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# Structure and Bonding in Some *S*-methylsulfonium Halides

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ABSTRACT: *Density functional theory (DFT) calculations have been carried out at the B3LYP 6-311+G(d,p) level to characterize the geometric and electronic characteristics of a series of S-methylsulfonium halides that possess unusual molecular structures. Atoms-in-molecules (AIM), electron localization function (ELF), and NMR data support the idea that the binding in these gas phase species is predominately ionic with some small degree of covalent bonding.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:263–270, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20087

## *INTRODUCTION*

In a recent theoretical study of $^{31}$S nuclear magnetic resonance (NMR) shieldings [1], our attention was drawn to *S*-methylthiolanium (*S*-methyltetrahydrothiophenium) iodide whose NMR shielding was thought to be very much downfield and, indeed, the most downfield-shifted sulfur compound for which experimental data currently existed at that time. Our calculations indicated either theory was failing in this particular case or that the early experimental results were in error. We have recently carried out a redetermination of the experimental shieldings in the *S*-methylthiolanium iodide and theoretical calculations on the cation and its F, Cl, and Br halides [2]. We showed that our theory was correct, that the shielding in these compounds is not far downfield, so that the early experimental results are in error. In addition, experiment and theory were examined for the related trimethylsulfonium cation and the F, Cl, and Br halides. Agreement between experiment and theory was very good in both cases.

Because the experiments on the iodide salts were carried out in aqueous solution, it was felt that the ions would be dissociated and that a proper comparison between theory and experiment would involve the isolated cations. We did go on to point out, however, that one can obtain stable gas-phase structures in which the halide anion is situated on either “side” of the pyramidal sulfonium cation: that side where one expects the lone pair to be located (the “front” side) where direct interaction between the halide and sulfur can occur, or that side opposite the lone pair (the “back” side) where interaction with sulfur is minimized by the intervening carbon and hydrogen atoms. The differences in energies in the two cases are, as we discuss later, rather small.

Because the structure of those compounds is rather unusual, the purpose of this paper is to characterize in detail the structure and bonding of sulfur in a series of gas phase *S*-methylsulfonium halides not only by molecular geometries but also by electronic characteristics as determined from the atoms-in-molecules (AIM) approach [3] and the electron localization function (ELF) [4,5].

## *THEORETICAL METHODS AND BACKGROUND*

### *Computational Details*

We have carried out calculations on the *S*-methyl cations of dimethylsulfide, the cyclic systems $SC_2H_4$

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(thiirane), $SC_3H_6$ (thietane), $SC_4H_8$ (thiolane), and $SC_5H_{10}$ (thiane) and their fluorine, chlorine, and bromine salts. Geometries were optimized at the B3LYP [6–8] 6-311+G(d,p) level with frequency determinations affirming the stability of the structures. Chemical shieldings were performed at the GIAO [9,10] B3LYP/6-311+G(nd,p) level where two sets of Cartesian $d$-functions ($n = 2$) were used for sulfur and $n = 1$ for all other elements. Accurate energies were determined from the model chemistry G3 [11] or G3MP2 [12] methods. Gaussian 03 [13] was used in these calculations. ELF and AIM characteristics were determined from the code of Noury et al [14] with extensions of 5 Å from the outermost nuclear centers and a spacing of 0.1 or 0.15 Å.

We employed our scaled DFT method [15] for the chemical shieldings, a method resulting from the discovery that a simple constant rescaling of the paramagnetic contribution in the B3LYP approach can be made such that quantitative predictions are possible. A scaled DFT shielding is obtained as

$$\sigma_{\mathrm{s,DFT}} = \sigma_{\mathrm{dai}} + k\sigma_{\mathrm{para}} \tag{1}$$

where $\sigma_{\mathrm{s,DFT}}$ is the new estimate of the shielding. The redetermined shieldings are in good agreement with experiment and rival some of the more sophisticated ab initio approaches, and, because density functional theory is involved, the shielding calculations are extremely fast. For sulfur we initially found $k = 0.871(\pm 0.010)$ [15]; a retreatment the experimental and theoretical data from our extensive sulfur study [1] leads to the improved value of $k = 0.888(\pm 0.010)$, the value we use in this study.

### *Theoretical Background*

The theoretical tools we employ in this study are the atomic charge and delocalization index [16] from atoms-in-molecules (AIM) theory [3] and the basin populations from the electron localization function (ELF) [4,5].

