

Theoretical studies of the preferred connectivity in X_3NZ ($X = H, F; Z = O, S$) types of molecules

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Abstract

B3LYP/6-311+G* calculations were performed on a series of structural isomers of nitrosyl trifluoride (**1a**), thiazyl trifluoride (**3d**), and their hydrogen analogues (**2** and **4**). Computational results show that the most stable isomeric form varies among the four series. For example, in the hydride series, the molecule with the formula H_2NZH , with Z being either O or S, has the highest thermal stability. In contrast, the most stable isomers in the two fluoride series were found to be F_3NO and *cis*- $FNSF_2$. The relative energetics and the structural differences among the constitutional isomers in each series, as well as those between the isovalent series, are discussed. Natural bond orbital analysis results are presented, and new structures for F_3NO and F_3NS are proposed.

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1. Introduction

Sulfur–nitrogen-containing compounds continue to capture the interest of both experimental chemists and theoreticians [1–9], because many of these compounds possess nonclassical structures and display puzzling features [10]. Theoretically, these molecules present an enormous challenge to the current chemical bonding theory [11], and therefore may serve as excellent models for further research in order to modify and improve the existing theory. Practically, the SN group has recently emerged as a new functional group, and much effort has been focused on synthesizing new SN-containing compounds [12–14]. For instance, new

heterocyclic compounds have been prepared via traditional methods such as Diels–Alder reactions, by using various thionitrosyl derivatives as the dienophiles [15–17]; and, $(CH_3OCH_2CH_2)_2NSF_3$ was reported as a breakthrough in air-product research to be the newest, safe, inexpensive, yet efficient deoxofluorinating agent [18].

Recently, we reported density functional theory (DFT) studies of the preferred connectivity in two isovalent series of RNO (vs. NOR) and RNS (vs. NSR), where R is an organic or inorganic substituent [19,20]. Computational results are consistent with the experimental reports, and have shown that the more stable form for the nitrosyl molecules is $X-N=O$, whether X be a hydrogen or a halogen; in contrast, a switch in connectivity is observed in the NS analogues [21–31], such that thionitroso hydride (HNS) is more stable than HSN, whereas the thiazyl halides (NSX , with X being

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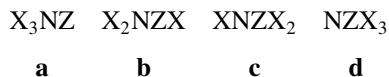
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F, Cl or Br) have considerably lower electronic energy than the corresponding thionitrosyl forms (XNS).

By using the frontier molecular orbital (FMO) theory, we showed that the reason why all the substituents overwhelmingly prefer to bond to N is because of the larger atomic coefficients on N in the π^* orbitals, which results in stronger interactions between the two singly occupied molecular orbitals (SOMOs). In the NS case, it is still true for most substituents, except for the most electronegative substituents such as halogens. The small energy gap between the high-lying NS π bonding orbital and the low-lying SOMO in the electronegative substituents invites bonding with S, which leads to the thiazyl form.

Closely related to the mono-substituted triatomic thionitrosyl and thiazyl molecules are the tri-substituted pentatomic analogues, namely, nitrosyl trifluoride (F_3NO) and thiazyl trifluoride (F_3SN). Both of these compounds have been synthesized [32,33]. Similar to the mono-substituted cases, the F atoms prefer to bond to N in the former, but to S in the latter. However, if one pauses for a moment to inspect the hydrogen analogue, one would realize that the assumption of H atoms favoring bonding to N does not lead to the correct structure for the most stable isomer in the tri-substituted forms. In fact, H_3NO exists only transiently, while hydroxyl amine (H_2N-OH), on the other hand, is a familiar, stable, inorganic compound. This example shows that the tri-substituted pentatomic molecules are not simple extensions of the mono-substituted triatomic molecules, but there are underlying new reasons for the preferred connectivity. Furthermore, while no other structural isomer of F_3NO has been observed experimentally, there yet exists another structural isomer of F_3SN , which has the molecular formula F_2SNF . This compound was reported to have a low bp of $-6.7^\circ C$ [10].

