ and $HNO_2$ as suggested by calculated bond lengths.

from the force constant matrix obtained analytically at the HF/4-31G* level. In order to obtain more reliable energetics, the effect of electron correlation was taken into account by the second- (MP2) and the third- (MP3) order Møller-Plesset perturbation method[7] with frozen core orbitals with the 6-31G**[8] basis functions at the HF/4-31G* optimized geometries. For a few isomers we also carried outt calculations up to the MP4 level with the Huzinaga-Dunning basis set with polarization functions, denoted hereafter as the D95** basis set.[9] For dithionitro and nitro compounds, we also used the CASSCF method[10] to examine the need of a multiconfigurational wave function. It is conceivable that for some isomers there exist low-lying open-shell states, which will be left for future studies.

## III. Structure and Bonding

The geometries optimized at the HF/4-31G* level for most possible isomers for both sulfur and oxygen analogues are shown in Figure 1. All the geometries are optimized without any symmetry constraint, and converged to planar forms except for the isomers D which are nonplanar. Furthermore, vibrational frequency analysis has been carried out for all the isomers, and they are verified to be true local minima. A qualitative discussion on the single- and double-bond nature of various bonds in these isomers can be presented as follows, based on a comparison of

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**Table I.** Calculated and Experimental Bond Distances (Å) and Angles (deg) of *N*-Thiosulfinylamines

| compd | N=S | S=S | RNS | NSS | ref |
|---|---|---|---|---|---|
| (*Z*)-HNSS | | | | | |
| $A_S$[a] | 1.517 | 1.912 | 115.2 | 117.9 | this work |
| $A_S$[b] | 1.510 | 1.910 | 115.2 | 117.8 | this work |
| $A_S$[c] | 1.510 | 1.899 | 115.0 | 118.0 | this work |
| **5b**[d] | 1.548 | 1.898 | 126.4 | 119.7 | 23 |
| **7**[d] | 1.569 | 1.912 | 119.2 | 114.9 | 24 |
| **8**[d] | 1.592 | 1.908 | 120.9 | 111.4 | 25 |
| $A'_S$[e] | 1.586 | 2.175 | 116.1 | 111.3 | this work |
| $B'_S$[e] | 1.596 | 2.158 | 113.6 | 110.5 | this work |

[a] Calculated with HF/D95** (see Figure 3). [b] Calculated with HF/6-31G** (See Figure 3). [c] Calculated with HF/4-31G** (See Figure 1). [d] Determined by X-ray crystallographic analysis. All of these compounds have a *Z* configuration. [e] Calculated without the d function (4-31G).

**Table II.** Calculated and Experimental Bond Distances (Å) and Angles (deg) of Nitro Compounds

| compound | N–O | ∠ONO | ref |
|---|---|---|---|
| $HNO_2$[a] | 1.185 | 128.6 | this work |
| $CH_3NO_2$[b] | 1.222[c] | 123.4 | 30 |
| $C_6H_5NO_2$[b] | 1.21[c] | 124.5 | 31 |
| $CH_3NO_2$[d] | 1.240 | 126.2 | 32 |
| $CH_3NO_2$[e] | 1.192 | 125.8 | 32 |

[a] Optimized at the HF/4-31G* level (see Figure 1). [b] Determined by X-ray crystallographic analysis. [c] An average value of the two N–O bonds. [d] Calculated by 3-21G. [e] Calculated by 6-31G*.

known bond distances; the resultant formal bonding representations are shown in Figure 2.

**(a) Isomers A and B.** Both the N–S and the S–S bonds in sulfur analogues $A_S$ and $B_S$ are double bonds, while the O–O bond in oxygen analogues ($A_O$ and $B_O$) is between a single and a double bond, judging from the reported bond lengths of S=S[11] (1.892 Å for S=S=O[12] and 1.868 Å for $S{=}SF_2$[13]), N=S (1.510 Å for Me—N=S=O[14]), S—S (2.029 Å for $Me_2S_2$[15]), N—S (1.668 Å for $(OC_2H_4NS_2)_2$[16]), N=O (1.211 Å for $CH_3NO$[17]), N—O (1.463 Å for $H_2NOCH_3$[18]), O=O (1.20752 Å for $O_2$[19]), and O—O (1.475 Å in HOOH[20]). Although the N—O bond is also expected to be between a single and double bond, the calculated bond length (1.187 Å) is shorter than that of $CH_3NO$[17] and rather close to that of (*Z*)-$CH_3ONO$ (1.182 Å).[21]

**(b) Isomer C.** $C_S$ is of a nitro type, since its N—S bond length is between that for N=S and N—S. As for $C_O$, its N—O bond is shorter than that of $CH_3NO$ although it is considered to be a nitro compound. This point will be discussed again in a later section.

**(c) Isomer D.** N—X and X—X bonds (X = S and O) in $D_S$ and $D_O$ are normal single bonds.

**(d) Isomers E and F.** These can be described essentially as H—X—N=X, although slight shortening in X—N and slight lengthening in N=X suggest a small contribution of a canonical structure $H{-}X^+{=}N{-}X^-$. However, here again, the bond between the nitrogen and the terminal oxygen is shorter than that of $CH_3NO$.

