into the carbon–fluorine bond. This result is significant because it provides a useful example of a competition experiment whereby the insertion reaction occurs at the carbon–fluorine bond in the 4-position, rather than at the 4-position in the phenyl carbon–hydrogen bonds.

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Supplementary Material Available: Tables of positional parameters, bond distances, bond angles, general displacement parameters, and torsion angles (13 pages); a table giving values of F_o and F_c (40 pages). Ordering information is given on any current masthead page.

Notes

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^{19}F NMR Chemical Shift of SF_2 in the Gas Phase

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In the series of fluorides SiF_4, PF_3, SF_2, and ClF, sulfur difluoride can be considered as a laboratory curiosity. It is unstable with respect to disproportionation into SSF_2 and SF_4.[1] Due to this instability the existence of SF_2 could not be verified until 1969, when the compound was detected by mass and microwave spectroscopy in the gas phase at low pressures (≤0.1 mbar).[2,3] All efforts to enhance the partial pressure by condensation failed because SF_2 dimerizes spontaneously even at temperatures as low as −196 °C.[1] The well-characterized dimer SF_3SF[4,5] is not a suitable precursor for SF_2, because its dissociation is kinetically hindered.[1] However, by reaction of F_2 with COS under suitable conditions, partial pressures of more than 30 mbar of SF_2 could be obtained, and it became possible to record a high-resolution IR spectrum.[6] The new synthesis initiated extensive research into the macroscopic properties of SF_2.[1] Although SF_2 has already been characterized by mass,[2] microwave,[3,7] infrared,[6,8] and photoelectron[9] spectroscopy, its ^{19}F NMR spectrum has not been reported. Recently, ^{19}F and ^{33}S chemical shifts have been calculated with the IGLO method[10] and compared with experimental values for related compounds.[11] The $\delta(^{19}F)$ values in the series of compounds SiF_4, PF_3, SF_2, and ClF do not change monotonically, and it was questionable whether the shielding in SiF_4 or ClF is unusual. The chemical shifts of SF_2 are therefore of great interest.

Experimental Section

Sulfur difluoride was prepared from COS (Baker) and F_2 (Kali-Chemie) according to the published method.[6] The concentration of SF_2 was monitored by FTIR spectroscopy. Unreacted COS is observed, and CO, SF_4, and traces of SF_6 are formed as byproducts. The NMR tube, equipped with a rotational symmetrically valve[12] (type VNMR-10, Young, London), was treated with boiling hydrochloric acid, vacuum-dried, and finally passivated with the COS/F_2 reaction products. The molar ratio COS/F_2 of approximately 1/1 was adjusted to yield a maximum concentration of SF_2. Then the NMR tube was filled with about 100 mbar of the reaction products containing about 30 mbar of SF_2 and inserted into the probe of the NMR spectrometer, which was cooled to −30 °C. For a fast pulse sequence of 7 s^{-1}, the measurement of the ^{19}F NMR gas spectrum took about 20 min. According to the FTIR spectrum of the sample, the concentration of SF_2 had decreased by about 50% after that time, and the dimer of SF_2 as well as the decomposition products SF_4 and SSF_2 was formed. The ^{19}F chemical shift of SF_2 was referenced to the signals of SF_3SF. In a separate experiment, a mixture of CCl_3F and SF_3SF was measured under the same conditions.

The NMR spectrum was recorded on a Bruker MSL 200 spectrometer at 188.31 MHz using a 10-mm $^1H/^{19}F$ dual probe. The FTIR spectra were measured with a Nicolet MX 3600 instrument using a DTGS detector.