In order to understand the nature of bonding in these NO- and NS-containing pentatomic molecules, as well as to find the real causes for the preferred connectivity, we decided to theoretically investigate a model system which consists of four series of such molecules



1. X = F, Z = O;

2. X = H, Z = O;

3. X = F, Z = S;

4. X = H, Z = S.

Series **1** and **2** are the NO derivatives, and **3** and **4**, the NS derivatives. A total of six possible isomers have been included in each series. Molecules **a–d** are the four structural isomers; for **b** and **c**, each has the *cis* and the *trans* conformational isomers. H and F were chosen as substituents because the electronegativity of the substituent was found to play a central role in affecting the electronic energy of each isomeric form. Comparative studies between the H- and F-substituted derivatives are, therefore, expected to allow for an effective analysis of the results. Furthermore, the mono-substituted analogues, namely, HNO, FNO, HNS, and NSF, have been extensively studied by spectroscopic work [21–25] as well as ab initio methods [26–31].

Besides the intriguing thermodynamic properties, there are interesting structural features associated with these pentatomic molecules. For example, F_3NO was found, both by experimental work [10] and theoretical investigations [34,35] to contain a long F–N bond, and an exceptionally short NO bond. The short NO bond, which indicates multiple bond character, is certainly not predicted by a first attempt of writing its Lewis structure as $F_3N^+-O^-$.

In the following sections of the paper, we report the DFT computational results for the 24 molecules in the model system as well as ab initio calculations for F_3NO and F_3NS . The NBO analysis results are presented, followed by a discussion of the bonding structure in F_3NO .

2. Computational methodology

All DFT and ab initio calculations were carried out with the GAUSSIAN 98W program package [36]. The Becke three-parameter hybrid exchange functional [37] and the nonlocal correlation functional of Lee, Yang and Parr [38] was employed in the DFT calculations, and ab initio calculations were

Table 1
Computed (B3LYP/6-311+G*) bond length and energy data for **1a–d**

Molecules		r_{FN} (Å)	r_{NO} (Å)	r_{OF} (Å)	Energy (Hartree)	Relative energy (kcal/mol)
F ₃ NO		1.45	1.15	–	–429.3991668	0
F ₂ NOF	<i>cis</i>	1.39	1.23	1.59	–429.3433884	35.0
	<i>trans</i>	1.39	1.38	1.43	–429.3285985	44.3
FNOF ₂	<i>cis</i>	1.36	1.18	1.74	–429.2606534	86.9
	<i>trans</i>	1.40	1.19	1.74	–429.2399987	99.9
NOF ₃		–	1.08	1.87	–429.1833296	135.4

performed using the MP2 [39,40], MP4 [41] and QCISD(T) [42,43] methods. The basis set employed was 6-311+G*, which is triple zeta, and has included diffuse functions, as well as d polarization functions on the heavy atoms [44–46]. Diffuse functions were found to lower the total electronic energies significantly for compounds containing highly electronegative atoms. Higher basis sets were tested, but showed no further significant improvement of the geometries at stationary points. Natural bond orbital (NBO) analysis calculations were performed with the same suite of programs by using the methods primarily developed by Weinhold and coworkers [47,48].

In all four series, X₃NZ and NZX₃ are of C_{3v} symmetry, and, X₂NZX and XNZX₂ have nonplanar geometries with C_s symmetry. In the latter, the plane of symmetry contains N, Z, and the unique X atom, with the two identical X atoms lying above and below the plane. Vibrational frequency analyses were performed at all optimized geometries, and each was confirmed to be a stationary point on the potential energy surface.

3. Results

The bond angles of ∠XNZ and ∠NZX for all of the pentatomic molecules are between 100 and 119°, which resemble the mono-substituted molecules. Other structural data and the energy results computed with the DFT methods are collected in Tables 1–4.

Consistent with the experimental observations, the short NO bond in F₃NO (**1a**) was reproduced by calculations. The calculated NO bond length is 1.15 Å, which is close to the experimentally determined value of 1.16 Å. The relatively long F–N bond distance, computed to be 1.45 Å, also agrees well with the experimental value of 1.43 Å. In order to confirm the credibility of the DFT methods, we carried out additional calculations for F₃NO and F₃NS with three ab initio methods with the same 6-311+G* basis set as implemented in the B3LYP calculations. The results of the ab initio calculations using MP2, MP4, and QCISD(T) methods are collected in Table 5. Clearly, all four methods predict similar structural parameters, which are also in very good agreement with the experimental data. In terms of computational

