Chalcogen Bonding between Tetravalent SF₄ and Amines

Vincent de Paul N. Nziko and Steve Scheiner*

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, United States

Supporting Information

ABSTRACT: The N→S chalcogen bond between SF₄ and a series of alkyl and arylamines is examined via ab initio calculations. This bond is a strong one, with a binding energy that varies from a minimum of 7 kcal/mol for NH₃ to 14 kcal/mol for trimethylamine. Its strength derives in large measure from charge transfer from the N lone pair into the σ*(SF) antibonding orbitals involving the two equatorial F atoms, one of which is disposed directly opposite the N atom. Decomposition of the total interaction energy reveals that the induction energy constitutes more than half of the total attraction. The positive region of the molecular electrostatic potential of SF₄ that lies directly opposite the equatorial F atoms is attracted to the N lone pair, but the magnitude of this negative region on each amine is a poor predictor of the binding energy. The shortness and strength of the N→S bond in the dimethylamino-·SF₄ complex suggest it may better be described as a weak covalent bond.

INTRODUCTION

Of the various noncovalent bonds, the H-bond is arguably the most important and prevalent. It is typically formulated as the positioning of two molecules such that the H atom of one molecule, A−H, acts as a bridge to an atom D of another molecule. Although its earliest conception applied highly electronegative atoms like O, F, and N as donor and acceptors, a great deal of work since that time has broadened the picture to include other atoms such as C, S, and Cl. In addition, the proton need not interact with a lone pair of the acceptor atom but also with other electron sources such as the π-systems of unsaturated molecules. It is not only a proton that can serve as a bridge between two molecules. The anisotropically charged distribution around halogen atoms (X) allow them to act in a similar capacity.

Unsurprisingly, the chalcogen family is not excluded from this sort of noncovalent bonding. A chalcogen bond is formed when a member of this family of atoms (e.g., S or Se) engages in an attractive and direct noncovalent interaction with an electronegative atom like N or O. The importance of chalcogen bonds has been underscored by their strength, which is comparable to and sometimes exceeds that of HBs. For instance, there is a direct interaction of S of FHS with N of NH₃, forming a strong S···N noncovalent bond with a binding energy of 8 kcal/mol.

With respect to S, prior study of its chalcogen bonding has centered around the divalent bonding situation, e.g., SO₂, HSF, thioethers, or thiazole nucleosides. Unlike its congener O, the S atom commonly engages in higher order bonding, as, for example, the tetravalent S in H₂SO₄ or SF₄.

The present study is thus meant to fill this gap in our present knowledge about S chalcogen bonding. SF₄ is taken as the prototypical tetravalent S molecule. Experimentally, SF₄ is widely used in fluorination of alcohols, aldehydes, ketones, and carboxylic acids. SF₄ is reacted with primary amines to yield sulfur difluoro imide and sulfur diimides. Although alternative methods for the synthesis of these compounds exist, the most common one is the reaction of compounds containing the primary amino group (NH₂) with SF₄. This tetravalent S is allowed to interact with a series of electron donor amines, covering a range of both alkylamines and N-containing heteroaromatic rings. It is found that the S···N chalcogen bonds are all quite strong, greater in magnitude than the prototypical H-bond within a water dimer. Indeed, the binding energy ranges up to as much as 14 kcal/mol, so that some of these interactions may be considered as having crossed the threshold from noncovalent to weak covalent S···N bond.

COMPUTATIONAL PROCEDURES

Calculations were carried out with the Gaussian09 program. Geometries were fully optimized at the MP2/aug-cc-pVDZ level. This method has demonstrated its reliability for a range of...
nearly opposite the N atom, \( \text{Fc} \) represents one of the two binding energy, with the exception of a small increase for TMA. The interaction energy was dissected using SAPT methodology.\(^{66} \) The SAPT0 calculations\(^{68,69} \) were carried out at the HF/cc-pVDZ computational level, using the MOLPRO program.\(^{70} \) The Natural Bond Order (NBO) method\(^{71,72} \) was used to evaluate charge transfer effects using the NBO-3 program, incorporated in the Gaussian09 program.

