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(Trifluoroethylidyne)sulfur Trifluoride, $F_3CC\equiv SF_3$: Two Solid-State Structures and Reactivity as a Carbene

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Abstract: The known solid-state structure of $F_3CC\equiv SF_3$ (phase I) is revised (a = 629.4 (6), b = 755.1 (6), c = 569.2 (7) pm, β = 105.25 (10)°, Z = 2, $P2_1/m$). The C—C—S angle is found to be 171.4 (3)°. A second solid-state structure with very different packing (phase II) was observed (a = 948.2 (7), b = 694.6 (5), c = 890.3 (7) pm, β = 118.47 (2)°, Z = 4, $P2_1/n$) with a C—C—S angle of 162.9 (2)°. In connection with the gas-phase structure (C—C—S angle of 155°), these data show the bending force constant to be very small (nonclassical molecular structure). These findings are explained in terms of a low-lying carbene state, F_3CCSF_3. The dimerization reaction of $F_3CC\equiv SF_3$ is first order with an activation energy of 55 kJ mol^{-1}. Beside the E dimer $F_3C(SF_3)C{=}C(SF_3)CF_3$, a linear trimer is formed over very long reaction times. Reaction of $F_3CC\equiv SF_3$ and $F_5SC\equiv SF_3$ with fluorinated isonitriles yields alkylidenesulfur difluorides. For $C_6F_5N{=}CFC(SF_5){=}SF_2$ the structure was established by single-crystal X-ray investigation as the Z isomer with respect to the CS double bond (a = 730.4 (1), b = 740.6 (2), c = 1202.5 (4) pm, α = 85.53 (3)°, β = 86.08 (2)°, γ = 71.03 (2)°, Z = 2, $P\bar{1}$).

Introduction

The structures of $F_3CC\equiv SF_3$ and $F_5SC\equiv SF_3$ have been investigated in the solid state[1,2] and the gas phase[3,4] with the C—C—S angle varying between 180° and 155°. This finding is paralleled by ab initio calculations. First a linear geometry was found,[5,6] and an enlarged basis set and inclusion of electron correlation resulted in an angle of 160°.[3] Even though these calculations disagreed on the location of the minimum, they agreed on the fact that the bending potential is very shallow. The best calculated result so far gives an energy that is only 0.92 kJ mol^{-1} lower for the bent system than for the linear geometry.

At this point it became clear that the C—C—S bond angle in crystal structures of the molecule would reflect even minor influences of the packing. Furthermore, the need arose to repeat the crystal structure determination of $F_3CC\equiv SF_3$ when it became clear that the chosen space group $P2_1$ in the first solid-state structure might be incorrect. Even if crystal structures cannot illustrate anything about bending potentials directly, the existence of two different solid-state phases with quite different C—C—S angles in connection with kinetic measurements allows one to establish the bending potential, at least qualitatively. The reason for this "nonclassical" behavior[7] of the CS triple bond will be discussed in terms of a carbene state, which also governs the reactivity of these compounds.

Structure Analysis of $F_3CC\equiv SF_3$, Phase I

The previously reported structure of $F_3CC\equiv SF_3$ served as proof for the existence of this novel type of molecule.[1] However, the structure determination was not very accurate. The nonlinearity of the C—C—S bond especially was not beyond doubt, if an error limit of 3σ was allowed. Also, it turned out that the reported space group $P2_1$ was possibly incorrect. A recalculation of the structure with space group $P2_1/m$ results in the same structure, but with higher accuracy (see Table II). Nevertheless, a new single-crystal X-ray investigation was performed that led to the determination of two different solid-state crystalline phases. For the crystal of the known phase, hereafter called phase I, the crystallization temperature was −125 °C. The results of the least-squares refinement of the atomic parameters with five atoms fixed in the mirror plane can be seen in Figures 1a and 2 and Tables I and II. Vibrational amplitudes are now smaller, when compared to the previous measurement, and so are the standard deviations. Roughly the same structure as before was established. The C—C—S bond angle of 171.4 (3)° now indicates nonlinearity without a doubt. The crystal data and further details of the X-ray diffraction experiment are stated in Table I and the Experimental Section; Table II gives bond lengths and angles and Figure 1a the molecule. With the new data set atomic parameters were calculated for both space groups $P2_1$ and $P2_1/m$. Only for the second space group was the refinement convergent.

