but experimental evidence does exist for facile rotation about the MoMo triple bond in some systems. Recent work from Chisholm's laboratory[12] suggests a wide range of values for metal–metal rotation barriers: <8 kcal mol^{-1} in 1,1-Mo$_2$(O-*t*-Bu)$_2$R$_4$, R = CH$_2$SiMe$_3$; 14.0 kcal mol^{-1} in 1,1-Mo$_2$-(NMe$_2$)$_2$R$_4$; 15.6 kcal mol^{-1} in 1,2-Mo$_2$(NMe$_2$)$_2$R$_4$; >16 kcal mol^{-1} in *anti*-1,2-Mo$_2$Cl$_2$(NMe$_2$)$_4$.

The very low barriers reported by Hall for Mo$_2$H$_6$,[6a] obtained from Hartree–Fock as well as partially correlated molecular orbital models, may be due to the use of assumed equilibrium geometries. STO-3G calculations using these geometries (taken, as previously mentioned, from the crystal structure of Mo$_2$(NMe$_2$)$_6$)[3] reveal an energy difference of only 0.5 kcal mol^{-1} between the staggered and eclipsed forms of Mo$_2$H$_6$, the former being the preferred. For comparison, Hall's data place the energy of the staggered conformer 0.1 kcal mol^{-1} below that of the eclipsed form.

The present theoretical results for Mo$_2$H$_6$ may be rationalized with the aid of an orbital-energy correlation diagram connecting staggered and eclipsed forms (Figure 1). (Here, in order to separate energy differences due to conformation from those associated with other geometry changes, bond lengths and angles for the eclipsed conformer have been constrained to those of the staggered form. This results in a modest increase in barrier to 9.4 kcal mol^{-1}.) Note that the energy of the 7e$_u$ molecular orbitals (7e′ in the eclipsed structure) that constitute the two π bonds is essentially unaffected. Furthermore, orbital photographs[13] of these or-

bitals in staggered and eclipsed complexes (Figure 2) are visually nearly identical. Thus, the calculations at this level do not support significant participation of δ-symmetry functions in the π bonds. The only significant change in energy levels noted between the staggered and eclipsed conformers is an increased splitting of the 6e$_g$ and 6e$_u$ levels (6e′ and 6e″ in the eclipsed form). The molecular orbitals to which these correspond are essentially the bonding (6e$_g$) and antibonding (6e$_u$) combinations of the metal–hydrogen linkages on the two MoH$_3$ fragments. It is clear from the orbital photographs in Figure 3 that the two fragments interact more strongly in an eclipsed geometry than in a staggered arrangement.

Rotation barriers in Mo$_2$F$_6$ and Mo$_2$(OH)$_6$ would be expected to be smaller, as here the metal–ligand bonding molecular orbitals are much lower in energy (compared to the hydride) and more tightly localized. Their energies are not significantly affected upon twisting.

Even though the present quantum-chemical calculations are relatively simple, they present a picture of the bonding in Mo$_2$L$_6$ complexes that is consistent both with the known experimental structures and with the apparent absence of stable eclipsed forms. They suggest that conformation is dictated in large part by vicinal interactions between metal–ligand bonding orbitals.

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Structure and Bonding in Thiazyl Fluorides

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Electronic structure calculations at the SCF and, in part, at the CEPA level are reported for SN$^+$, NSF, NSF$_3$, [HNSF]$^+$, [HNSF$_3$]$^+$, and [CH$_3$NSF]$^+$. The equilibrium distance obtained for SN$^+$, r_e = 1.44 ± 0.01 Å, is expected to be definitive. Computed equilibrium distances and the results of a population analysis show a marked stabilization of SN and SF bonds if electrons are removed from the thiazyl group, e.g. in going from NSF to NSF$_3$ or by complexing NSF or NSF$_3$ with electron acceptors. This effect appears to be correlated with the increasing positive net charge on sulfur. The population analysis indicates that bonding to acceptors is most likely at the nitrogen end, with NSF$_3$ being a better donor than NSF.

