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Ground-State Potential Surface of NSF. An ab Initio Study

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The ground-state potential surface of thiazyl fluoride (NSF) has been calculated with use of ab initio Hartree-Fock methods. Two minima corresponding to the structural isomers NSF and FNS are located. Their relative stability has been investigated by applying extended basis sets. An estimate of correlation effects is included and shows NSF to be more stable than FNS by 21 kcal mol⁻¹. The isomers are separated by a barrier of 29 kcal mol⁻¹ relative to NSF. A modified bond order-bond length relation of SN compounds is suggested.

Introduction

The structure of thiazyl fluoride (NSF) was subject to several experimental and theoretical investigations³ since it was first synthesized by Glemser, Schröder, and Haesler.⁴ Although its stoichiometry was clear from the beginning, its structural formula has been debated. The first structure proposed was SNF in analogy to nitrosyl fluoride, ONF.⁴⁻⁶ Its structure finally has been settled by microwave^{7,8} and infrared spectroscopy.⁹ The resulting geometrical parameters are $r(\text{NS}) = 1.448 \text{ \AA}$, $r(\text{SF}) = 1.643 \text{ \AA}$, and $\angle\text{NSF} = 116^\circ 55'$. Stabilized as a ligand in $[\text{Co}(\text{NSF})_6]^{2+}$, it has been investigated by X-ray analysis.¹⁰

The electronic structure of NSF has been discussed in connection with photoelectron spectra¹¹⁻¹⁵ which were interpreted by a vibrational analysis and in terms of semi-empirical¹¹⁻¹³ and ab initio Hartree-Fock models.^{14,15} The theoretical treatment implies three questions that will be discussed in this paper: (1) Does the isomer FNS exist as a thermally stable compound and what is its stability compared to that of NSF? (2) Are FNS and NSF the only isomers? (3) What role is played by higher order angular momentum functions?

The first question has been treated to some extent by So et al.¹⁶ and by Collins et al.,¹⁷ who carried out a geometry optimization on both species using Hartree-Fock theory and a minimal basis set that was augmented with d functions. Both calculations predicted NSF to be more stable than FNS by about 6 kcal mol⁻¹, but the calculated bond distances and

angles differed appreciably. Collins et al. obtained a shorter SN bond in NSF than in FNS whereas So et al. found the reversed order. Thus some more detailed theoretical investigations are certainly appropriate.

In order to obtain information about the structure of all possibly existing isomers and their relative stability and rearrangement paths, we investigated a sufficiently large section of the electronic potential surface of thiazyl fluoride. We used closed-shell Hartree-Fock techniques and allowed the free geometrical parameter to relax completely.

To contribute to the third question, we redetermined the stationary points on the potential surface, corresponding to NSF, FNS, and the saddle point, with an extended basis set containing d functions.

The influence of correlation effects has been included in terms of Møller-Plesset theory to second order.

Methods of Computation and Basis Sets

The computations were carried out with a GAUSSIAN system¹⁸ integrated on a Perkin-Elmer 8/32 using parallel processing techniques¹⁹ and a monitor comprising particularly the needs of quantum-chemical calculations. We applied the spin-restricted Hartree-Fock (RHF) version of the conserved-state method²⁰ to obtain converged results as close as possible to the given starting vector by quasi-continuous energy minimization. With use of a second-order energy variation procedure²¹ it was assured that this converged, i.e., stationary, Hartree-Fock energy corresponded to a minimum with respect to small changes of the wave function.