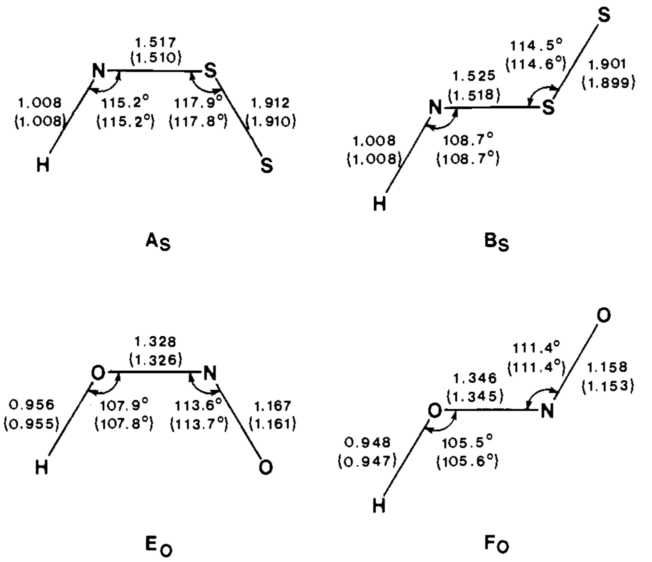
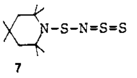


**Figure 3.** Geometrical parameters (in Å and deg) optimized at the HF/D95** and the HF/6-31G** (in parentheses) level.

**(e) Isomers G and H.** The S—S and the O—O bond are single bonds, while the S—N and the O—N bonds are a triple and a double bond, respectively, since the former is shorter than an S=N double bond and the latter is close to a normal double bond.

Now let us compare our results directly with the experimental geometries. Of the isomers calculated as local minima on the potential energy surface, only *N*-thiosulfinylamine ($A_S$ and $B_S$), nitro compound $C_O$, and nitrites $E_O$ and $F_O$ are known so far.[22] For these four isomers, we have further optimized geometries with larger basis sets, 6-31G** and D95**. The results are shown in Figure 3. The observed geometries for these compounds are listed in Tables I–III along with those calculated in the present work. There generally exists a satisfactory agreement between calculated and observed geometries.

**A. *N*-Thiosulfinylamines.** An X-ray structural analysis has been performed for **5b**,[23] **7**,[24] and **8**[25] and all of them have been shown to have a *Z* configuration. This is consistent with the



7

$Ph_3P{=}N{-}S{-}N{=}S{=}S$

8

theoretical prediction obtained here that the *Z* form $A_S$ is more stable than the *E* form $B_S$ (vide infra). Table I also shows that the calculated S–S bond length (1.899–1.912 Å) and N–S–S bond angle (117.8–118.0°) in $A_S$ are in good agreement with those observed for **5b** (1.898 Å and 119.7°, respectively), whereas the calculated N=S bond length (1.510–1.517 Å) and R–N–S bond angle (115.0–115.2°) are somewhat smaller than the observed values (1.548 Å and 126.4°). The small deviation of the R–N–S bond angle from its experimental value is most likely due to the presence of the bulky 2,4-di-*tert*-butyl-6-methylphenyl group on the nitrogen in **5b**, since a similar deviation due to a bulky group has been observed for sulfinylamines (R—N=S=O): for HNSO from microwave spectroscopy[26] 1.512 Å (N–S), 1.451 Å (S–O), 115.8° (HNS), and 120.4° (NSO); for ArNSO (Ar = 2,4,6-tri-*tert*-butylphenyl) from X-ray crystallography[27] 1.494 Å, 1.436

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**Table III.** Calculated and Experimental Bond Distances (Å) and Angles (deg) of Nitrites ($R—O_1—N=O_2$)

