reagent would coordinate to either of two equivalent lone pairs of electrons on the carbonyl oxygen (cf. structures **2–4**).[12] Spectroscopic results corresponding to a time average of these two complexes were expected, and this has been labeled the *two-site* model. However, some of us have found that results for Eu(fod)$_3$ complexes of symmetrical ketones are consistent only with a *linear* complex having a C=O—Eu angle of 180° (*one-site* model; cf. structures **5–7**).[13] Since lanthanide ions are highly electropositive and possess vacant d or f orbitals having the requisite symmetry, they may adopt a linear geometry in their complexes with ketones. Our results suggest that the *one-site* model[13] may not just be a computational convenience but rather may be a proper description of the actual complex.

Acknowledgment. Most of this work was carried out at the Friedrich-Alexander-Universität Erlangen-Nürnberg. We thank the Alexander von Humboldt Stiftung for the award of a Fellowship to D.J.R. The Fonds der Chemischen Industrie provided additional support. We thank the staff of the Regionales Rechenzentrum, Erlangen, for their cooperation.

Note Added in Proof. Scatter plot analysis of X-ray data involving hydrogen-bonding interactions to a variety of oxygen functional groups reveals a statistical preference for the conventional lone-pair directions involving ketones (Murray-Rust, P.; Glusker, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 1018). X-ray structures of an Ag^+–acetophenone complex (Crist, D. R.; Hsieh, Z.-H.; Quicksall, C. O.; Sun, M. K. *J. Org. Chem.* **1984**, *49*, 2478) and of a [LiBr·2(acetone)]$_2$ complex (Seebach, D. Proceedings, 27th Welch Conference in Chemical Research, 1983, in press) also indicate nonlinear C=O—M^+ interactions. More data of this type are needed before reliable conclusions can be drawn about the shape of the potential energy surface.

Registry No. CH_2=O, 50-00-0; CH_2=O—H^+, 18682-95-6; CH_2=O—Li^+, 53259-65-7; CH_2=O—BeH^+, 91744-02-4; CH_2=O—BH_2^+, 91744-03-5; CH_2=O—CH_3^+, 41879-84-9; CH_2=O—Na^+, 57450-19-8; CH_2=O—MgH^+, 91744-04-6; CH_2=O—AlH_2^+, 91744-05-7; CH_2=O—SiH_3^+, 91744-06-8.

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X-ray Photoelectron Spectroscopic Study of Sulfur–Nitrogen–Fluorine Compounds

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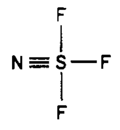
The gas-phase core binding energies of NSF, NSF_3, and several compounds of the types NSF_2R and F_2SNR have been determined. Qualitative interpretation of the data shows that N(pπ)→S(dπ) bonding is probably important in the NSF_2R compounds and in NSF_3, that the bonding of the sulfur atom in NSF is similar to that in SO_2, and that the nitrogen atom of NSF_3 is more negatively charged than that of NSF (in spite of a stronger N–S bond in NSF_3). Quantitative interpretation of the data for NSF and NSF_3, together with literature valence ionization potentials, shows that the HOMO of each molecule has principally nitrogen 2p character and is stabilized by interaction with a higher lying sulfur 3d orbital. The approximate atomic orbital contributions to the other molecular orbitals of these molecules are deduced.

We have obtained the gas-phase X-ray photoelectron spectra of the compounds[2] shown in Chart I in order to attempt clarification of the π bonding in the compounds. The structures in Chart I are Lewis octet structures, which imply the use of only s and p valence orbitals. The indicated charges are merely *formal charges*, i.e., the charges that the atoms would have if bonding electrons were equally shared between bonded atoms. It is of particular interest to determine whether pπ → dπ bonding is involved, i.e., to determine whether structures such as

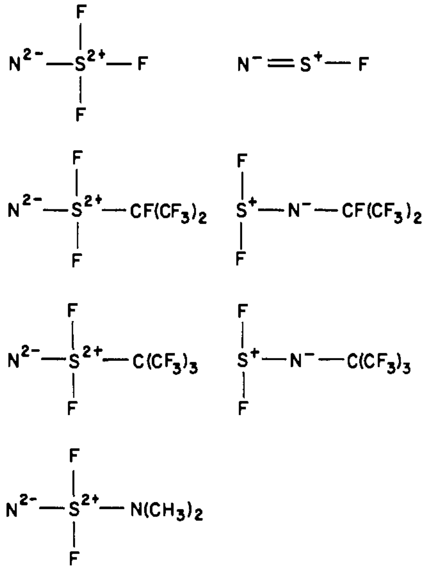


$N{\equiv}\overset{F}{\underset{F}{S}}{-}F$

must be considered.