Each point of the potential surface, the setup of which will be described in the next section, was calculated with the split-valence 4-31G basis.²² The internal degree of freedom that was not determined as a parameter of the potential surface, i.e., the SN bond length, was optimized by the Fletcher-Powell-Davidon method.²³

In order to refine the parameters of distinguished points, we started from the graphically located stationary points of the potential surface. They were optimized by a full geometry search according to the methods of Fletcher, Powell, and Davidon²³ and McIver and Komornicki.²⁴ On these refined structures single-point calculations were carried out in order to evaluate a sufficiently flexible basis set including d functions. As criteria we used the Mulliken gross orbital population²⁵ and the energy lowering due to additional functions. The basis set finally chosen consisted for sulfur of the [12s 9p] set of Veillard²⁶ contracted to s(6,2,1,1,1,1) and p(5,1,1,1,1) and for nitrogen and fluorine of a [9s 5p] set of Huzinaga²⁷ contracted to s(5,1,1,1,1) and

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Table I. Calculated Total Energies (au)^a and Dipole Moments (D) of NSF, the Saddle Point, and FNS

geom optimizn	method/ basis set	NSF		saddle point		FNS	
		<i>E</i>	μ	<i>E</i>	μ	<i>E</i>	μ
RHF ^b	RHF ^b	-550.581 35	2.69	-550.485 94	5.90	-550.576 04	2.09
	RHF ^c	-551.326 18	2.68	-551.219 05	6.59	-551.291 72	1.99
	RHF ^d	-551.334 56	2.53	-551.226 82	6.42	-551.296 84	1.99
	RHF ^e	-551.331 96	2.58	-551.224 97	6.45	-551.295 06	2.01
	RMP2 ^b	-550.905 94		-550.883 20		-550.915 01	
RHF ^e	RHF ^e	-551.208 59	2.98	-551.125 57	6.90	-551.206 11	1.99
RHF ^f	RHF ^f	-551.349 44	2.31	-551.229 92	6.97	-551.301 89	1.67

^a 1 au = 627.53 kcal mol⁻¹. ^b 4-31G. ^c (12,9,1/9,5,1) (5d). ^d (12,9,2/9,5,1) (6d). ^e (12,9/9,5). ^f (12,9,2/9,5,1) (5d).

p(2,2,1). Two sets of five d functions were used for sulfur with exponents of 0.6 and 0.3 and one set of five d functions for fluorine and nitrogen with exponents of 1.62 and 0.95, respectively.²⁸ With this basis the atomic Hartree-Fock energies obtained were N(⁴S) = -54.39440 au, S(³P) = -397.48245 au, and F(²P) = -99.39470 au. These values should be compared to the estimated Hartree-Fock limits²⁹ of the three atoms (N = -54.40093 au, S = 397.50487 au, and F = -99.40933 au). As an examination of the completeness in the molecular environment each atomic basis was augmented with one more set of diffuse p functions with an exponent of one-third of each smallest atomic p exponent. This leads to an energy lowering of about 1.2 kcal mol⁻¹ for both isomers with no significant occupation of the additional functions. The test was repeated with larger p exponents about half of each smallest p exponent. The results obtained remained essentially the same. Thus we concluded that the s and p parts of the atomic basis sets were sufficiently flexible to describe the molecular environment adequately.

In a similar test the set of five d functions was replaced by a set of six d functions, which corresponds to the inclusion of an additional s function (RHF (12,9,2/9,5,1) (6d)) in Table I). An energy lowering in the same order of magnitude as before was observed, mainly for NSF. In this case the supplementary s function was occupied more strongly than in FNS.

A further expansion of the s and p sets gave no considerable improvement of the basis, thus the (12,9,2/9,5,1) set described above was used to reoptimize the minima and the saddle point of the potential surface (last entry in Table I).

For a given geometry the change from a smaller basis set to a more elaborate one was carried out by a least-squares technique projecting the converged wave function to the larger basis set. This projected and reorthogonalized wave function was then used as the new starting vector. In this way the conservation of a selected electronic configuration was ensured.

Electron correlation has been included by single-point calculations applying Møller-Plesset theory to second order³⁰ with the 4-31G basis set (RMP2/4-31G).

