# Bis(trifluoromethyl)trisulfane, $CF_3SSSCF_3$, and Bis(trifluoromethyl)tetrasulfane, $CF_3SSSSCF_3$: Simple Syntheses, Spectroscopic Data, and Gas-Phase Structures[1]

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Bis(trifluoromethyl)trisulfane, $CF_3SSSCF_3$, and bis(trifluoromethyl)tetrasulfane, $CF_3SSSSCF_3$, have been prepared in good yield and high purity by reacting $CF_3SSH$ with $CF_3SCl$ and $CF_3SSCl$, respectively, at 298 K. The IR, Raman, and $^{13}C$ and $^{19}F$ NMR data are reported. The gas-phase structures and conformations were determined by electron diffraction (ED) and ab initio calculations (HF/3-21G*). The ED intensities of the trisulfane are consistent only with the trans conformation, in agreement with the ab initio calculations ($E_{cis} - E_{trans} = 2.4$ kcal/mol). The experimental intensities of the tetrasulfane are reproduced equally well with a cis–trans and a trans–trans structure. Comparison between experimental and calculated dihedral angles leads to a preference of the cis–trans form. The relative ab initio energies are 0.0, 0.3, and 1.1 kcal/mol for cis–trans, trans–trans, and cis–cis conformers.

## Introduction

Bis(trifluoromethyl)monosulfane, $CF_3SCF_3$, and the analogous disulfane, $CF_3SSCF_3$, are readily synthesized in high yields and high purity. Both compounds are well characterized.[3-10] Various synthetic routes have been reported in the literature for the preparation of the corresponding tri- and tetrasulfanes.[11-13]

$$CS_2 + IF_5 \xrightarrow{60-200\,°C} CF_3SSCF_3 + SF_4 + CF_3SSSCF_3 \quad (1)$$

$$CF_3I + S \xrightarrow[36\,h]{310\,°C} CF_3SSCF_3 + CF_3SSSCF_3 + CF_3SSSSCF_3 \quad (2)$$

$$C_2F_6 + S_8 \xrightarrow[h\nu]{>165\,°C} S_n + CF_3 \rightarrow CF_3SSSCF_3 + CF_3SSSSCF_3 + ... \quad (n = 1\text{–}8) \quad (3)$$

All methods require elevated temperatures and produce mixtures of three or more components, which are difficult to separate. Tri- and tetrasulfanes are obtained only in low yields. These compounds have so far been characterized only by mass, $^{19}F$ NMR, and incomplete IR spectra.[11,12,14] An early ED investigation of the trisulfane resulted only in partial structural data without identifying its conformation.[15]

In this report we describe a simple synthetic method for the preparation of the tri- and tetrasulfanes which uses condensation reactions of trifluormethyldisulfane, $CF_3SSH$, with $CF_3SCl$ and $CF_3SSCl$, respectively.

$$CF_3SSH + CF_3S_nCl \xrightarrow{25\,°C} CF_3SSS_nSCF_3 + HCl \quad (n = 1, 2) \quad (4)$$

Besides small amounts of starting products, the trisulfane contains only traces of di- and tetrasulfanes and the tetrasulfane contains a trace of trisulfane. After fractional condensation samples of high purity are obtained which were used for spectroscopic characterization and gas-phase structural studies. The structure determinations are made complicated by the possible presence of two (trisulfane) or three (tetrasulfane) conformers. Whereas geometric structures of disulfanes depend only on short-range interactions between lone pairs, bonds, and substituents, the structures and conformational properties of tri- and tetrasulfanes provide information about such long-range interactions. Since geometric parameters (especially dihedral angles) and conformational properties of polysulfanes can be strongly affected by *intermolecular* interactions in the crystal (see below), only gas-phase studies provide information about these *intramolecular* interactions. The experimental investigations are supplemented by ab initio calculations at the HF/3-21G* level, using the GAUSSIAN 86 program system.[16] As demonstrated in previous studies, such calculations reproduce experimental geometries and conformational properties of disulfanes ($CF_3SSX$,[17] X = H, F, Cl, and Br, and FC(O)SSC(O)F[18]) closely. From this we expect a similar agreement between experiment and theory for the polysulfanes. Unfortunately, calculations with larger basis sets and inclusion of electron correlation are not feasible for molecules of this size.