Structure Analysis of $F_3CC\equiv SF_3$, Phase II

As $F_3CC\equiv SF_3$ has quite strong X-ray reflection intensities even at high Bragg angles, crystallization was attempted repeatedly in order to obtain data good enough for electron density mapping. During these experiments a second solid phase was detected, hereafter called phase II. Its crystallization temperature was −142 °C. For the crystal data and details of the X-ray diffraction experiment, see Table I and the Experimental Section. Here the molecule is in no special position. Bond lengths and angles are given in Table II, and the molecule is shown in Figure 1b.

As can be seen in Figure 2, the packings of phase I and phase II are completely different. Phase I has an all-antiparallel orientation of the molecules, while phase II shows a herringbone pattern. Phase II is a little more densely packed, as the cell volume per molecule is 1% smaller, so that phase II may be considered the thermodynamically more stable phase.

Even the overall structure of the molecule in phase II differs from that in phase I. The C–C–S bond angle is now 162.9 (2)°. This shows the softness of the bending potential. Moreover, the orientation of the three fluorine atoms on each side of the molecule differs: in phase I two fluorine atoms are in a plane with and on the narrow side of the S–C–C configuration (see Figure 1a). In phase II, two fluorine atoms are also in a plane with but on the wide side of the S–C–C configuration (see Figure 1b).

Reactions of $F_3CC\equiv SF_3$

It turned out that the chemistry of $F_3CC\equiv SF_3$ is very difficult to investigate. All attempts to have it react in a controlled manner with hydrogen-containing materials, except HF, failed; normally

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(1) Pötter, B.; Seppelt, K.; Simon, A.; Peters, E.-M.; Hettich, B. *J. Am. Chem. Soc.* **1985**, *107*, 980.

(2) Gerhardt, R.; Grelbig, T.; Buschmann, J.; Luger, P.; Seppelt, K. *Angew. Chem.* **1988**, *100*, 1592; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1534.

(3) Christen, D.; Mack, H.-G.; Marsden, C. J.; Oberhammer, H.; Schatte, G.; Seppelt, K.; Willner, H. *J. Am. Chem. Soc.* **1987**, *109*, 4009; **1990**, *112*, 5388.

(4) Weiss, J.; Oberhammer, H.; Gerhardt, R.; Seppelt, K. *J. Am. Chem. Soc.* **1990**, *112*, 6839.

(5) Boggs, J. E. *Inorg. Chem.* **1984**, *23*, 3577.

(6) Dixon, D. E.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 2688.

(7) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303.

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Table I. Crystal Data and Experimental Conditions

formula	$F_3CC\equiv SF_3$ (phase I)	$F_3CC\equiv SF_3$ (phase II)	$C_6F_5N{=}CFC(SF_5){=}SF_2$
fw (g/mol)	170.07	170.07	421.19
space group	$P2_1/m$	$P2_1/n$	$P\bar{1}$
Z	2	4	2
d (g/cm^3)	2.164	2.191	2.283
V (10^{6}pm^3)	260.99	515.48	612.64
a (pm)	629.4 (6)	948.2 (7)	730.4 (1)
b (pm)	755.1 (6)	694.6 (5)	740.6 (2)
c (pm)	569.2 (7)	890.3 (7)	1205.5 (4)
α (deg)	90	90	85.53 (3)
β (deg)	105.25 (10)	118.46 (2)	86.08 (2)
γ (deg)	90	90	71.03 (2)
ϑ (°C)	−135	−155	−165
abs coeff (cm^{-1})	6.70	6.78	5.17
wavelength (pm)	71.068	71.068	71.068
scan method	ω–2θ	ω–2θ	ω–2θ
2θ range (deg)	4–90	3–100	4–50
Miller indices	$-8 \le h \le 10$ $-10 \le k \le 0$ $-11 \le l \le 7$	$-20 \le h \le 16$ $-14 \le k \le 6$ $-19 \le l \le 18$	$-8 \le h \le 8$ $-11 \le k \le 11$ $0 \le l \le 14$
no. reflns measd	1639	9183	2270
unique reflns	1049	5228	2155
thereof obsd	837, $F \ge 3\sigma(F)$	3277, $F \ge 2\sigma(F)$	1857, $F \ge 3\sigma(F)$
parameters	49	82	217
R_{int}	0.022	0.050	0.048
R	0.043	0.075	0.073
R_w	0.025	0.047	0.071