Table 2
Computed (B3LYP/6-311+G*) bond length and energy data for **2a–d**

Molecules		r_{HN} (Å)	r_{NO} (Å)	r_{OH} (Å)	Energy (Hartree)	Relative energy (kcal/mol)
H ₃ NO		1.03	1.36	–	–131.7211773	21.1
H ₂ NOH	<i>cis</i>	1.02	1.43	0.97	–131.7450300	6.2
	<i>trans</i>	1.02	1.44	0.96	–131.7548313	0
HNOH ₂	<i>cis</i>	1.04	1.66	0.97	–131.6432773	70.0
	<i>trans</i>	1.03	1.69	0.96	–131.6526483	64.1
NOH ₃		–	–	–	–	–

Table 3
Computed (B3LYP/6-311+G*) bond length and energy data for **3a–d**

Molecules		r_{FN} (Å)	r_{NS} (Å)	r_{SF} (Å)	Energy (Hartree)	Relative energy (kcal/mol)
F ₃ NS		1.45	1.59	–	–752.3574337	55.2
F ₂ NSF	<i>cis</i>	1.40	1.67	1.64	–752.4184893	16.9
	<i>trans</i>	1.41	1.75	1.64	–752.4120543	20.9
FNSF ₂	<i>cis</i>	1.40	1.54	1.66	–752.4453490	0
	<i>trans</i>	1.44	1.57	1.65	–752.4307943	9.1
NSF ₃		–	1.43	1.62	–752.4428759	1.6

cost, both B3LYP and MP2 are much less expensive than MP4, but QCISD(T) is extremely costly. Ironically, the least expensive B3LYP calculations seem to produce data that are the closest to those predicted by the most costly QCISD(T) methods. Therefore, taking the advantage of the efficiency as well as the good performance of the DFT methods, we carried out the rest of the study at the B3LYP/6-311+G* levels of theory.

As shown in Table 1, the F–N bond length, r_{FN} , remains somewhat constant in all the other structural isomers (**1b–d**), with a value between 1.36 and 1.40 Å, which is in the range of a normal F–N bond length of 1.37 Å [49]. While the F–N distance is insensitive to the different connectivity, the NO bond length alters dramatically throughout the series. The longest NO bond appears in the *trans* form of **1b**, with $r_{\text{NO}} = 1.38$ Å. The value of r_{NO} decreases consistently, as each additional F atom is ‘transferred’ from N to O down the column. Likewise, the O–F bond length is also highly sensitive to the isomeric form, except that the O–F bond length alters in the opposite fashion as the NO bonds. Specifically, r_{OF} is

the *shortest* in *trans-1b*, and *increases* steadily and drastically down the column, with an extremely large r_{OF} of 1.87 Å in **1d**.

Listed in Table 2 are the hydrogen analogues of series **1**. The alteration of the bond length in molecules **2a–d** displays a strikingly different pattern from the fluorides in **1**. First, no stationary point could be located for NOH₃, as opposed to the NOF₃ case, as all attempts to optimize the geometries for NOH₃ led to a convergence to the optimized geometry for H₃NO. Secondly, both the r_{HN} and r_{OH} values remain essentially constant. The H–N bonds are around 1.02 Å and the O–H bonds are between 0.96 and 0.97 Å, both of which reflect a typical N–H and O–H bond, respectively. Thirdly, the NO bonds show an *increase* in bond length down the column, from **2a** (1.36 Å) → **2b** (1.43 and 1.44 Å) → **2c** (1.66 and 1.69 Å).

The third series, **3a–d**, is isovalent to **1**. The two isovalent series show similarities as well as differences in their structural profiles. Parallel to **1a–d**, r_{FN} varies very little between **3b** and **3c** (Table 3), with values slightly higher than those in **1b** and **1c**.

Table 4
Computed (B3LYP/6-311+G*) bond length and energy data for **4a–d**

Molecules		r_{HN} (Å)	r_{NS} (Å)	r_{SH} (Å)	Energy (Hartree)	Relative energy (kcal/mol)
H ₃ NS		1.02	1.87	–	–454.7469938	11.1
H ₂ NSH	<i>cis</i>	1.01	1.71	1.37	–454.7633487	0.8
	<i>trans</i>	1.01	1.74	1.36	–454.7646075	0
HNSH ₂	<i>cis</i>	1.02	1.59	1.40	–454.6841105	50.5
	<i>trans</i>	1.02	1.61	1.38	–454.6812840	52.3
NSH ₃		–	1.47	1.41	–454.5817564	114.7

