$(Me_2NCN)(SN)_2$, generated in situ from **2a**. To test this possibility we added a solution of **2a** in CCl_4 to a green solution of $(NSCl)_3$ in CCl_4 at 60 °C.[29] However, this reaction resulted in the dechlorination of $(NSCl)_3$ by **2a** to give S_4N_4 and **1a**. An alternative mechanism for the production of **3a** involves the formation of the monosubstituted derivative of **1a**, $(Me_2NCN)(NSCl)(NSNSO)$, which undergoes *intermolecular* elimination of SO_2 to give $RN{=}S{=}NR$ (where R = $(Me_2NCN)(NSCl)(NS)$). When R = $(Ph_2PN)_2(SN)$, this type of compound readily undergoes a six- to eight-membered-ring expansion to give a spirocyclic compound, which forms a monocyclic eight-membered ring on thermal decomposition.[30] A similar sequence of transformations could account for the formation of **3a**.[31]

Conclusions

The metathetical reaction of **1a–c** with $Me_3SiNSNSiMe_3$ gives good yields of the corresponding bicyclic derivatives, **2a–c**.[32] The same compound **2a** is formed when **1a** is treated with 2 mol of Me_3SiNSO. In the latter reaction a ring expansion to give the eight-membered ring 1,5-$Me_2NC(NSN)_2SCl$ also occurs. Although the synthetic applications of this transformation are limited by the low yield and long reaction time, it may provide an initial approach to novel, ring-expanded heterocyclothiazenes from heterocyclothiazyl chlorides. The compounds **2a–c** are potential sources of the eight-π-electron six-membered rings $R_2NCS_2N_3$ via loss of N_2S on thermolysis, but the mass spectra indicate that the fragmentation of the bicyclic rings may involve more than one pathway.

Acknowledgment. We thank Dr. E. A. Dixon for assistance with recording the ^{13}C NMR spectra, the Natural Sciences and Engineering Research Council of Canada for financial support, the Dr. K. A. Kerr for use of the diffractometer.

Registry No. **1a**, 85869-54-1; **1b**, 99618-21-0; **1c**, 99618-22-1; **2a**, 99618-23-2; **2b**, 99618-24-3; **2c**, 99618-25-4; **3a**, 99618-26-5; $Me_3SiNSNSiMe_3$, 18156-25-7; Me_3SiNSO, 7522-26-1; $(NSCl)_3$, 5964-00-1.

Supplementary Material Available: Tables containing anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, best planes, and observed and calculated structure factors for 1,5-$Me_2NC(NSN)_2SCl$ and IR data for compounds **2a–c** (11 pages). Ordering information is given on any current masthead page.

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(31) It is, of course, possible that the initial product is the 1,3- rather than the 1,5-isomer. In solution, however, ionization of the S–Cl bond would provide a mechanism for the isomerization of the 1,3- to the presumably more stable 1,5-isomer, **3a**.

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Gas-Phase Structures of Bis(pentafluorothio)difluoromethane and Tetrafluoro-1,3-dithietane Octafluoride

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The structures of $(SF_5)_2CF_2$ and $(SF_4CF_2)_2$ have been studied by gas electron diffraction. Very long S–C bonds (1.908 (7) Å) and a large SCS bond angle (124.3 (7)°) have been determined for $(SF_5)_2CF_2$. These results are compared to the skeletal parameters of $(SF_5)_2O$ and $(SF_5)_2NF$. A simple bonding model based on polar effects is proposed. For the cyclic $(SF_4CF_2)_2$ the SCSC four-membered ring is planar with S–C = 1.886 (4) Å, SCS = 96.2 (3)°, and CSC = 83.8 (3)°. The effects of ring formation are discussed in connection with those for the analogous oxygen and nitrogen compounds.