In AIM theory it is the electron density, $\rho(\bar{r})$, that is used to partition the space into "atoms." The number of electrons, $N_j$, in a particular atomic basin is obtained by integrating the electron density over a particular atomic basin, $\Omega_j$. Likewise, the number of electron pairs, $N_{jk}$, involved in two basins $\Omega_j$ and $\Omega_k$, is obtained by integrating the spinless electron pair density over the two basins. By expressing the pair density in terms of a correlation factor used in defining the Fermi hole [17,18], the delocalization index [16], $\delta_{jk}$, is given by

$$\delta_{jk} = 2(N_j N_k - N_{jk}) \tag{2}$$

According to Fradera et al. [16], the delocalization index is a measure of the number of electron pairs shared by two basins. While they do not claim this function to be a bond order, in the case of single determinate functions (such as employed here in the Kohn–Sham wavefunction) it is identical to the covalent bond order defined by Ánglyán et al. [19]. We shall use it here as a particular measure of covalent bond order.

ELF is a robust descriptor of chemical bonding based on topological analyses of local quantum mechanical functions related to the Pauli exclusion principle. Basins corresponding to core electrons, bond electrons, and lone pair electrons are found in this approach with the various basin populations obtained again by integrating the electron density over the basins. ELF is of special interest to chemists in that the resulting isosurfaces of the ELF density conform well with the classical Lewis picture of bonding. Indeed, ELF has given quantitative credence to the valence shell electron pair repulsion (VSEPR) theory [20,21].

## *RESULTS AND DISCUSSION*

### *Structural Data*

With the exception of the thianium halides discussed below, most of the sulfonium halide structures are unique. Typically for the front-side complexes, the halide and the $S$-methyl group are in axial positions with respect to the other carbon atoms adjoining sulfur and the sulfur lone pair which occupy essentially equatorial positions; for the back-side complexes, the halide sits over the cyclic ring (or, in the case of trimethylsulfide, over the three methyl groups). Figure 1 illustrates these facts for the two thiiranium fluoride isomers. Although $S$-methylthietane has both axial and equatorial isomers (differing by only 0.33 kcal/mol via G3 theory), the presence of a halide flattens the cyclic ring enough (ring-bend angle of less than three degrees) so that the front-side complexes are unique. So, too, are the back-side complexes, which have basically the appearance of the equatorial $S$-methylthietane; if one starts from the axial $S$-methyl form, the equatorial complex results as the equilibrium form (with a ring-bend angle of from 35° (F) to 31° (Cl, Br).

The thianium complexes are more complicated in that different structures are obtained starting with the $S$-methyl group in an axial or equatorial position. For the back-side complexes, the halide ion again situates itself over the ring atoms as in the other, simpler compounds. The situation is also different for the front-side complexes as illustrated in Fig. 2. There one sees that it is one of the ring atoms along with a fluorine atom that occupy axial positions, one