Introduction

The chemistry of thiazyl fluoride (NSF) and thiazyl trifluoride (NSF$_3$)—which has recently been reviewed in detail by Glemser and Mews[2]—shows some interesting and fascinating features. In adducts with electrophilic compounds, e.g. A(NSF$_{(3)}$)$_n$, A = Ni^{2+}, Co^{2+}, etc., one finds always a strengthening of SN and SF bonds (as measured by bond distances and the corresponding infrared frequencies). This is in marked contrast with the corresponding behavior of ligands such as CO, SN$^+$, and OPF$_3$.[3,4]

In this article we report and discuss results of electronic structure calculations for the systems SN$^+$, NSF, NSF$_3$, [HNSF]$^+$, [HNSF$_3$]$^+$, and [CH$_3$NSF]$^+$, where H$^+$ and CH$_3$$^+$ serve as simple (and strong) electron acceptors. These investigations mainly deal with the properties of the SN bond and its changes—due to different chemical environments—in order to get a better understanding of the chemistry of thiazyl fluorides. The present results are certainly more accurate for the smaller systems (SN$^+$ and NSF), which also serve as test cases for approximations—use of pseudopotentials, neglect of electron correlation—made in the treatment of the "larger" molecules.

The results of the present computations together with an analysis of bonding and electron distributions yield a consistent model that allows for a rationalization of experimental facts. A crucial role for an understanding of the chemistry of NSF

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Table I. Computed Equilibrium Distance r_e and Force Constant K of SN$^+$

line no.	basis[a]	method[a]	r_e, Å	K, mdyn/Å	ω_e, cm^{-1}	comment
1	(7,3,1;10,6,1)	SCF	1.397	17.34	1732	ref 24
	[421,641] "DZP"	PNO-CI(D)	1.425	14.35	1576	
		CEPA-PNO(D)	1.443	12.60	1477	
2	DZP	SCF	1.393	17.5	1741	this work
		CEPA-1(SD)	1.446	11.9	1435	
		CEPA-2(SD)	1.457	10.6	1353	
3	(8,4,1;10,6,2)	SCF	1.388	17.7	1750	this work[b]
	[4,2,1;6,5,2]	CEPA-1(SD)	1.440	12.0	1441	
4	(9,5,2;12,8,2)	SCF	1.394	17.5	1740	this work
	[5,3,2;7,5,2]					
5	(10,6,2;12,8,2)	SCF	1.393	17.8	1755	this work
	[6,4,2;7,5,2]					
6	DZP	SCF-PP	1.370	18.2	1773	this work (PP)
		CEPA-1(SD)	1.423	12.3	1457	
		CEPA-2(SD)	1.434	11.0	1379	

^{a} As explained in the text. ^{b} Including L-shell correlation of S; i.e., only the K-shell orbitals of S and N are frozen.

and NSF$_3$ plays the great ease with which the S atom gives off electrons, e.g. in going from NSF to NSF$_3$, or NSF$_{(3)}$ to A(NSF$_{(3)}$)$_n$, where A denotes again an acceptor. This enhances covalent bonding—e.g. through increased tendency of S to hypervalency—and leads to a strengthening of SN and SF bonds. This mechanism, together with other results, yields a simple interpretation of properties of NSF and NSF$_3$—structure, stability, reactivity, and donor properties—and their somewhat unexpected properties in complexes with acceptors.

Surprisingly few nonempirical theoretical investigations of NSF compounds have been published to date.[5-9] They are exclusively concerned with properties of NSF such as structure, stability of isomers, and ionization potentials. None of these studies deals with the problems sketched above.

Method of Computation

For all molecules considered in this work we have performed at least SCF computations. As long as the computational expenses were not prohibitive, we have accounted for effects of electron correlation by means of CEPA(SD)[10-12] calculations. Within the CEPA(SD) method one includes all single and double excitations (out of valence MOs) explicitly and accounts for the most important higher substitutions—the so-called unlinked cluster terms—in an approximate way. This guarantees size consistency. Various CEPA versions have been proposed; they differ in the way in which the higher substitutions are (approximately) included.[12] In this work only CEPA-1 and CEPA-2 are used. It should be noted that these two versions bracket the full CI result (within the given basis) in the few cases where comparisons are possible.[12,13] All computations were performed with the KARLSRUHE program system developed by the present authors.[12,13] The method of computation is closely related to Meyer's SCEP[14] and procedures developed by Pople and co-workers,[15] which are altogether related to the direct CI techniques of Roos and Siegbahn.[16]

In order to save computation time, we have (for the larger molecules) taken advantage of the pseudopotential method (PP) of Habitz,

Schwarz, et al.;[17] i.e. only valence electrons were treated explicitly whereas core electrons were simulated by the pseudopotential. The PP method leads to slight errors, which were investigated in systematic studies of SN$^+$ and NSF.