Table 5
Structural parameters for F₃NO and F₃NS at B3LYP, MP2, MP4 and QCISD(T)/6-311+G* levels of theory

Structural parameters		B3LYP	MP2	MP4	QCISD(T)
F ₃ NO	$r_{\text{F-N}}$	1.445	1.448	1.462	1.438
	$r_{\text{N-O}}$	1.154	1.148	1.163	1.163
	a_{FNO}	117.38	117.75	117.63	117.37
	Energy	-429.3991669	-428.4876765	-428.5329066	-428.5169231
F ₃ NS	$r_{\text{F-N}}$	1.449	1.477	1.497	1.446
	$r_{\text{N-S}}$	1.594	1.543	1.563	1.602
	a_{FNS}	118.57	119.56	119.48	118.47
	Energy	-752.3574337	-751.0553904	-751.1128595	-751.0990956

The long F–N bond is, again, observed in **3a**, with the bond length identical to that in **1a**. The profile of r_{NS} is also similar to that of r_{NO} in series **1**, such that the NS bond is the longest in **3b**, being 1.67 and 1.75 Å, for the *cis* and the *trans* conformations, respectively, and decreases consistently down the column to the smallest value of 1.43 Å in **3d**. Similarly, the NS bond length of 1.59 Å in **3a** is shorter than a normal NS single bond of 1.71 Å [49]. The differences between the two series lie in the bond lengths of the S–F and O–F bonds. Instead of having very different r_{OF} values in **1**, the S–F bond remains fairly constant in **3**, with a value around 1.64 Å. The calculated S–F bonds in these molecules are slightly longer than a normal S–F bond, such as in SF₂ or SF₆, which is around 1.59 Å [49].

The structural data in **4** exhibit features similar to their fluoro analogues of **3**. As presented in Table 4, neither r_{HN} nor r_{SH} changes much between the isomers, with values close to the normal bond lengths of N–H and S–H. The NS bond distance varies, with a pattern largely resembling that in **3**, such that r_{NS} decreases in the order of **3b** > **3c** > **3d**. The only difference between the two series is the exceptionally long NS bond in **4a**. In fact, **4a** contains the longest NS bond among all the NS-containing molecules.

The energy results have shown that the form of the most stable isomer varies among the different series. The four molecules that have been found to possess the greatest thermal stability, in comparison to the other isomers, are F₃NO (**1a**), H₂NOH (**2b**), FNSF₂ (**3c**), and H₂NSH (**4b**). The computational results are, again, consistent with the experimental reports, since

all four of these compounds have been synthesized. Calculations also predict that NSF₃ is virtually isoenergetic with FNSF₂; their energy differs by only 1.6 kcal/mol. This result agrees with the experimental reports, since, as mentioned earlier, both NSF₃ and FNSF₂ have first been synthesized several decades ago [10,33].

In Table 1, the relative energies increase down the column drastically, with the least stable form in **1d** being 135.4 kcal/mol higher in energy than the most stable isomer **1a**. With each transfer of F from N to O, the molecular energy increases by an amount between 35.0 and 64.9 kcal/mol, which is somewhat close to the calculated energy difference of 43.6 kcal/mol between FNO and NOF [19]. For both **1b** and **1c**, the *cis* conformation is considerably more stable than the *trans* conformation by as much as 13.0 kcal/mol.

However, the energy profile for **3** is not similar to the isovalent series **1**. For example, the most stable form in **3** is the *cis*-**3c**, and **3d** is very close to it in energy; and opposed to the prediction that F₃NO is the most stable isomer in **1**, F₃NS is, on the other hand, the least stable form in the entire series of **3**.

For the two hydrogen-substituted series (Tables 2 and 4), similar profiles for the relative energies were observed. For both series, the most stable isomer is *trans*-H₂NZH. The least stable isomer in **4** is **4d**. If the nonexistence of NOH₃ (**3d**) indicates its extreme thermal instability, it adds to the similarities between the two series. The energy gaps between the different isomers in **4** are smaller than those in **2**. The small energy difference of

11.1 kcal/mol between **4a** and the most stable form of **4b** suggests that **4a** might possess enough thermal stability to be synthesized in the future or observed spectroscopically.

