Geometries and Stabilities of NSF and SNF

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A theoretical consideration of the relative stabilities of the known molecule NSF and the unreported isomer SNF suggests that the latter is potentially stable.

Thiazyl fluoride NSF was first prepared by Glemser et al.[1] and characterized by its i.r. spectrum.[2]   Its microwave spectrum has been studied by Kirchhoff et al.,[3, 4] and the molecule shown by isotopic substitution to be bent in the ground state with sulphur as the central atom.

To the authors' knowledge, the SNF molecule is still unknown.   It is thus thought desirable to study theoretically the possibility of its existence and the relative stability of NSF and SNF.

Ab initio LCAO-MO SCF calculations were performed, as described earlier,[5] using minimal STO-3G basis functions augmented by sulphur $3d$ orbital with an exponent of 1.2.   Basis sets of similar size, in particular when augmented with $3d$ orbitals for the second row elements (e.g., P, S, Cl), have been well demonstrated [5-8] to give reasonably good molecular geometries.   The calculated geometries and energies of NSF and SNF are listed in table 1.

TABLE 1.—Geometries and energies of NSF and SNF

	NSF	SNF
r(N–S)/Å	1.548 (1.448)*	1.486
r(N–F)/Å	1.615 (1.643)	—
r(N–F)/Å	—	1.397
angle/deg	119.83 (116.92)	112.50
E_T/a.u.	−545.118 108	−545.028 284

* Expt. values are in parentheses.

NSF was calculated to be lower in energy than SNF by 2.44 eV without correlation corrections.   The prediction that NSF is more stable agrees with observation and is supported by considerations discussed below.   However, the present work also shows that SNF may be potentially stable molecule, the potential curves for bond-stretching going through a minimum.   In fact, it was found that stretching its bonds by 0.2 Å did not lead to bond-breaking.   (Root-mean-square amplitudes of internal vibrations of a molecule along internuclear distances are usually of the order of 0.05 Å at room temperature).

The overlap populations of NSF and SNF are shown in tables 2 and 3. If one assumes both σ and π bonds to be of equal strength, it is then seen that the N—S bond is a double and triple bond in SNF and NSF, respectively. The overlap populations of the N—F bond of SNF is significantly smaller than that of the S—F bond of NSF though the former bond is very much shorter. This is probably due to the larger difference in electronegativity of the S and F atoms (1.7) as compared with that of the N and F atoms (1.0) and the availability of empty $3d$ orbitals of the S atom to accept back donation of electrons from the F atom. Consequently, the S—F bond is stronger. One thus sees, in part at least, why NSF is more stable than SNF.

TABLE 2.—OVERLAP POPULATIONS OF NSF

		1s	2s	2pσ	2pπ	3s	3pσ	3pπ	3dσ	3dπ	Σσ	Σπ
N:	1s	0.000	0.000	0.000	0.000	0.001	−0.003	0.000	−0.004	0.000		
	2s	0.000	0.002	−0.002	0.000	−0.087	−0.035	0.000	0.031	0.000		
	2pσ	0.000	−0.008	−0.007	0.000	0.090	0.232	0.000	−0.026	0.000		
	2pπ	0.000	0.000	0.000	−0.002	0.000	0.000	0.185	0.000	0.197		
	Σσ										0.184	
	Σπ											0.380
F:	1s	0.000	0.000	0.000	0.000	0.001	0.000	0.000	−0.002	0.000		
	2s	0.000	0.001	0.000	0.000	−0.039	−0.025	0.000	0.025	0.000		
	2pσ	0.000	−0.001	−0.002	0.000	0.022	0.154	0.000	0.099	0.000		
	2pπ	0.000	0.000	0.000	−0.001	0.000	0.000	0.008	0.000	0.089		
	Σσ										0.233	
	Σπ											0.096

TABLE 3.—OVERLAP POPULATIONS OF SNF

		1s	2s	2pσ	2pπ	Σσ	Σπ
S:	1s	0.000	0.000	0.000	0.000		
	2s	0.000	−0.001	−0.009	0.000		
	2pσ	0.000	−0.004	−0.009	0.000		
	2pπ	0.000	0.000	0.000	−0.002		
	3s	0.001	−0.082	0.067	0.000		
	3pσ	−0.005	0.043	0.218	0.000		
	3pπ	0.000	0.000	0.000	0.142		
	3dσ	−0.003	0.023	−0.035	0.000		
	3dπ	0.000	0.000	0.000	0.112		
	Σσ					0.204	
	Σπ						0.252
F:	1s	0.000	0.001	0.000	0.000		
	2s	0.000	−0.053	−0.017	0.000		
	2pσ	−0.001	0.044	0.178	0.000		
	2pπ	0.000	0.000	0.000	0.014		
	Σσ					0.152	
	Σπ						0.014

It is interesting to note that the bond angle of SNF is smaller than that of NSF. This agrees with Gillespie's VSEPR theory [9] in that lone pairs of electrons in a filled valence shell exert greater repulsion than those in an incompletely filled one.

Analysis of the eigenfunctions reveals that for both NSF and SNF the highest filled a' m.o. gives mainly the in-plane p–p overlap. On the other har q, populating the lowest vacant a'' m.o. leads to the out-of-plane pure p–p and p–d oʌerlaps. In both these a' and a'' m.o.s, the p a.o.s of the central atom are of phase opposite to that of the end atoms' orbitals. Consequently, the above-mentioned overlaps will become more positive and the orbital energies lower as the bond angles decrease. The drop in the a'' m.o.s orbital energy was found to be larger for NSF but smaller for SNF with respect to that of the a' m.o. NSF is therefore expected to close up its bond angle on electron excitation. Such a conclusion has in fact been reached by Barrow et al.[10] from the vibrational analysis of its $\tilde{A}^1 A'' \leftarrow \tilde{X}^1 A'$ 4050 Å band system.

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