Qualitative Interpretation of Core Binding Energies

The core binding energy data for the compounds of Chart I are given in Table I.



$N^{2-}{-}\overset{F}{\underset{F}{S^{2+}}}{-}F$ $\quad N^-{=}S^+{-}F$

$N^{2-}{-}\overset{F}{\underset{F}{S^{2+}}}{-}CF(CF_3)_2$ $\quad \overset{F}{\underset{F}{S^+}}{-}N^-{-}CF(CF_3)_2$

$N^{2-}{-}\overset{F}{\underset{F}{S^{2+}}}{-}C(CF_3)_3$ $\quad \overset{F}{\underset{F}{S^+}}{-}N^-{-}C(CF_3)_3$

$N^{2-}{-}\overset{F}{\underset{F}{S^{2+}}}{-}N(CH_3)_2$

Sulfur. It can be seen that replacement of a fluorine atom in NSF_3 by the $C(CF_3)_3$ or $N(CH_3)_2$ group causes a decrease in the sulfur $2p_{3/2}$ binding energy in qualitative accord with the relative electronegativities of the groups. As expected, replacement by the $CF(CF_3)_2$ group causes a decrease similar to that of the $C(CF_3)_3$ group, but inexplicably the $CF(CF_3)_2$ group causes a greater decrease than the $C(CF_3)_3$ group. Of course, removal of two fluorine atoms from NSF_3 to form NSF would be exected to cause a marked drop in the sulfur binding energy, and the observed drop of 2.96 eV is entirely

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[1] (a) University of California and Lawrence Berkeley Laboratory. (b) University of Göttingen.

[2] For a review of these compounds, see: Glemser, O.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 883.

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Table I. Core Binding Energies (eV) of Sulfur-Nitrogen-Fluorine Compounds

	S $2p_{2/3}$		N 1s		F 1s		C 1s	
	E_B	fwhm[a]	E_B	fwhm	E_B	fwhm	E_B	fwhm
NSF	174.14 (4)[b]	1.24 (15)	406.88 (2)	1.31 (6)	692.74 (2)	1.79 (10)		
NSF_3	177.10 (4)	1.08 (16)	406.10 (3)	1.53 (19)	695.32 (2)	1.76 (7)		
$NSF_2CF(CF_3)_2$	175.82 (4)	1.49 (12)	405.43 (3)	1.37 (9)	695.01 (2)	1.90 (2)	295.87 (4) 299.92 (2)[c]	1.61 (23) 1.34 (7)
$NSF_2C(CF_3)_3$	175.88 (5)	1.52 (14)	405.58 (4)	1.50 (11)	695.11 (2)	1.98 (4)	294.19 (5) 299.95 (2)[c]	1.44 (16) 1.41 (6)
$NSF_2N(CH_3)_2$	174.85 (5)	1.23 (19)	404.28 (3) 406.58 (3)[d]	1.24 (6) 1.35 (8)	693.37 (3)	1.86 (8)	292.50 (3)	1.31 (9)
$F_2SNCF(CF_3)_2$	175.64 (5)	1.64 (12)	406.46 (4)	1.52 (12)	694.82 (3)	2.04 (9)	295.79 (5) 299.37 (2)[c]	1.62 (14) 1.49 (8)
$F_2SNC(CF_3)_3$	175.43 (6)	1.58 (15)	406.54 (3)	1.38 (10)	694.86 (3)	1.97 (5)	294.25 (6) 299.60 (3)[c]	1.49 (15) 1.46 (7)

[a] Full width at half-maximum. [b] Uncertainty in last digit (2σ value of least-squares fit of data) indicated in parentheses. [c] CF_3 carbon. [d] $N(CH_3)_2$ nitrogen.

reasonable. Indeed, the sulfur binding energy of NSF is of similar magnitude to that of SO_2 (174.80 eV),[3] with which NSF is isoelectronic.