## Experimental Section

**Materials and Apparatus.** The disulfanes $CF_3SSH$ and $CF_3SSCl$ were synthesized and purified according to literature methods.[19,20] $CF_3SCl$ was kindly supplied by Prof. Dr. mult. A. Haas, University of Bochum,

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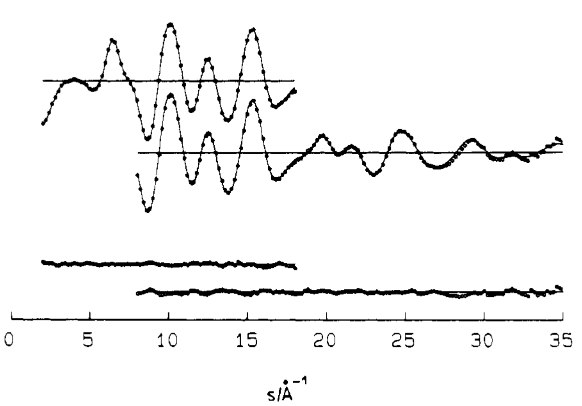


**Figure 1.** Experimental (dots) and calculated (full line) molecular intensities and differences for $CF_3SSSCF_3$.

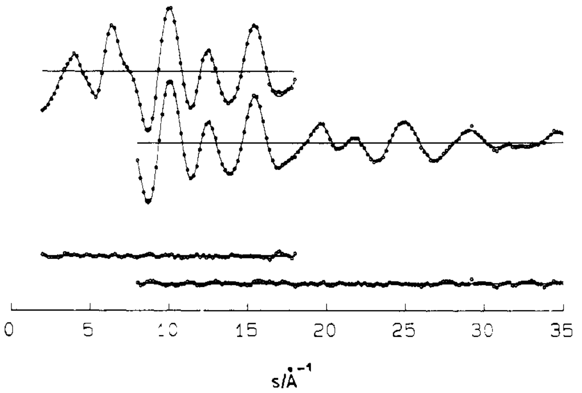


**Figure 2.** Experimental (dots) and calculated (full line) molecular intensities and differences for $CF_3SSSSCF_3$.

Germany. Its purity was checked by $^{19}F$ NMR and Raman spectra. Gas-phase IR spectra were recorded at 298 K with a Bruker IFS 113V FT spectrometer, using a 10-cm stainless steel cell equipped with silicon windows. The Raman spectra were measured at 298 K with a Coderg T800 spectrometer using excitation at $\lambda = 514.5$ nm. The NMR spectra were recorded with a Bruker AM300 ($CF_3SSSCF_3$, at 298 K) and with a Bruker AC 200 spectrometer ($CF_3SSSSCF_3$, at 263 K). TMS and F11, respectively, were used as external standards.

**Preparation of $CF_3SSSCF_3$ and $CF_3SSSSCF_3$.** A 2.0-mmol sample of $CF_3SSH$ (268 mg) and 2.0 mmol of $CF_3SCl$ (273 mg) or 2.0 mmol of $CF_3SSCl$ (337 mg), respectively, are condensed into a glass ampule at 77 K. After 3 days at 298 K the formed HCl is pumped off at 178 K. The products are purified by fractional condensation. After repeated purification the yield is ca. 35%.

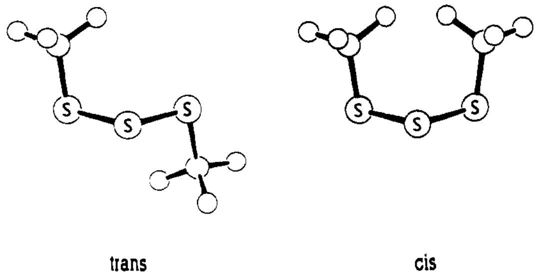
**Electron Diffraction.** The scattering intensities were recorded with a Model KD-G2 gas diffractograph at camera (nozzle-to-plate) distances of 25 and 50 cm with an accelerating voltage of ca. 60 kV. The electron wavelength was calibrated by ZnO powder patterns. The sample reservoirs were kept at −15 °C ($CF_3SSSCF_3$) and +5 °C ($CF_3SSSSCF_3$), and the inlet system and nozzle were maintained at room temperature. The camera pressure during the experiments was below $2 \times 10^{-5}$ mbar. Two plates for each compound and camera distance were analyzed by the usual procedures.[9] Numerical values of the total scattering intensities in the $s$-ranges 2–18 Å$^{-1}$ and 8–35 Å$^{-1}$ in steps of $\Delta s = 0.2$ Å$^{-1}$ are available as supplementary material and averaged molecular intensities are shown in Figures 1 and 2.