Introduction

Bis(pentafluorothio)difluoromethane was synthesized 30 years ago by electrochemical fluorination of carbon disulfide.[2] Recently a simple procedure, which is based on direct fluorination of CS_2 and which is suitable for high-yield preparation, was reported by Waterfeld et al.[3] From the structural point of view the skeletal parameters of $(SF_5)_2CF_2$ are interesting in comparison with those of the isoelectronic analogues, $(SF_5)_2O$ and $(SF_5)_2NF$, whose gas-phase structures have been determined previously.[4,5] Such a comparison provides information on the structural effects and steric requirements of SF_5 groups. Tetrafluoro-1,3-dithietane octafluoride has been synthesized by direct room-temperature fluorination of tetrafluoro-1,3-dithietane with chlorine monofluoride.[6] The comparison of the sulfur–carbon skeleton in the unstrained $(SF_5)_2CF_2$ with the SCSC four-membered ring in $(SF_4CF_2)_2$ provides information on the effects of ring formation. These effects can be compared to those for the nitrogen analogues $(SF_5)_2NF$ vs. $(SF_4NCl)_2$ and for the oxygen compounds $(SeF_5)_2O$ vs. $(SeF_4O)_2$. Furthermore, the structure of $(SF_4CF_2)_2$ is interesting in relation to those of other four-membered sulfur–carbon ring systems where sulfur is found in different oxidation states and with different coordination numbers.

Experimental Section

Bis(pentafluorothio)difluoromethane. $(SF_5)_2CF_2$ was prepared according to the published method.[3] It was separated from byproducts (SF_6, CF_3SF_5) by fractional condensation (−70, −100, −196 °C) under vacuum. The pure compound remained in the trap at −100 °C. The purity was checked by IR and NMR spectroscopy. The compound is stable at room temperature and inert toward acids and bases.

Tetrafluoro-1,3-dithietane Octafluoride.[6] A reaction mixture of 0.33 g (2.0 mmol) of tetrafluoro-1,3-dithietane and 22.0 mmol of ClF in a 75-mL stainless-steel bomb was held at −20 °C for 2 h. Then it was warmed to 25 °C and held there overnight. Initial separation was conducted by passing the mixture through a trap held at −40 °C. Further

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(1) (a) University of Idaho. (b) Universität Göttingen. (c) Universität Tübingen.

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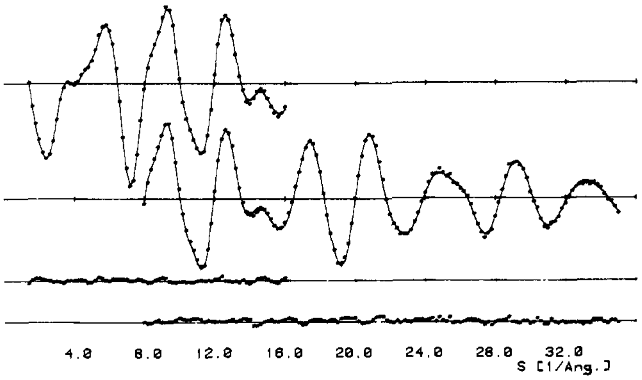

Figure 1. $(SF_5)_2CF_2$: Experimental (···) and calculated (—) molecular intensities and differences.

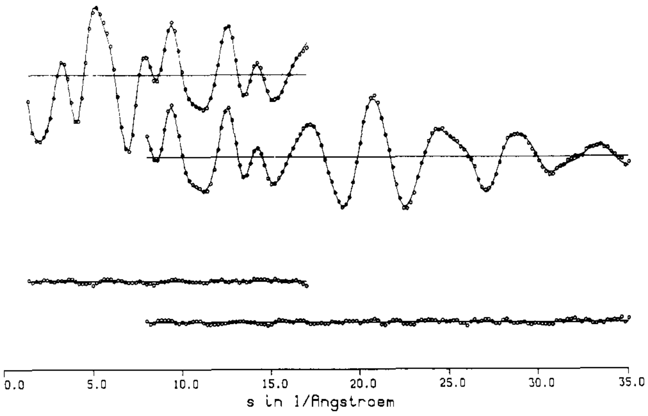

Figure 2. $(SF_4CF_2)_2$: Experimental (O) and calculated (—) molecular intensities and differences.