On going from $NSF_2C(CF_3)_3$ to the isomeric $F_2SNC(CF_3)_3$, the sulfur binding energy decreases by 0.45 eV, and on going from $NSF_2CF(CF_3)_2$ to $F_2SNCF(CF_3)_2$, it decreases by 0.18 eV. These changes are qualitatively consistent with the formal charges of the structures in Chart I. However, one might have expected a more pronounced change in binding energy associated with the change in sulfur formal charge of 1 unit. (For example, on going from SO_2F_2 to SOF_2, the sulfur binding energy decreases by 1.47 eV.)[3,4] The relatively small binding energy changes are consistent with an exceptional degree of $p\pi \rightarrow d\pi$ charge transfer from nitrogen to sulfur in the compounds with the N–S–C skeleton (and presumably also in NSF_3). Such $p\pi \rightarrow d\pi$ bonding is expected because of the high positive formal charge on the sulfur atom and the unusually high negative *formal* charge on the peripheral nitrogen atom.

Nitrogen. Two peaks of equal intensity were clearly resolved in the nitrogen 1s spectrum of $NSF_2N(CH_3)_2$. We assign the peak at higher binding energy (406.58 eV) to the $N(CH_3)_2$ nitrogen atom because binding energies of that magnitude are typical for nitrogen atoms in similar environments (urea, 406.09 eV; formamide, 406.41 eV)[5]. We assign the peak at lower binding energy (404.28 eV) to the peripheral nitrogen atom because then the trend in peripheral nitrogen binding energy, in the series NSF_3, $NSF_2C(CF_3)_3$, $NSF_2CF(CF_3)_2$, and $NSF_2N(CH_3)_2$, is reasonable in terms of the electronegativities of the groups. (Again, however, the relative values for $NSF_2CF(CF_3)_2$ and $NSF_2C(CF_3)_3$ seem slightly unreasonable.)

On going from NSF to NSF_3, the nitrogen 1s binding energy decreases by 0.78 eV. Because of the importance of the interpretation of this result, we wished to be assured in this case of the validity of the assumption that a decrease in binding energy corresponds to an increase in negative charge. Therefore, we estimated the effect of the changes in relaxation energy and potential associated with this binding energy shift. (The details of the calculations are described in the Calculations.) The calculations indicate that the assumption is valid and that on going from NSF to NSF_3 the negative charge on the nitrogen atom increases. The same result has recently been obtained from extended basis set ab initio calculations on NSF and NSF_3.[6] Offhand, this increase in charge appears surprising in view of the gain of two electronegative fluorine atoms. But, the increase becomes reasonable when one considers the fact that, even in the complete absence of hyperconjugation or $p\pi \rightarrow d\pi$ bonding, the octet rule would require π bonding between the nitrogen and sulfur atoms of NSF, with a consequent lower negative formal charge on the nitrogen atom of NSF. If we assume that the charge on the nitrogen atom is a measure of the total degree of π bonding between the N and S atoms, we are forced to the conclusion that the total covalent N–S bond order in NSF is greater than that in NSF_3. In order to rationalize this conclusion with the obviously greater strength of the bond in NSF_3 (as measured by bond length and stretching frequency[2]), we propose that the σ N–S bond is stronger in NSF_3 than in NSF. This proposal seems reasonable when one considers the bond angles and orbital hybridizations in these compounds. In NSF_3, the FSF bond angles[2] are only 94°, corresponding to a high degree of p character in the sulfur orbitals used in forming the S–F bonds. Consequently, the sulfur orbital used in forming the σ N–S bond must have a high degree of s character and would be expected to form an exceptionally strong σ bond.[7] In NSF, the σ lone pair on the sulfur atom would be expected to occupy an orbital having a high degree of s character. Therefore, the sulfur orbital used in forming the σ N–S bond must have considerable p character and would be expected to form a relatively weak σ bond.[7] In other words, we believe that the strong σ N–S bond of NSF_3 more than compensates for the fact that there is less π N–S bonding in NSF_3 than in NSF.

On going from NSF_3 to the NSF_2R compounds, the nitrogen binding energy decreases markedly (by an amount depending on the electronegatively of the group R). These decreases parallel the corresponding decreases in the sulfur binding energies. Because NSF_3 and the NSF_2R compounds have similar structures, it is probably safe to conclude that the N–S bond orders are lower in the NSF_2R compounds. Such a conclusion is readily explained by assuming a reduction either in the degree of $p\pi \rightarrow d\pi$ bonding (caused by an expansion of the sulfur $d\pi$ orbitals) or in the degree of N($p\pi$)/S–F(σ) hyperconjugation (caused by the reduction in the number of S–F bonds).