## Results and Discussion

**Vibrational Spectra.** Raman and IR spectra of tri- and tetrasulfanes are collected in Table I. The assignment is made by comparison with the spectra of the analogous mono- and disulfanes. The latter was assigned on the basis of ab initio calculations.[8] The $CF_3$ stretches, deformations, and rockings are typical for such groups. The Raman spectrum of the trisulfane shows two S–S stretches at 496 and 518 cm$^{-1}$, and that of the tetrasulfane, only one vibration at 509 cm$^{-1}$. The C–S stretches are nearly equal at 460 and 458 cm$^{-1}$. This vibration has the highest Raman intensity in tetrasulfane. The skeletal deformations (three in trisulfane and four in tetrasulfane) occur below 300 cm$^{-1}$, and a plausible assignment is given in Table I. All three torsional vibrations are observed in the tetrasulfane spectrum, the lowest one being the $CF_3$ torsion at 54 cm$^{-1}$.

**NMR Spectra.** The $^{19}F$ singlets and $^{13}C$ quartets of the two equivalent $CF_3$ groups in di-, tri-, and tetrasulfanes occur at nearly equal positions ($\delta(^{19}F) = -46.6, -46.50$, and $-45.19$ ppm; $\delta(^{13}C) = 125.8, 129.05$, and 128.60 ppm), and also the $^1J_{CF}$ coupling constants are very similar (313.7, 309.55, and 313.81 Hz).

**Gas-Phase Structures and Conformations. Bis(trifluoromethyl)trisulfane.** Assuming gauche conformations around the S-S bonds with dihedral angles near 90°, two different conformers are conceivable for trisulfane, +g +g or trans ($C_2$ symmetry) and −g +g or cis ($C_s$ symmetry). X-ray crystallographic studies for trisulfanes RSSSR demonstrate that trans and cis conformers occur in the solid, depending on the groups R.[21] Besides the incomplete ED study of $CF_3SSSCF_3$[15] the only gas-phase structure investigation reported in the literature is that of the parent compound $H_2S_3$.[22] Its strongest transitions in the microwave spectrum are unambiguously assigned to the cis form. This is in contrast to a vibrational study which assigns the IR and Raman spectra of this compound to the trans conformer.[23] Both molecular mechanics[24] and ab initio calculations[25] predict a very small energy difference of only 0.3 kcal/mol, with slight preference for the trans structure. This theoretical result does not contradict the interpretation of the microwave spectrum. The ab initio value for the dipole moment of the cis form is almost three times larger than that of the trans structure, which predicts the transitions of the cis form to be about five times stronger than those of the trans conformer, despite its lower population.



The experimental radial distribution curve of $CF_3SSSCF_3$ (Figure 3) was calculated by Fourier transform of the molecular intensities (Figure 1) by applying an artificial damping function $\exp(-0.002\,s^2)$. Comparison with calculated curves demonstrates that the ED data are consistent only with a trans conformation possessing SSSC dihedral angles of ca. 90°. Contributions of the cis form larger than 10% can be excluded. In the least-squares refinement $C_2$ overall symmetry and local $C_{3v}$ symmetry of the $CF_3$ groups were assumed. Constraints for vibrational amplitudes are evident from Table II. Eight geometric parameters and nine vibrational amplitudes were refined simultaneously. Only two correlation coefficients had values larger than $|0.7|$: tilt/$u_5$ = 0.91 and $u_3/u_4$ = 0.75. The full correlation matrix is available as supplementary material. Final results and numbering of vibrational amplitudes are given in Tables II and III.