Results and Discussion

Potential Surface. The potential surface was spanned by a two-dimensional grid of points. For each point the nitrogen and sulfur atoms were arranged on the z axis with the origin bisecting the SN bond. The fluorine atom was placed in the x, z plane adopting positions in the range -1.75 ≤ z ≤ 1.75 Å and 1.25 ≤ x ≤ 2.35 Å.

The spacings between two subsequent sites of F were chosen as Δz = 0.5 Å and Δx = 0.275 Å, resulting in a lattice of 40 points. A contour plot of the interpolated potential surface is shown in Figure 1. It was constructed from the calculated values by a two-dimensional cubic spline fit data densifier.³¹

The potential surface shown in Figure 1 exhibits two minima corresponding to the structures NSF and FNS. One distinct path of isomerization connects the minima traversing a saddle point, which is located about halfway between the isomers. Along this path the relaxed SN bond length varies smoothly.

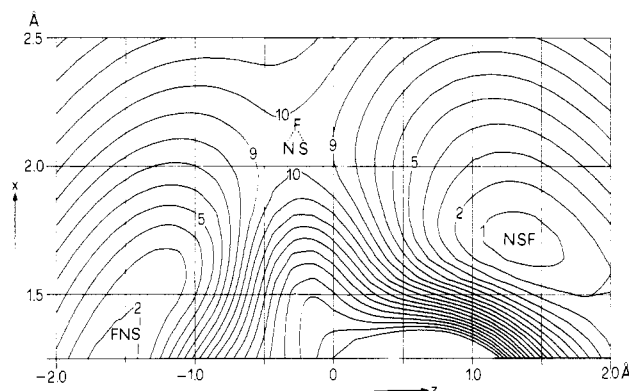


Figure 1. Split-valence potential surface of NSF with relaxed SN bond length. The energy difference between the contours amounts to 0.01 au; contour 1, -550.580 00 au. The contours 1, 2, 5, 9, and 10 are indicated separately. For the definition of x and z see text.

Table II

Calculated Total Energies (au) of NS ⁺ and F ⁻			
geom optimizn	method	NS ⁺	F ⁻
RHF/4-31G	RHF/4-31G	-450.976 49	-99.247 82
RHF/(12,9,2/9,5,1)	RHF/(12,9,2/9,5,1)	-451.587 83	-99.415 36

Optimized Bond Distances of NS ⁺			
RHF/4-31 G	1.445 Å	RHF/(12,9,2/9,5,1)	1.398 Å

At the 4-31G level NSF is found lower in energy than FNS by about 3 kcal mol⁻¹. The energy difference between the saddle point and NSF amounts to 60 kcal mol⁻¹.

In order to estimate a lower limit of the barrier of a possible decay channel to the fragments SN⁺ and F⁻, we calculated their energies and compared them with the lowest minimum NSF. The results obtained with different basis sets are listed in Table II. At the 4-31G level this barrier is found to be 224.1 kcal mol⁻¹ (9.7 eV) and 217.3 kcal mol⁻¹ (9.4 eV) with the (12,9,2/9,5,1) basis set. As anticipated these values lie below the appearance potential of 11.8 eV for the fragmentation of NSF to NS⁺ and F,³² where it is assumed that the products are in their vibronic ground state and possess no excess energy. For this process we obtain 9.9 eV using the (12,9,2/9,5,1) basis. Thus, under thermal conditions, isomerization seems to be considerably more likely than fragmentation.