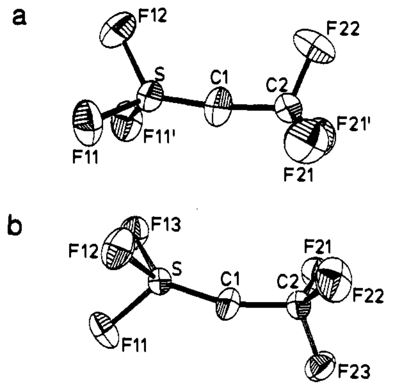


Figure 1. ORTEP drawing of (2,2,2-trifluoroethylidyne)sulfur trifluoride, $F_3CC\equiv SF_3$: (a) solid phase I; (b) solid phase II.

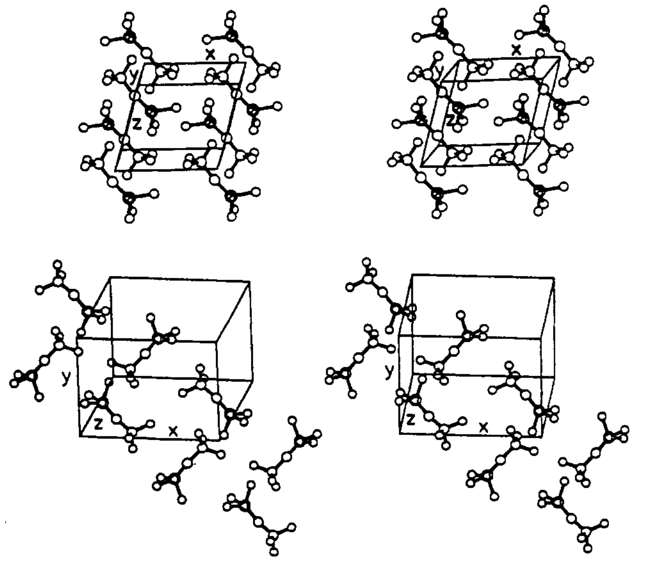


Figure 2. Packing of (2,2,2-trifluoroethylidyne)sulfur trifluoride, $F_3C\text{-}C\equiv SF_3$, XP-plot: (top) solid phase I; (bottom) solid phase II. The cell shown is that of the measurement, space group $B2_1/a$, a = 941.8 (2), b = 694.6 (5), c = 1580.0 (15) pm, β = 94.10 (2)°. This cell is transformed by (−0.5 0 0.5) (0 1 0) (−0.5 0 −0.5) to the conventional cell of space group $P2_1/n$.

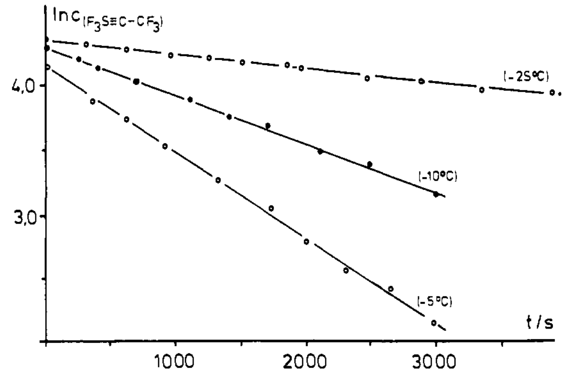


Figure 3. Kinetics of dimerization of $F_3CC\equiv SF_3$ at various temperatures, as followed by ^{19}F NMR.

hydrogen is abstracted, and in a complicated reaction sequence, $F_3CCH{=}SF_4$ and $F_3CCH_2SF_5$ are observed, just as if only HF was added.[1] Also, all reactions failed when $F_3CC\equiv SF_3$ was tried as a heteroalkyne ligand in organometallic chemistry; here the material turned out to be a very strong oxidizing and fluorinating agent. The dominant reaction in the absence of such "reactive" counterparts was always the dimerization to $SF_3(CF_3)C{=}C(CF_3)SF_3$ (E isomer). This already established reaction was investigated further. A kinetic study of this reaction shows that the disappearance of $F_3CC\equiv SF_3$ follows first-order kinetics over a range of 1 order of magnitude in concentration, at temperatures between −25 and +5 °C (see Figure 3). The rate-determining step has to be an excitation of $F_3CC\equiv SF_3$, before it will react further. This finding, in connection with other reactions described below, indicates a carbene state F_3CCSF_3 as the excited state, with a barrier of 47.7 kJ mol^{-1} in between.