| compound | basis set | $N—O_1$ | $N=O_2$ | $R—O_1—N$ | O—N—O | $R—O_1$ | ref |
|---|---|---|---|---|---|---|---|
| (*Z*)-HONO | D95** | 1.328 | 1.167 | 107.9 | 113.6 | 0.956 | this work |
| (*E*)-HONO | | 1.346 | 1.158 | 105.5 | 111.4 | 0.948 | this work |
| (*Z*)-HONO | 6-31G** | 1.326 | 1.161 | 107.8 | 113.7 | 0.955 | this work |
| (*E*)-HONO | | 1.345 | 1.153 | 105.6 | 111.4 | 0.947 | this work |
| (*Z*)-HONO | 4-31G* | 1.328 | 1.159 | 107.4 | 113.7 | 0.960 | this work |
| (*E*)-HONO | | 1.348 | 1.151 | 105.2 | 111.4 | 0.952 | this work |
| (*Z*)-HONO | 4-31(N*)[a] | | | | | | |
| (*E*)-HONO | | 1.36 | 1.15 | 108.0 | 110.6 | | 33 |
| (*Z*)-HONO | 4-31G | 1.377 | 1.177 | 111.6 | 113.9 | 0.965 | 34a,b |
| (*E*)-HONO | | 1.400 | 1.166 | 107.9 | 111.4 | 0.953 | |
| (*Z*)-HONO | 3-21G | 1.420 | 1.189 | 107.2 | 112.3 | 0.978 | 34a |
| (*E*)-HONO | | 1.442 | 1.179 | 104.8 | 110.2 | 0.969 | |
| (*Z*)-HONO | DZ | 1.425 | 1.179 | 108.5 | 113.1 | 0.972 | 35 |
| (*E*)-HONO | | 1.447 | 1.169 | 105.2 | 110.4 | 0.962 | |
| (*Z*)-HONO | exptl[b] | 1.392 | 1.185 | 104.0 | 113.6 | 0.982 | 36 |
| (*E*)-HONO | | 1.432 | 1.170 | 102.1 | 110.7 | 0.958 | |
| (*Z*)-$CH_3ONO$ | 4-21G | 1.413 | 1.195 | 115.7 | 114.1 | 1.468 | 37a,c |
| (*E*)-$CH_3ONO$ | | 1.441 | 1.186 | 110.3 | 109.7 | 1.461 | 37a |
| (*Z*)-$CH_3ONO$ | exptl[b] | 1.398 | 1.182 | 114.7 | 114.8 | 1.437 | 21a |
| (*E*)-$CH_3ONO$ | | 1.415 | 1.164 | 109.9 | 111.8 | 1.436 | |

[a] A set of d functions is added only on the N atom. [b] Determined by microwave spectroscopy.

**Table IV.** Relative Energies (kcal $mol^{-1}$) for Isomers of $HNS_2$ and $HNO_2$[a]

| | | isomers | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| compd | method for energy | A | B | C | D | E | F | G | H |
| $HNS_2$ | RHF/4-31G[b] | 0 | 4.9 | | | −8.6 | | | |
| | RHF/4-31G* | 0[c] | 4.8 | 9.2 | 25.8 | 7.0 | 7.8 | 14.0 | 15.0 |
| | RHF/6-31G** | 0[d] | 4.2 | 5.4 | 5.6 | 5.8 | 6.1 | 15.2 | 15.8 |
| | MP2/6-31G** | 0[e] | 4.4 | 2.6 | 16.2 | 13.8 | 14.0 | 25.7 | 27.5 |
| | MP3/6-31G** | 0[f] | 3.9 | 1.0 | 9.8 | 9.9 | 9.9 | 21.4 | 22.5 |
| | CASSCF/4-31G* | 0[g] | | 2.4<br>(1.9)[h] | | | | | |
| $HNO_2$ | RHF/4-31G[b] | 76.6 | | | | | | | |
| | RHF/4-31G* | 94.1 | 99.5 | 14.4 | 87.9 | 0[i] | 1.6 | 78.7 | 78.8 |
| | RHF/6-31G** | 95.5 | 100.8 | 15.7 | 89.7 | 0[j] | 1.4 | 79.0 | 78.9 |
| | MP2/6-31G** | 85.1 | 86.9 | 6.1 | 83.8 | 0[k] | 1.4 | 74.0 | 65.8 |
| | MP3/6-31G** | 86.6 | 89.4 | 11.6 | 81.1 | 0[l] | 1.0 | 73.3 | 67.6 |
| | CASSCF/4-31G* | | | 8.9<br>(8.2)[h] | | 0[m] | | | |

[a] At RHF/4-31G* optimized geometries, unless otherwise noted. [b] At RHF/4-31G optimized geometry. [c] −849.1059 hartrees. [d] −849.9742 hartrees. [e] −850.4077 hartrees. [f] −850.4196 hartrees. [g] −849.1436 hartrees. [h] At CASSCF/4-31G* optimized geometires. See section VII. [i] −204.4461 hartrees. [j] −204.6461 hartrees. [k] −205.1704 hartrees. [l] −205.1667 hartrees. [m] −204.4847 hartrees.

Å, 131.7°, and 121.9°, respectively. Although the reason for the deviation in the N=S bond length is not clear at present, it is likely to be a consequence of the influence of the crystalline structure, considering the facts: (i) the optimizations of HNSS ($A_S$) with larger basis sets still give 1.510 Å (6-31G**) and 1.517 Å (D95**)[28] and (ii) the optimization of *cis*-$CH_3NSS$ (at the 4-31G* level) for a check of effect of replacing H by $CH_3$ again gives 1.508 Å. Of three *N*-thiosulfinylamines **5b**, **7**, and **8** for which geometrical information is available, **5b** is considered to have the most unperturbed features of the N=S=S compound, since the presence of a sulfur atom adjacent to the N=S=S group in **7** and **8** should enhance the contribution of the following polarized structures, causing elongation of the N=S and S=S bonds and decrease of the N—S—S angle.

$$—S—N=S=S \leftrightarrow —S^{+}=N—S^{-}=S \leftrightarrow —S^{+}=N—S—S^{-}$$

In order to see the effect of the d polarization function, which is already well know,[29] we have also carried out optimization without the d function (the 4-31G basis), and the optimized structures are shown as $A'_S$ and $B'_S$ in Table I. Without a d function, the S=S and the N—S bonds become too long by 0.28 and 0.08 Å, respectively, and the NSS angle becomes too small by 7°, in comparison with the results with the d function. The polarization d function is essential in describing both S=S and N=S bonds.