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**Table I.** Vibrational Frequencies ($cm^{-1}$) of $CF_3S_nCF_3$ ($n$ = 1–4)

| $CF_3SCF_3$[a] | $CF_3SSCF_3$[b] | $CF_3SSSCF_3$ | | $CF_3SSSSCF_3$ | | |
|---|---|---|---|---|---|---|
| RA[c] | RA | RA[c] | IR | RA[c] | IR | |
| 1220 (1) | 1206 vw | | | | | $\nu(CF_3)$ |
| 1190 (1.5) | 1184 vw | | 1181 s | | 1180 s | $\nu(CF_3)$ |
| 1160 (1.5) | 1125 m | 1120 (3) | 1106 s | 1116 (5) | 1105 s | $\nu(CF_3)$ |
| 1070 (1) | 1088 w | 984 (3) | | 900 (9) | | $\nu(CF_3)$ |
| 768 (100) | 759 vs | 764 (46) | 757 m | 763 (39) | 756 m | $\delta_s(CF_3)$ |
| 593 (2) | 574 m | 570 (9) | | 567 (6) | 569 w | $\delta_{as}(CF_3)$ |
| 545 (2) | 543 sh | | | | | $\delta_{as}(CF_3)$ |
| | 536 m | 518 (64) | | 509 (75) | 512 w | $\nu(SS)$ |
| | | 496 (15) | | | | $\nu(SS)$ |
| 475 (40) | 453 s | 460 (44) | 453 w | 458 (100) | 452 mw | $\nu(CS)$ |
| | 447 sh | | | | | $\nu(CS)$ |
| 358 (1) | 357 w | 349 (3) | | | | $\rho(CF_3)$ |
| 304 (73) | 339 m | 335 (5) | | 341 (7) | | $\rho(CF_3)$ |
| 286 (13) | 284 s | 320 (26) | | 325 (27) | 319 w | $\rho(CF_3)$ |
| | 156 sh | 200 (100) | | 234 (22) | | $\delta(SSC)$ |
| | 147 s | | | | | $\delta(SSC)$ |
| | | 182 (23) | | 212 (65) | | $\delta(SSS)$ |
| 130 (4) | | | | | | $\delta(CSC)$ |
| | | | | 134 (98) | | $\tau(SSSS)$ |
| | | 118 (66) | | 116 (88) | | $\tau(SSSC)$ |
| | 78 sh | | | | | $\tau(CSSC)$ |
| 75 sh | | | | | 54 w | $\tau(CF_3)$ |

[a] Reference 7. [b] Reference 8. [c] Relative intensities are given in parentheses.

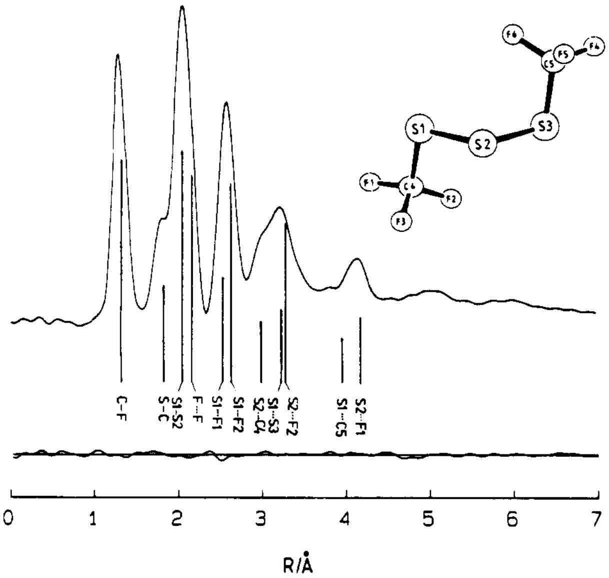

**Figure 3.** Experimental radial distribution function and difference curve for $CF_3SSSCF_3$. The positions of the most important interatomic distances are indicated by vertical bars.