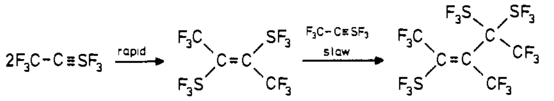
At a lower temperature (−40 °C), the dimerization is not only quite slow but a second product besides (E)-$F_3S(CF_3)C{=}C(CF_3)SF_3$ is also observed. This new compound is not the expected Z isomer. It contains, according to its ^{19}F and ^{13}C NMR spectra, three different ab_2 spectra of SF_3 groups, three different CF_3 groups, and three different quaternary skeleton carbon atoms. A cyclopropane structure can be ruled out not only for reasons of the inherent symmetry of such molecules but also because of the downfield ^{13}C shift of the skeleton carbon atoms. This trimer is most likely a pentene, $(F_3S)_2C(CF_3)C(CF_3){=}C(CF_3)SF_3$. This would be formed by carbene insertion into a CS bond. Under

Table II. Bond Lengths (pm), Selected Valence Angles (deg), and Selected Dihedral Angles (deg)

(a) $F_3CC{\equiv}SF_3$, phase I[a]			
S–F(11)	154.9 (2), 153.6 (3), 156.4	C(2)–F(22)	133.8 (3), 132.3 (5), 135.8
S–F(12)	155.0 (2), 153.2 (3), 156.2	F(11)–S–F(11)	94.6 (1), 94.4 (2)
S–C(1)	142.4 (3), 140.0 (4), 142.2	F(11)–S–F(12)	92.9 (1), 92.9 (1)
C(1)–C(2)	142.8 (3), 142.0 (5), 145.8	C(2)–C(1)–S	171.4 (3), 172.7 (4)
C(2)–F(11)	133.7 (2), 132.2 (3), 136.0		
(b) $F_3CC{\equiv}SF_3$, phase II			
S–F(11)	154.3 (2)	C(2)–F(22)	133.0 (2)
S–F(12)	154.8 (2)	C(2)–F(23)	134.9 (2)
S–F(13)	154.9 (2)	F(11)–S–F(12)	92.98 (9)
S–C(1)	143.1 (2)	F(11)–S–F(13)	93.20 (8)
C(1)–C(2)	143.5 (2)	F(12)–S–F(13)	93.88 (9)
C(2)–F(21)	134.0 (2)	S–C(1)–C(2)	162.90 (20)
(c) $C_6F_5N{=}CFC(SF_5){=}SF_2$			
F(1)–C(1)	134.8 (6)	S(1)–F(11)	156.9 (4)
F(2)–C(2)	133.7 (6)	S(1)–F(12)	158.8 (3)
F(3)–C(3)	133.2 (6)	S(2)–F(21)	156.6 (3)
F(4)–C(4)	135.2 (6)	S(2)–F(22)	156.6 (3)
F(5)–C(5)	134.0 (6)	S(2)–F(22)	156.6 (3)
C(1)–C(2)	137.3 (8)	S(2)–F(23)	157.0 (3)
C(2)–C(3)	137.6 (7)	S(2)–F(24)	156.8 (3)
C(3)–C(4)	137.7 (7)	S(2)–F(25)	157.3 (3)
C(4)–C(5)	136.8 (7)	C(6)–N–C(7)	121.4 (4)
C(5)–C(6)	139.4 (7)	N–C(7)–C(8)	122.4 (5)
C(6)–C(1)	138.6 (7)	C(7)–C(8)–S(1)	111.0 (3)
C(6)–N	141.1 (6)	C(7)–C(8)–S(2)	121.7 (3)
C(7)–N	125.1 (7)	S(1)–C(8)–S(2)	127.3 (3)
C(7)–F(7)	134.6 (6)	C(8)–S(1)–F(11)	107.6 (2)
C(7)–C(8)	146.0 (7)	C(8)–S(1)–F(12)	109.5 (2)
C(8)–S(1)	160.1 (5)	F(11)–S(1)–F(12)	89.6 (2)
C(8)–S(2)	179.7 (5)		

[a] First value, this work; second value, recalculation with data from ref 1; third value, bond length after librational correction with data from ref 1.

the assumption of hindered rotation of the CC single bond, due to sterical hindrance by the very large substituents, all NMR data fit with this formula. At temperatures above −90 °C, coalescence of two SF_3 groups is observed, indicative of a partially hindered rotation. The temperature sensitivity of the trimer, its nonvolatility, and the fact that so far it has been observed only in mixtures with the *E* dimer have prevented the determination of physical data other than NMR.