**B. Nitro Compounds and Nitrites.** As shown in Tables II and III, the calculated geometrical parameters on the whole are in acceptable agreement with experimental values. First, for the hitherto unknown nitro compound $C_O$, the calculated geometry was compared with the experiments for nitromethane[30] and nitrobenzene[31] (Table II). The calculated NO distance (1.185 Å), shorter than the experimental values 1.22 and 1.21 Å, can be attributed to the deficiency of a single determinant, as will be discussed later.

As to the nitrites ($E_O$ and $F_O$), our results are compared with other theoretical and experimental results as well as with those of methyl nitrite (Table III). An improvement of the basis set from 3-21G through D95** makes the N—O and the N=O distances shorter.[33] The bond angle ONO is reproduced well with

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(28) See also Stromberg, A.; Wahlgren, V.; Pettersson, L.; Siegbahn, P.E.M. *Chem. Phys.* **1984**, *89*, 323. Following their analysis, we have carried out the geometry optimization for $A_S$ at the HF/D95 level augmented with one p function on H (same as D95**) and with two d functions ($\zeta$ = 2.12 and 0.67), as their analysis indicates that these two d functions are most effective in improving bond distances. The results are 1.496 Å for NS, 1.890 Å for SS, 117.4° for HNS, and 118.6° for SSN. The calculated N=S distance is even shorter than those in Table I.

(29) (a) For example, Magnusson, E. *J. Comput. Chem.* **1984**, *5*, 612 and references therein. (b) Cruickshank, D. W. J.; Eisenstein, M. *J. Mol. Struct.* **1985**, *130*, 143.

(30) Trevino, S. F.; Prince, E.; Hubbard, C. R. *J. Chem. Phys.* **1980**, *73*, 2996.

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(32) McKee, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1900.

(33) Baird, N. C.; Taylor, K. F. *Chem. Phys. Lett.* **1981**, *80*, 83.

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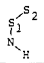
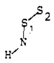
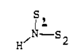
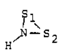
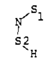
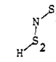
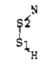
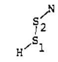
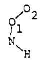
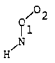
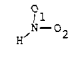
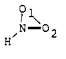
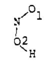
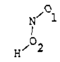
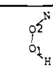
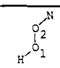
**Table V.** Mulliken Gross d Orbital Population[a]

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| |  |  |  |  |  |  |  |  |
| N | 0.036 | 0.036 | 0.084 | 0.056 | 0.065 | 0.064 | 0.031 | 0.032 |
| $S_1$ | 0.250 | 0.251 | 0.086 | 0.119 | 0.105 | 0.105 | 0.084 | 0.087 |
| $S_2$ | 0.074 | 0.074 | 0.086 | 0.119 | 0.128 | 0.122 | 0.202 | 0.203 |
| |  |  |  |  |  |  |  |  |
| N | 0.073 | 0.071 | 0.196 | 0.094 | 0.149 | 0.130 | 0.060 | 0.064 |
| $O_1$ | 0.135 | 0.141 | 0.058 | 0.090 | 0.064 | 0.084 | 0.060 | 0.050 |
| $O_2$ | 0.055 | 0.059 | 0.058 | 0.090 | 0.065 | 0.063 | 0.118 | 0.113 |

[a] $q = d_{xx} + d_{yy} + d_{zz} + d_{xy} + d_{yz} + d_{xz}$ at the HF/6-31G** level.

any split-valence or better basis set. For better reproduction of the HON angle, the polarization function is important, and even the best HF calculation seems to give a consistent deviation (~2°) from the experimental value. A calculation at the HF/4-21G level for methyl nitrite again suggests the need of a d function for a better reproduction of the CON angle.[37]

## IV. Relative Stability

The energetics at various levels of calculation for the HF/4-31G* optimized structures of $HNS_2$ and $HNO_2$ isomers are shown in Table IV. Among the calculated isomers of $HNS_2$, only $A_S$- and $B_S$-type isomers are known experimentally,[38] where the H atom is replaced by a bulky aryl or alkyl group.[4] Our theoretical prediction at the highest level of calculation (MP3), however, suggests the possibility that other isomers may exist within a reasonable energy range (less than 23 kcal/mol). Since we have not determined the barrier height for isomerization, decomposition or coupling (except isomerization between $A_S$ and $B_S$ which will be discussed later), we cannot say much about their kinetic stability.