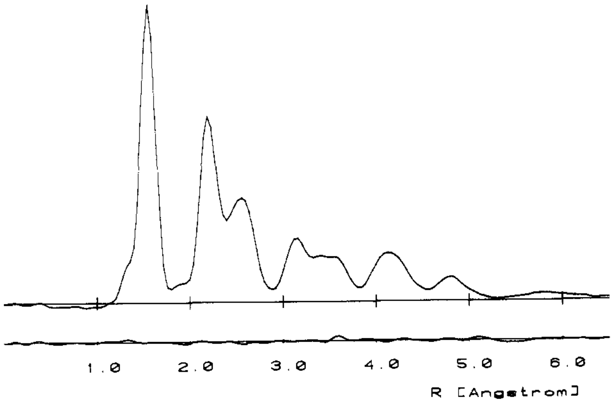

Figure 3. $(SF_5)_2CF_2$: Experimental radial distribution function and difference curve.

purification by gas chromatography yielded 0.25 g (0.79 mmol) of tetrafluoro-1,3-dithietane octafluoride. The purity of the sample was checked by IR and NMR spectroscopy. The compound is resistant to photolysis, thermolysis (300 °,C), and chemical attack by 10% aqueous NaOH solution. It is solid at room temperature with a high sublimation pressure.

Electron diffraction intensities were recorded with a Balzers gas diffractograph Model KD-G2[7] at two camera distances (25 and 50 cm) and an accelerating voltage of about 60 kV. The electron wavelength was calibrated by ZnO diffraction patterns. The sample temperatures were −33 °C ($(SF_5)_2CF_2$) and −20 °C ($(SF_4CF_2)_2$), respectively. The inlet system and nozzle were at room temperature. The camera pressure never exceeded 1.5×10^{-5} torr. Exposure times were 4–8 and 15–25 s for the long and short camera distances, respectively. For each compound and camera distance two photographic plates were selected and analyzed by the usual procedures.[8a] The averaged molecular intensities for the scattering range 1.4–17 $Å^{-1}$ and 8–35 $Å^{-1}$ in steps of $\Delta s = 0.2$ $Å^{-1}$ are presented in Figures 1 and 2.

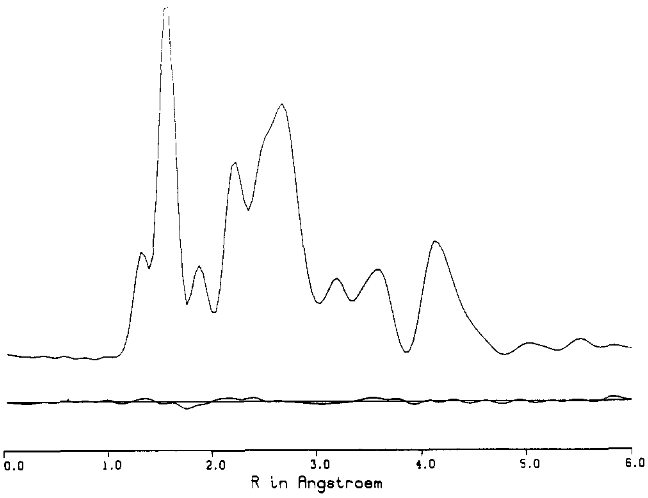

Figure 4. $(SF_4CF_2)_2$: Experimental radial distribution function and difference curve.