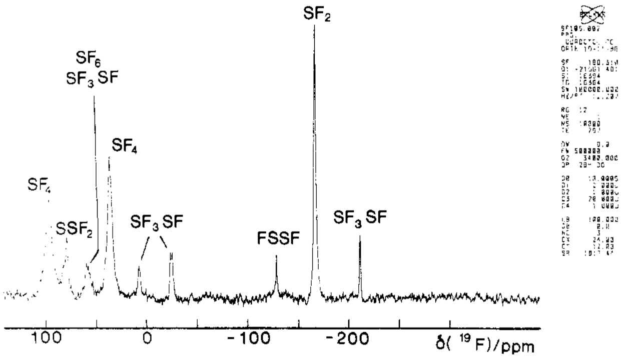

Figure 1. Gas-phase ^{19}F NMR spectrum of a sample containing SF_2 and other binary sulfur fluorides.

Table I. ^{19}F Chemical Shifts for Gaseous and Liquid Binary Sulfur Fluorides (Referenced to CCl_3F)

	$\delta(^{19}F)$/ppm	
	gas phase at −30 °C	liquid state
SF_2	−167.0	
SF_4 (ax)	93.0	88.4[a]
SF_4 (eq)	34.2	34.1[a]
SF_6	54.9	56.5[a]
SSF_2	77.8	79.0[a]
FSSF	−128.8	−123.2[b]
S_2F_4 (1)	54.9	53.2[c]
S_2F_4 (2)	7.0	5.7[c]
S_2F_4 (3)	−24.7	−26.3[c]
S_2F_4 (4)	−211.1	−204.1[c]

[a] Reference 13; −50 °C. [b] Reference 14; −50 °C. [c] Reference 4; −100 °C.

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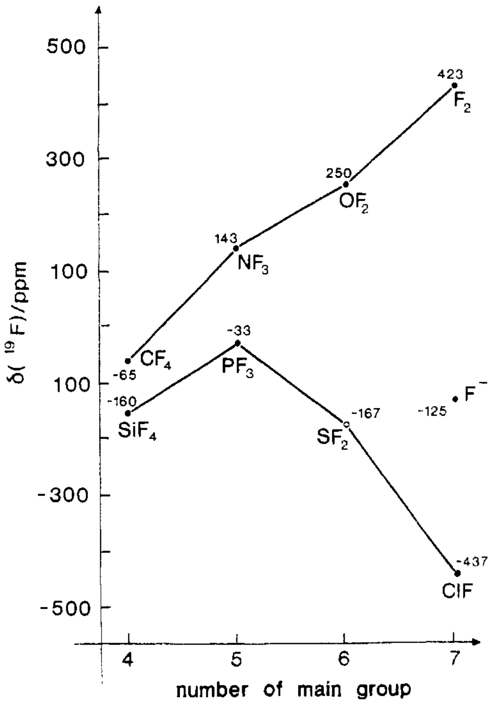

Figure 2. ^{19}F chemical shifts of element fluorides of the first and second period referenced to CCl_3F.

Results and Discussion

^{19}F NMR spectra of the product formed in the reaction of COS with F_2 in the gas phase are recorded repeatedly. A typical spectrum is shown in Figure 1. The intensity of the signal at −167 ppm corresponds well to the concentration of SF_2, measured by FTIR spectroscopy. Since the resonance is close to that of SiF_4, the IR spectrum of the gaseous product is checked for the presence of this compound, which is found to be present only in traces. Furthermore, the decrease of this signal and simultaneous increase of the signals of the dimer, SF_3SF, is observed as expected.[1] Hence the signal at −167 ppm is attributed to SF_2. All other signals can be assigned to other binary sulfur fluorides. The chemical shifts of these compounds in the liquid state are well established. The ^{19}F NMR spectrum reported here of the reaction products yields the chemical shifts in the gas phase. Some values show considerable phase-dependent shifts. The results are listed in Table I and compared to the values for the liquid compounds.

The experimental ^{19}F chemical shift of SF_2 of −167 ppm is in reasonable agreement with the predicted value of −182 ppm.[11] In Figure 2, chemical shifts of binary fluorides of p-block elements are compared. The fluorides in the first period exhibit the predicted decrease in their ^{19}F NMR shifts with increasing negative charge on the fluorine atoms caused by an increasing difference in electronegativity between the bonded element and fluorine (decreasing atomic number of central atom).