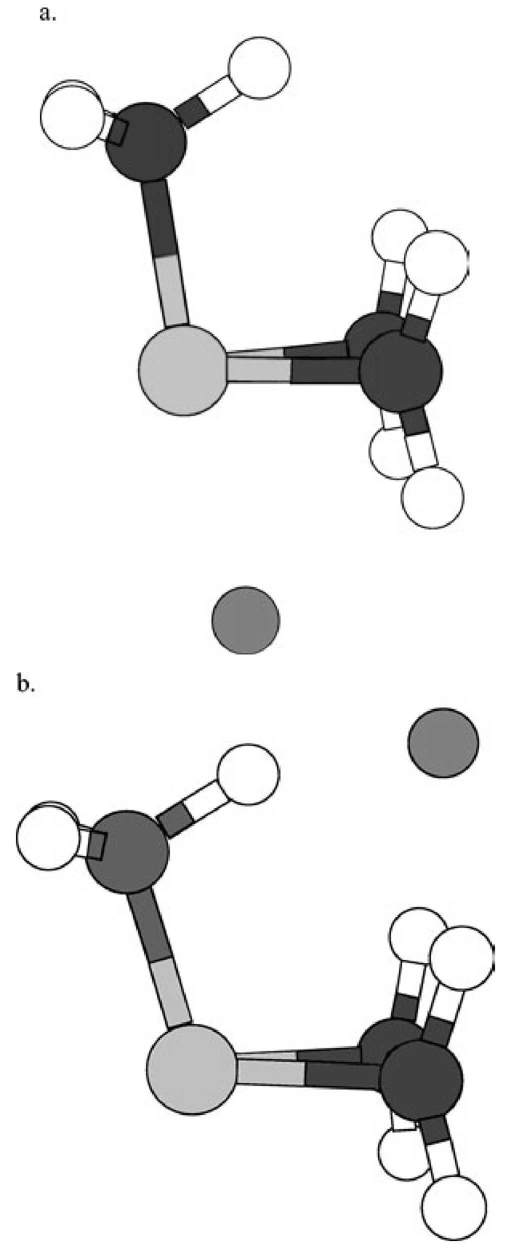


**FIGURE 1** Structures (to scale) of (a) the front-side and (b) the back-side complexes of *S*-methylthiiranium fluoride.

of the other sulfide-adjoined ring carbons and the *S*-methyl group being in equatorial positions. As we discuss later, we are selective when describing the various characteristics of the thianium compounds.

In our study of the front- and back-side halide complexes with various sulfonium cations, we found that the quantitative characterization of the species differing by the carbon substituents on sulfur varied little, as perhaps one might have expected. Accordingly, for the most part we shall concentrate on just one of the species, the halides of the *S*-methyl thiiranes, $SMXC_2H_4$, $X = F, Cl, Br$, and note where significant differences occur for other compounds. This species has a high degree of symmetry and is simple to illustrate. Our goal is not only to present theoretical structural data but more importantly to characterize the bond(s) formed between the halides and the sulfonium cationic species.

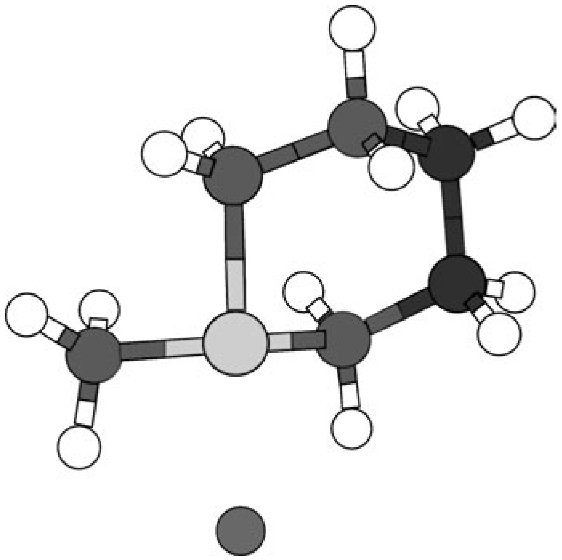
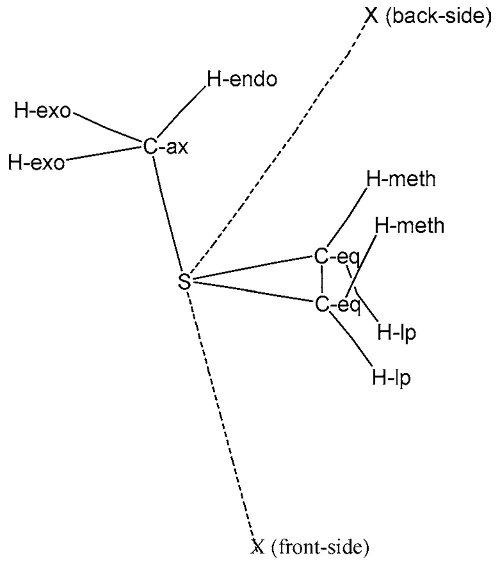


**FIGURE 2** Structure (to scale) of (equatorial) *S*-methylthianium fluoride. The fluorine and one ring carbon occupy axial positions while the *S*-methyl and another ring carbon occupy equatorial sites.

One might at first glance guess that a halide approaching an *S*-methyl sulfonium cation might well prefer the front-side situation where direct interaction with sulfur may occur, as illustrated in Fig. 1a for *S*-methylthiiranium fluoride. However, the back-side complex shown in Fig. 1b also represents a stable species which is, in a number of cases, the stabler form. In the back-side complex the halide closest approach contacts are with hydrogens, particularly that *S*-methyl hydrogen that points back over the hydrocarbon portion of the sulfonium species (H-endo; see Scheme 1). The front-side compound is interesting in that it resembles the trigonal bipyramid structure that one would predict on the basis of the VSEPR model for five electron pairs about a central atom: the sulfur lone pair and the ring carbons essentially occupying equatorial positions with the *S*-methyl group and halide in axial positions. There is clearly some distortion of the ideal trigonal bipyramid structure, a feature we discuss later.

