A Theoretical Investigation of the Structure of some Small Nitrogen–Sulphur Molecules

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The structure of the nitrogen–sulphur compounds NSF, HSN, N_2S, N_2S_2, and H_3NS has been investigated using the L.C.A.O.M.O. *ab initio* method and a moderately large basis set. The compound NSF is found to be more stable than SNF in agreement with experiment, HNS is predicted to be more stable than HSN, NNS (linear) is more stable than NSN, and the order of stability of the isomers of H_3NS is predicted to be $H_2SNH < H_3SN < HSNH_2 < SNH_3$. The compound N_2S_2 is shown to be square planar in agreement with recent experimental evidence.

THE chemistry of nitrogen–sulphur compounds has attracted much recent interest[1] but there are still several species whose structures are not fully characterised. Surprisingly, there have been few *ab initio* molecular-orbital studies of such compounds, although this technique is known to accurately predict the structures and geometries for small molecules if sufficient care is taken with the choice of basis set. In this study we have investigated a number of small molecules containing N–S bonds. The structure of NSF has now been assigned unambiguously,[2,3] but HSN or HNS is so far unknown. The compound N_2S was prepared[4] only after our calculation had been completed and initial structural data have now been published.[4] Similarly, little is known of the possible isomers of H_3NS. The geometry of N_2S_2 in its adduct with $SbCl_5$ has been determined,[5] but recently this has been shown to be different from the free molecule.[6] Our objective has been to study the geometry of these systems using a moderately large basis set of Gaussian orbitals in the usual L.C.A.O.M.O. *ab initio* technique. The role of *d* functions in predicting accurate geometries is found to be particularly important.

METHOD

The *ab initio* molecular-orbital method using a basis set of contracted Gaussian orbitals (g.t.o.s) was employed. The basis set was selected after extensive tests on H_2S and NSF and was a compromise between economy and accuracy. It is nevertheless moderately large and gives good optimised geometries. Calculations on H_2S reported elsewhere[7] and on NSF reported here indicate that the inclusion of *d* orbitals on sulphur is crucially important in predicting accurate geometries, even though the effect of these orbitals on the variational energy may be small. For economy we used single-zeta contractions for the core orbitals and double-zeta contractions for the valence orbitals. This results in energies somewhat above those reported elsewhere. Total energy is not necessarily a good measure of the accuracy of a wavefunction. Improvements in the prescriptions of the core orbitals, especially the nuclear cusps, leads to dramatic changes in the molecular energy without necessarily improving the representation of the valence regions of the molecule. The quality of the valence basis seems to be an important factor in describing bonding and obtaining optimal geometries. For NSF the following basis sets were contrasted.

SP.—This was the foundational set employed. It possessed Basch–Snyder[8] double-zeta functions for the valence orbitals of the light nuclei and Clementi–Reotti[9] STO-3G double-zeta representations for the sulphur orbitals. Clementi–Raimondi[10] STO-3G single-zeta formulations were used for all the core orbitals.

SPP′.—The sulphur *p* space was improved by the addition of an optimal *p* STO-3G function.

SPP′P″.—The nitrogen *p* space was further improved (with respect to SPP′) by the incorporation of an optimal 3*p* STO-3G orbital.

SPD.—Initially, an optimised STO-1G (exponent 1.2) *d* orbital was added to the SP set. Further *d* functions were subsequently added to produce SPDD′ and SPDD′D″ sets.

Results of optimising the N–S bond length and NSF bond angle are shown in the Table. Bond lengths and bond angles at the lowest energy are accurate to 0.005 Bohr ‡ and 0.5° respectively. It is clear that only basis sets containing a *d* function give results close to the experimental ones. The importance of *d* orbitals, both for predicting accurate bond lengths and angles as well as gross structural features, has been recently discussed by several workers (see ref. 7 and refs. therein). For further work the basis set SP was used as above for S, F, and N with the P″ improvement of the N *p* space but without the extra S *p* function. This was augmented by an optimum (for NSF) STO-1G *d* orbital on S, although the results are very insensitive to the actual value of the *d*-orbital exponent. For hydrogen a