To possibly simplify further potential surface investigations of similar small systems, we calculated a second potential surface with a fixed SN bond length of 1.5644 Å, the average of the 4-31G optimized values for NSF and FNS. Qualitatively this second surface resembled very much the optimized one with a deviation of at most 0.1 Å for minima and saddle point. However, a shortcoming should be noted: The region around FNS is predicted to be lower in energy than that

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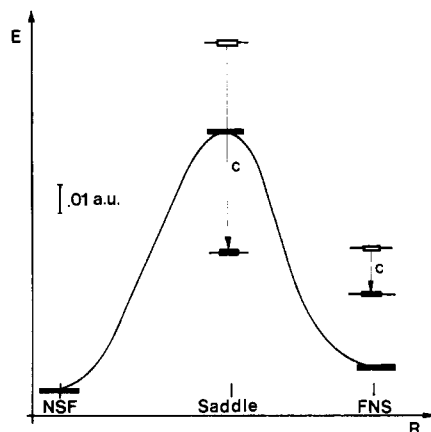


Figure 2. Energy profile along the path NSF, saddle point, FNS: (—) section through the 4-31G potential surface (Figure 1) along the path of isomerization, R; (—) stationary points on the potential surface; (---) stationary points calculated with the (12,9,2/9,5,1) basis. The energies are shifted that the value for NSF coincides with the 4-31G result; (---) correlation correction (c) included.

Table III. Population Analyses for NSF, the Saddle Point, and FNS

(a) Total Atomic Population						
	NSF		saddle point		FNS	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
N	7.474	7.375	7.257	7.030	7.146	7.012
S	15.000	15.197	15.160	15.290	15.551	15.786
F	9.526	9.428	9.583	9.680	9.303	9.202

(b) Total d Population ((12,9,2/9,5,1) Basis Set)			
	NSF	saddle point	FNS
N	0.037	0.044	0.067
S	0.375	0.176	0.117
F	0.005	0.005	0.008

^a 4-31G basis set. ^b (12,9,2/9,5,1) basis set.

around NSF. This result is opposite to the findings of the optimized surface. In the region of $z > 1.5 \text{ \AA}$ and $x > 2.0 \text{ \AA}$ some irregularities occurred which were not found on the smoother relaxed surface. Such disturbances, however, can be ascribed to the lack of a simple cubic spline fit to represent functions with strongly varying curvatures as they are found in boundary regions of the surface or in the region where fluorine gets close to N or S, causing a steep ascent of energy.

Minima and Saddle Point. The total energies of the three stationary points on the potential surface calculated with different basis sets and including electron correlation are listed in Table I. In Figure 2 we have shown the potential energy along the path of minimum energy between NSF and FNS for two different basis sets. At all levels of Hartree-Fock theory NSF is predicted to be more stable than FNS. The difference in energy between the two isomers, however, strongly depends on the quality of the basis set. With the less flexible 4-31G and (12,9/9,5) basis sets FNS lies about 3 kcal mol⁻¹ above NSF. The inclusion of d functions in the extended (12,9,2/9,5,1) basis set increases the difference to about 30 kcal mol⁻¹. This reflects the fact that the energy lowering due to d participation is not the same for both isomers. In going from the (12,9/9,5) to the (12,9,2/9,5,1) basis set, the total energy of NSF decreases by 0.1408 au whereas the predicted lowering for FNS and the saddle point is only 0.1044 and 0.0958 au, respectively. An explanation for these differences may be found by inspecting the total d population of the sulfur atoms for the three structures (see Table III). In NSF the sulfur d functions are populated with 0.38 electron (0.26 electron populate the first set of d functions and 0.12 electron

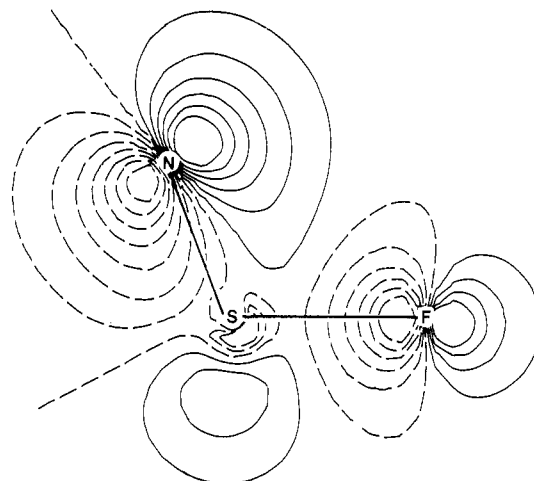


Figure 3. Canonical highest occupied molecular orbital (HOMO) of NSF.