In summary, our results have shown that: (1) the X–N and Z–X bond lengths remain somewhat constant among all the isomers, except for the O–F bonds; (2) in all cases, the NZ bonds were found to be shorter in the *cis* form than in the corresponding *trans* form; (3) the NZ bond order profiles are parallel in the two fluoride series, but essentially the opposite between the two hydride series; (4) in contrast to the structural profiles, the energy profiles exhibit similar features in the two hydride series, i.e. the most stable isomers show the same structural connectivity, however are very different between the two fluoride series.

4. Discussion

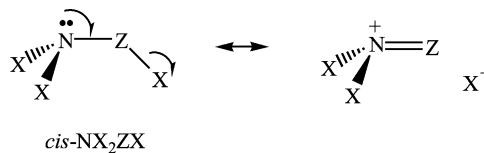
4.1. The energetics among the isomers

The observation in the mono-substituted triatomic molecules that H prefers to bond to N in both NH and NS, but F switches preference from N in NO to S in NS, is largely repeated in these tri-substituted pentatomic molecules. As shown by the energy data, the energy profiles for the hydride series (**2** and **4**) are similar, whereas those in the fluoride series (**1** and **3**) are largely the opposite.

Secondly, whether a molecule may be represented by reasonable Lewis structures gives good indication to its stability. For example, in the hydride series, **2b** and **4b** are the most stable isomer in their respective series. This can be understood as, firstly, H prefers to bond to N, which leads one to expect that the molecular forms of **a** and **b** being better than **c** or **d**; secondly, between **a** and **b**, the latter is understandably more stable molecule due to the not-so-good Lewis structure in the former in which charge separation exists.

The relative energies between the *cis* and *trans* conformations are determined by two opposite factors, namely, the steric repulsion which favors *trans* over *cis*, and the contribution from the zwitterionic resonance structures, which is

facilitated by the *cis* conformations and adds extra stability to this form.



Therefore, for each conformational isomer pair in the fluoro-molecules, the energy for the *cis* conformation is lower than the *trans* conformation, due to the large resonance stabilization. In contrast, the resonance contribution is expected to be much smaller in the hydrogen analogues. Consequently, the energy differences between *cis* and *trans* in the hydro-molecules are much smaller, and in some cases, *trans* is more stable.

4.2. Structures

Among all the structural data, those for the NZ bond length are of the most interest because they allow for comparisons between the H- and the F-series. In addition, they directly reflect the interactions between the substituents and the NZ groups, which may elucidate the bonding structures in these molecules. The NZ bond length results for the six isomers in each of the four series are presented in Fig. 1.

As discussed in Section 3, the NS bond lengths for molecules with the same connectivity in **3** and **4** are remarkably close, in spite of the large difference in electronegativity between F and H. Displayed in Fig. 1, the r_{NS} data points are more or less on top of each other in the two series, except for those in X₃NS, where X stands for either F (**3a**) or H (**4a**). The similarities can readily be explained by their Lewis structures; since, whether it be H or F, the normal Lewis structures for **b–d** are the same, namely, X₂N–SX (**b**), XN=SX₂ (**c**), and N≡SX₃ (**d**). Furthermore, the corresponding bond orders described in the Lewis structures are consistent with the calculated r_{NS} values. Specifically, r_{NS} values between 1.67 and 1.75 Å in **3b** and **4b** are in the range of a single bond distance; those between 1.54 and 1.61 Å in **3c** and **4c** are inline with an N=S, such as that in F–N=S (1.55 Å); and the bond length of 1.43 and