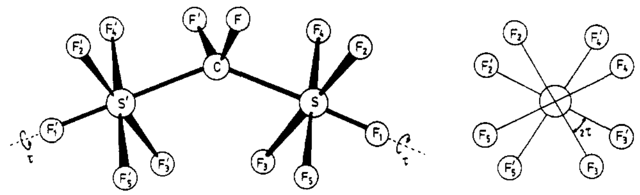

Figure 5. $(SF_5)_2CF_2$: Molecular model with atom numbering and Newman projection along S···S direction.

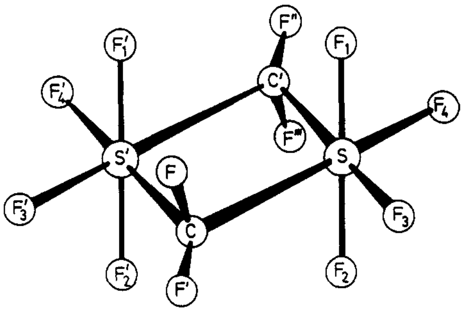

Figure 6. $(SF_4CF_2)_2$: Molecular model with atom numbering.

Structure Analysis

Preliminary molecular models were derived from the radial distribution functions (Figures 3 and 4) and were refined by least-squares procedures based on the molecular intensities. A diagonal weight function[8] was applied to the intensities, and the scattering amplitudes and phases of Haase[9] were used.

$(SF_5)_2CF_2$. Model calculations demonstrate that the SF_5 groups are not in the doubly eclipsed position as found in $(SF_5)_2O$[4] or $(SF_5)_2NX$[5] (X = F, H), but are rotated around the C–S bonds in opposite directions by an angle τ, resulting in C_2 overall symmetry. $\tau = 0$ corresponds to the doubly eclipsed position (F_3 eclipsed to F'_3 and F_5 eclipsed to F'_5, see Figure 5). A tilt angle between the S–C bond direction and the C_4 axis of the SF_5 group converged toward a value that was smaller than its standard deviation, and therefore it was set to zero in the final analysis. Assuming C_{4v} symmetry for the SF_5 groups, 8 geometric parameters and 10 vibrational amplitudes were refined simultaneously. Constraints for the vibrational amplitudes are evident from Table I. The following correlation coefficients had values larger than |0.7|: $SF_e/SF_a = -0.96$, $SF_e/F_eSF_a = 0.70$, $SCS/FCF = -0.73$, $SF_e/l(SF) = -0.81$, $SF_a/l(SF) = 0.82$. All refinements result in shorter axial S–F bonds ($S–F_1$) than

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Table I. Geometric Parameters and Vibrational Amplitudes for $(SF_5)_2CF_2$[a]

(a) Geometric Parameters

S–F$_a$	1.544 (10)	SCS	124.3 (7)
S–F$_e$	1.566 (4)	FCF	103.0 (15)
Δ(S–F)[b]	0.022 (11)	SCF[b]	106.9 (5)
S–C	1.908 (7)	F$_a$SF$_e$	89.6 (2)
C–F	1.335 (6)	$\tau(SF_5)$[c]	16.6 (8)

(b) Vibrational Amplitudes[d]

atom pair	dist	m[e]	amplitude	atom pair	dist	m[e]	amplitude
C–F	1.33	2	0.045[f]	S··S	3.38	1	0.100 (37)
S–F$_a$	1.54	2	0.046 (3)	S··F$'_5$	3.09	2	0.118 (14)
S–F$_e$	1.57	8		S··F$'_3$	3.40	2	
S–C	1.91	2	0.055[f]	S··F$'_2$	4.03	2	0.128 (23)
F··F′	2.09	2	0.062 (3)	S··F$'_4$	4.27	2	
F$_1$··F$_2$	2.19	8		S··F$'_1$	4.80	2	0.100[f]
F$_2$··F$_4$	2.22	8		F··F	2.33–3.35	15	0.11 (2)
C··F$_2$	2.48	8	0.067 (11)	F··F	3.61–4.45	23	0.21 (9)
S··F	2.63	4	0.103 (27)	F··F	4.91–6.11	7	0.15[f]
F$_2$··F$_3$	3.13	4	0.057 (14)				
C··F$_1$	3.45	2					