Nitrogen–sulphur bond length and bond angle in NSF as a function of the choice of basis set

Basis	Total energy (Hartree)	N–S Distance (Bohr)	N–S–F Angle (°)
SP	−544.898 2	3.23	108
SPP′	−545.092 8	3.13	108
SPP′P″	−545.153 6	3.13	109
SPD	−545.086 1	2.88	113
SPDD′	−545.143 9	2.83	116
SPDD′D″	−545.172 5	2.78	116
Experiment		2.75	116.77

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‡ Throughout this paper: 1 Bohr ≈ 5.29×10^{-11} m; 1 Hartree ≈ 2.62×10^{3} kJ mol^{-1}; 1 D ≈ 3.33×10^{-30} C m.

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Basch–Snyder double-zeta basis plus a STO-1G $2p$ polarisation function (exponent 0.75) was employed.

For each molecule, different geometries and different isomers were studied. The results for the geometries are likely to be more accurate than those for the differences in energy between structural isomers. In each case accurate results are dependent on there being no change in correlation energy with change in geometry. From many recent calculations it appears that this assumption must be reasonably accurate. The use of the *ab initio* molecular-orbital method for predicting structural isomers is now widespread. At worst, it gives encouragement to experimentalists to study a particular system and at best it gives very accurate predictions. It gives better estimates of energy differences for systems having the same number of electron pairs than it does for binding energies or bond-breaking processes.

RESULTS AND DISCUSSION

Thionitrosyl Fluoride, NSF.—Although this molecule is now well characterised,[2,3] it is interesting to note that when first investigated it was assigned as SNF rather than NSF.[11-13] A full geometry search was therefore carried out on both species with the following results (all distances are in Bohrs):

SNF	Calc.	NSF	Calc.	Expt.
S–N–F	120°	N–S–F	115°	116.46°
N–F	3.08	N–S	2.85	2.75
N–S	2.90	S–F	3.21	3.11

Mulliken charges		
F	−0.003 6	−0.004 2
N	0.011 7	−0.001 8
S	−0.008 1	0.006 0

The compound NSF is more stable than SNF by 0.011 2 Hartree. This, of course, is in contrast to the oxygen analogue, where ONF is more stable than NOF. In each case the electronegative fluorine atom is bonded to the more electropositive atom. In an *ab initio* calculation on ONF, Peslak *et al.*[14] found the energy difference to be 0.074 Hartree. The CNDO/2 method also predicts NSF as the most stable isomer although with a much exaggerated energy difference in comparison to the *ab initio* result. The CNDO/2 structure also has very short bonds (N–S 2.43 Bohr) even though the bond angle is accurate.

HNS *or* HSN.—This system is apparently unknown and it is therefore unclear whether the most favoured structure would be HSN or HNS. A full geometry search gives the following results:

HNS		HSN	
N–S	2.93	N–S	3.08
N–H	1.90	S–H	2.56
H–N–S	100°	H–N–S	104°

HNS is more stable than HSN by 0.040 8 Hartree. Similarly HNO is more stable than HON by 0.039 Hartree according to an *ab initio* calculation by Peslak *et al.*[14] As a ligand NS behaves differently to H than it does to F, and the energy difference is fairly substantial. There is no experimental support for this prediction, but there are some analogies. For example, in $N_4S_4F_4$ the fluorine is co-ordinated to sulphur, but in $N_4S_4H_4$ the hydrogen is attached to the nitrogen. In the first-row oxygen congeners the F or H atom is always bound to the nitrogen. Lithium, however, is thought to bond more favourably with the oxygen in LiON,[14] and a similar situation may exist[15] in the matrix-isolated metal tricarbonyls $[M(CO)_3]$ ($M = K$ or Cs). CNDO/2 disagrees with the *ab initio* prediction and favours HSN. However, the *ab initio* result seems to be a clear theoretical prediction and the experimental investigation of this system is awaited with interest.