In order to visualize electron distributions and to relate the latter to simple concepts of chemical bonding, we have further performed a population analysis (vide infra). The procedure applied for this purpose is a slight modification of Davidson's method[18] and has been described in detail elsewhere.[19] It is based on occupation numbers, e.g. of AOs, and in general gives results that are less basis set dependent than the Mulliken population analysis.[19]

Basis Sets

All computations were performed within the LCAO method in using CGTO basis sets. If it is not stated differently, we have used the following DZP basis sets, with primitive GTOs from Huzinaga's tables:[20]

$$C, N, F: \quad (8,4,1)/[4,2,1]$$

$$S: \quad (10,6,1)/[6,4,1]$$

with the orbital exponents η of d functions

$$C, 0.65; N, 0.8; F, 1.2; S, 0.7$$

For hydrogen we used a (4)/[2] basis.

In the PP computations we took the four most diffuse functions of s and p type in a DZ contraction, i.e. (4,4,1)/[2,2,1] for C, N, F, and S, with the d functions as specified above. The contraction coefficients were obtained from PP calculations of the corresponding atomic ground states.

In some computations of NSF we have augmented the above basis set for F by an additional diffuse p set with $\eta = 0.1$; the basis is described as DZP + p(F).

For SN$^+$ we could afford to perform computations with two sets of polarization functions; the corresponding orbital exponents are as follows:

$$S, 0.7, 5.0 \quad \text{(line 3, Table I)}$$

$$N, 0.5, 1.5; S, 0.33, 1.0 \quad \text{(lines 4 and 5, Table I)}$$

Results of Computations for SN$^+$, NSF, NSF$_3$, [HNSF]$^+$, [HNSF$_3$]$^+$, and [CH$_3$NSF]$^+$

(a) SN$^+$. Our investigations of SN$^+$ had two purposes mainly. We wanted to perform a definitive computation of r_e since previously published results show an unusually large scatter from 1.25 Å[21] over 1.42 Å[22] to 1.44 Å.[23,24] We further

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wanted to study in detail some computational aspects such as accuracy of the SCF approximation—i.e. the influence of correlation effects—basis set saturation effects, and the quality of the PP approximation. This appeared necessary since the larger molecules, e.g. NSF_3, could only be treated within the SCF and PP approximation.

Karpfen et al.[24] have already published a careful theoretical study of SN^+ at the SCF and CEPA–PNO levels. Therefore, we need to discuss only those points that are new. The present study employs an improved method of computation—no PNO approximation and inclusion of single substitutions—and thus removes some possible sources of uncertainty.

In Table I we have collected our most instructive results for SN^+. Let us consider the results of line 2, obtained with a DZP basis, as reference for the discussion. The SCF result for r_e (1.393 Å) does not vary if the valence shell basis set is extended (compare with lines 4 and 5). This is in agreement with the results of Karpfen et al.,[24] who obtained $r_e = 1.394$ Å (SCF) for larger basis sets. However, an increased flexibility for the L shell of S leads to a decrease by 0.005 Å for r_e (1.388 Å, line 3).

Electron correlation effects (of valence shell MOs) increase r_e by about 0.06 Å (CEPA-1, 0.05 Å; CEPA-2, 0.06 Å) for the DZP basis (line 2 of Table I). This is accompanied by a corresponding decrease of the force constant K from 17.5 mdyn/Å (SCF) to 11.2 mdyn/Å (average of CEPA-1 and CEPA-2), Karpfen et al.[24] find a slightly smaller effect of electron correlation, e.g. an increase of 0.05 Å for r_e in CEPA-2. This is probably a result of the PNO approximation and the neglect of single substitutions in their computations. An inclusion of correlation of L shell MOs of sulfur seems to have no marked effect on r_e and K (compare lines 2 and 3). CEPA-2 computations performed with large valence basis sets lead only to a slight reduction of r_e as compared to that for the DZP basis. The present results as well as those of Karpfen et al.[24] indicate strongly that the DZP basis overestimates r_e only slightly. In order to account for this effect, we select the smaller of the CEPA values (CEPA-1) as the recommended value

SN^+: $r_e = 1.44 \pm 0.01$ Å, $K =$

11.9 ± 0.5 mdyn/Å, $\omega_e = 1435$ cm^{-1} (^{32}S, ^{14}N) (1)

where the error estimates are based on the authors' experience only and ω_e denotes the harmonic spectroscopic constant. r_e from eq 1 is in excellent agreement with the experimental result of Dyke et al.[23] (1.440 Å); it also confirms a recent solid-state result of Clegg et al.[22] who reported 1.42 Å. The present result for ω_e is also very close to an experimental value[2] of 1437 cm^{-1}.