(c) Agreement Factors for the Two Camera Distances
$R(50\text{ cm}) = 0.037$ $R(25\text{ cm}) = 0.059$

[a] r_a values in Å, angles in deg. For error limits see text. [b] Dependent parameter. [c] Torsional angle of SF_5 group around the S–C bond. $\tau = 0°$ corresponds to the doubly eclipsed configuration. [d] See Figure 5 for atom numbering. [e] Multiplicity of distance. [f] Not refined.

Table II. Geometric Parameters and Vibrational Amplitudes for $(CF_2SF_4)_2$[a]

(a) Geometric Parameters

S–F$_e$	1.572 (6)	CSC[b]	83.8 (3)
S–F$_a$	1.590 (6)	F$_e$SF$_e$	88.6 (10)
Δ(S–F)[b]	0.018 (9)	CSF$_e$[b]	93.8 (8)
S–C	1.886 (4)	F$_a$SF$_e$	90.1 (8)
C–F	1.324 (3)	FCF	109.4 (7)
SCS	96.2 (3)		

(b) Vibrational Amplitudes[c]

atom pair	dist	m[d]	amplitude	atom pair	dist	m[d]	amplitude
C–F	1.32	4	0.046 (6)	S··F$'_1$	3.22	4	0.097 (12)
S–F$_e$	1.57	4	0.043 (3)	F$_1$··F$_2$	3.18	2	0.059 (11)
S–F$_a$	1.59	4		C··F$_4$	3.46	4	
S–C	1.89	4	0.053 (4)	C··F″	3.46	4	0.080[e]
F··F′	2.16	2	0.066 (7)	F$_1$··F′	3.63	8	0.073 (9)
F$_3$··F$_4$	2.19	2		S··F$'_3$	4.08	4	0.083 (11)
F$_1$··F$_3$	2.24	8		F··F″	4.05	2	0.120[e]
C··F$_1$	2.46	8	0.061 (7)	F··F‴	4.59	2	
C··F$_3$	2.53	4		F$_1$··F$'_4$	4.16	8	0.098 (16)
S··S′	2.81	1	0.065[e]	F$_1$··F$'_2$	4.23	2	0.144 (27)
C··C′	2.52	1		F$_1$··F$'_3$	4.38	8	
S··F	2.69	8	0.074 (8)	F$_3$··F$'_3$	5.06	2	0.120[e]
F··F$_1$	2.51	4	0.142 (26)	F$_3$··F$'_4$	5.52	2	
F$_1$··F$'_1$	2.80	2					
F··F$'_3$	2.91	8					

(c) Agreement Factors for the Two Camera Distances
$R(50\text{ cm}) = 0.049$ $R(25\text{ cm}) = 0.066$

[a] r_a values in Å, angles in deg. For error limits, see text. [b] Dependent parameter. [c] See Figure 6 for atom numbering. [d] Multiplicity of distance. [e] Not refined.

Table III. Correlation Coefficients for $(CF_2SF_4)_2$

SF$_a$/SF$_e$	−0.97	F$_a$SF$_e$/FCF	−0.87	SF$_a$/l(F··F)[b]	−0.80
SF$_a$/F$_e$SF$_e$	−0.80	SF$_a$/l(SF)[a]	−0.84	SF$_e$/l(F··F)	0.79
SF$_a$/F$_a$SF$_e$	0.91	SF$_e$/l(SF)	0.84	F$_e$SF$_e$/l(F··F)	0.80
SF$_e$/F$_e$SF$_e$	0.78	F$_a$SF$_e$/l(SF)	−0.77	F$_a$SF$_e$/l(F··F)	−0.88
SF$_e$/F$_a$SF$_e$	−0.91				

[a] Vibrational amplitude for S–F bonds. [b] Vibrational amplitude for F··F′, F$_3$··F$_4$, and F$_1$···F$_3$ distances.