Table IV. Activation Parameters of Isomerization (kcal mol⁻¹)

	NSF/ saddle point	FNS/ saddle point	NSF/ FNS
RMP2/4-31G	14.27	19.96	-5.69
RHF/(12,9,2/9,5,1) + estd correlation energy	29.40	8.58	20.82

the second one) while FNS and the saddle point only distribute 0.12 and 0.18 electron, respectively, to these functions.

A comparison of the canonical MO's of NSF and FNS shows that the SN σ bond is strengthened in both isomers by occupation of d functions in the 8a' orbital (and 11a' in FNS). Similarly the SN π in-plane bond of the 12a' orbital and the SN π out-of-plane bond of the 3a'' orbital are strengthened. The striking difference in d participation between the two isomers is found in the highest occupied orbital, 13a' (Figure 3). For NSF a strong p_x - d_x bond is predicted. The d_{xz} orbital of sulfur is contracted by the more electronegative neighbors, and thus the interaction with the lone pairs of F and N is intensified. In the case of FNS with its terminal sulfur such an interplay is not possible.

As anticipated the d functions of N and F do not play the same important role as the d functions of S. As shown in Table III the d functions of F and N are populated with at most 0.07 electron in all three structures.

Besides the inclusion of d functions on sulfur which is required for a reliable quantitative description of the relative stability of the isomers, the contribution of electron correlation has to be taken into account. We have applied second-order Møller-Plesset theory³⁰ to the 4-31G structures (RMP2/4-31G in Table I). At this level of theory the correlation energy is calculated to be 0.3246 au for NSF, 0.3390 au for FNS, and 0.3973 au for the saddle point. With application of these corrections FNS is predicted to be more stable by 5.7 kcal mol⁻¹ than NSF (Tables I and IV). However, it should be kept in mind that this result is based only on nonrelaxed single-point calculations. Assuming that the relative correlation effects do not change significantly, we corrected the total energies obtained with the (12,9,2/9,5,1) basis set. The activation parameters calculated for both basis sets mentioned are given in Table IV. The results for the (12,9,2/9,5,1) basis set together with the inclusion of correlation energy are presented in Figure 2. We obtain a saddle point 29 kcal mol⁻¹ above NSF and 9 kcal mol⁻¹ above FNS, while NSF is about 21 kcal mol⁻¹ more stable than FNS.

This would mean that it might be possible to make FNS accessible to experiment. The dipole moments of the three structures depending on the basis set are given in Table I. The

Table V. Optimized Geometric Parameters^a of NSF, the Saddle Point, and FNS

	NSF			saddle point			FNS		
	$r(\text{N-S})$	$r(\text{S-F})$	$\angle\text{NSF}$	$r(\text{N-S})$	$r(\text{S-F})$	$r(\text{N-F})$	$r(\text{N-S})$	$r(\text{N-F})$	$\angle\text{FNS}$
RHF/4-31G	1.541	1.720	108.0	1.469	2.235	2.078	1.588	1.413	112.3
RHF/(12,9/9,5)	1.541	1.758	107.4	1.472	2.304	2.128	1.588	1.408	113.1
RHF/(12,9,2/9,5,1)	1.432	1.634	112.9	1.413	2.318	2.063	1.528	1.347	113.4

^a Bond lengths in angstroms; angles in degrees.

experimental value for NSF⁶ calculated from the Stark effect is found to be 1.902 ± 0.012 D. The value of 2.31 D obtained with the (12,9,2/9,5,1) basis set is somewhat larger in agreement with other Hartree-Fock calculations on NSF.^{15,33} As anticipated the dipole moment was found to depend on the basis set approaching the experimental value as it becomes more flexible.