The results obtained within the PP method are easily discussed (compare lines 2 and 6 of Table I). Within the SCF as well as in the CEPA approximation one finds a consistent decrease of r_e by 0.02 Å and an increase of K by ~0.4 mdyn/Å. These deviations have to be attributed to the approximations inherent in the PP method.

(b) NSF. The still relatively modest computational expenses for a theoretical treatment of NSF allowed for an additional check of the just discussed results obtained for SN^+, e.g. basis set and correlation effects and reliability of the PP approximation. The results of the present investigations are collected in Table II. Let us first consider the SN bond we are mainly

Table II. Equilibrium Geometry of NSF As Obtained by Different Methods[a]

line no.	basis[b]	method[b]	r_e(SN)	r_e(FS)	∠NSF
1	DZP	SCF	1.42	1.60	114
2	DZP + p(F)	SCF	1.42	1.62	114
3	DZP	SCF/PP	1.40	1.60	114
4	DZP + p(F)	SCF/PP	1.40	1.61	(114)
5	DZP − d(F)	SCF/PP	1.40	1.63	(114)
6	DZP	CEPA-1(SD)/PP	1.450	(1.60)	(114)
7	DZP + p(F)	CEPA-1(SD)/PP	1.448	(1.64)	(117)
8		exptl[c]	1.448	1.643	116.9

[a] Distances are in Å and angles in degrees; quantities in parentheses were not optimized. All valence MOs are correlated in the CEPA treatment. [b] As explained in the text. [c] Reference 28.

concerned with. Here we find the very same trends as for SN^+. The PP approximation again underestimates r_e by 0.02 Å (compare lines 1 and 3, and 2 and 4, of Table II, respectively). The SCF method underestimates r_e(SN) by 0.05 Å (lines 3 vs. 6 and 4 vs. 7), as compared to a corresponding effect of 0.05 Å (CEPA-1) for SN^+.

The SF bond is expected to be between a purely covalent and a dominantly ionic bond. Ionic fluorine bonds are usually well described within the SCF approximation, with errors of ~1% for r_e, provided the rather diffuse electron distribution of F^- is appropriately described.[25] SCF treatments of dominantly covalent fluorine bonds, e.g. in F_2 or F_2O, usually underestimate r_e considerably, by ~0.08 Å, and only highly correlated wave functions yield r_e with an accuracy of a few thousands of an angstrom.[26,27] The SN distance appears to be relatively independent of the actual description of the SF bond, as measured by the dependence on the F basis (see e.g. line 1 vs. line 2 of Table II). Since we are mainly interested in the SN bond, no SF bond optimizations were performed on the CEPA level to save computation time.

On the DZP–SCF level we get r_e(SF) = 1.60 Å, which is 0.04 Å shorter than the experimental value (see lines 1 and 8 of Table II). Addition of a diffuse p set on F improves r_e(SF) to 1.62 Å (line 2 of Table II). The PP approximation yields r_e(SF) by 0.005–0.01 Å too short. Our least expensive calculation, in which the fluorine d functions were deleted (line 5), actually yields the "best" r_e(SF) of 1.63 Å, which is due to a fortuitous cancellation of errors. The computed NSF angles of 114° are within tolerable deviations from experiment[28] (116.9°).

Let us now consider r_e(NS). Our most sophisticated computation (line 7) yields r_e(NS) = 1.448 Å, in perfect agreement with experiment.[28] For these computations we fixed r_e(SF) = 1.64 Å, as a compromise between experiment and SCF value, and used the experimental bond angle. However, the PP method applied in these computations underestimates r_e-(NS) by ~0.02 Å. If we correct for this feature, we get

NSF: r_e(NS) = 1.47 Å (2)

In order to resolve the slight discrepancy to the experimental value of 1.45 Å, it would be desirable to perform additional more sophisticated computations and possibly new measurements, especially since Kirchhoff and Cook[28] estimated the error of their r_e(NS) to ~0.01 Å. Seeger et al.[9] have recently published a large basis set (12,9,2/9,5,1) treatment of NSF (and SNF, as well as of the saddle point for the isomerization). Their SCF results r_e(SN) = 1.432 Å, r_e(SF) = 1.634 Å, and ∠NSF = 112.9° differ only slightly from those of the DZP

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+ p(F) basis set (line 2): our r_e(SN) is 0.009 Å shorter, r_e(SF) is 0.016 Å shorter, and the angle is 2° larger.