Table IV. Skeletal Parameters of $(SF_5)_2X$ (X = O, NF, CF_2)

	S–X, Å	$(S{-}X)_{SS}$,[a] Å	SXS, deg
$(SF_5)_2O$[b]	1.586 (11)	1.70	142.5 (16)
$(SF_5)_2NF$[c]	1.685 (5)	1.74	138.3 (10)
$(SF_5)_2CF_2$	1.908 (7)	1.81	124.3 (7)

[a] Schomaker–Stevenson values. [b] Reference 4. [c] Reference 5.

the equatorial S–F bonds, independent of the starting values (S–F$_a$ > S–F$_e$ or S–F$_a$ < S–F$_e$). The results are summarized in Table I. Error limits for the geometric parameters are 2σ values and include a possible scale error of 0.1% for bond lengths. Error limits for vibrational amplitudes are 3σ values.

$(SF_4CF_2)_2$. Model calculations indicate that the CSCS ring is planar or very nearly planar. Thus, D_{2h} symmetry was assumed. Constraints for the vibrational amplitudes are evident from Table II. In the final analysis 8 geometric parameters and 13 vibrational amplitudes were refined. Although several correlations between parameters have values larger than |0.7| (Table III) the 8 geometric parameters are well determined by the 12 "characteristic features" (peaks and shoulders) of the radial distribution function. The final results are listed in Table II. For error limits see above.

Discussion

Summarized in Table IV are the skeletal parameters of the isoelectronic series $(SF_5)_2X$ where X = O, NF, or CF_2. The S–X bond lengths are compared to the Schomaker–Stevenson values,[10] which are based on the S(II) covalent radius of 1.04 Å. The S–O and S–N bond lengths are shorter than the predicted values by 0.11 and 0.05 Å, respectively, while the S–C bonds are longer by 0.10 Å. The SXS bond angles are extremely large compared with standard bond angles, which in all three cases would approach tetrahedral. These structural features can be rationalized qualitatively by strong polar contributions to the S–X bonds in combination with steric repulsions between the SF_5 groups. The polarity of the S–X bonds is estimated to be much higher than accounted for by the Schomaker–Stevenson expression. This expression is based on electronegativity differences in diatomic molecules and severely underestimates the polarity of X–SF_5 bonds. Due to the high positive net charge of sulfur in the SF_5 group and a negative oxygen net charge this polar contribution is expected to be strongly attractive in $(SF_5)_2O$. A reduced, but still attractive, contribution is expected for the S–N bonds, in agreement with the intermediate bond shortening of 0.05 Å. The polar contribution to the S–C bonds, however, will be repulsive, since both atoms, sulfur and carbon, carry positive net charges. The S–C bonds in $(SF_5)_2CF_2$ are the longest such bonds known for gas-phase molecules. They are longer than S(VI)–C bonds in CF_3SF_5 (1.887 (8) Å[11]) or $(CF_3)_2SO_2$ (1.858 (5) Å[12]), which in turn are considerably longer than such bonds in S(II) compounds (e.g. 1.819 (3) Å in $(CF_3)_2S$[8a]).

The large bond angles in all three SF_5 compounds are a consequence of steric repulsions between the SF_5 groups. The shortest F··F contacts between the two SF_5 groups are 2.40 Å in $(SF_5)_2O$, 2.44 Å in $(SF_5)_2NF$, and 2.55 Å in $(SF_5)_2CF_2$. These nonbonded F··F distances are considerably shorter than the F··F van der Waals distance of 2.70 Å.[10] The large bond angles at the central atom leads to increased s character of the covalent S–X bonds. This effect enhances the bond shortening for the S–O and S–N bonds and diminishes bond lenghtening due to the repulsive polar contribution for the S–C bonds.