In order to prove the existence of the separate carbene state, numerous trapping reactions were attempted. For reasons described before, only the hydrogen-free isonitriles F_3CNC[8,9] and C_6F_5NC[10,11] gave clean 1:1 reactions. In all cases an addition is observed, and the resulting alkylidenesulfur difluoride can be rationalized by a subsequent 1,3 fluorine shift reaction.

The products are always mixtures of *E* and *Z* isomers at the carbon–sulfur double bond. The nitrogen–carbon double bond could also give rise to *E* and *Z* isomers, but it seems that *E* isomers are only formed in traces, if at all. The structure of these compounds was confirmed by the crystal structure of $C_6F_5N{=}CFC(SF_5){=}SF_2$ (see Tables I and II and Figure 4). With this measurement, the CS double bond length of 160.1 (5) pm of an alkylidenesulfur difluoride is experimentally established for the first time. Previously known alkylidenesulfur difluorides are $(F_3C)_2C{=}SF_2$ and $F_5S(F_3C)C{=}SF_2$, and the calculated CS double bond length of the latter molecule is 159 pm.[12] It is remarkable that the *Z* isomer (with respect to the CS double bond) is always formed in higher amounts than the *E* isomer. There is no isomer equilibration even by heating to 200 °C, which is indicative of considerable double bond character.

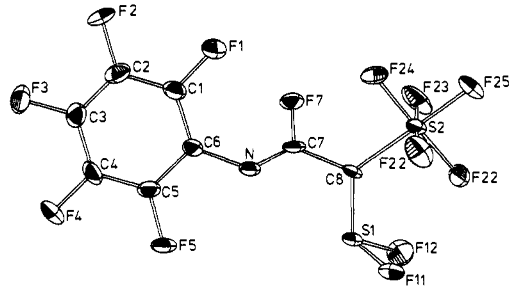
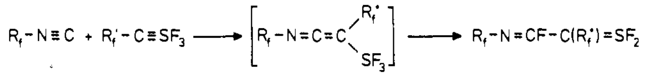


Figure 4. ORTEP plot of the structure of $C_6F_5N{=}CFC(SF_5){=}SF_2$, *Z*/*E* isomer.



Discussion

The criteria for a triple bond are the following: (1) the bond length should be considerably shorter, by almost 20%, than a comparable single bond; (2) the overall geometry should be linear; and (3) an intense electron density of cylindrical symmetry should be found between the triple-bonded atoms.[13] The first criterion is fulfilled for $RC{\equiv}SF_3$ compounds. The most accurate measurement gives 140.9 (2) pm for $F_3CC{\equiv}SF_3$ (phase II), and the values for phase I and $F_5SC{\equiv}SF_3$ are the same within the error limits. The criterion of an intense electron density is also fulfilled.

With its nonlinearity, the specialty of this triple bond system becomes obvious. If all measurements and calculations are considered, all CCS bond angles between 180° and approximately 155° are observed. The existence of two different solid phases of $F_3CC{\equiv}SF_3$ with quite different angles (162.9 (2)° and 171.4 (3)°) in connection with the bond angle of 180° in solid F_5S-

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(8) Makerov, S. P.; Englin, M. A.; Videuko, T. V. *Zh. Obshch. Khim.* **1967**, *37*, 2781.

(9) Lentz, D. *J. Fluorine Chem.* **1984**, *24*, 523.

(10) Banks, R. E.; Haszeldine, R. N.; Wiloughby, B. G. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2451.

(11) Lentz, D.; Graske, K.; Preugschat, D. *Chem. Ber.* **1988**, *121*, 1445.

(12) Damerius, R.; Seppelt, K.; Thrasher, J. *Angew. Chem.* **1989**, *101*, 783; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 769.