The structures presented in Fig. 1 are further clarified by those in Fig. 3 that show the ELF 0.8 isosurfaces for the *S*-methylthiiranium cation (a), and the front- (b) and back-side (c) fluorine complexes. Figure 3a clearly indicates the sulfur lone pair



**SCHEME 1**

occupying essentially a tetrahedral position, the lone pair, and sulfur-ring-carbon bond basins joined at this level (0.8) of ELF. Figure 3b clearly parallels the structure shown in Fig. 1a and confirms the location of the sulfur lone pair, as does Fig. 3c. It is important to note that while bond basins are apparent for the sulfur–carbon and carbon—hydrogen bonds, *there are no bond basins* found between the fluorine atom and other atomic species. This situation is that typically found for ionic species, a point we stress later.

Table 1 shows the G3 (and B3LYP) energy differences (at 0 K) for the compounds studied here, negative entries indicating a relative stability of a front-side complex. For only the fluorides are all the front-side species the lower G3 energy form; of the chlorides only the *S*-methylthiolanium chloride ($SMXC_4H_8$, X=Cl) shows the front-side complex to be lower in energy. G3 cannot handle bromine, but the B3LYP energy differences suggest that the behavior of bromine would parallel that of chlorine. With the exception of the thiolanium fluoride, the energy differences are rather small, and since G3 (and G3MP2) theory predicts energies to about ±1–2 kcal/mol the front- and back-side forms of the complexes are very similar in energy.

This near equality in energy does not suggest a small energy of formation. The G3 energy changes (G3MP2 for the thianium salts) upon formation of the complexes from the sulfonium cations and the halide anions are essentially the same for the front-side complexes ($-125.4 \pm 2.4$ kcal/mol) and the same but somewhat lower for the back-side complexes ($-102.5 \pm 1.4$ kcal/mol). Clearly bonding is involved between the halide and the sulfonium species being

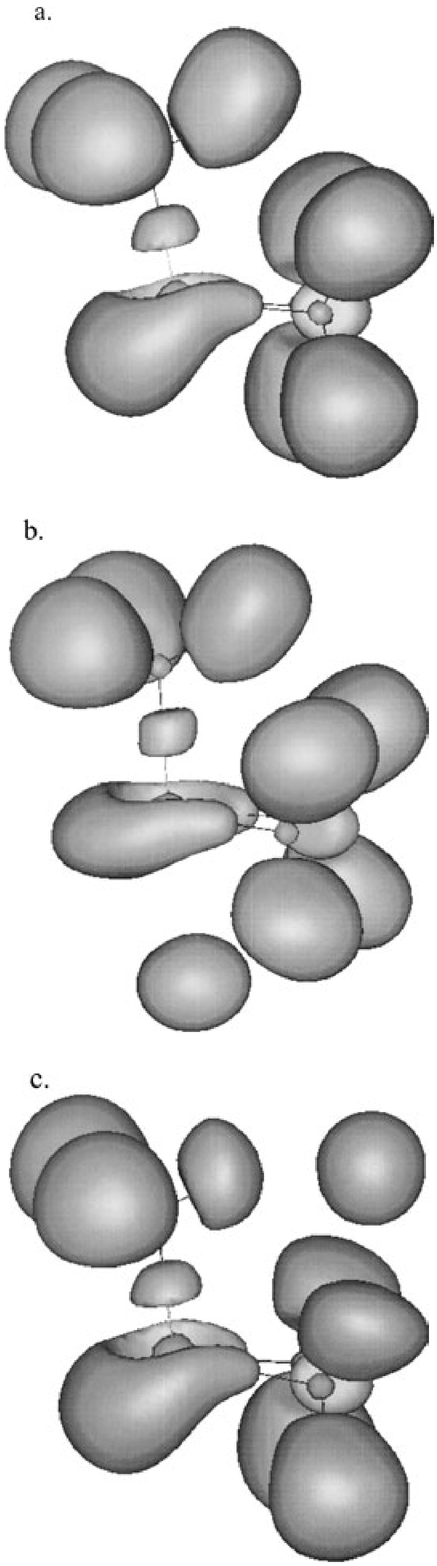


**FIGURE 3** ELF 0.8 isosurfaces for (a) the *S*-methylthiiranium cation, (b) the front-side *S*-methylthiiranium fluoride, and (c) the back-side *S*-methylthiiranium fluoride. The *S*-methyl hydrogen basins are in the top left portion of the figures, while the fluoride core basin is at the bottom of 2b and at the upper right of 2c.