**Table II.** Interatomic Distances and Vibrational Amplitudes for $CF_3SSSCF_3$ and $CF_3SSSSCF_3$[a]

| | $CF_3SSSCF_3$ (trans) | | $CF_3SSSSCF_3$ (cis–trans) | |
|---|---|---|---|---|
| | dist | ampl | dist | ampl |
| C–F | 1.33 | 0.044 (2) | 1.33 | 0.041 (2) ($u_1$) |
| S–C | 1.82 | 0.051 (5) | 1.82 | 0.054 (6) ($u_2$) |
| S–S | 2.04 | 0.060 (5) | 2.05 | 0.055 (2) ($u_3$) |
| F···F | 2.16 | 0.061 (5) | 2.16 | 0.059 (6) ($u_4$) |
| S···F | 2.54, 2.64 | 0.068 (7) | 2.55, 2.63 | 0.072 (8) ($u_t$) |
| S···C | 2.94 | 0.089 (11) | 2.98 | 0.093 (8) ($u_6$) |
| S···S | 3.25 | | 3.26 | |
| S···F | 3.25 | 0.24 (2) | 3.18, 3.27 | 0.20 (3) ($u_7$) |
| S···F | 3.53 | 0.30[b] | 3.47 | 0.30[b] |
| S···C | 3.94 | 0.17 (5) | 3.91 | 0.29 (13) ($u_8$) |
| S···S | | | 4.37 | |
| S···F | 4.18 | 0.10 (2) | 4.17 | 0.09 (2) ($u_9$) |
| S···F | 4.58, 5.05 | 0.30[b] | 4.52–5.27 | 0.30[b] |
| S···C | | | 4.11, 5.53 | |
| S···F | | | 6.25, 6.49 | 0.40[b] |
| C···C | 5.20 | 0.40[b] | 5.42 | 0.40[b] |
| C···F | 5.03–6.13 | | 4.71–6.68 | |
| F···F | 5.07–7.01 | | 5.02–7.67 | |

[a] Values in Å. Error limits are $3\sigma$ values and refer to the last digit. [b] Not refined.

The HF/3-21G* calculations predict the cis conformer to be higher in energy by 2.4 kcal/mol and are in accord with the ED result concerning the conformation of this trisulfane. If the SSSC angles for the cis form are set equal to that of the trans conformer, an F···F contact of ca. 1.7 Å occurs between the two $CF_3$ groups. In the ab initio structure optimization for the cis form, the SSSC dihedral angles increase by more than 10° and the $CF_3$ groups rotate ca. 10° from their staggered positions. These distortions and the remaining F···F repulsion (ca. 2.5 Å) are responsible for the energy difference between cis and trans conformers of $CF_3SSSCF_3$, which is much larger than that for $H_2S_3$ (0.3 kcal/mol).

**Bis(trifluoromethyl)tetrasulfane.** Provided again that only gauche conformations around the three S–S bonds occur, three pairs of enantiomers are conceivable for a tetrasulfane: +g +g +g or trans–trans ($C_2$ symmetry), –g +g +g or cis–trans ($C_1$ symmetry), and –g +g –g or cis–cis ($C_2$ symmetry). In the solid phase tetrasulfanes can adopt the trans–trans, trans–cis, and cis–cis[28] conformation, indicating rather similar conformational energies. This is also confirmed by ab initio calculations (HF/3-21G*) for $H_2S_4$ which predict the cis–trans form to be only slightly more stable than the trans–trans (+0.2 kcal/mol) and cis–cis (+0.3 kcal/mol) conformers.[29] No experimental gas-phase structure for an $S_4$ compound has been reported so far.

Suprisingly, the experimental radial distribution curve (Figure 4) can be reproduced almost equally well with a trans–trans or a cis–trans model, if the SSSS and SSSC dihedral angles are adjusted accordingly. Thus, the ED data alone do not allow a distinction between trans–trans and cis–trans conformations or a mixture of both. The cis–cis form fits the experimental curve considerably worse and can be excluded as the prevailing conformer of this compound. Least-squares analyses were performed for the trans–trans and the cis–trans structures. For the cis–trans form ($C_1$ symmetry) the geometric parameters of both halves of the molecule, $CF_3S_1S_2$– and $–S_3S_4CF_3$, were set equal, except for the sign of the SSSC dihedral angles ($S_3S_2S_1C$

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(29) Pseudopotential SCF calculations for the trans–trans and cis–cis conformers of $H_2S_4$ predict the former to be lower in energy by 0.03 kcal/mol.[25] The cis–trans form of the tetrasulfane is not considered in this publication.