This possibility of vast variety of isomers for $HNS_2$ contrasts with the limited number of stable isomers in $HNO_2$. For instance, $A_O$ and $B_O$ are higher in energy than $E_O$ or $F_O$ by more than 85 kcal/mol. Practically only $E_O$, $F_O$, and $C_O$ are reasonably considered as thermodynamically stable species, which is in accordance with the experimental fact that only nitrites and nitro compounds are known. Our result that the nitrite is more stable than the nitro compound is in agreement with the observation that thermolysis of nitromethane gives methyl nitrite.[21b]

These differences between oxygen and sulfur compounds can be attributed in part to the difference in the electronegativity between oxygen and sulfur and in part to the hypervalent capacity of the sulfur atom. It should be noted in Table IV that calculations either with or without d functions predict that A and E are relatively close in energy in $HNS_2$ compared with those in $HNO_2$. However, the prediction of the correct order, $A_S$ being more stable than $E_S$, requires the polarization function. In A or B, for example, the inner sulfur atom is formally tetravalent (see Figure 2), which can be easily achieved with the hypervalency; in the oxygen analogues, however, this is possible only via resonance of two forms, probably with high energy or as biradical species,[22] which explains the stability of $A_S$ or $B_S$ compared to $A_O$ or $B_O$.

Though there are several proposals as to the quantitative definition of hypervalency,[39] here we consider it simply as the availability of d orbitals and use the Mulliken population on d orbitals as its measure. As is shown in Table V, the inner sulfur atom in $A_S$ and $B_S$ has a larger d population, 0.250 and 0.251, respectively, than the oxygen atom in $A_O$ and $B_O$, 0.135 and 0.141, respectively. Similarly the fact that $G_S$ and $H_S$ are relatively more stable than $G_O$ and $H_O$, as referenced to the most stable isomers ($A_S$ and $E_O$), respectively, can also be attributed to the contribution of the d orbitals of the sulfur atom bonded to N.

**Table VI.** Energy Differences (kcal mol$^{-1}$)[a] between *E* and *Z* Isomers Calculated with MP3/6-31G**[b]

| compd | B-A | F-E | H-G |
|---|---|---|---|
| $HNS_2$ | 3.82 | -0.07 | 0.94 |
| $HNO_2$ | 2.93 | 0.92 | -6.33 |

[a] $E_E - E_Z$. [b] The zero-point energy correction is included, based on the HF/4-31G* vibrational frequencies.

It is interesting, as shown in Table VI, that a *Z* isomer is often more stable than the corresponding *E* isomer, except for the two cases where the $G_O$–$H_O$ pair distinctly and the $E_S$–$F_S$ pair very slightly deviate from the trend. Among the values in Table VI, experimental results are available for the two $A_S$–$B_S$ and $E_O$–$F_O$ pairs. The preference of $A_S$ over $B_S$ is consistent with our recent experiments for the related compound **5b**. On the other hand, for the nitrous acid isomers $E_O$ and $F_O$, our theoretical result shows that the *Z* isomer is slightly more stable than the *E* isomer by 0.9 kcal/mol at the MP3/6-31G**//HF/4-31G* level. This is in disagreement with the recent experimental results,[40] where the *E* isomer is more stable by about 0.4 kcal/mol. Though there exist some previous calculations which support the more stable *E* isomer such as those with a small STO-3G basis set,[41] or with the 4-31G[34a] (without a d function), other calculations using larger basis sets[35] predict the more stable *Z* isomer.[42] In order to resolve this discrepancy, we carried out calculations up to the MP4 level at the HF/6-31G** and the HF/D95** optimized geometries, for $E_O$ and $F_O$ as well as $A_S$ and $B_S$. The results are shown in Table VII. While the results for HNSS are in agreement with experiment and the calculations in Table VI, for HONO at all the levels of calculation the *Z* isomer is more stable than the *E* isomer, consistent with results in Table VI but in disagreement with experiment. We might suspect that there might be some room about the reliability of the experimental results, as was also pointed out by Nguyen.[34a]

In an attempt to find a simple explanation for the geometrical preference for the *Z* isomer over the *E* isomer, we examined such effects as the lone pair–lone pair[43] and the lone pair–bond interactions, the steric interaction (exchange interaction), and the electrostatic interaction, based on the localized orbital[44] or the energy decomposition method.[45] No simpler clearcut explanation

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(38) Although derivatives of isomer $B_S$ have not been known as a stable, isolable compound, we have recently observed photochemical formation of (*Z*)-**5b** at low temperatures.[5]

(39) Mayer, I. *Int. J. Quantum Chem.* **1986**, *10*, 477.

(40) (a) Varma, R.; Curl, R. F. *J. Phys. Chem.* **1976**, *80*, 402. (b) McGraw, G. E.; Bernit, D. L.; Hisatsune, I. C. *J. Chem. Phys.* **1966**, *45*, 1392. (c) Shirk, A. E.; Shirk, J. S. *Chem. Phys. Lett.* **1983**, *97*, 549.

(41) Dargelos, A.; El Ouadi, S.; Chaillet, M.; Elguero, J.; Liotard, D. *Chem. Phys. Lett.* **1977**, *51*, 545.