**TABLE 1** Energy Differences (kcal/mol) Between Front- and Back-side Complexes of the Various Sulfonium Halides in the Model Chemistry G3[a] and B3LYP/6-311+G(d,p) (in parentheses) Approaches

| | *X* = *F* | *Cl* | *Br* |
|---|---|---|---|
| $(CH_3)_3SX$ | −0.29 (1.83) | 1.69 (3.25) | (3.00) |
| $SMXC_2H4$ | −1.34 (3.16) | 0.60 (3.05) | (2.59) |
| $SMXC_3H_6$ | −2.62 (1.12) | 0.70 (2.71) | (3.82) |
| $SMXC_4H_8$ | −5.65 (−1.57) | −1.94 (0.46) | (0.07) |
| $SMXC_5H_{10}^{a}$ | −0.36 (2.42) | 2.41 (3.65) | (3.44) |

All energies include zero-point corrections and are energies at 0 K. A negative energy difference indicates the front-side complex to be more stable than the back-side isomer.

[a] The equatorial $SMXC_5H_{10}$ compounds were calculated in the G3MP2 model chemistry [12].

formed. On the basis of two electronic charges a distance *R* apart, these two energies yield *R* values of 2.6 Å and 3.2 Å, respectively, distances comparable to the “size” of these molecular complexes.

Table 2 exhibits the distances between the sulfur and halides in the front-side complexes and the halide with the endo methyl hydrogen (H-endo, Scheme 1) in the back-side compounds. The various distances are very similar for a given halide. At the bottom of each part of Table 2 are given Pauling covalent bond and van der Waals distances for comparison. Quantitatively the various distances are about midway between the associated covalent bond and van der Waals distances. Clearly “bonds” are being formed, but they are obviously not standard covalent bonds.

**TABLE 2** Key Distances (Å) for the Ion Pair Complexes

| | *X* = *F* | *Cl* | *Br* |
|---|---|---|---|
| (A) Front-side sulfur-halide distances | | | |
| $(CH_3)_3SX$ | 2.151 | 2.902 | 3.088 |
| $SMXC_2H_4$ | 2.145 | 2.852 | 3.021 |
| $SMXC_3H_6$ | 2.140 | 2.856 | 3.034 |
| $SMXC_4H_8$ | 2.152 | 2.873 | 3.052 |
| $SMXC_5H_{10}$ | 2.171 | 2.932 | 3.111 |
| SX covalent bond | 1.68 | 2.03 | 2.18 |
| SX van der Waals | 3.20 | 3.65 | 3.80 |
| (B) Back-side halide-nearest-H distances | | | |
| $(CH_3)_3SX$ | 1.811 | 2.360 | 2.521 |
| $SMXC_2H_4$ | 1.571 | 2.216 | 2.396 |
| $SMXC_3H_6$ | 1.691 | 2.306 | 2.447 |
| $SMXC_4H_8$ | 1.654 | 2.283 | 2.448 |
| $SMXC_5H_{10}$ | 1.807 | 2.377 | 2.535 |
| XH covalent bond | 0.94 | 1.29 | 1.44 |
| XH van der Waals | 2.55 | 3.00 | 3.15 |

Sulfur-halide distances are tabulated for the front-side complexes, while the halide-nearest-H distances (the *S*-methyl endo hydrogen) are displayed for the back-side species.

Pauling covalent bond and van der Waals distances are given above each set of data for comparison.

## *AIM Data*

The atoms-in-molecule (AIM) treatment can provide atomic charges and, from the delocalization index, a measure of covalent bond order. Scheme 1 provides a roadmap for the atomic designations.

Of particular importance are the charges on sulfur and the halides, both of which have sizeable values. Sulfur has a larger charge in the front-side complexes, while the opposite is true for the halides. Generally speaking, hydrogen will be slightly positive and carbon slightly negative as illustrated by the H-exo and both carbon species regardless of the sidedness of the complex. When the halides are situated on the front side the H-lp species are noticeably more positive, while when one considers the back-side complexes the H-meth and H-endo hydrogens have enhanced positive charges. Since one expects little interaction with other species by the halides in the back-side complexes, these sizeable hydrogen charges (along with the large negative charge on the halides) clearly suggest a dominating ionic interaction in this case.