On going from $NSF_2C(CF_3)_3$ to $F_2SNC(CF_3)_3$, the nitrogen binding energy increases by 0.96 eV, and on going from $NSF_2CF(CF_3)_2$ to $F_2SNCF(CF_3)_2$, it increases by 1.03 eV. These changes are qualitatively consistent with the formal charges of the structures in Chart I. The fact that the increases are considerably greater than the corresponding decreases in

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(3) Siegbahn, K. "ESCA Applied to Free Molecules"; North-Holland Publishing Co.: Amsterdam, 1969.

(4) Corrected datum for SO_2F_2 from: Perry, W. B. Ph.D. Thesis, University of California, Berkeley; Lawrence Berkeley Laboratory Report LBL-3133, Oct, 1974.

(5) Bakke, A. A.; Chen, H. W.; Jolly, W. L. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *20*, 333.

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Table II. Localized Orbital Ionization Potentials (LOIP) for NSF and NSF_3

molecule	LOIP, eV N 2p	 F 2p	 S 3p
NSF	11.1	14.80	13.62
NSF_3	10.4	16.87	15.99

the sulfur binding energies is also expected; because of the difference in the $\langle 1/r \rangle$ values of the nitrogen and sulfur valence electrons, nitrogen core binding energies change about twice as much for a given change in charge as do sulfur core binding energies.[8]

Fluorine. Replacement of a fluorine atom in NSF_3 by an $N(CH_3)_2$ group causes the binding energy of the remaining fluorine atoms to decrease by 1.95 eV, in accord with the relatively low electronegativity of the $N(CH_3)_2$ group. Only one peak was observed in the fluorine 1s spectra of $F_2SNCF(CF_3)_2$ and $F_2SNC(CF_3)_3$. Because this peak corresponds to both the SF and CF fluorines, the binding energy of the peak is a weighted average and has little significance.

Removal of two fluorines from NSF_3 to form NSF causes the binding energy of the remaining fluorine to drop by 2.58 eV. This drop reflects the fact that, in NSF, the fluorine atom has no competition in the withdrawal of electron density from the NS group.

Carbon. The carbon 1s spectra of all four of the carbon-containing compounds consist of two well-resolved peaks that are easily assigned to the two kinds of carbon atoms. In each case, on going from the NSF_2R compound to the F_2SNR compound, the binding energy of the unique carbon atom is essentially constant, whereas that of the CF_3 groups decreases slightly. The decrease is probably due to the attachment of the fluorocarbon group to a nitrogen atom, as opposed to a highly positively charged sulfur atom.

Interpretation of Valence Ionization Potentials with Core Binding Energies

By use of appropriate core binding energy data, it is possible to delete from shifts in valence ionization potential the contributions (to these shifts) of changes in potential and relaxation energy.[9] We assume that the pπ lone pairs of H_2S, HF, and planar NH_3 are strictly nonbonding. We have used the lone pair ionization potentials and core binding energies of these molecules,[9] together with the core binding energies of NSF and NSF_3, to calculate the ionization potentials that the valence p orbitals of NSF and NSF_3 would have *if they were nonbonding*. These calculated localized orbital ionization potentials (LOIPs) are listed in Table II. It is instructive to compare the LOIP values with the actual ionization potentials of molecular orbitals (MOs) that involve the nitrogen, fluorine, and sulfur p orbitals in order to quantify the bonding or antibonding character of the MOs.

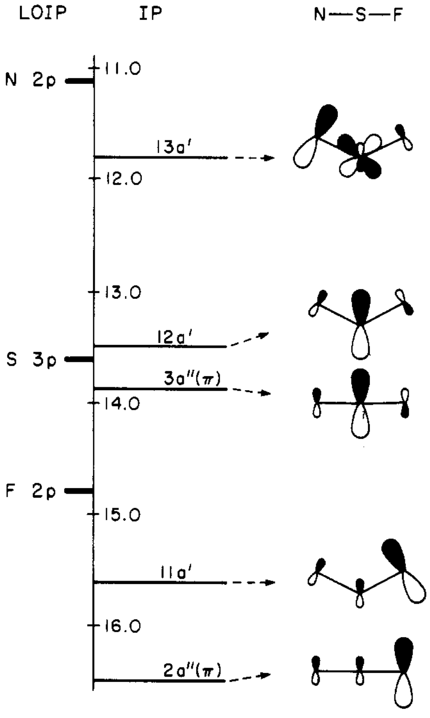
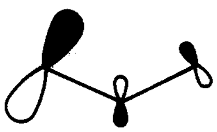


Figure 1. Molecular orbital energy level diagram for NSF, showing the LOIP values for the nitrogen 2p, sulfur 3p, and fluorine 2p orbitals.