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**Table VII.** Total Energy of $Z$ Isomers (in Hartrees) and the Energy Difference $E_E - E_Z$ (in kcal $mol^{-1}$)

| | | HNSS | | HONO | |
|---|---|---|---|---|---|
| optimization | energy | $E_Z$ | $E_E - E_Z$ | $E_Z$ | $E_E - E_Z$ |
| HF/6-31G** | HF/6-31G** | -849.9742 | 4.21 | -204.6462 | 1.35 |
| | MP2/6-31G** | -850.4079 | 4.53 | -205.1704 | 1.44 |
| | MP3/6-31G** | -850.4197 | 3.97 | -205.1667 | 0.97 |
| | MP4(SDQ)/6-31G** | -850.4285 | 4.45 | -205.1796 | 1.26 |
| HF/D95** | HF/D95** | -849.9828 | 4.03 | -204.6962 | 1.02 |
| | MP2/D95** | -850.4287 | 4.25 | -205.2135 | 1.04 |
| | MP3/D95** | -850.4402 | 3.69 | -205.2108 | 0.62 |
| | MP4(SDQ)/D95** | -850.4480 | 4.13 | -205.2239 | 0.93 |

**Table VIII.** Mulliken Net Charge on H and Terminal Atom X of Z Isomers with HF/4-31G*

| | | A | E | G |
|---|---|---|---|---|
| $HNS_2$ | H | +0.324 | +0.048 | +0.095 |
| | X | -0.347 | -0.483 | -0.419 |
| $HNO_2$ | H | +0.318 | +0.349 | +0.341 |
| | X | -0.405 | -0.337 | +0.030 |

**Table IX.** Energy of the Transition State for $E$–$Z$ Isomerization (in kcal $mol^{-1}$ Relative to $A_S$ and $E_O$)

| method for energy[a] | $A_S \rightarrow B_S$ | $E_O \rightarrow F_O$ |
|---|---|---|
| HF/4-31G* | 25.1 | 12.8 |
| HF/6-31G** | 24.6 | 12.5 |
| MP2/6-31G** | 26.1 | 14.3 |
| MP3/6-31G** | 26.1 | 12.6 |

[a] Structure determined at the HF/4-31G* level.

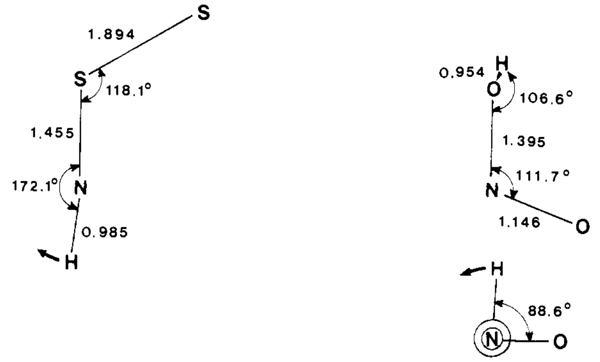

**Figure 4.** Structures (in Å and deg) of the transition structure between $A_S$ and $B_S$ (left) and $E_O$ and $F_O$ (right). The arrows indicate the approximate direction of the reaction coordinate, i.e., the normal coordinate with an imaginary frequency, at the transition state.

**Table X.** Assignment of HF/4-31G* Calculated (Scaled) and Experimental Vibrational Frequencies ($cm^{-1}$)

| ($Z$)-HONO | | ($E$)-HONO | | ($Z$)-RNSS | | ($E$)-HNSS |
|---|---|---|---|---|---|---|
| | | | | R = H | R = $CH_3$ | |
| calcd[a] | exptl[b] | calcd[a] | exptl[b] | calcd[a] | calcd[a] | calcd[a] |
| 670 | 638.5 | 530 | 543.0 | 340 | 200 | 360 |
| torsion | torsion | torsion | torsion | wSSN | wSSN + wSNR | wSSN |
| 700 | 609.0 | 700 | 595.6 | 630 | 620 | 640 |
| wONO | wONO | wONO | wONO | nSS | nSS | nSS |
| 1030 | 851.9 | 970 | 790.1 | 770 | 340 | 700 |
| nO—N | nO—N | nO—N | nO—N | torsion | NS torsion | torsion |
| 1370 | | 1350 | 1263.2 | 1060 | 480 | 1080 |
| wHON | | wHON | wHON | wSNH | wSNR − wSSN | wSNH |
| 1770 | 1640.5 | 1820 | 1699.8 | 1140 | 1240 | 1120 |
| nN=O | nN=O | nN=O | nN=O | nNS | nNS | nNS |
| 3490 | 3426.2 | 3620 | 3590.7 | 3310 | 860 | 3300 |
| nOH | nOH | nOH | nOH | nNH | nCN | nNH |

[a] A uniform scale factor of 0.89 is used. [b] Reference 49a.

was found than Müller[46] and Farnell[34b] mentioned. We show only the results of net charge obtained by Mulliken population analysis in Table VIII, where every case except for $G_O$ indicates that there should be an electrostatic attraction between H and the terminal atom. This is consistent with the fact that the $Z$ isomer is more stable than the $E$ isomer in all cases, except for $G_O$ at the HF/4-31G* level, although at the MP3/6-31G** level this order is reversed slightly for $E_S$. We can say that the electrostatic attraction between the terminal atoms should play an important, if not exclusive, role in determining the relative stability of $Z$ and $E$ isomers.[47] The replacement of the terminal H by an alkyl or aromatic group probably would further obscure the decisive factor.