(13) van Nes, G. J. H. Ph.D. Dissertation, University of Groningen, Groningen, The Netherlands, 1978.

Table III. $C{-}C{\equiv}S$ Bond Angles of Alkylidenesulfur Trifluorides

$F_3C{-}C{\equiv}SF_3$	solid, phase I[a]	171.4 (3)°
	solid, phase II[a]	162.9 (2)°
	gas, electr diffr[b]	155 (3)°
	SCF-MP2[b]	148°
$F_5S{-}C{\equiv}SF_3$	solid[c]	180°
	gas, electr diff[d]	159 (3)°

[a] This work. [b] Reference 3. [c] Reference 2. [d] Reference 4.

$C{\equiv}SF_5$[2] proves the bending potential barrier to be very small if not zero within the given limits. This finding is novel for a triple-bonded molecule, although a similar situation has been established for cumulated species such as $H_2C{=}C{=}C{=}O$[14] or $Ph_3P{=}C{=}PPh_3$,[15] which also have nonlinear geometries with very soft bending motions. Solid $Ph_3P{=}C{=}PPh_3$ even has two different molecules with PCP angles of 130.1° and 143.8° in the unit cell.[15]

Since alkynes and some other known heteroalkynes like $RC{\equiv}N$ and $RC{\equiv}P$ do not exhibit such behavior, we feel that the key to understanding may be found in the unusual reactivity of the $RC{\equiv}SF_3$ compounds. Except for the addition of HF across the triple bond, in the few cases where $F_3CC{\equiv}SF_3$ reacts in a clean manner, it behaves like a carbene species F_3CCSF_3. The reaction with isonitriles can be understood as a ketene imine intermediate undergoing a 1,3 fluorine shift reaction to give the final alkylidenesulfur difluoride. Carbene–isonitrile reactions are known to give ketene imines,[16-20] and these are known to rearrange.[21] Alternatively, an intermediate thiirene ring can be formulated that could open under 1,2 fluorine migration, forming the final product. Addition of isonitriles to triple bonds is also well documented.[22,23]

The first-order kinetics of the $F_3CC{\equiv}SF_3$ dimerization reaction to (E)-$F_3S(CF_3)C{=}C(CF_3)SF_3$, however, can only be understood if activation of one starting molecule is the rate-limiting step; this could hardly be anything else than activation to a carbene, if the product is kept in mind. The activation barrier of 47 kJ mol^{-1} is low, and the energy difference between the triple-bonded state and the (triplet?) carbene state is then even smaller. Even the formation of the trimer is best described as a carbene insertion into a CS single bond. All arguments may be summarized in Figure 5, which shows the bending potential.

A full theoretical understanding of the bending potential is hindered by the fact that the carbene F_3CCSF_3 can have a singlet or triplet state. In cases where the singlet state is stabilized by one ligand carrying nonbonding electron pairs, the singlet and triplet states are very close, HCF has a singlet state marginally lower in energy,[24] and F_3CCSF_3 could be another case. Carbene reactions of the latter can be explained in such a way that at first a decrease of the CCS angle generates a singlet carbene state. At 115° the CS bond length has increased to 148.1 pm and at 100° to 151.6 pm, while the total geometrically optimized MP2 energy has increased to 16.8 and 54.4 kcal mol^{-1}. The activation barrier of 47.7 kJ mol^{-1} corresponds to a bond angle of approximately 105°.[25] A crossing over to the triplet carbene state may occur, followed by a relaxation to the larger CCS bond angle of this state.