We have finally computed a rough estimate ω^* of the SN vibration frequency in assuming a complete decoupling of **F** and **G** matrices:

$$\omega_e \approx \omega^* = (K^*G^*)^{1/2} \qquad G^* = \frac{1}{m_S} + \frac{1}{m_N} \quad (^{32}\text{S}, \, ^{14}\text{N}) \quad (3)$$

K^* denotes here an "effective" force constant obtained for frozen r(SF) and ∠NSF (as in line 7 of Table II). Within the PP approximation we get

$$\text{SCF:} \quad K^* = 13.4 \text{ mdyn/Å}, \, \omega^* = 1523 \text{ cm}^{-1} \quad (4)$$

$$\text{CEPA-1:} \quad K^* = 9.7 \text{ mdyn/Å}, \, \omega^* = 1296 \text{ cm}^{-1} \quad (5)$$

$$\text{extrapolated:} \quad K^* = 9.3 \text{ mdyn/Å}, \, \omega^* = 1269 \text{ cm}^{-1} \quad (6)$$

The extrapolated value was obtained in correcting the deficiency of the PP approximation by applying a shift of 0.4 mdyn/Å for K^* as found for SN$^+$. By virtue of the rather rough approximations made, one obtains a surprisingly close agreement with the experimental result $\omega_e = 1361$ cm^{-1}. In any case, these results show beyond doubt the shortcomings of the SCF approximation, which seriously overestimates ω_e.

Let us summarize briefly the main methodological results obtained for NSF. The properties of the SN bond are relatively insensitive with respect to the basis set chosen for F. The trends found for SN$^+$ were (fortunately) confirmed for NSF: the PP approximation appears to underestimate r_e(NS) by ~0.02 Å, and the SCF approximation underestimates r_e(NS) by ~0.05 Å, such that r_e(SN) is underestimated by ~0.07 Å on the PP–SCF level. This is, of course, accompanied by corresponding shifts of force constants.

(c) NSF$_3$. For NSF$_3$ we could only afford to perform computations on the PP–SCF level with a DZP basis set. The results so obtained may be extrapolated to correct for deficiencies of the PP approximation and the neglect of correlation effects with the aid of experiences gathered for SN$^+$ and NSF as just described. We then obtain the following comparison of computed, extrapolated, and experimental results:[29-32]

NSF$_3$ (C_{3v})	PP–SCF–DZP	extrap	exptl
r_e(SN), Å	1.36	1.43	1.42
r_e(SF), Å	1.51		1.55
∠FSF, deg	95.5		94.0
ω^*(SN), cm^{-1}	1740	1523	1515

ω^*(SN) was obtained by means of the same approximate procedure as discussed for NSF. The agreement of computed (∠FSF) and extrapolated (r_e(NS), ω^*(SN)) results with experiment is actually much better than could have been expected. The deviation between computed and experimental values for r_e(SF) is roughly the same as found for NSF, where r_e(SF) was also underestimated by 0.04 Å on the PP–SCF–DZP level.

Especially gratifying is a consideration of trends—which are often predicted quite reliably by even approximate theoretical treatments—found in a comparison of experimental and theoretical data of NSF and NSF$_3$. In going from the former to the latter, we compute on the PP–SCF–DZP level (experimental trends in parentheses) a decrease of r_e(SN) by 0.04 Å (0.03 Å) and a corresponding one of 0.09 Å (0.09 Å) for r_e(SF).

(d) The Molecular Ions [HNSF]$^+$, [HNSF$_3$]$^+$, and [CH$_3$NSF]$^+$. These ions were studied in order to investigate

theoretically the experimentally observed marked strengthening in SN and SF bonds in complexes of NSF$_{(3)}$ with Lewis acids. H$^+$ and CH$_3^+$ serve here as strong acceptors, which are admittedly not too typical since they are strong σ acceptors but only weak π donors (CH$_3^+$) or have no donor potential at all (H$^+$).