## V. *Z* and *E* Isomerization

We have determined, with the analytical energy gradient method, transition states for isomerization of the $Z$ and the $E$ isomers between the most stable isomers, $E_O$ and $F_O$ for $HNO_2$ and $A_S$ and $B_S$ for $HNS_2$. The geometries of the transition states optimized at the HF/4-31G* level are shown in Figure 4, and their energies at various levels of calculation are given in Table IX.

Between $A_S$ and $B_S$, the transition state we found represents an in-plane inversion of the HNS bending mode. Its barrier height, 26 kcal/mol relative to the more stable $Z$ isomer $A_S$, is quite high. An extensive search for other paths such as the N–S rotation or the inversion at the S atom gave rather high energies and did not result in any transition state. We may say that no other easily accessible transition state exists for unimolecular isomerization of $A_S$. Experimentally we have observed the thermal isomerization of ($E$)-**5b** to ($Z$)-**5b** at a low temperature, 150 K. The source of this discrepancy is not clear at present. A possibility of a bimolecular or catalyzed process may be suggested.

For the isomerization of nitrous acids $E_O$ and $F_O$, a transition state has been located along the N–O internal rotation mode (Figure 4). The calculated MP3/6-31G** barrier height of 12.6 kcal/mol agrees quite well with the experimental value of 11.6 kcal/mol determined as a torsional barrier by microwave technique.[40b] A "transition state" found along the HON inversion mode has two imaginary frequencies and is not a true transition state.

## VI. Vibrational Frequencies

The HF/4-31G* harmonic vibrational frequencies have been calculated at the optimized geometries. Calculated normal frequencies shown in Table X, together with known related experimental fundamental frequencies, have been scaled by a uniform scale factor of 0.89, as proposed by DeFrees and McLean[48] so as to give a best overall fit at this level of calculation. Experimentally assigned values[40b,49] are available for the ($Z$)- and ($E$)-nitrous acids ($E_O$ and $F_O$). Our scaled frequencies and their assignments are in reasonable agreement with them, except for

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(46) Modduller, R. P.; Monellar, M.; Russegger, P.; Huber, J. R. *Chem. Phys.* **1984**, *87*, 351.

(47) A similar electrostatic interaction has been invoked to explain the higher stability of $E$ isomer vs. $Z$ isomer of inorganic anion $^{-}S_2$—N=S=S: Gleiter, R.; Bartetzko, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36b*, 492. Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1980**, *102*, 5773.

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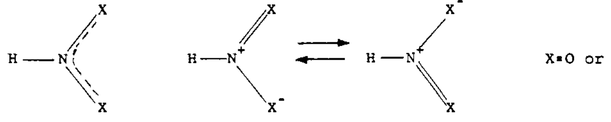
N–O stretching where the scaled value is still a substantial overestimate, which is probably related to a too short N–O distance, a deficiency of the present calculation.

Though infrared spectra of various *N*-thiosulfinylanilines have been reported,[50] no assignment of vibrational frequencies has been made. For instance, we have presented IR spectra for *N*-thiosulfinyl-2,4-di-*tert*-butyl-6-methylaniline (**5b**).[3a,5] Here we report our theoretical assignments of normal frequencies for model compounds HNSS ($A_S$ and $B_S$) and $CH_3NSS$ (Table X). Based on these results, we propose a possible assignment of vibrational spectra of **5b**, which are complicated because of a large substituent. The SS stretching may be assigned to the experimental 620- or 695-cm$^{-1}$ band, which is comparable with 718-, 697-, and 693-cm$^{-1}$ bands for $SSF_2$,[51] $SSCl_2$,[52] and SSBr,[52] respectively, and with 672 cm$^{-1}$ for $S_2O$.[53] The NS stretching may possibly be assigned to one of experimental 1275- and 1227-cm$^{-1}$ bands, similar to the experimental values for related compounds such as Ph–NSO[54] (1284 cm$^{-1}$), $CH_3NSNCH_3$[54] (1218 cm$^{-1}$), $CH_3NSO$[55] (1252 cm$^{-1}$), and others.[56] Though the CN stretching 860-cm$^{-1}$ band of $CH_3NSS$ corresponds well to the experimental 830-cm$^{-1}$ band in $CH_3NSO$,[55] the substitution of $CH_3$ by $C_6H_5$ (1299 cm$^{-1}$ in pH–NSO[54]) prevents us from proposing an assignment for the CN stretching band in **5b**, except for suggesting one of the 1275- and 1381-cm$^{-1}$ bands as a candidate in comparison with Ph–NSO. The lower frequency bands (480, 340, and 200 cm$^{-1}$) calculated for $CH_3NSS$ would be further shifted to lower frequencies by substitution of $CH_3$ by a substituted phenyl, and therefore any of experimental 400-, 440-, and 480-, and 525-cm$^{-1}$ bands observed in **5b** is a candidate for the SSN and SNR bending modes and the torsion around the SN bond.