NSF. The first five bands in the ultraviolet photoelectron spectrum of NSF lie at 11.82, 13.50, 13.87, 15.61, and 16.47 eV.[10–13] The corresponding MOs have been characterized as π or quasi-π orbitals, derived mainly from the valence p orbitals of the three atoms.[10–12] The LOIP data strongly suggest that the 11.82-eV band corresponds to an MO derived mainly from a nitrogen 2p orbital (LOIP = 11.1 eV), with 0.7 eV of bonding character. The data indicate that the bands at 13.50 and 13.87 eV correspond to MOs derived mainly from sulfur 3p orbitals (LOIP = 13.62 eV), with very slight antibonding and bonding character, respectively. The bands at 15.61 and 16.47 eV appear to correspond to bonding MOs derived mainly from fluorine 2p orbitals (LOIP = 14.80 eV). We believe that the MO assignments and qualitative MO pictures shown in the energy level diagram of Figure 1 are logical deductions from the data. The symmetry assignments are largely in agreement with those of the UPS investigators,[10–13] but in most cases the indicated atomic orbital contributions to the MOs are quite different from those given by those investigators. The differences are mainly due to the LOIP values, which show that the nonbonding nitrogen 2p level lies well above the nonbonding sulfur 3p level. The earlier workers assumed an ordering consistent with the electronegativities of the neutral atoms, i.e., the reverse ordering.

The HOMO, which we characterize as an S–N bonding orbital located mainly on the nitrogen atom, has been described variously as a sulfur lone pair[12] and as an orbital centered mainly on nitrogen and fluorine.[13] The bonding character of the orbital is inconsistent with the involvement of only valence p orbitals in the bonding. If we restricted the bonding to p orbitals, the HOMO would be expected to look something like



The orbital picture implies a net antibonding interaction. Hence, the LOIP data indicate that the HOMO has been stabilized by interaction with a higher lying orbital, presumably a sulfur d orbital, and therefore that the HOMO has considerable N(pπ) → S(dπ) character, as indicated crudely by the sketch in Figure 1. The experimental data do not rule out the possibility that the out-of-plane 4a″(π) orbital might be stabilized by N(pπ) → S(dπ) interaction so much more than the 13a′ orbital that it ends up as the HOMO. However, we abide by the ab initio calculations of Seeger et al.,[14] which

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(8) Jolly, W. L.; Perry, W. B. *Inorg. Chem.* **1974**, *13*, 2686.

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indicate that the HOMO is the in-plane orbital, 13a′. The electron density contour plots of the HOMOs of NSF[14] and the isoelectronic molecule, SO_2,[15] are very similar in the region of the sulfur atom. However, the plot for NSF shows the greatest density in the region of the nitrogen atom, thus confirming our interpretation of this orbitals as one mainly located on the nitrogen atom.

We consider the 12a′ and 3a″(π) orbitals as essentially sulfur lone pairs rather than as a nitrogen lone pair and S–N π-bonding orbital,[12,13] respectively. And finally, we believe that 11a′ and 2a″(π) are S–F bonding orbitals, located mainly on the fluorine atom, rather than an S–N bonding orbital and fluorine lone pair,[12,13] respectively.

NSF_3. The first four bands in the ultraviolet photoelectron spectrum of NSF_3 lie at 12.50, 14.15, 16.65, and 18.35 eV, and the corresponding MOs have been characterized as derived mainly from the valence p orbitals of the atoms in the molecule.[11] The first band has been assigned to the 7e(π) orbitals, corresponding to π bonding between the nitrogen and sulfur atoms. However, the LOIP data are not at all consistent with a description of this π bonding, based only on valence p orbitals. If only p orbitals were involved in the S–N π bonding, the first ionization potential of the molecule would be *lower* than the nitrogen atom LOIP, 10.4 eV. It is clear that the 7e(π) orbitals have been strongly stabilized by interaction with higher lying orbitals, presumably a pair of sulfur d orbitals.