If one considers only these charges, the corresponding fluorine atoms in compounds of the second period should be more shielded. The lowest value should be that of SiF_4, which should be similar to that of the fluoride ion. The experimental ^{19}F chemical shifts show that simple electronegativity arguments are not applicable for this series of compounds and that an increasing diamagnetic effect plays an important role in the series PF_3, SF_2, and ClF. The extremely negative ^{19}F shift of ClF corresponds to an extremely high shielding of the fluorine nucleus, which is attributable to a $\pi^* \rightarrow \sigma^*$ excitation, caused by the external magnetic field.[21] It can be concluded from the curvature in the plot in Figure 2 that the same effect is also of considerable importance for SF_2.

If we proceed from ClF via SF_2 and PF_3 to SiF_4, the number of fluorine atoms competing for π orbitals with the central atom increases. Therefore, the π-bond order to a specific F atom decreases in this series, and the diamagnetic effect attributed to the $\pi^* \rightarrow \sigma^*$ transition becomes less important. If F is replaced by CF_3 or CH_3 groups that are not capable of π-interaction with the central atom, the shielding of the remaining fluorine atom increases considerably (Table II) because of the higher π-bond order. The highest ^{19}F shielding of all compounds of the general type X–F listed in Table II is that of CF_3SF (X = CF_3S). Thus, the CF_3S group appears to be the best "parachlorine" in the sense of the element displacement principle.[20]

Table II. ^{19}F NMR Chemical Shifts of SF_2, PF_3, SiF_4, and Derivatives in ppm from CCl_3F

SF_2	−167	CF_3SF	−351[a]		
PF_3	−33[b]	$(CF_3)_2PF$	−218[b]	$(CH_3)_2PF$	−196[c]
SiF_4	−142[d]			$(CH_3)_3SiF$	−155[d]

[a] Reference 16. [b] Reference 17. [c] Reference 18. [d] Reference 19.

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Registry No. SF_2, 13814-25-0; SF_4, 7783-60-0; SF_6, 2551-62-4; S_2F_2, 13709-35-8; S_2F_4, 27245-05-2.

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Synthesis and Spectroscopic Characterization of 1,2-Bis(trimethylsilyl)-1,2-dicarba-*closo*-hexaborane(6) Derived from *closo*-Stannacarborane and the X-ray Crystal Structure of the Precursor 1-Sn-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$

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It has been demonstrated that the C–$SiMe_3$-substituted stannacarboranes are important precursors in the production of a number of main-group and transition-metal metallacarboranes.[1] For example, the apical tin in the *closo*-stannacarboranes has been replaced by an $Os(CO)_3$ unit in the production of *closo*-osmacarboranes.[2] The *commo*-germacarboranes[3] were synthesized from the direct reaction of $GeCl_4$ with the corresponding stannacarboranes, while the reaction with a different molar ratio of reactants produced the mixed-valence germacarborane *closo*-1-Ge^{II}-2,3-$(SiMe_3)_2$-5-$(Ge^{IV}Cl_3)$-2,3-$C_2B_4H_3$.[4] It has also been shown that the *C,C'*-dimethyl-substituted stannacarborane reacts with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ to yield a cobaltacarborane via an air-sensitive intermediate $(\eta^5\text{-}C_5H_5)CoSnMe_2C_2B_4H_4$.[5] In all of these cases there was no evidence of the oxidative closure of the carborane cage even when the apical tin was eliminated reductively as Sn^0 in some instances, such as in the production of the *closo*-osmacarborane[2] and the cyclopentadienylcobaltacarborane[5] derivatives. However, it has been reported that the icosahedral stannacarborane analogue 1-Sn-2,3-$C_2B_9H_{11}$ eliminates the apical tin as Sn^0 at 450 °C to produce the 11-vertex polyhedron *closo*-2,3-$C_2B_9H_{11}$.[6] Furthermore, the reaction of $SnCl_2$ with the dianion $[1,7\text{-}C_2B_9H_{11}]^{2-}$ also produced *closo*-2,3-$C_2B_9H_{11}$ as the

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