The geometries obtained for the three structures are listed in Table V. A comparison of the experimental values for NSF⁶ with the 4-31G and (12,9/9,5) results shows that the bond lengths are overestimated. The more flexible (12,9,2/9,5,1) basis, on the other hand, underestimates somewhat the experimental values. These results parallel the findings of Karpfen et al. in a study on S₂N₂.³⁴ The bond angle calculated with the 4-31G basis is underestimated by 9°, while it comes closer (4°) to the experimental value with the larger basis.

The contraction of bond lengths changing from the 4-31G and (12,9/9,5) basis to the (12,9,2/9,5,1) basis is also found for FNS and the saddle point. An exception is the weak SF bond of the saddle point. The SN bond in FNS and the saddle point is contracted by about 0.06 Å; in NSF this effect is nearly doubled (0.11 Å). This is certainly caused by a different extent of d participation, which has been discussed above, and conversely the SN contraction calculated may be considered as a measure of d participation. The contraction of the SF bond in NSF by about 0.09 Å is influenced by d effects as well. The same d function responsible for the SN p_x-d_x bond also serves to support the SF bond (Figure 3). For the saddle point, however, a similar p_x-d_x interaction is not present since the fluorine atom is bound only loosely to the SN moiety. The opening of the NSF bond angle from 108 to 113° (Table V) when going from the smaller to the larger basis can also be rationalized by the formation of the p_x-d_x bond. By an opening of the angle the 2p orbitals at S and N adopt a local symmetry with respect to S particularly suitable for d participation (see also Figure 3). In FNS there is no similar environment, and thus the bond angle opens up by 1° only when the basis set is changed.

Another aspect should be discussed comparing NSF and FNS with their "hypervalent" and "valent" sulfur atoms, respectively. It was proposed³⁵ that sulfur d orbitals may be expected to effectively participate in bonding when the attached atoms remove inner-shell density and thereby decrease the shielding of the nuclear charge. This led to the conclusion³⁶ that there is a parallel between the participation of d orbitals in a bond and the ionic character of a bond. It was shown in several examples by using bases with strongly contracted inner-shell regions, however, that the inclusion of d functions on sulfur decreases the ionic character of the SN bond in hypervalent molecules.³⁶

We find a decrease of the ionic character of the SN bond for both isomers by inclusion of d functions. This effect is even

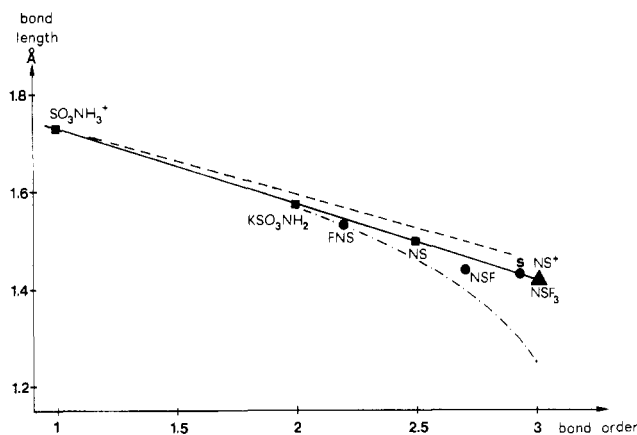


Figure 4. Correlation between bond order and bond length of the SN bond: (—) this publication; (---) ref 34; (····) ref 36 (■) values from ref 36; (▲) bond length from this publication and bond order from ref 36; (●) bond length from this publication).