## RESULTS

The optimized structure of \( \text{H}_3\text{N} \cdots \text{SF}_4 \) is illustrated in Figure 1, which is representative of all of these heterodimers involving an alkylamine. \( \text{F}_a \) and \( \text{F}_b \) are the equatorial F atoms, with \( \text{F}_a \) lying nearly opposite the N atom, \( \text{F}_b \) represents one of the two symmetrically disposed axial F atoms. The first row of Table 1 indicates the binding energy grows rapidly as methyl groups are added, from a minimum of 6.62 kcal/mol for \( \text{NH}_3 \) and peaking at 14.39 kcal/mol for trimethylamine (TMA). The enhanced strength arising from each methyl addition is consistent with the idea that alkyl groups are electron-releasing, and can hence facilitate the donation of electron charge from the amine. The next row shows a corresponding contraction of the intermolecular separation with each succeeding increase in binding energy, with the exception of a small increase for TMA. The N atom sits nearly exactly opposite one of the two equatorial F atoms of \( \text{SF}_4 \), with a \( \theta(\text{N} \cdots \text{SF}_4) \) angle within 10° of 180°. Concomitant with the binding, there is a stretch in this \( \text{S} \cdots \text{F}_a \) bond, between 18 and 66 mÅ, and this stretch correlates with the overall binding energy. The other equatorial \( \text{S} \cdots \text{F}_b \) and axial \( \text{S} \cdots \text{F}_c \) bonds also undergo a stretch, albeit not quite as large. The full thermodynamic quantities in the remaining rows of Table 1 indicate that the zero-point vibrational energies introduce a small decrease in the magnitude of \( \Delta E \) on going to \( \Delta H \). When the entropic loss is factored in, \( \Delta G \) hovers around zero (slightly positive for the three most weakly bound complexes and slightly negative for TMA), suggesting the presence of the dimer even at room temperature.

A similar sort of analysis was also carried out for a set of N-containing heteroaromatics shown in Figure 2. Pyridine is a six-membered ring containing a single N. Pyrazine, pyridazine, and pyrimidine add a second N to the ring, in the 1,4, 1,2, and 1,3 positions, respectively. Imidazole retains two N atoms but reduces the ring size to five atoms. The properties of their complexes with \( \text{SF}_4 \) are reported in Table 2 where it may first be noted that the binding energies all vary within the relatively narrow range of 7.4 to 9.4 kcal/mol. This range makes these complexes intermediate in strength between \( \text{NH}_3 \) and

### Table 1. Energetic (kcal/mol) and Geometric Aspects of Alkylamine:SF\(_4\) Complexes

<table>
<thead>
<tr>
<th>Amine</th>
<th>( \Delta E ) (kcal/mol)</th>
<th>( R(N\cdots S) ) (Å)</th>
<th>( \theta(N\cdots SF_4) ) (deg)</th>
<th>( \Delta r(S\cdots F_a) ) (mÅ)</th>
<th>( \Delta r(S\cdots F_b) ) (mÅ)</th>
<th>( \Delta H ) (298 K)</th>
<th>( \Delta S^* ) (cal mol(^{-1}) K(^{-1}))</th>
<th>( \Delta G ) (298 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>–6.62</td>
<td>–9.72</td>
<td>2.571</td>
<td>173.3</td>
<td>18.5</td>
<td>8.7</td>
<td>–5.26</td>
<td>–27.00</td>
</tr>
<tr>
<td>Methylamine</td>
<td>–13.25</td>
<td>2.188</td>
<td>170.3</td>
<td>52.9</td>
<td>27.9</td>
<td>43.3</td>
<td>–8.32</td>
<td>2.47</td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>–14.39</td>
<td>2.158</td>
<td>169.7</td>
<td>65.9</td>
<td>36.9</td>
<td>43.7</td>
<td>–11.63</td>
<td>0.12</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>–12.66</td>
<td>2.227</td>
<td>171.3</td>
<td>62.4</td>
<td>32.4</td>
<td>45.2</td>
<td>–12.66</td>
<td>–0.63</td>
</tr>
</tbody>
</table>

\(^{64} \)Evaluated at 25 °C.