The extent to which other than ionic interactions are taking place for the front-side complexes can be examined by considering the appropriate delocalization indices shown in Table 3. In part A of that table, the delocalization indices are given for some

**TABLE 3** AIM Delocalization Indices, $\delta_{jk}$, for (A) Some Reference Compounds with Sulfur–Fluorine (and sulfur–carbon) Covalent Bonds and (B) the Halides Interacting with Various Atoms (as Indicated in Scheme 1) of the *S*-Methylthiiranium Halides

(A) Reference Compounds

| | *SF* | *SC* |
|---|---|---|
| $(CH_3)_2S$ | – | 1.12 |
| $CH_3SF$ | 1.01 | 1.12 |
| $SF_2$ | 1.05 | – |
| $SF_4$ Axial | 0.81 | – |
| Equatorial | 0.88 | – |

(B) The *S*-Methylthiiranium Halides

| | *X* = *F* | *Cl* | *Br* |
|---|---|---|---|
| XS | 0.446 | 0.316 | 0.312 |
| | 0.032 | 0.032 | 0.034 |
| XH-lp | 0.042 | 0.068 | 0.072 |
| | 0.006 | 0.006 | 0.006 |
| XH-meth | 0.010 | 0.010 | 0.010 |
| | 0.086 | 0.100 | 0.106 |
| XH-endo | 0.008 | 0.008 | 0.008 |
| | 0.188 | 0.156 | 0.148 |

The data in part B on the first line of each entry is for the front-side complex while that on the second line is for the back-side ion pair.

reference compounds containing what one would characterize as basically covalent SF (and SC) bonds. The simple compounds have indices of essentially one, indicating the sharing of one pair of electrons. Those for $SF_4$ are somewhat reduced; according to Cioslowski and Mixon [22], if the Lewis octet rule is to be obeyed, $SF_4$ must consist of three structures with one lone pair on sulfur, three fully covalent bonds, and one fully ionic bond. This gives on average a bond ionicity of 25% or an average sharing of three quarters of a pair of electrons, consistent with the reduced delocalization indices.

Of key interest here are the delocalization indices involving sulfur and the halides. The very small values for the back-side complexes are expected since in these cases the halides are far removed from sulfur and shielded from it by the intervening carbons and hydrogen atoms. The values for the front-side complexes are not negligible but neither are they of the order one expects for a normal covalent bond. We are led to the conclusion that some small degree of covalent bonding does exist in these cases.

As pointed out by Fredera et al. [16] "nonbonded" species will have a nonvanishing delocalization index, and whether or not one characterizes two AIM atoms as bonded or not will depend on the magnitude of the delocalization index. Table 3 also includes values for the halide–hydrogen atom pairs. They are in many cases very small, but certainly for the case of the back-side endo hydrogen the value is significant. To be consistent one must consider a very small but nozero degree of covalent bond character to be present in those cases as well.

## *ELF Data*

The most significant aspect of the electron localization function is in its graphical representation of core, lone pair, and bond electrons as was illustrated in Fig. 3. Of these the graphical representation of lone pairs is of considerable chemical interest. One can derive basin populations by integrating the electron density and these are often useful in characterizing the molecular electronic space, although not as consistently as does the delocalization index [23].

We present in Table 4 basin populations for some representative fluorine-containing molecules and those for both the front-and back-side *S*-methylthiiranium fluorides. Populations for a normal covalent bond should ideally be close to 2 as should those representing a lone pair. These numbers are often modified, however, by the effects of polarization with bond basin populations being less than 2 and lone pair basin populations being larger than 2. Such is evident in the data in Table 4.

**TABLE 4** ELF Basin Populations for (A) Some Reference Compounds with Sulfur–Fluorine Covalent Bonds and (B) *S*-Methylthiiranium Fluoride

(A) Reference Compounds

| | *SF* | *SC* | *S Lone Pair* | *F Lone Pairs*[a] |
|---|---|---|---|---|
| $(CH3)_2S$ | – | 1.59 | 2.25[b] | – |
| $CH_3SF$ | 0.49 | 1.61 | 2.28[b] | 7.04 |
| $SF_2$ | 0.63 | – | 2.32[b] | 6.87 |
| $SF_4$ Axial | 0.70 | – | 2.48 | 7.00 |
| Equatorial | 0.94 | – | | 6.79 |

(B) The *S*-Methylthiiranium Halides

| | *Front-Side* | *Back-Side* |
|---|---|---|
| SC-ax | 1.69 | 1.71 |
| SC-eq | 1.17 | 1.05 |
| CC | 1.97 | 2.00 |
| S lone pair | 3.43 | 3.44 |
| F lone pair | 7.62 | 7.33 |
| SF | Absent | Absent |

The data in part B on the first line of each entry are for the front-side complex while that on the second line is for the back-side ion pair.