The computations were performed on the PP–SCF level. Basis sets were usually of DZP type, except that no p set was used on H and no d set was used on F for [CH$_3$NSF]$^+$. For the sake of simplicity we considered only the linear acceptor–N–S arrangement. As a justification we note that a linear or almost linear (deviations ≲10°) structure has been found experimentally in various complexes, e.g.[2] [M(NSF)$_6$]$^{2+}$ (M = Ni, Co), F$_5$AsNSF$_3$, and [Mn(NSF$_3$)$_4$][AsF$_6$]. We also could afford only a rather approximate determination of equilibrium geometries: we first optimized the acceptor–N distance and then reoptimized r_e(SN)—and r_e(SF) for [HNSF]$^+$—in the corresponding compounds. The following results were obtained; nonoptimized distances and angles are given in parentheses:

[HNSF]$^+$: r_e(HN) = 1.02 Å, r_e(SN) = 1.38 Å, r_e(SF) = 1.51 Å (∠NSF = 117°)

[HNSF$_3$]$^+$: r_e(HN) = 1.02 Å, r_e(SN) = 1.34Å (r_e(SF) = 1.60 Å, ∠FSF = 95.5°)

[CH$_3$NSF]$^+$: r_e(CN) = 1.44 Å, r_e(SN) = 1.39 Å (r_e(SF) = 1.60 Å, r_e(CH) = 1.11 Å, ∠HCH = 109.5°, ∠NSF = 117°)

In a comparison of these results with those obtained for NSF and NSF$_3$ on the same level of sophistication (PP–SCF–DZP), one has to bear in mind the rather rough approximations made for the molecular ions, e.g. the constraint geometry optimization or the use of slightly smaller basis sets. Quantitatively reliable results would have required much more elaborate computations than the present ones, which were not feasible. Nevertheless, the following trends of computed properties of NSF$_{(3)}$ as compared with those of ANSF$_{(3)}$, A = H$^+$, CH$_3^+$, are obvious

(i) There is a shortening of r_e(SN) by ~0.02 Å on the average. This is accompanied by a marked increase in the force constant K^*(SN) by ~7 mdyn/Å. Since we could use only three points to evaluate K^*(SN), this result is only of qualitative nature.

(ii) r_e(SF) decreases by 0.09 Å in going from NSF to [HNSF]$^+$.

These trends compare favorably with those found experimentally. The SF distance in M(NSF)$_6$ (M = Ni^{2+}, Co^{2+}) is ~0.07 Å shorter than in NSF, and that in [Mn(NSF$_3$)$_4$]$^{2+}$ is about 0.05 Å shorter than in NSF$_3$. The experimentally observed shortenings of r_e(SN) between NSF$_{(3)}$ and the corresponding complexes A(NSF$_{(3)})_n$ cluster around 0.04 Å, which is about twice as large as the one found in our study. The SN frequency of [CH$_3$NSF$_3$]$^+$ (1788 cm^{-1})[33] is about 18% larger than that of NSF$_3$ (1515 cm^{-1}). This corresponds to an increase of 37% for the force constant, again in good agreement with the rather rough theoretical estimate (an increase by ~7 mdyn/Å corresponds to an increase of ~40% in K^*(SN)).

Despite these agreements we want to point out that further and more elaborate computations and also further experimental data are necessary for a more quantitative discussion.

Electronic Structure and Bonding in Thiazyl Fluorides: Results of a Population Analysis

In order to relate the necessarily abstract results of electronic structure calculations to familiar simple ideas of chemical

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(32) Ramaswamy, K.; Sathianandan, K.; Cleveland, F. F. *J. Mol. Spectrosc.* **1962**, *9*, 107.

(33) Mews, R., private communication.

bonding, we will now report and discuss results of a population analysis for SN^+, NSF, NSF_3, and $[HNSF]^+$. These results should be considered with caution, since quantum mechanics does not provide an unambiguous definition of nonmeasurable quantities such as atomic charge or bond order in a molecule.

The population analysis applied was originally proposed by Davidson[18] and later further discussed by Roby[34] as well as Heinzmann and Ahlrichs.[19] The method is based on occupation numbers of AOs (or spaces spanned by sets of AOs) or modified AOs that incorporate, e.g., effects of polarization from which one computes atomic net charges and especially "shared electron numbers". The shared electron number gives the number of electrons shared by bonded atoms which cannot be assigned to either atom in a unique way. The shared electron numbers can be considered as a measure of covalent bond strength. We list the following simple examples to give the reader an idea of the size of shared electron numbers (SEN) in typical cases:[19,35]