### Table 2. Energetic (kcal/mol) and Geometric Aspects of Heteroaromatic Amine:SF\(_4\) Complexes

<table>
<thead>
<tr>
<th>Amines</th>
<th>( \Delta E ) (kcal/mol)</th>
<th>( R(N\cdots S) ) (Å)</th>
<th>( \theta(N\cdots SF_4) ) (deg)</th>
<th>( \Delta r(S\cdots F_a) ) (mÅ)</th>
<th>( \Delta r(S\cdots F_b) ) (mÅ)</th>
<th>( \Delta H ) (298 K)</th>
<th>( \Delta S^* ) (cal mol(^{-1}) K(^{-1}))</th>
<th>( \Delta G ) (298 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>–9.39</td>
<td>–7.69</td>
<td>2.308</td>
<td>171.9</td>
<td>43.3</td>
<td>15.5</td>
<td>–8.24</td>
<td>–33.01</td>
</tr>
<tr>
<td>Pyrazine</td>
<td>–8.62</td>
<td>–7.43</td>
<td>2.338</td>
<td>172.5</td>
<td>31.1</td>
<td>11.5</td>
<td>–6.46</td>
<td>–37.03</td>
</tr>
<tr>
<td>Pyridazine</td>
<td>–7.43</td>
<td>–9.14</td>
<td>2.416</td>
<td>173.7</td>
<td>32.4</td>
<td>23.7</td>
<td>–7.25</td>
<td>–30.46</td>
</tr>
<tr>
<td>Pyrimidine</td>
<td>–8.32</td>
<td>–6.23</td>
<td>2.285</td>
<td>173.1</td>
<td>27.1</td>
<td>9.0</td>
<td>–7.90</td>
<td>–31.03</td>
</tr>
<tr>
<td>Imidazole</td>
<td>–13.25</td>
<td>–9.39</td>
<td>2.39</td>
<td>146.0</td>
<td>43.9</td>
<td>14.6</td>
<td>–9.72</td>
<td>–35.35</td>
</tr>
</tbody>
</table>

\(^{44} \)Evaluated at 25 °C.

Figure 1. Atomic labeling used to define geometries of complexes of amines with \( \text{SF}_4 \).

Figure 2. Heteroaromatic amines, (a) pyridine, (b) pyrazine, (c) pyridazine, (d) pyrimidine, and (e) imidazole, used in this study.
CH$_3$NH$_2$. Pyridine forms the strongest complex, followed by
the disubstituted rings, of which pyridazine with its adjacent N
atom forms the strongest. The five-membered ring of imidazole
is stronger still, despite the presence of two N atoms. Like the
binding energies, the intermolecular $R$(N···S) distances are also
fairly similar to one another, with the general trend of shorter
distances associated with strong bonds. Also like the alkyl-
amines, the S–F bonds elongate upon formation of each
complex. $\Delta H$ lies in the range between −6.2 and −8.2 kcal/
mol, while $\Delta G$ is positive, between 2.7 and 4.2 kcal/mol.

**Energy Decomposition.** The total interaction energy in
each of these dimers was dissected via SAPT to provide the
various attractive and repulsive components. These quantities
are displayed graphically in Figure 3 from which one can
quickly see their relative magnitudes. It is immediately clear
that induction makes the largest contribution to the binding
followed by electrostatic and then dispersion. The magnitudes
of these quantities vary from one system to the next, but their
relative proportions are surprisingly constant. Specifically, the
induction accounts for more than half of the total attractive
relative proportions are surprisingly constant. Specifically, the
induction accounts for more than half of the total attractive
energy, with a correlation coefficient $R^2$ of 0.88, as is ES. The
correlation improves when these two components are
compared with the MP2 values of $\Delta E_i$ with $R^2 = 0.95$
Although small in magnitude, DISP also scales linearly with $\Delta E_i$
with $R^2 = 0.97$.

**Comparison of Tetravalent with Divalent S.** As this
work represents the first examination of the chalcogen bonds
formed by tetravalent S, it would be informative to draw a
comparison with the more common divalent S. The properties
of the complexes formed by SF$_4$ with both NH$_3$ and
trimethylamine are displayed in Table 3 and are compared
with those in which SF$_4$ is replaced by both H$_2$S and HSF. The
first three rows of the table indicate the strong similarities of the
three complexes involving NH$_3$, with a small advantage for FHS. Adding three methyl groups to the amine approximately
doubles the strength of the interaction, but shows even less of a
distinction between the divalent and tetravalent S complexes,
even though the intermolecular distance is slightly longer in the
latter case.