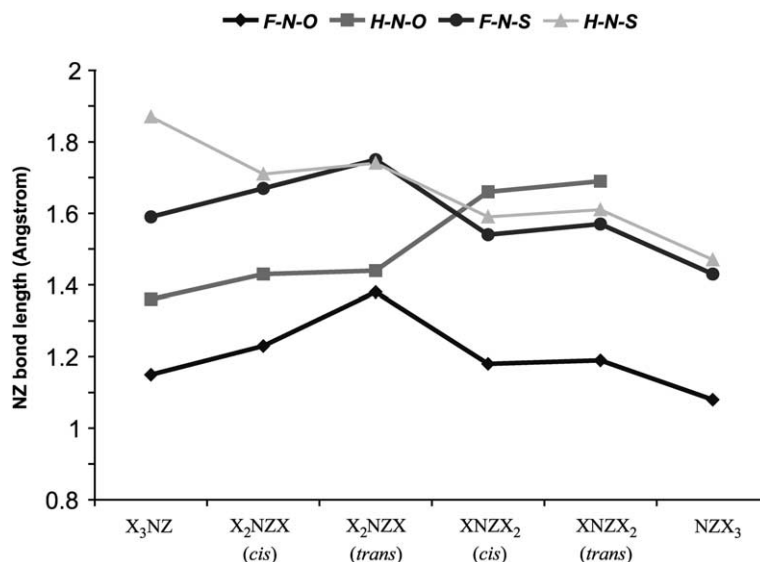


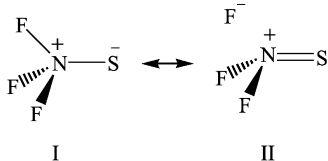
Fig. 1. The NO and NS bond length profiles for the four series.

1.47 Å in **3d** and **4d**, respectively, are typical of those in an N≡S.

The r_{NS} values for the fluorides all lie slightly lower than their hydrogen counterparts, except for *trans*-X₂NSX, in which r_{NS} values are right on top of each other. These results are in accord with what is predicted by Bent's rule [50], that the NS bonds are more contracted in the fluorides, due to the higher s character in the N, as a result of its using more p character in bonding with the more electronegative F atoms.

The extremely long NS bond in **4a** (1.87 Å) is consistent with its Lewis structure, H₃N⁺ → S⁻, where a dative bond is formed between N and S. However, the much shorter NS bond in **3a** (1.59 Å) is closer to an N=S bond.

One way to explain the short NS bond in **3a** is by drawing the zwitterionic resonance structures II,



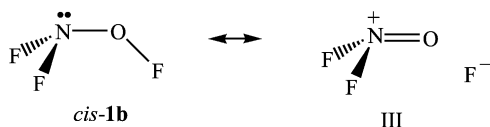
with, of course, three identical structures as described in II contributing equally to the overall structure. The NBO analysis results, indeed, support such resonance

structures, which show that the total occupancy for the lone pair orbitals in S (1.9776, 1.6093 and 1.6093) is summed to be 5.196. If it is assumed that the 'total occupancy of the lone pair orbitals' from the NBO calculations directly correlate with the number of lone pair electrons, and, the overall structure of F₃NS is adequately represented by just these two types of resonance structures, the weight of contribution from I and II may, then, be estimated. For example, the percentage contribution of I and II can be estimated as 58.8 and 40.2%, respectively, by a simple calculation of solving for I%, in equation I%·6 + (1 - I%)·4 = 5.196, where I% stands for the weight of contribution of type I resonance structure; (1 - I%), the weight of contribution from the type II resonance structures; and 6 and 4 are the number of lone pair electrons on S in I and II, respectively.

The NO bond order for each of the isomers in **2** can all be represented by a single conventional Lewis structure. For instance, the NO bond length (1.36 Å) in **2a** is consistent with the structure of H₃N⁺ - O⁻. In contrast to a long N-S dative bond, the NO bond in **2a** is slightly shorter than other NO single bonds such as that in hydroxyl ammonium ion or in trimethylamine oxide (CH₃)₃NO (the organic analogue of **2a**), both of which are around 1.40 Å [49]. This difference in the NZ bond order between **3a** and **4a** is probably due to

the higher electronegativity and compatible size of O in comparison to S. The bond distances $r_{\text{NO}} = 1.43$ and 1.44 \AA in **2b** are close to that of an NO single bond, which is indicated by the Lewis structure for hydroxyl amine, $\text{H}_2\text{N}-\text{OH}$. For **2c**, the exceptionally long NO bond lengths of 1.66 and 1.69 \AA indicate very weak bonding between N and O, and the structure may be visualized as a dative bond between O and N, as in $\text{HN}^- \leftarrow \text{O}^+\text{H}_2$.

The NZ bond order profiles in the two fluoride-series, **1** and **3**, display similar features. As shown in Fig. 1, the data profile for the r_{NO} values in **1** and the r_{NS} values in **3** are almost parallel to each other. The $r_{\text{NO}} = 1.15 \text{ \AA}$ in **1a** is close to that in the NO radical, which is between 1.12 and 1.13 \AA . Hence, it corresponds to a bond order of 2.5, as is the case in the NO radical. As in **3**, r_{NO} in **1** continues to decrease from **1b** \rightarrow **1c** \rightarrow **1d**, with the bond lengths in **1c** being 1.18 – 1.19 \AA and 1.08 \AA in **1d**, suggesting the $\text{N}=\text{O}$ and $\text{N}\equiv\text{O}$ structures in these two molecules, respectively. In **1b**, r_{NO} is 1.23 \AA for the *cis* and 1.38 \AA for the *trans* conformation. The latter indicates an NO single bond, parallel to those in **3b**. However, the bond length in the *cis* form corresponds rather closely to an $\text{N}=\text{O}$ bond. This can be accounted for by the zwitterionic resonance structure, III, as a result of the interactions, which is facilitated by the anti-coplanar configuration in the *cis* conformation, between the lone-pair electrons on N and the $\sigma_{\text{O}-\text{F}}$ electrons.