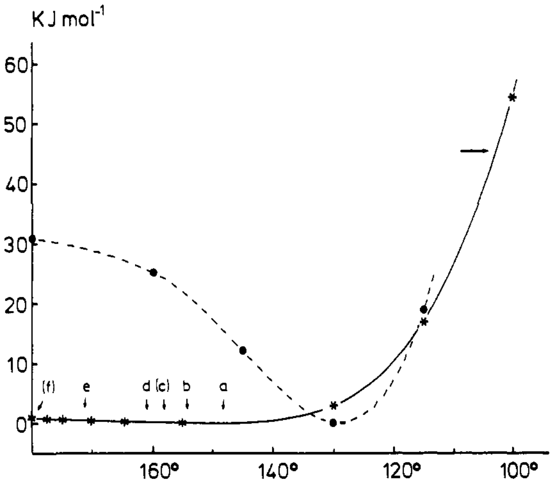

Figure 5. Bending potential of $F_3CC{\equiv}SF_3$(—) from the MP2/6-31G*/HF/6-31G* calculation:[3] (a) calculated minimum; (b) gas-phase structure of $F_3CC{\equiv}SF_3$;[3] (c) gas-phase structure of $F_5SC{\equiv}SF_3$;[4] (d) $F_3CC{\equiv}SF_3$ solid phase II; (e) $F_3CC{\equiv}SF_3$ solid phase I; (f) $F_3SC{\equiv}SF_3$ solid.[2] The horizontal arrow indicates the activation energy of the F_3C-$C{\equiv}SF_3$ dimerization reaction, which corresponds to an angle of ~105°. Bending potential of $FC{\equiv}SF_3$ (- - -), calculated values. Its minimum is set arbitrarily at the same energy as the $F_3CC{\equiv}SF_3$ minimum.

The widely observed hydrogen abstraction reaction that limits clean reactions to compounds without hydrogen favors the intermediacy of a triplet carbene. However, attempts to observe its EPR signal have so far been unsuccessful. As of yet it is also not possible to calculate the energy of the triplet state.

Another argument for the existence of a separate carbene state is that only the strongly singlet carbene *destabilizing* groups CF_3 and SF_5 form at least moderately stable triple-bonded species. The singlet carbene stabilizing fluorine ligand, as in $FCSF_3$, will lead to a C–C–S angle of 130° and a typical sulfur(IV) geometry (pseudo-trigonal-bipyramidal), according to calculations[3] (see Figure 5).

If substitution of one carbon atom in $RC{\equiv}CR$ by a sulfur atom brings the triple bond to the limits of its existence, one can speculate that $F_3S{\equiv}SF_3$ will exist only as "dicarbene" F_3SSF_3, and the known FSSF and F_3SSF will have very short SS bonds, reminiscent of unknown $FS{\equiv}SF$ and $F_3S{\equiv}SF$.[24-27] This picture is in accord with predictions about the nonclassical behavior of double or triple bonds, depending on the singlet–triplet or doublet–quartet separations of their fragments:[7] in second row elements the singlet or doublet state is more favored than the triplet or quartet state, in comparison to first row elements. In recent years a parallel phenomenon has become known: phosphinocarbenes $R_2PCSiR_3' \leftrightarrow R_2P{\equiv}CSiR'_3$ are described as triple-bonded species on account of their characteristic NMR data, but preferentially react as carbenes.[28-30]

Experimental Section

Spectra: Infrared spectra, Perkin-Elmer 885; Raman, Cary 82, Ar laser excitation; mass spectra, Varian 711, 80 eV, EI; and NMR spectra, JEOL FX 90Q (90 MHz) and Bruker AUX 500 (500 MHz).

Reagents. $F_3CC{\equiv}SF_3$ was prepared from $F_3CCH{=}SF_4$[31] as described previously.[32] $F_5SC{\equiv}SF_3$,[2] $F_3CN{\equiv}C$,[9] and $C_6F_5N{\equiv}C$[11] were prepared from literature methods.

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(14) Farrel, C.; Radom, L. *Chem. Phys. Lett.* **1982**, *91*, 373. Brown, R. D.; Dittman, R. D. *Chem. Phys.* **1984**, *83*, 77.

(15) Vincent, A. T.; Wheatley, P. J. *J. Chem. Soc., Chem. Commun.* **1971**, 592; *J. Chem. Soc., Dalton Trans.* **1972**, 617.

(16) Halleux, A. *Angew. Chem.* **1964**, *76*, 889; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 752.

(17) Boyer, J.; Beverung, W. *J. Chem. Soc., Chem. Commun.* **1969**, 1377.

(18) Green, J. A.; Singer, L. A. *Tetrahedron Lett.* **1969**, 5093.

(19) Obata, N.; Takizawa, T. *Tetrahedron Lett.* **1969**, 3404.

(20) Ciganek, E. *J. Org. Chem.* **1970**, *35*, 862.

(21) Krow, G. R. *Angew. Chem.* **1971**, *83*, 455; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 435.

(22) Suzuki, Y.; Obata, N.; Takizawa, T. *Tetrahedron Lett.* **1970**, 2667.