## VII. Quality of the One-Determinant Description for Nitro and Thionitro Compounds

Several authors have noted[57] that a reasonable description of the ground state of nitromethane and other simple nitro compounds requires a multiconfigurational wave function and a basis set of at least double-$\zeta$ quality. For example, a biradical character of nitromethane has been suggested by a recent theoretical study.[57b] This problem is related to ozone, studied with the GVB method by Hay et al.,[58] which also is a three-center 4$\pi$-electron system.

In order to obtain a better description of the wave function for $HNO_2$ $C_O$ and $HNS_2$ $C_S$ (which again has a three-center 4$\pi$-electron system), we have carried out a CASSCF[10] energy gradient calculation taking these four electrons in three $\pi$ orbitals as the active space at the 4-31G* level. The geometry optimization should show whether there is one minimum (I) or two minima (II) in the potential energy surface of the ground state. Starting from a nonsymmetric structure, the CASSCF geometry optimization gave the symmetric geometry (I), for both nitro and dithionitro compounds, as in the HF optimization. We may now reasonably say both compounds have a symmetric equilibrium structure corresponding to the representation I.



I

II

**Table XI.** Optimized Geometry of $C_S$ and $C_O$ at the CASSCF/4-31G* Level

| | | XN (Å) | XNX (deg) | HN (Å) |
|---|---|---|---|---|
| $HNS_2$ | $C_S$ | 1.628 | 130.6 | 1.006 |
| $HNO_2$ | $C_O$ | 1.201 | 127.5 | 1.013 |

**Table XII.** CASSCF Natural Orbital Occupation Numbers

| | $A_S$[a] | $C_S$[a] | $C_S^{OPT}$[b] | $A_O$[a] | $C_O$[a] | $C_O^{OPT}$[b] |
|---|---|---|---|---|---|---|
| $1_\pi$ | 1.993 | 1.990 | 1.990 | 1.999 | 1.988 | 1.988 |
| $2_\pi$ | 1.857 | 1.728 | 1.712 | 1.917 | 1.893 | 1.883 |
| $3_{\pi*}$ | 0.150 | 0.282 | 0.298 | 0.084 | 0.118 | 0.129 |

[a] CASSCF natural orbitals at the HF/4-31G* optimized geometry. [b] CASSCF natural orbitals at the CASSCF/4-31G* optimized geometry.

In Table XI we show the geometries optimized with the CASSCF gradient. The N–O bond distance, 1.201 Å, is improved from the HF/4-31G* level of 1.185 Å (see Table II). Although we do not know the experimental NS distance, the CASSCF value 1.628 Å is also substantially larger than the HF/4-31G* value of 1.608 Å. These trends can be accounted for by the occupation number of the $\pi^*$ orbital which was vacant at the HF level. The occupation numbers of the natural orbitals obtained by CASSCF are shown in Table XII, for $C_O$ and $C_S$ as well as for $A_S$ and $A_O$ for comparison. These values indicate that the multiconfigurational description is more important in C than in A, and in the sulfur analogues than in the corresponding oxygen analogues.

The relative energies calculated at the CASSCF/4-31G* level are shown in Table IV. As expected from the MP results in Table IV, the CASSCF relative energies of $C_S$ and $C_O$, with respect to the most stable isomers, $A_S$ and $E_O$, are substantially lower than the HF energies.

## VIII. Concluding Remarks

A systematic comparison for the geometry and stability of many possible isomers of $HNO_2$ and $HNS_2$ has been carried out. The geometry optimization at the HF/4-31G* level and the energetics at the MP3/6-31G** level show for $HNS_2$ that, although *N*-thiosulfinylamine, H—N═S═S, is the most stable, several other isomers may exist within a reasonable energy range. This suggests a wider variety of chemistry of $RNS_2$ than is known, in which only *N*-thiosulfinylamines are established. For $HNO_2$, only the nitrous acid H—O—N═O and the nitro compound H—N(┅O)$_2$ are reasonably considered as thermodynamically stable. This difference of sulfur compounds compared with the oxygen analogues has been attributed to the availability of sulfur d orbitals for facile hypervalency. Though the preferred stability of *Z* isomers relative to *E* isomers has been examined in several ways, no simple explanation has been established, except that the electrostatic contribution is suggested. The geometrical structures of the transition states for *Z–E* isomerization (the rotation in HONO and the inversion in HNSS) have been determined and their barriers are found to be relatively high. Vibvrational spectra have been calculated for some isomers and a tentative assignment of experimental spectra has been made.

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