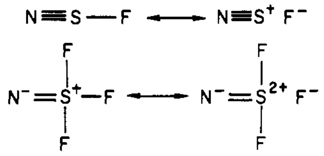
The second band has been assigned to the $10a_1(\sigma)$ orbital, which has been described as a "nitrogen lone pair".[11] The ionization potential and LOIP values are consistent with this interpretation if the orbital is described as having strong S–F antibonding character and weak S–N bonding character. When NSF_3 forms an adduct with a Lewis acid, the electrons in this orbital largely transfer to the Lewis acid. Because of the depopulation of the S–F antibonding region of the orbital, the S–F bonds are strengthened,[2] and because of rehybridization at the nitrogen atom (in which the s character of the N–S σ-bonding orbital increases), the N–S bond is strengthened.[2]

The third band is intense and broad and has an ionization potential close to the fluorine LOIP value. Therefore, we believe the band is a composite, assignable to the nonbonding fluorine lone pair orbitals, $1a_2$, 6e, and 5e. Cowan et al.[11] assign this band to 6e alone, without comment.

The ionization potential of the fourth, weak band (18.35 eV) is consistent with an orbital located mainly on the fluorine atoms, with bonding character. We believe that a reasonable assignment is $9a_1(\sigma)$, the bonding counterpart to $10a_1(\sigma)$. The orbital would be expected to have both S–F and S–N bonding character and to be located mainly on the fluorine atoms. Cowan et al.[11] tentatively assign this band to $1a_2$, a nonbonding fluorine orbital that we have included in the composite third band.

Summary

We have shown that N(pπ) → S(dπ) bonding is important in all the compounds of chart I that have a sulfur atom bonded to a peripheral nitrogen atom. Other XPS data[16] have indicated strong N(pπ)/S–F(σ) hyperconjugation in NSF_3, and the long S–F bond[17] in NSF suggests similar hyperconjugation in that molecule. Because of structural similarities, the other compounds of Chart I probably also have considerable hyperconjugation. However, we do not believe that the data of this study give information regarding this point. Nevertheless, in describing the bonding in NSF and NSF_3, it is clear that we must include not only the simple s,p σ bonding implied by the structures of Chart I but also both hyperconjugation and N(pπ) → S(dπ) bonding. There is no simple way to indicate the relative importance of these bonding contributions in a structural formula, and even the concept of bond order is difficult to define meaningfully when such different types of bonding are involved. However, we can approximately represent NSF and NSF_3 as resonance hybrids:



The left-hand structures imply N(pπ) → S(dπ) bonding, and the right-hand structures imply N(pπ)/S–F(σ) hyperconjugation. These representations are consistent with our finding that the nitrogen atom of NSF_3 is more negatively charged than that of NSF.

Experimental Section

Thiazyl fluoride (NSF) was prepared by the thermal decomposition of $Hg(NSF_2)_2$.[18] Thiazyl trifluoride (NSF_3) was prepared by the reaction of SbF_5NSF_3 with KF.[19] The dimethylamido complex $NSF_2N(CH_3)_2$ was prepared by the reaction of NSF_3 with $(CH_3)_3SiN(CH_3)_2$.[20] The perfluoroalkyl complexes $NSF_2CF(CF_3)_2$[21] and $NSF_2C(CF_3)_3$[22] were prepared by the reaction of NSF_3 with $F_2C{=}CFCF_3$ and $F_2C{=}C(CF_3)_2$, respectively.[21] The S–N–C isomers $F_2SNCF(CF_3)_2$ and $F_2(SNC(CF_3)_3$ were prepared from the corresponding N–S–C linked compounds via a sealed tube reaction at 110 °C for 24 h.[21] Vapor-phase infrared spectroscopy showed the purity of the samples to be better than 95%.