Dinitrogen Sulphide.—The compound N_2S can be considered as a nitrogen atom bonded to NS and is thus similar to the previous systems. It was discovered during the course of our work by Powell[4] who has published initial structural data and is currently working on its structural refinement.[16] No other properties such as dipole moment, ionisation potential, *etc.*, are available. The following possible forms were considered; N(NS) linear and bent (analogous to N_2O) and N(SN) linear and bent similar to SO_2. The most favoured structure is NNS linear with N–N 2.13 Bohr and N–S 3.08 Bohr. The tentative experimental results agree well with this theoretical assignment giving N–N 2.15 Bohr and N–S 2.99 Bohr. The dipole moment is predicted to be 0.18 D and the Mulliken charges are:

$$\underset{-0{\cdot}0945}{N}\text{——}\underset{0{\cdot}0280}{N}\text{——}\underset{0{\cdot}0665}{S}$$

The N–S bond length is again overestimated but the experimental results are not certain.

Dinitrogen Disulphide.—Experimentally, the structure of this free species was not known before this computation was initiated, although the geometry of the adduct with $SbCl_5$ had been determined. Our results, which have appeared in a preliminary communication,[17] predict the molecule to be square planar with a N–S distance of 3.06 Bohr, in close agreement with the recent experimental result[6] of N–S 3.11 Bohr and N–S–N 89.58°, and in conflict with the results for the $SbCl_5$ adduct where the angle N–S–N was found to be 85°. CNDO/2 predicts a bond length of 3.23 Bohr and N–S–N 88°. A minimum basis-set (STO-3G) calculation has recently been reported[18] for N_2S_2 which gives an optimum N–S distance of 3.203 Bohr and N–S–N 86.5°. This result is in accordance with our conclusion that, without the inclusion of d functions on sulphur, the N–S distance will be overestimated. Neither the bond distance nor the angle is in good agreement with experiment.

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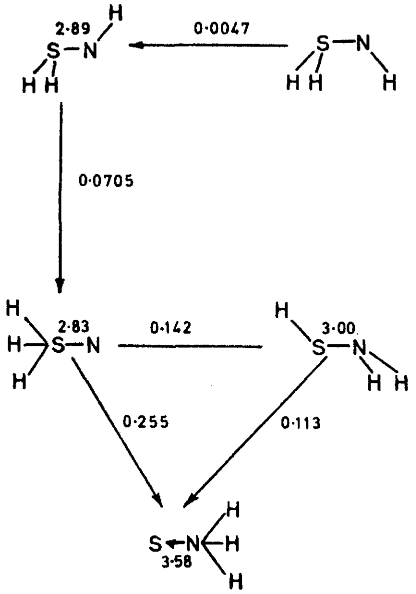
H_3SN, H_2SNH, $HSNH_2$, *and* SNH_3.—It was anticipated that the most favourable isomer of H_3SN would be H_2NSH analogous to $PH_2(SH)$.[19] It was only after completion of these calculations that we became aware that Kerouanton *et al.* [20] had synthesised and characterised H_3NS, which thus appears to be the most stable isomer. This indeed appears to be the most favourable system as shown in the Figure. The stability sequence $H_2SNH < H_3SN < HSNH_2 < SNH_3$ is not quite in accord with the trend for the siting of the protons, but the energy difference between the first two systems is very small. The tendency for the hydrogen atoms to be bonded to the more electronegative nitrogen of NS, noted for HSN, comes out strongly in this case.



Energy changes (Hartree) and optimal N–S distances (Bohr) for for various H_3NS isomers

Only the bond lengths were fully optimised. The angles were idealised for H_3SN and SNH_3 and the values of Mezey *et al.*[21] were used for sulphimide. For SNH_3 the bond lengths are predicted to be **3.58** and **1.91** Bohr for the N–S and N–H bonds respectively. The N–S distance is very long and, with the Mulliken densities, might be used as evidence that the bond is dative $H_3N \rightarrow S$. Mezey *et al.*[21] studied sulphimide using a split valence-shell basis which also described the cores very well. Although their energy is lower than ours, —**452.948 1** compared with —**449.648 1** Hartree, the inversion barriers are similar, **10.1** and **12.3** kJ mol^{-1}. Again we feel that our calculations provide a chemically significant structural prediction for a molecule where little experimental evidence is available.

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