strong covalent σ bonds (e.g. H–H, C–H, C–C): SEN $\approx$ 1.4

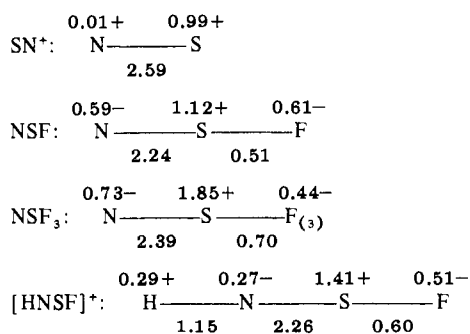weak, reactive σ bonds (F_2, Cl_2): SEN $\approx$ 0.6

polar σ bonds: SEN $\approx$ 1.0 (HF) to $\approx$ 0.3 (NaF)

double bonds (C=C in C_2H_4): SEN $\approx$ 2.2

triple bonds (C≡C, N_2,
C≡P in HCP or CH_3CP): SEN $\approx$ 3.0

The population analysis based on occupation numbers has been shown to be markedly less basis set dependent than the conventional Mulliken population analysis.[19] The method requires as input the number of modified AOs per atom (which are then determined from the requirement that occupied MOs can be represented as closely as possible by linear combinations of modified AOs) to be used in the population analysis. For SN^+, NSF, and $[HNSF]^+$ we have not encountered problems in this respect, since four modified valence AOs for N, S, and F turned out to be sufficient (i.e. the unassigned charge was smaller than 0.05). NSF_3 turned out to be more difficult, as will be discussed below.

The population analysis results (net charges and shared electron numbers) of SCF–DZP wave functions are collected in the following diagrams:

```
        0.01+     0.99+
SN⁺:    N————————S
             2.59

      0.59-      1.12+     0.61-
NSF:  N————————S————————F
           2.24     0.51

       0.73-     1.85+     0.44-
NSF₃:  N————————S————————F₍₃₎
            2.39     0.70

         0.29+    0.27-    1.41+    0.51-
[HNSF]⁺: H————————N————————S————————F
              1.15    2.26     0.60
```

The atomic net charges do not add up to the total molecular charge (the largest deviation of 0.2 e is found for NSF_3), since we have not accounted for three-center contributions.[19] The sign of these deviations indicates weak-bonding three-center contributions.

The net charges of SN^+ clearly indicate an electronic structure S^+≡N, although the shared electron number points to a weak triple bond. Since electronic structure and bonding in thiazyl fluorides has previously[36] been discussed in terms

of valence bond structures (and since the potential reader may not be too familiar with the concepts of occupation and shared electron numbers), we will try to visualize the results of our population analysis by means of valence bond structures, although this approach has to be considered with the necessary care. Net charges and shared electron numbers of NSF are compatible with a 1:1 mixture of the valence structures

$$N{\equiv}S^+F^- \qquad N^-{=}S^+{-}F$$

Since the MOs could be well represented by four modified valence AOs, contributions with a hypervalent sulfur structure play a minor role; i.e. d AOs serve as polarization functions only. Our results indicate a covalent SN bond order of $\sim$2.5; the additional stabilization by ionic contributions justifies our speaking of a (weak) triple bond.

As a consequence of the net charges one certainly expects a nitrogen attack of electrophilic groups; sulfur is positively charged and fluorine should be attached to hard Lewis acids only since it binds its electrons rather tightly. By virtue of the SN triple bond one further expects bond angles acceptor–N–S of $\sim$180°, in agreement with experiment.

The net charges obtained for $[HNSF]^+$ indicate a shift of 0.7 e from NSF to H^+, of which 0.3 e is coming from both N and S and 0.1 e from F. Although 0.6 e is removed from the SN group, we find an insignificant but slight increase in the SEN as compared to that of NSF, indicating an increase in covalent bond strength.

We encountered problems in specifying the number of valence sulfur AOs in NSF_3. With four modified valence AOs one gets an unassigned charge that is too large (0.15), which reduces to 0.05 if six AOs are used (the additional ones turned out to be dominantly of dπ type with respect to the SN axis), which has been considered acceptable in a previous study.[19] Since the results of the present population analysis depend on the number of modified AOs employed and, furthermore, tend to become unbalanced if weakly occupied modified AOs are included, we have reported in the above diagram the corresponding averaged results obtained with four and six sulfur AOs. This is certainly an unsatisfactory procedure. However, the subsequent discussions are not affected since the changes between NSF and NSF_3 show the very same trends in both procedures. These considerations show in any case that sulfur d orbitals are more important in NSF_3 than in NSF.