Gas-phase X-ray photoelectron spectra were obtained on a GCA/McPherson ESCA-36 spectrometer utilizing a Mg anode. Samples were held in a Monel reservoir at a temperature sufficient to give a vapor pressure of 10–100 torr. Flow through the all-metal inlet system was controlled with a micrometer-type needle value. The Ne 1s, Ne 2s, and the N_2 1s photolines were used as calibration standards. Peak positions and their uncertainties were determined by the computer program CURVY.[23]

The binding energy data for thiazyl trifluoride replace less accurate data that we earlier reported for that compound.[16,24]

Calculations

The change in charge of the nitrogen atom (ΔQ_N) on going from NSF to NSF_3 may be calculated from[25]

$$\Delta Q_N = (1/k)(\Delta E_B - \Delta V + \Delta E_R)$$

where ΔE_B is the change in the N 1s binding energy, k is 26.53 eV/charge,[26] ΔV is the change in potential due to the charges of the other atoms, and ΔE_R is the change in relaxation energy. The E_R values were calculated by the transition-state method,[27] using CNDO/2 wave functions[28] and the equivalent cores approximation.[29] The

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experimental geometries of NSF and NSF_3 were used.[2] Straightforward application of the method involves the relation

$$E_R = 0.5[\Phi_{val}(N) - \Phi_{val}(O^+)]$$

where $\Phi_{val}(N)$ is the valence potential in the ground-state molecule and $\Phi_{val}(O^+)$ is the valence potential in the ion, approximated by replacing the N nucleus by the O nucleus. Calculations based on this relation yield $\Delta E_R = 0.8$ eV, a value almost exactly equal to $-\Delta E_B$. Previous studies[30,31] have shown that ΔE_R values calculated by this method are usually too large and must be reduced by a factor of about half to give satisfactory correlations of E_B data. Thus, we conclude in this case that $\Delta E_R + \Delta E_B \leq 0$. The sulfur atom of NSF_3 is surely more positively charged than that of NSF, and therefore $\Delta V > 0$. Hence, the calculations, even allowing for uncertainty in ΔE_R, indicate that $\Delta Q_N < 0$.

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Metal-Nitroxyl Interactions. 41. Comparison of Electron-Electron Spin-Spin Interactions in Spin-Labeled Silver Porphyrins in Fluid Solution, in Frozen Solution, and on Imbiber Beads

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EPR spectra were obtained for three spin-labeled silver porphyrins in fluid solution, in frozen solution, and on imbiber beads. The values of the electron-electron spin-spin coupling constant, *J*, obtained in the three media, were in good agreement, which indicated that the molecular conformations were substantially unchanged by immobilization. Therefore, the values of the interspin distance, *r*, obtained from the rigid-lattice spectra, reflect the geometries of the molecules in fluid solution as well as in the solid state. For a tetraphenylporphyrin that had the spin label attached to the ortho position of one of the phenyl rings, the large solvent dependence of *J* observed in fluid solution persisted in frozen solution. The analysis of the frozen-solution spectra indicated that the change in *J* was accompanied by a change of about 2 Å in the interspin distance. The strong solvent dependence of *J* is consistent with the hypothesis that the solvent influences the molecular conformation and that in some conformations there is weak orbital overlap between the ortho substituent and the porphyrin π system.

Introduction

The determination of molecular structure in fluid solution is a problem of longstanding interest to chemists. Although X-ray crystallography provides detailed information concerning the structure of molecules in the solid state there is always the concern that structures in solution may differ from structures in the solid state. Therefore a structure-dependent observable that can be measured both in the solid and in fluid solution is important as an indicator of whether other parameters measured in the solid state pertain to the structure in fluid solution.

The electron-electron coupling constants, *J*, obtained from the EPR spectra of spin-labeled complexes of slowly relaxing metals in fluid solution, arise from the isotropic exchange interaction between the two unpaired electrons. For small molecules in fluid solution, molecular tumbling averages away the electron-electron splitting due to the anisotropic dipolar interaction that is dependent on the interspin distance. However when molecules are immobilized, the ESR spectra reflect the combined effects of the isotropic exchange and anisotropic dipolar interactions. Thus, analysis of the spectra can provide the value of *J* as well as the interspin distance.[1-3]

We have shown previously that the values of *J* are sensitive to changes in the conformations of the bonds between the metal and the nitroxyl.[1,4-6] Thus, agreement between the values of *J* obtained from spectra run in fluid and frozen solutions indicates that the conformations of the metal-nitroxyl linkage are similar in the two states. In cases where there is agreement between the values of *J* in fluid solution and in the solid states, the value of *r* obtained from the immobilized spectra should also pertain to the fluid-solution structure.

More detailed geometrical information can be obtained from the analysis of EPR spectra obtained on doped single crystals than from powder samples. However, not all molecules can readily be doped into single crystals. Furthermore, the analysis of single-crystal data is time-consuming. We are therefore exploring the extent to which geometrical information can be

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