**Table III.** Experimental and Calculated Geometric Parameters for $CF_3SSSCF_3$ and $CF_3SSSSCF_3$

| | $CF_3SSSCF_3$ (trans) | | $CF_3SSSSCF_3$ (cis–trans) | |
|---|---|---|---|---|
| | ED[a] | HF/3-21G* | ED[a] | HF/3-21G* |
| C–F | 1.330 92) | 1.345 | 1.331 (2) ($p_1$) | 1.345 |
| S–C | 1.820 (5) | 1.787 | 1.818 (6) ($p_2$) | 1.786 |
| $(S–S)_{mean}$[b] | 2.040 (4) | 2.044 | 2.041 (3) ($p_3$) | 2.048 |
| ΔSS[c] | | | 0.020[e] | 0.020 |
| $S_1$–$S_2$ | 2.040 (4) | 2.044 | 2.034 (3) | 2.041 |
| $S_2$–$S_3$ | 2.040 (4) | 2.044 | 2.054 (3) | 2.061 |
| ∠SSS | 105.3 (6) | 104.6 | 106.8 (5) ($p_4$) | 104.7 |
| ∠SSC | 101.0 (7) | 99.6 | 101.6 (8) ($p_5$) | 100.1 |
| ∠FCF | 108.3 (3) | 108.1 | 108.3 (4) ($p_6$) | 108.1 |
| tilt($CF_3$)[d] | 4.2 (8) | 3.3 | 4.5 (7) ($p_7$) | 3.4 |
| δ(SSSS) | | | 98 (5) ($p_8$) | 99.3 |
| δ(SSSC) | 89 (3) | 87.5 | 84 (6) ($p_9$) | 86.3 |

[a] $r_a$ distances in Å, $\angle_\alpha$ angles in deg. Error limits are 3σ values and refer to the last digit. [b] $(SS)_{mean} = {}^1/_3((2(S_1–S_2) + (S_2–S_3))$. [c] $\Delta SS = (S_2–S_3) – (S_1–S_2)$. [d] Tilt between $C_3$ symmetry axis of $CF_3$ group and S–C bond, away from vicinal S–S bond. [e] Not refined.

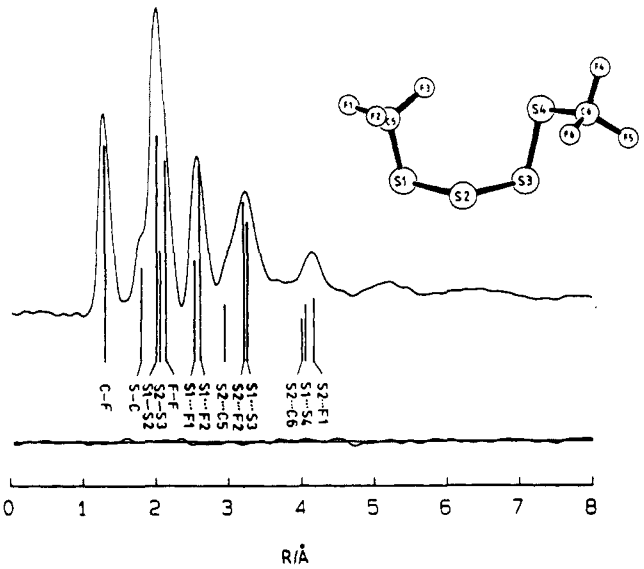
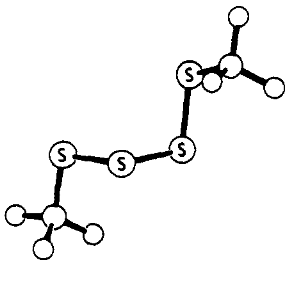
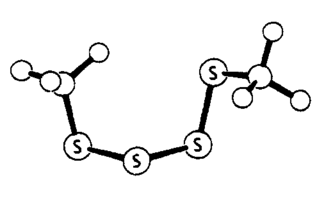
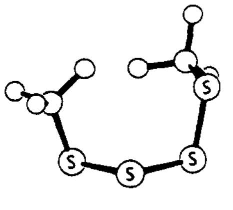


**Figure 4.** Experimental radial distribution function and difference curve for $CF_3SSSSCF_3$. The positions of the most important interatomic distances are indicated by vertical bars.