In an attempt to correlate the results of the population analysis to familiar valence structure, we consider structures a–e. The present net charges are consistent with a roughly
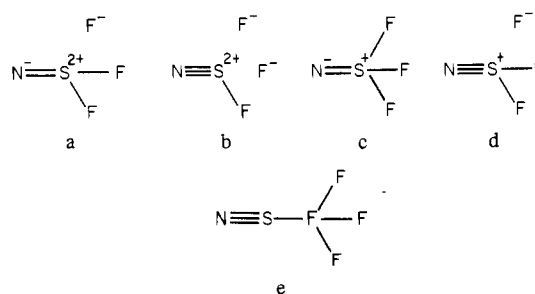
3:1 mixture of structures a and b, but the hypervalent structures c–e should also play a minor role as is obvious from the foregoing discussion. Jolly, Lazarus, and Glemser[36] have tried to relate measured core binding energies to atomic charges and bond structures. These authors favored structure a but did not consider structure b.

For NSF_3 we find, as compared to NSF, a decrease of electronic charge on sulfur and fluorine but an increase for

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nitrogen. Whereas the first effect is expected, the latter appears surprising at first glance. However, our result is in line with experimental findings, which indicate NSF_3 to be a better donor than NSF. A rather large electron density of nitrogen has also been conjectured from an investigation of the photoelectron spectrum[37] of NSF_3. With reference to the above discussion for NSF, a nitrogen attack of Lewis acids is even more likely for NSF_3 than for NSF, again with expected bond angles of $\sim 180°$.

The population analysis results are consistent with the trends of computed bond distances and force constants reported in the preceding section. In going from NSF to $[HNSF]^+$ or NSF_3, we find increased bond strength—as measured by the shared electron numbers—of SN and SF bonds. The slightly weaker bonds in NSF imply increased reactivity of this molecule (as compared to that of NSF_3), which trimerizes in fact to $(NSF)_3$ at room temperature.[2] As compared to NSF, we find a marked reduction of sulfur electronic charge in $[HNSF]^+$ and especially NSF_3. This leads to at least some contraction of sulfur AOs and a lowering of d levels; both effects should enhance covalent bond strength (better matching of sulfur AOs with those of N or F) and increase the tendency toward hypervalency. This is in agreement with the increased stability of NSF in complexes with acceptors.[2]

Our results and conjectures basically confirm the ideas advanced by Glemser and Mews.[2] They also demonstrate a typical feature of sulfur chemistry: the ease with which this atom may assume formal charges between 1– and 2+, if it is placed in the appropriate chemical environment.

The problem of back-bonding may be raised in connection with transition-metal complexes such as $[Mn(NSF_3)_4]^{2+}$. First of all, back-bonding occurs mainly in neutral transition-metal complexes, e.g. $Ni(CO)_4$; donation of transition-metal cations is unlikely by virtue of the high cation ionization potential and has never been established. Furthermore, we expect NSF or NSF_3 to behave differently than CO. The carbon end of CO is a good σ donor and a good π acceptor (the CO π^* MO is dominantly located at C), but the negatively charged nitrogen atom in NSF or NSF_3 should act rather as a barrier for π back-donation.

Conclusions

We have reported and discussed results of electronic structure calculations for several thiazyl fluorides. The accuracy of our treatment had to be reduced from SN^+—where the present treatment definitely settles the equilibrium distance (see eq 1)—to the larger molecules such as NSF_3, which could not be treated with the accuracy desired by the authors. However, since the approximations introduced (neglect of correlation effects, PP method) could be systematically checked for SN^+ and NSF, and since we get a consistent pattern of trends that is in agreement with experiment, we are confident that this does not impair our basic conclusions.

Our results mainly show a marked stabilization of SN and SF bonds—as measured by computed bond distances and results of the population analysis—whenever electrons are removed from the thiazyl group, e.g. in going from NSF to NSF_3 or by forming complexes with Lewis acids. The corresponding changes of atomic net charges are most pronounced for sulfur. In the authors' opinion, this effect plays a crucial role in the stabilization of $NSF_{(3)}$ in complexes with electron acceptors.

By virtue of the computed charge distributions, Lewis acids should be preferably attached to nitrogen, with a linear or almost linear acceptor–N–S arrangement. NSF_3 should be a better donor than NSF. Effects of π back-bonding are expected to be of lesser importance than for CO, to give an example.

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