[a] Sum of the fluorine lone pair basin populations.

[b] The population is for each of two lone pairs.

The key result in Table 4, and as seen in Fig. 2, is the complete absence of a bond basin between sulfur and fluorine in the sulfonium salts. Such is expected for the back-side complex and clearly indicates ionic stabilization in that case. The fact that such a bond basin is also absent for the front-side complex suggests the same conclusion as to the type of bonding involved.

Another useful result of the ELF analyses is the location of the basin attractors in the front-side *S*-methylthiiranium fluoride as illustrated in Fig. 4 along with those for the *S*-methylthiiranium cation. In the latter case it is clear, as was pointed out earlier in Fig. 2, that the sulfur lone pair takes up an essentially tetrahedral orientation with respect to the sulfur and carbon atoms, as we would predict. The relative orientation of the basin attractors for the front-side complex gives us further insight to the nature of the bonding in this molecule. As mentioned earlier, for five electron pairs around a central atom, VSEPR predicts a trigonal bipyramid arrangement of the atoms, such as that seen in (the slightly distorted) $SF_4$ molecule. Here, however, it is clear that the totally planar arrangement of the equatorial species is not present, but rather they are somewhat distorted toward the tetrahedral arrangement seen in the cation. VSEPR theory presumes that the electron pairs it deals with are involved in predominately covalent bonds, and, strictly speaking, is not applicable when the bonding is mainly ionic. The