= –$S_2S_3S_4C$). The difference between the SS bond lengths ΔSS = $(S_2–S_3) – (S_1–S_2)$ could not be determined from the ED intensities and was constrained to the ab initio value. For assumptions concerning the vibrational amplitudes, see Table II. In addition to the two large correlations occurring in the trisulfane, the two dihedral angles in the tetrasulfane also correlate strongly: SSSS/SSSC = –0.87, tilt/$u_5$ = 0.87, $u_3/u_4$ = 0.75. The full correlation matrix is available as supplementary material.

The refinements for cis–trans and trans–trans conformers lead to almost identical agreement factors. Comparison between experimental and calculated dihedral angles, however, suggests that the cis–trans conformer is present in the gas phase or is, at least, the prevailing one. Only for this structure do the experimental and calculated SSSS and SSSC dihedral angles agree very closely (see Table III), whereas these values differ by ca. 10° for the trans–trans conformer (SSSS = 83 (6) vs 91.1° and SSSC = 92 (5) vs 83.7°). Since the applied ab initio method reproduces the experimental SSSC dihedral angle in the trisulfane within its uncertainty (89 (3) vs 87.5°), we expect a similar agreement in the tetrasulfane. The calculations predict the cis–trans structure to be slightly more stable than the trans–trans form (+0.3 kcal/mol), whereas the cis–cis conformer is higher by +1.1 kcal/mol. From the calculated relative energies a cis–trans:trans–trans ratio of ca. 3:1 is estimated, if the different degeneracies are taken into account. Such a mixture of the two conformers is consistent with the above interpretation of the ED data.

Table III compares experimental and calculated geometric parameters of the tri- and tetrasulfane. The experimental C–F and S–C bond lengths are equal in both compounds and are very similar to those in the corresponding disulfane $CF_3SSCF_3$ (C–F = 1.333 (2) Å, S–C = 1.835 (5) Å).[10] The S–S distances in the trisulfane and the mean S–S bond length $(S–S)_{mean}$ in the tetrasulfane are equal. These bond lengths are intermediate between that in $CF_3SSCF_3$ (2.030 (5) Å) and that in the solid state of elemental $S_8$ (2.048 (2) Å).[30] The dihedral angles around the S–S bonds depend strongly on the atoms or groups attached to the sulfur atoms. The CSSC angle in disulfanes increases from 85 (4)° in $CH_3SSCH_3$[31] to 104 (4)° in $CF_3SSCF_3$. The CSSS dihedral angles in both compounds of the present study are slightly smaller than 90° (89 (3)° in $CF_3SSSCF_3$ and 84 (6)° in $CF_3SSSSCF_3$). The experimental SSSS angle in the tetrasulfane is near 100°, in perfect agreement with the corresponding ab initio value (99.3°). The same theoretical method predicts the SSSS angle in $H_2S_4$ to be nearly 20° smaller (81.1°). A still smaller SSSS dihedral angle of 65° has been observed in the crystal structure of bis(octadecyl)tetrasulfane.[26] This large variation of the SSSS dihedral angles indicates a strong influence of substituents and packing effects in the crystal.

All experimental structural parameters are reproduced very closely by ab initio calculations at the HF/3-21G* level. The calculated C–F bond lengths are systematically longer and the S–C bonds shorter than the experimental values. Especially, the bond and dihedral angles are reproduced within their experimental error limits.

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**Supplementary Material Available:** Tables listing numerical values for total electron diffraction intensities and full correlation matrices for $CF_3SSSCF_3$ and $CF_3SSSSCF_3$ (6 pages). Ordering information is given on any current masthead page.

**Registry No.** $CF_3SSSCF_3$, 372-06-5; $CF_3SSSSCF_3$, 372-07-6; $CF_3SSCF_3$, 55860-39-4; $CF_3SCl$, 421-17-0; $CF_3SSCl$, 53268-50-1.

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