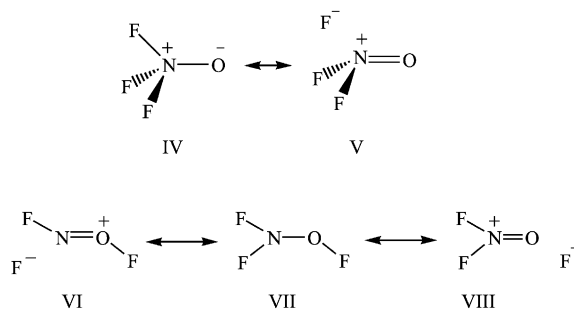


In fact, such a zwitterionic resonance structure exists in all of the *cis* conformations, although it contributes most significantly in *cis-1b*, due to the high electronegativity of F. The resonance contribution is evident in the observation that the NZ bond lengths in *cis* are all shorter than in *trans*.

While the NZ bond orders exhibit similar behavior between the two fluoride series, owing to the fundamental differences between O and S, a second row and a third row element, respectively, no reasonable conventional Lewis structures may be written in many of the isomers in **1** as opposed to **3**. For instance, if one imposes the correct bond orders

determined from the bond length results, the Lewis structures for **1c** and **1d** would have to look like $\text{FN}=\text{OF}_2$ (**1c**) and $\text{N}\equiv\text{OF}_3$ (**1d**), which are, obviously, troublesome structures. The fact that they are extremely high in energy, and can only exist hypothetically on the potential energy surface, is consistent with their problematic structures.

The zwitterionic resonance structures are, again, adopted in order to account for the bond length results for **1a** and **1b**, both of which contain NO bonds that are shorter than what the conventional Lewis structures predict.



The weights of contribution to the overall structure for **1a** are, again, estimated to be 58.5% from IV and 41.5% from V, as the total lone pair orbital occupancy (1.971, 1.5985, and 1.5985) in O is 5.168. The percentage contribution of VI, VII, and VIII in **1b** is calculated to be 23.1, 53.1, and 13.8%, respectively, based on the averaged number of lone pair electrons of 1.7237 in N and 3.5378 in O.

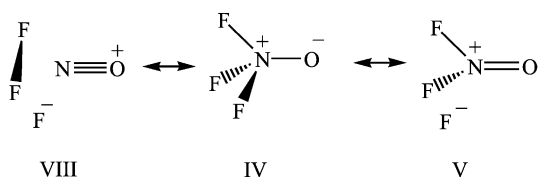
4.3. The nature of bonding in F_3NO revisited

The nature of bonding in F_3NO has been studied by several groups. Reed and Schleyer [34] used the same resonance hybrid approach as we have discussed here, and described the process of achieving the zwitterionic resonance structures as back-bonding or negative hyperconjugation. Gillespie et al. [35] used the ligand close packing (LCP) model to discuss the overall structure in terms of ligand–ligand interactions and packing of the ligands around the central atom. Since the negative hyperconjugation model is supported by the NBO results with two key components, namely, the occupancy of the lone pair orbitals (with values in-between those indicated in the conventional Lewis structure and

the zwitterionic resonance structures), and the sizable coefficients for the σ^* orbitals, we decide to stick to the resonance-hybrid approach to further explore the bonding structures in F_3NO .

While the negative hyperconjugation model works well in explaining the structural trends in a long list of related inorganic molecules which were investigated by Reed and Schleyer, certain aspects of the F_3NO structure cannot be adequately explained by this model alone. The main problem is that, an ionic bond with a lower bond order than a covalent bond does not suggest a weaker bond, nor does it predict a bond longer than a single covalent bond. Therefore, the contribution of resonance hybrids IV and V does not account for the long F–N bond, nor is it necessarily consistent with a weak F–N bond structure.