**Molecular Electrostatic Potentials.** With regard to the
electrostatic segment of the interaction energy, examination of the
molecular potentials of the various electron donors all show a
negative region in the vicinity of the N atoms. These regions
can be quantitatively assessed via the value of the most negative
point on a surface that corresponds to an isodensity contour of
0.001 au. The values of this quantity, $V_{min}$, are presented in the

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**Table 3. Properties of Divalent and Trivalent S Complexes**

<table>
<thead>
<tr>
<th>complex</th>
<th>$E_b$ (kcal/mol)</th>
<th>$R$(N···S) (Å)</th>
<th>$\theta$(FS···N) (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FHS–NH$_3$</td>
<td>−7.92</td>
<td>2.466</td>
<td>171.0</td>
</tr>
<tr>
<td>F$_3$S–NH$_3$</td>
<td>−6.95</td>
<td>2.480</td>
<td>173.0</td>
</tr>
<tr>
<td>F$_3$S–NH$_3$</td>
<td>−6.62</td>
<td>2.573</td>
<td>173.3</td>
</tr>
<tr>
<td>FHS–TMA</td>
<td>−14.56</td>
<td>2.183</td>
<td>170.6</td>
</tr>
<tr>
<td>F$_3$S–TMA</td>
<td>−14.48</td>
<td>2.158</td>
<td>172.3</td>
</tr>
<tr>
<td>F$_3$S–TMA</td>
<td>−14.39</td>
<td>2.227</td>
<td>171.3</td>
</tr>
</tbody>
</table>
first column of Table 4. The alkyamines in the first four rows show a diminishing trend as methyl groups are added. This trend is opposite to the pattern of binding energies in Table 1 or even the ES terms in the SAPT decomposition. Within the context of the heteroaromatics, \( V_{\text{min}} \) varies as pyrazine < pyridazine < pyridine < pyrimidine < imidazole, which again differs from the binding energies in Table 2, where, for example, pyrimidine is the most weakly bound and pyridine the strongest. In summary, then, \( V_{\text{min}} \) is a poor indicator of binding strength or even of the electrostatic component.

On the positive side, MEPs do offer some insight into the similarity between divalent and tetravalent S with respect to its chalcogen bonding. The MEPs are illustrated in Figure 5 for Table 4. Extrema in the Molecular Electrostatic Potentials (kcal/mol) on an Isodensity Surface Corresponding to 0.001 au

<table>
<thead>
<tr>
<th></th>
<th>( V_{\text{min}} )</th>
<th>( V_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_3 )</td>
<td>−39.39</td>
<td>+42.15</td>
</tr>
<tr>
<td>methylamine</td>
<td>−38.04</td>
<td>+39.16</td>
</tr>
<tr>
<td>dimethylamine</td>
<td>−35.63</td>
<td>+42.19</td>
</tr>
<tr>
<td>trimethylamine</td>
<td>−33.45</td>
<td></td>
</tr>
<tr>
<td>pyridine</td>
<td>−29.76</td>
<td></td>
</tr>
<tr>
<td>pyrazine</td>
<td>−23.10</td>
<td></td>
</tr>
<tr>
<td>pyridazine</td>
<td>−25.45</td>
<td></td>
</tr>
<tr>
<td>pyrimidine</td>
<td>−35.60</td>
<td></td>
</tr>
<tr>
<td>imidazole</td>
<td>−36.27</td>
<td></td>
</tr>
</tbody>
</table>

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Figure 5. MEP of HSF, SF\(_2\)_d and SF\(_2\)_c, all calculated on isodensity surface of \( \rho = 0.001 \) au.

divalent \( \text{H}_2\text{S} \) and FHS, followed by tetravalent SF\(_4\). The similarities are evident. All potentials contain a red (negative) area along the extension of the S–F bonds, particularly the axial SF bonds of SF\(_4\).

More importantly, there is a blue (positive) region near the S atom, along the extension of each F–S bond, a so-called \( \sigma \)-hole. Quantitative of this hole via an evaluation of \( V_{\text{max}} \), the maximum of this potential on the \( \rho = 0.001 \) au isodensity contour, leads to the values reported in Table 4. It is immediately plain that the depth of this hole is nearly independent of the valency of the S atom. Whether \( \text{H}_2\text{S} \), FSH, or SF\(_4\), \( V_{\text{max}} \) lies within the narrow range of 39 to 42 kcal/mol. It should be finally noted that there is no positive \( \sigma \)-hole opposite the axial F atoms of SF\(_4\) due to the presence of one axial F atom directly opposite the other.