An alternative rationalization for the short S–O and S–N bonds and the increased oxygen and nitrogen bond angles would be partial delocalization of the central atom lone pairs into the empty sulfur d orbitals with formation of (p–d)π bonds. The normal bond angles in SF_5OF (SOF = 108°[13]) and SF_5NF_2 (SNF =

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Table V. Effects of Ring Formation on Bond Lengths (Å) and Bond Angles (deg)[a]

	Y-X[b]	Δ(Y-X)	YXY	Δ(YXY)
$(SeF_5)_2O$[c] $(SeF_4O)_2$[d]	1.697 (13) 1.779 (7)	0.082 (15)	142.4 (19) 97.5 (5)	−44.9 (20)
$(SF_5)_2NF$[e] $(SF_4NCl)_2$[f]	1.685 (5) 1.734 (4)	0.049 (7)	138.3 (10) 99.3 (6)	−39.0 (12)
$(SF_5)_2CF_2$ $(SF_4CF_2)_2$	1.908 (7) 1.886 (4)	−0.022 (9)	124.3 (7) 96.2 (3)	−28.1 (8)

[a] All geometric parameters are r_a values. [b] Y = S or Se; X = O, N, or C. [c] Reference 4. [d] Reference 15. [e] Reference 5. [f] Reference 16.

111.4 (3)° and FNF = 98.1 (8)°[14]), however, do not indicate partial delocalization of the oxygen or nitrogen lone pairs. Thus, the concept of (p–d)π bonding does not appear to be required to rationalize the structural parameters of $(SF_5)_2O$ and $(SF_5)_2NX$. Polar effects are very strong in these molecules and, in combination with steric repulsions, do qualitatively explain their structural features. Furthermore, the concept of polar effects can also be applied to $(SF_5)_2CF_2$. The long S–C bonds can be explained by strong $C^{\delta+}$–$S^{\delta+}$ repulsion.

Table V compares the effect of ring formation on bond lengths and bond angles in $(SeF_5)_2O$ vs. $(SeF_4O)_2$, $(SF_5)_2NF$ vs. $(SF_4NCl)_2$, and $(SF_5)_2CF_2$ vs. $(SF_4CF_2)_2$. Since the cyclic sulfur compound $(SF_4O)_2$ has not been observed, the analogous selenium compound is used in this comparison. This seems to be justified, since the structural features of all three $(YF_5)_2O$ oxides (Y = S, Se, and Te) are very similar (short Y–O bonds and YOY angles around 145°)[4] and the effects of ring formation are, within experimental error limits, the same for the Se and Te compounds (lengthening of the Y–O bonds by 0.082 (15) and 0.086 (15) Å and decrease of the YOY angles by 44.9 (2.0) and 46.0 (2.2)° for the selenium and tellurium compounds, respectively).[15] Thus very similar effects upon ring formation are expected for the analogous sulfur compounds. Also for the nitrogen compounds, strict comparison between the bis(pentafluorothio)amine and the dimeric tetrafluorosulfur imide is not possible. The only imide that exists as cyclic dimer is the chloro derivative $(ClNSF_4)_2$. The corresponding noncyclic compound, $(SF_5)_2NCl$, has been synthesized, but its structure has not been studied. A comparison of the structural data for $(SF_5)_2NH$ and $(SF_5)_2NF$ demonstrates that the nitrogen substituents with different electronegativities have only small effects on the skeletal parameters of the amine.[5] Thus, the comparison between $(SF_5)_2$ NF and $(SF_4NCl)_2$ should give a very nearly correct picture of the effect of ring formation for the nitrogen compounds. In the oxides the oxygen bond angle decreases by about 45° upon ring formation, and the bonds lengthen by about 0.08 Å. Similar, but smaller, variations are observed for the SNS angles (−39°) and the S–N bond lengths (+0.049 Å). Also for the carbon compounds the SCS angle decreases strongly (−28°) upon ring formation, but here the S–C bond lengths show the opposite trend. They are shorter in the four-membered ring than in the acyclic compound.