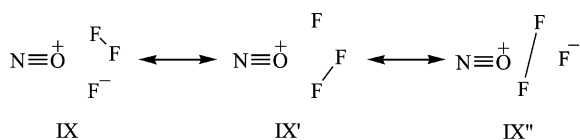
Here, we propose yet another type of resonance structures, i.e. VIII, as contributors to the overall structure of F_3NO , in addition to the zwitterionic resonance structures of V. As expected, there should be a total of three identical resonance structures as described in VIII.



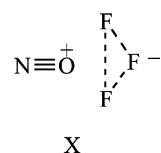
The distance between the F atoms are 2.22 Å, which is within the F–F van der Waals distance of 3 Å, and close to twice the ligand radius for F (1.06 Å), reported by Gillespie et al. [35]. Therefore, the F atoms may form partial bonds via ligand–ligand interactions. As there is no bond formed between the N and the F atoms in VIII, the contribution of such resonance structures would, indeed, lead to the lengthening as well as weakening of the NF bonds. Furthermore, recall that the NO bond length in F_3NO is close to that in the NO radical, which corresponds to a bond order of 2.5. Since neither IV nor V contains an NO bond of such high bond order, structure VIII becomes a plausible resonance contributor to account for the short NO bond length in F_3NO .

Resonance structure VIII may only be a minor contributor to the overall structure in F_3NO ; however, similar resonance structures are predicted by the NBO calculations to be the major contributors in NOF_3

(**1d**). The NBO analysis presents NOF_3 as three separate fragments, namely, NO, F, and F_2 , and the bonding orbitals show a triple bond between N and O, an anion F^- (with four lone pairs), and an F_2 fragment. Hence, the structure for NOF_3 may be represented as a hybrid of three equivalent resonance structures, IX, IX', and IX'',



The overall structure for **1d** is then,



where the three F atoms interact with each other, and form a 3-center-4-electron ligand system, which bonds weakly with the central atom via an ionic interaction.

The weak F–N bonds in F_3NO and F_3NS are also supported by the frequency analysis results. Table 6 has included the wavenumbers for the totally symmetric vibrations dominated by the NZ and NX stretching, and the bending normal mode of a_1 symmetry (denoted X_3 bending) of the three NX bonds, for the four X_3NZ molecules (**1–4a**). The weak F–N bonds in **1a** and **3a** are reflected in their low stretching frequencies, as well as the low F_3 bending frequencies, in comparison to those calculated in NF_3 of 1034.3 and 645.5 cm^{-1} , respectively. The frequency results for NOF_3 also show extremely weak OF bonds, which agree with structure X. The frequencies for the OF stretching is only 544.2 cm^{-1} , and the OF bending normal mode (a_1 symmetry) is as low as 365.3 cm^{-1} .

Table 6
Calculated vibrational frequencies (cm^{-1}) at B3LYP/6-311+G* levels of theory for the NZ and NX stretching and the bending normal mode of a_1 symmetry from the three NX bonds

Molecules	NZ stretching	NX stretching	X_3 bending
F_3NO (1a)	2169.7	824.5	459.2
H_3NO (2a)	1239.7	3412.9	1802.8
F_3NS (3a)	1368.8	727.7	399.7
H_3NS (4a)	574.0	3446.9	1408.3

In comparison to the hydrides, both the NO and NS stretching frequency in the fluorides are shown to be much stronger. These results are consistent with the suggested structures for the fluorides where both the NO and the NS bonds are of higher bond order.

5. Conclusions

The energy results predict that F_3NO , H_2NOH , and H_2NSH are no doubt the most stable isomeric forms for the particular composition, since the other structural isomers are all of much higher energy. On the other hand, $FNSF_2$ and NSF_3 are both among the most stable forms, with the energy calculated to be only 1.6 kcal/mol apart. All of these results are consistent with what has been known for these molecules, as all five of those most stable forms have been synthesized, while none of the others has been reported to exist to date.

Most of the structures for the molecules studied here are consistent with the ‘best’ Lewis structures. A few that cannot be represented by a single Lewis structure may be adequately represented by a myriad of resonance structures, in which the octet rule applies in each proposed resonance structure. Therefore, as the Lewis structures have reflected, the isovalent atoms, O and S, being a second row and third row element, respectively, behave very differently while involving in bonding in the pentatomic molecules studied here.

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