**Charge Rearrangement.** Treatment of the wave function via the NBO method leads to localized orbitals, which provide insights into the chemical nature of noncovalent interactions. In particular, the overlap of the N lone pair of the amine with the F_a–S \( \sigma^* \) antibonding orbital allows charge transfer/hyperconjugation from the former to the latter. This transfer has been shown to be a dominant factor in the formation of chalcogen bonds such as these. The magnitude of this transfer is listed in the first column of Table 5 as a perturbation energy.

![Figure 6](image)

Figure 6. Overlap between NBO N lone pair orbital and (a) \( \sigma^*(\text{FS}) \) and (b) \( \sigma^*(\text{SF}) \).

Table 5. NBO Second Order Perturbation Energy (kcal/mol) for Complexes with SF\(_4\)

<table>
<thead>
<tr>
<th></th>
<th>( E^*(2) ) (^a)</th>
<th>( E^*(2) ) (^b)</th>
<th>( E^<em>(2) + E^</em>(2) )</th>
<th>( \theta(\text{N–SF}_4) ) (^c)</th>
<th>( \theta(\text{N–SF}_4) ) (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>14.68</td>
<td>3.70</td>
<td>18.48</td>
<td>173.3</td>
<td>77.4</td>
</tr>
<tr>
<td>methylamine</td>
<td>41.49</td>
<td>16.77</td>
<td>58.26</td>
<td>170.3</td>
<td>80.6</td>
</tr>
<tr>
<td>dimethylamine</td>
<td>NA*</td>
<td>NA*</td>
<td>169.7</td>
<td>81.2</td>
<td></td>
</tr>
<tr>
<td>trimethylamine</td>
<td>41.28</td>
<td>20.65</td>
<td>61.93</td>
<td>171.3</td>
<td>81.7</td>
</tr>
<tr>
<td>pyridine</td>
<td>36.57</td>
<td>11.79</td>
<td>48.36</td>
<td>171.9</td>
<td>80.2</td>
</tr>
<tr>
<td>pyrazine</td>
<td>27.76</td>
<td>8.13</td>
<td>35.89</td>
<td>172.5</td>
<td>79.5</td>
</tr>
<tr>
<td>pyridazine</td>
<td>27.80</td>
<td>9.60</td>
<td>37.4</td>
<td>173.7</td>
<td>80.4</td>
</tr>
<tr>
<td>pyrimidine</td>
<td>24.59</td>
<td>6.93</td>
<td>31.52</td>
<td>173.1</td>
<td>79.4</td>
</tr>
<tr>
<td>imidazole</td>
<td>37.10</td>
<td>9.46</td>
<td>46.56</td>
<td>172.3</td>
<td>80.6</td>
</tr>
</tbody>
</table>

\( ^a \)NBO perturbation energy corresponding to \( \text{Nlp} \)–\( \sigma^*(\text{S–F}) \). \( ^b \)NBO perturbation energy corresponding to \( \text{Nlp} \)–\( \sigma^*(\text{S–F}) \). The interaction is strong enough that NBO places a covalent bond between N and S, i.e., considers the entire system as one unit.

\( E^*(2) \). This quantity is rather large, ranging from a minimum of 14.7 kcal/mol for \( \text{NH}_3 \) all the way up above 40 kcal/mol for methylamine and trimethylamine. The heteroaromatics also display large values of \( E(2) \), between 25 and 37 kcal/mol. Indeed, this interaction is so strong that in the case of dimethylamine, NBO assesses that there is a covalent bond linking the S and N atoms.

In a particularly interesting finding, the \( \sigma^*(\text{F}_n\text{S}) \) antibonding orbital, for which \( F_a \) lies opposite the N atom, is not the only one that can accept charge. Its overlap with the N lone pair is obvious in Figure 6a, but one can see in Figure 6b that the same

\( \sigma^*(\text{F}_n\text{S}) \) orbital can also engage with \( \sigma^*(\text{F}_n\text{S}) \) wherein \( F_n \) is the other equatorial F atom of SF\(_4\). Whereas \( F_a \) lies nearly opposite the N lone pair, so the \( \sigma^*(\text{SF}_4) \) orbital points directly at \( N \), the roughly 80° \( \theta(\text{N–SF}_4) \) angle reduces the overlap with this antibonding orbital. The amount of hyperconjugation associated with this second antibond is reported in the second column of Table 5 as \( E^*(2) \) and can be as large as 50% of \( E^*(2) \) (\( \text{Nlp} \rightarrow \sigma^*(\text{F}_n\text{S}) \)), so its effect cannot be ignored.