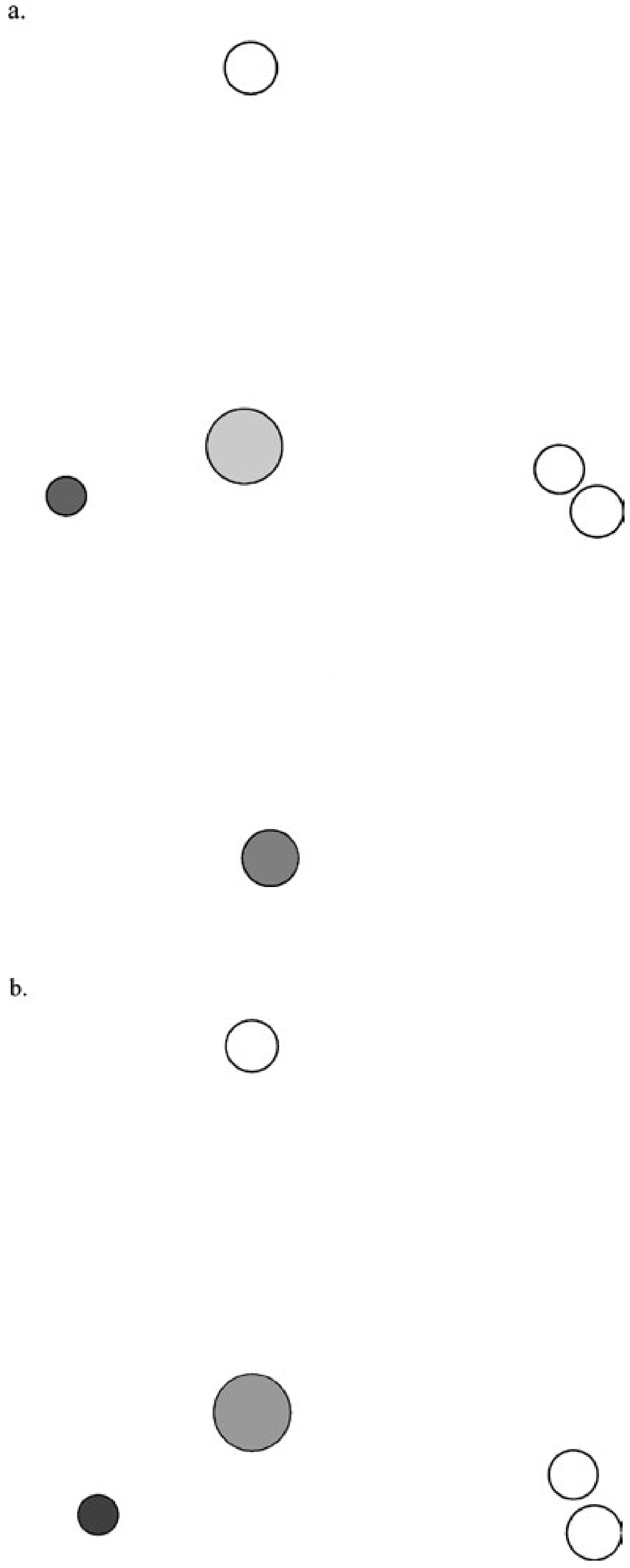


**FIGURE 4** ELF attractors for the lone pair and core basins in (a) *S*-methylthiiranium fluoride and (b) the *S*-methylthiiranium cation. Closed circles represent the sulfur lone pair basins, the gray-shaded circle the sulfur cores, and the open circles the carbon core basins.

"intermediate" nature of the relative location of the electron pairs in the front-side complexes further adds to our conclusions that the bonding between sulfur and the halides in these species is mainly ionic but with a small degree of covalent character.

### *NMR Data*

Finally we present in Table 5 absolute chemical shieldings for again some representative compounds containing covalent sulfur-fluorine bonds and for the *S*-methylthiiranium and *S*-methylthiolanium fluorides and some related compounds. It is quite clear from part A of that table that when SF covalent bonds are present a very large deshielding (movement to lower fields) of sulfur occurs relative to it all-carbon counterpart.

Such is not the case for the *S*-methyl sulfonium complexes as seen in part B of Table 5. The back-side complexes show very small and likely insignificant differences compared to the isolated cationic species, and the differences involving the front-side complexes are rather small. (Agreement between experiment and theory for sulfur shieldings in our scaled DFT approach is about ±30 ppm [1].). But note again that when we replace the *S*-methyl group with a fluorine atom ($SFC_2H_4$ and $SFC_4H_{10}$) very large deshieldings occur, commensurate with sulfur—fluorine covalent bonding. The NMR results

**TABLE 5** Absolute Sulfur Chemical Shieldings ($\sigma_S$, ppm) and Chemical Shifts Relative to $CH_3SCH_3$ ($\delta_S^{CH_3SCH_3}$, ppm), and the Sulfur–Fluorine Bond Distances ($R_{SF}$, Å) in (A) Some Simple Fluorosulfur Compounds, and (B) the *S*-Methylthiiranium and *S*-Methylthiolanium Fluorides and Related Compounds

| | $\sigma_S$ | $\delta_S^{CH_3SCH_3}$ | $R_{SF}$ |
|---|---|---|---|
| (A) Some simple fluorosulfur compounds | | | |
| $CH_3SCH_3$ | 584.7 | 0 | – |
| $SF_4$ | 40.4 | 544.3 | 1.650[a] |
| $CH_3SF$ | −297.8 | 882.5 | 1.680 |
| $SF_2$ | −946.6 | 1531.5 | 1.639 |
| (B) The *S*-methylthiiranium and *S*-methylthiolanium fluorides and related compounds | | | |
| $SMC_2H_4$ | 715.5 | −130.8 | |
| $SMFC_2H_4$ (back-side) | 723.0 | −138.3 | 3.294 |
| $SMFC_2H_4$ (front-side) | 749.8 | −165.1 | 2.145 |
| $SFC_2H_4$[b] | 269.1 | 315.6 | 1.611 |
| $SMC_4H_{10}$ | 425.7 | 159.0 | – |
| $SMFC_4H_{10}$ (back-side) | 428.9 | 155.8 | 3.232 |
| $SMFC_4H_{10}$ (front-side) | 455.9 | 128.8 | 2.152 |
| $SFC_4H_{10}$[c] | −34.7 | 619.4 | 1.622 |

[a] Average of the axial (1.704 Å) and equatorial (1.596 Å) distances.
[b] The *S*-fluorothiiranium cation.
[c] The *S*-fluorothiolanium cation.

are, as the other indicators we have presented, consistent with a predominant ionic interaction between sulfur and the halides in the *S*-methyl sulfonium salts.

## CONCLUSIONS

The *S*-methyl sulfonium halides possess unusual gas phase molecular structures. Our theoretical calculations, including AIM, ELF, and NMR data, support the idea that the binding in these gas phase species is predominately ionic with some small degree of covalent bonding.

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