Polar effects are expected to change little with ring formation. On the other hand, hybridization of O, N, or C will change strongly and the increased p character in the S–X ring bonds leads to lengthening of these bonds. Ring strain, which is expected to decrease with increasing ring size, i.e. in the sequence O > N > C, will cause further lengthening of the ring bonds. The S··S nonbonded distances (2.81 Å in $(SF_4CF_2)_2$, 2.64 Å in $(SF_4NCl)_2$, and 2.50–2.55 Å estimated for the hypothetical $(SF_4O)_2$) are much shorter than the van der Waals distance of 3.70 Å. Both effects, increased p character and ring strain, can rationalize the lengthening of the Se–O and S–N bonds upon ring formation and also the relative magnitude of these effects (Δ(Se–O) > Δ(S–N)). From these arguments we would expect a smaller effect, but still would expect lengthening of the S–C bonds upon ring formation. The experimental result, however, i.e. shorter S–C bonds in the SCSC ring, contradicts this rationalization. Very short nonbonded F··F contacts in $(SF_5)_2CF_2$ between SF_5 and CF_2 fluorines (F_2··F = 2.33 Å and F_4··F′ = 2.42 Å) are possibly responsible for the unexpected behavior of the S–C bonds. These nonbonded repulsions, which disappear upon ring formation, can explain the extremely long S–C bonds in $(SF_5)_2CF_2$.

Table VI. Geometric Parameters of CSCS Four-Membered Rings with Different Oxidation States of Sulfur

	S–C	CSC	SCS
$\overline{CF_2SCF_2S}$[a]	1.820 (2) (S^{II})	82.7 (2)	97.3 (2)
$\overline{CF_2SCF_2S}(OR_f)_2$[b]	1.744 (14) (S^{II}) 1.910 (13) (S^{IV})	86.5 (6) 77.4 (6)	98.1 (7)
$\overline{CF_2SOCF_2S}O$[c]	1.885 (4) (S^{IV})	79.4 (2)	100.6 (2)
$\overline{CF_2SF_2CF_2S}O_2$[d]	1.90 (S^{IV}) 1.88 (S^{VI})	85 86	94
$\overline{CF_2SF_4CF_2S}F_4$[e]	1.886 (4) (S^{VI})	83.8 (3)	96.2 (3)

[a] Electron diffraction study.[17] [b] X-ray study (mean values).[18] The values may be affected by decay of the compound in the X-ray beam and by disorder of the OR_f groups (R_f = $C(CF_3)_3$). [c] X-ray study (mean values).[18] [d] X-ray study.[19] No error limits are given. [e] This study.

It is of interest to compare the ring parameters in tetrafluoro-1,3-dithietane with some of its derivatives, where sulfur is in different, oxidation states with different coordination numbers (Table VI). S(II)–C bonds are definitely shorter than S(IV)–C and S(VI)–C bonds. The latter bond lengths in the four-membered rings are all very similar and are in the range 1.88–1.90 Å. The same dependence on the sulfur oxidation state is observed for the acyclic analogue $(CF_3)_2S$ (1.819 (3) Å[8a]) vs. $(CF_3)_2SO$ (1.885 (4) Å[20]), $(CF_3)_2SF_2$ (1.888 (4) Å[20]), or CF_3SF_5 (1.887 Å[11]). This comparison demonstrates that the S–C bond lengths depend strongly on the sulfur oxidation state (S(II) vs. S(IV) and S(VI)), but are almost unaffected by ring formation. For a given oxidation state no influence of the coordination number is evident from the limited data collected in Table VI. The CSC bond angles in the four-membered rings do vary considerably, but no definite correlation between these bond angles and oxidation state or coordination number can be observed. In all cases the CSC bond angles are smaller than the SCS angles by 10–20°.

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