As a means of further probing the influence of the two SF antibonding orbitals, the SF\(_4\) molecule was pivoted around the S–F\(_b\) axis by an angle \( \psi \), holding fixed the other geometrical parameters of the pyridine–SF\(_4\) complex. On the basis of the diagrams in Figure 6, this rotation ought to have little effect upon the overlap between the N lone pair and the \( \sigma^*(\text{SF}_4) \) orbital, but it would misalign the lone pair with \( \sigma^*(\text{SF}_4) \). The values of \( E(2) \) computed during this rotation support this supposition. As may be seen in Figure 7, \( E^*(2) \) remains nearly constant over a ±20° misalignment, while \( E^*(2) \) suffers an erosion of some 16%.

![Image](image)

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σ buildup may be noted behind the S atom, corresponding to a halogen, chalcogen, and pnicogen bonds. A purple charge immediately to the left of the S. This pattern is typical of a noncovalent N approximately the position of the center of what may be termed displayed in Figure 8a where increases in density correspond consistent with the observation that all four S \( \text{atom F}_b \) axis, \( \sigma_\text{SFb} \) antibonding orbital. In addition to the transfer from one specific localized orbital to another, there are charge rearrangements that involve the entire complex. The redistribution of total electron density that accompanies the formation of the NH\( _4 \cdot \cdot \cdot \text{SF}_4 \) complex is displayed in Figure 8a where increases in density correspond to purple and losses to yellow. One may note first that there is a charge buildup directly between the N and S atoms, in approximately the position of the center of what may be termed a noncovalent N\( \cdot \cdot \cdot \text{S} \) bond. A larger yellow region of loss occurs immediately to the left of the S. This pattern is typical of halogen, chalcogen, and pnicogen bonds. A purple charge buildup may be noted behind the S atom, corresponding to a \( \sigma_\text{F}^*(\text{SF}_b) \) antibonding orbital.

It is especially interesting to note that the four F atoms of \( \text{SF}_4 \) are all surrounded by a purple region of charge gain. This pattern does not much distinguish between the two equatorial F atoms whose \( \sigma_\text{F}^*(\text{SF}) \) antibonding orbital accept charge from the amine and the axial F atoms that do not. Indeed, the NBO atomic charges of these F atoms all become more negative, as reported in Table 6. Figure 8b displays the charge redistribution of the imidazole\( \cdot \cdot \cdot \text{SF}_4 \) complex, which is very much like that for the simpler NH\( _4 \) amine. Again, all four \( \text{SF}_4 \) F atoms acquire additional density, which is verified by NBO atomic charges in Table 6. This pattern is in fact characteristic of all of the complexes examined here, whether alkylamine or heteroaromatic amine. This similarity in charge redistribution is also consistent with the observation that all four S–F bonds of \( \text{SF}_4 \) elongate upon formation of the complex. In fact, there is a fairly strong linear relationship between the change in charge on the \( \text{F}_a \) atom and its elongation, with a correlation coefficient \( R^2 \) of 0.955. In terms of the hyperconjugation, the strength of the S– \( \text{F} \) bond might be measured in terms of the populations of its \( \sigma \) and \( \sigma^* \) orbitals. Since the former would act to strengthen this bond, and \( \sigma^* \) to weaken it, the overall effect can be assessed as \( (\sigma-\sigma^*) \). This population difference is also linearly related to \( \Delta r(\text{SF}_b) \), with \( R^2 = 0.945 \). Correlations exist for the other S–F bond lengths as well, but are of poorer quality.