more pronounced in FNS with its valent sulfur atom (see Table III). The decrease of ionic character does not seem to be a measure of d participation and is apparently not correlated with the valency of the sulfur atom. In order to elucidate the role of d functions, we optimized the structure of the three isomers with a basis set without d functions (12,9/9,5) using the same s and p contractions as for the basis set with d functions (12,9,2/9,5,1). The results are shown in Tables I and V. The geometries obtained with the (12,9/9,5) basis differ only slightly from the 4-31G results. This implies that d functions are important. For NSF a single-point calculation was carried out with replacement of the sulfur d functions in the (12,9,2/9,5,1) basis by s and p functions with the exponents of the d functions. This augmentation resulted in a minute energy lowering (0.007 au). The additional functions were nearly unoccupied. This supports our conclusion that the shortening of the SN bond together with the local symmetry around the sulfur atom as discussed above is a more reliable indication of d participation than the ionic character of a bond. The discrepancy between our findings in NSF and FNS and the examples given by others³⁶ may be explained by the different qualities of basis sets applied.

Bond Length-Bond Order Correlation. The strong variation of SN bond lengths going from NSF₃ (1.416 Å)⁷ to H₃NSO₃H (1.73 Å)³⁷ suggests that there exists a relationship between observed SN bond lengths and bond orders. Several correlations have been proposed.^{34,37-39} As shown in Table V the SN bond lengths obtained with the (12,9,2/9,5,1) basis differ also appreciably for NSF (1.432 Å), FNS (1.528 Å), and the saddle point (1.413 Å). To get an estimate of the SN bond orders using the bond length-bond order correlation of Chapman and Waddington,³⁷ we have to correct for our too-short SN distances. Assuming that the deviation from the experimental value in NSF remains the same for all three species, we may shift the calculated parameters by this dif-

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ference. This leads to the following values for the SN distance: FNS, 1.544 Å; saddle point (s in Figure 4), 1.429 Å. If we add the same correction to the calculated SN distance of NS⁺ (Table I), we obtain 1.414 Å. This latter value is considerably shorter than the value of 1.440 Å found for NS⁺ by Karpfen et al.³⁴ by CEPA calculations using a large basis set but close to the experimental value of 1.42 Å found in NS⁺Sb₂F₁₁⁻.⁴⁰ By application of the diagram of Karpfen et al. on NSF₃ with an experimental bond length of 1.416 Å^{5,10} a bond order of nearly 3.2 would be predicted.

If we modify the diagram of Chapman et al. according to our corrected bond length of 1.414 Å (which lies incidentally within the estimated error of 1–2% of CEPA calculations⁴¹), we obtain a bond order of 2.8 for NSF, of 2.15 for FNS, and of 2.9 for the saddle point. For NSF₃ a bond order of the SN bond of 3.0 is obtained (see Figure 4).

Using a larger set of crystal structure data, Nyburg proposed another bond length–bond order correlation diagram.³⁸ As in the diagram of Chapman et al. a bond distance of 1.25 Å for NS⁺ was taken as a basis corresponding to a bond order of 3.0. This leads, as already discussed, for NSF₃ to a bond order above 3.0. If we correct this diagram using our estimated bond length for NS⁺, SN bond orders in NSF, FNS, and the saddle point result that are somewhat below the values obtained by the modified Chapman correlation. Thus, in both

diagrams the deviation from linearity as well as the too-large bond order for NSF₃ can be corrected by biasing them with our proposed bond length for NS⁺.

Conclusions

Our calculations reveal that NSF, the isomer found experimentally, is more stable than FNS by 21 kcal mol⁻¹. The potential surface shows one saddle point on the path of isomerization at 29 kcal mol⁻¹ above NSF. The calculations furthermore reveal that the intramolecular isomerization FNS ⇌ NSF is energetically favored compared to fragmentation. For a quantitative description of the bonding properties, the inclusion of d functions on sulfur is required particularly in the case of NSF. A completely relaxed split-valence potential surface gives correct results with respect to the positions of the extrema and the relative stability of the isomers. An unrelaxed surface with fixed SN distances, however, describes only the positions of the extrema adequately.

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Supplementary Material Available: A listing of the calculated total energies as a function of the SN bond length (1 page). Ordering information is given on any current masthead page.

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