### SUMMARY

All of the amines, both alkyl and heteroaromatic, engage in strong chalcogen-bonds with \( \text{SF}_4 \). The alkylamine binding is very sensitive to the number of methyl groups; binding energies vary from 6.6 kcal/mol for NH\( _4 \) to 14.4 kcal/mol for trimethylamine. Heteroaromatics are less sensitive to the nature of the ring, all binding in the range between 7 and 9 kcal/mol. In all cases, one of the equatorial S–F bonds is arranged directly opposite the approaching N atom. It is into this \( \sigma_\text{F}^*(\text{S–F}) \) antibonding orbital that the N lone pair transfers some of its charge, which acts as a strong stabilizing influence on the complex. There is a lesser, but significant, amount of charge that is deposited into the \( \sigma_\text{F}^*(\text{S–F}) \) antibonding orbital of the other equatorial F atom of \( \text{SF}_4 \). The associated induction energy is the largest contributor to the binding of these complexes, constituting more than half of the total attractive energy, followed by electrostatic and then dispersion energy.

Examination of the charge rearrangements that accompany formation of each complex shows that the charge transferred from the amine to the \( \text{SF}_4 \) molecule is ultimately distributed among all four F atoms, as well as the central S atom. The ensuing increase in the partial negative charge on these F atoms explains the elongation of the S–F bonds. The molecular electrostatic potentials surrounding each monomer furnish some useful information about the binding. For example, the N lone pair is attracted to a positive region of the \( \text{SF}_4 \) potential surface, which is a strong stabilizing influence on the complex. There is a lesser, but significant, amount of charge that is deposited into the \( \sigma_\text{F}^*(\text{S–F}) \) antibonding orbital of the other equatorial F atom of \( \text{SF}_4 \).

### Table 6. Changes in NBO Atomic Charges (me) within \( \text{SF}_4 \) That Occur upon Formation of Complex with Indicated Amine

<table>
<thead>
<tr>
<th>Amine</th>
<th>( S )</th>
<th>( F_a )</th>
<th>( F_b )</th>
<th>( F_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>3.18</td>
<td>–23.25</td>
<td>–10.78</td>
<td>–15.01</td>
</tr>
<tr>
<td>methylamine</td>
<td>–86.9</td>
<td>–65.45</td>
<td>–22.03</td>
<td>–21.61</td>
</tr>
<tr>
<td>dimethylamine</td>
<td>–97.41</td>
<td>–52.89</td>
<td>–26.11</td>
<td>–27.29</td>
</tr>
<tr>
<td>TMA</td>
<td>–81.91</td>
<td>–46.64</td>
<td>–23.57</td>
<td>–18.71</td>
</tr>
<tr>
<td>pyridine</td>
<td>–27.22</td>
<td>–41.83</td>
<td>–8.86</td>
<td>–21.01</td>
</tr>
<tr>
<td>pyrazine</td>
<td>–12.50</td>
<td>–31.01</td>
<td>–6.34</td>
<td>–19.09</td>
</tr>
<tr>
<td>pyridazine</td>
<td>–7.06</td>
<td>–33.69</td>
<td>–5.56</td>
<td>–15.28</td>
</tr>
<tr>
<td>pyrimidine</td>
<td>–5.36</td>
<td>–29.29</td>
<td>–6.15</td>
<td>–22.80</td>
</tr>
<tr>
<td>imidazole</td>
<td>–25.11</td>
<td>–38.60</td>
<td>–9.76</td>
<td>–29.32</td>
</tr>
</tbody>
</table>

\( 0.10853 \)
determination to bind to an amine in the manner described here. In its complex with triethylamine, one of the equatorial F atoms of SF₅ lies 173° away from the N atom, within 2° of the structure described here with trimethylamine. Also quite similar is the R(N···S) distance of 2.38 Å, only slightly longer than the equivalent distance in our calculated TMA complex. Also confirmed by this crystal structure is the elongation of all of the S···F bonds upon formation of the complex.

There is an indication in the literature that a tetravalent S can engage in a chalcogen bond with an O atom as well. The complex between water and SO₂(CH₃)₂ contains what would appear at least geometrically to be a S···O chalcogen bond, of length 3.34 Å, and with the water O atom situated opposite one of the two O covalently bonded to S. However, there was little analysis of the nature of any possible S···O bond; furthermore, the energy of this bond could not be disentangled from the combined effects of several H-bonds.

**ASSOCIATED CONTENT**

Supporting Information

Full references S9 and 70. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: steve.scheiner@usu.edu.

Notes

The authors declare no competing financial interest.

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