(23) Krebs, A.; Kimling, H. *Angew. Chem.* **1971**, *83*, 401; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 409.

(24) Kuczkowsky, R. L. *J. Am. Chem. Soc.* **1964**, *86*, 3617.

(25) Carlowitz, U. V.; Oberhammer, H.; Willner, H.; Boggs, J. E. *J. Mol. Struct.* **1983**, *100*, 161.

(26) Singlet HCF is calculated to be only 13 kcal mol^{-1} more stable than the triplet state: Scuseria, G. E.; Duran, M.; Maclagan, R. G. A. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1986**, *108*, 3248.

(27) New calculations with the method described in ref 3: Mack, H. G.; Oberhammer, H. Private communication.

(28) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463.

(29) Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem.* **1989**, *101*, 617; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621.

(30) Gillette, G. R.; Baceiredo, A.; Bertrand, G. *Angew. Chem.* **1990**, *102*, 1486; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1429.

(31) Grelbig, T.; Pötter, B.; Seppelt, K. *Chem. Ber.* **1984**, *117*, 3255.

(32) Pötter, B.; Seppelt, K. *Angew. Chem.* **1984**, *96*, 138; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 150.

Crystallization for Single-Crystal X-ray Measurement. $F_3CC{\equiv}SF_3$, phases I and II: Crystals were grown on the computer-controlled four-circle diffractometer in a cold N_2 gas stream from an integrated special device[33] using an arcless low-temperature goniometer head. The substance liquid (0.6 mm^3) was brought by distillation in vacuo to the tip of a 25 mm long glass tube, which had a 0.5-mm diameter and a 0.01-mm wall thickness and was closed at both ends by melting the glass. Single crystals were obtained by a process described elsewhere.[34] Finally, the crystal was slowly cooled down further to the lowest possible temperature.

X-ray Diffraction. The single-crystal X-ray diffraction measurements were done with a Siemens four-circle diffractometer with an open X circle and the N_2 gas stream cooling device,[33] Mo Kα radiation, Nb-filtered. With the crystal of phase I, 55 reflections having $17° < 2\theta < 55°$ were centered to determine the lattice constants and orientation; with that of phase II, 64 reflections having $18° < 2\theta < 50°$ were centered for the same reason. The reflection intensities were Lp-corrected, scaled according to change in the standard reflections, and corrected both for the changing crystal volume hit by the X-ray beam[35] and for absorption. In both cases, close to 10 mismeasured reflections were left out. More details are listed in Table I. The least-squares refinement of phase I of the conventional atomic parameters with five atoms fixed in the mirror plane was carried out with the X-TAL program system.[36] The largest Δ/σ in the final cycle was 0.001; the largest residual peak in the ΔF Fourier map had a maximum of 100 e/nm^3. The corrections for anomalous dispersion[37] to the atomic form factors were included. The structure solution of phase II was performed with the direct methods program SHELXS86 (Sheldrick, 1990).[38] The largest Δ/σ in the final cycle was 0.002; the strongest F_c corrections by isotropic extinction were 0.94 for reflection (−2 0 2) and 0.96 for (0 1 2). The largest residual peak in the ΔF Fourier map had a maximum of 940 e/nm^3 and was located near the center of the C–S bond. Corrections for anomalous dispersion were again included.

Decomposition Kinetics of $F_3CC{\equiv}SF_3$. FEP tubes (4 mm o.d.) were sealed at one end, and on the vacuum line $F_3CC{\equiv}SF_3$ and $CFCl_3$ as solvent were distilled into it. The approximate molar ratio was 1:4. The tubes were sealed at the open end also. With ^{19}F NMR spectroscopy, the decrease of monomer was controlled at temperatures of −25, −10, and −5 °C.

The data were found to fit linearly into an ln c/T plot (see Figure 3). The activation energy ΔH^* at −15 °C was calculated to be 47.7 ± 5.1 kJ mol^{-1}.

Preparation of the (CF_3CSF_3) Trimer. A 500-mg sample of $F_3CC{\equiv}SF_3$ was kept in an FEP tube (which in turn would fit into a 10-mm NMR tube) at −40 °C for several days. By ^{19}F NMR monitoring, the decomposition was controlled and the process stopped when about 80% of the monomer had reacted. This took a few days; the ratio of dimer to trimer was then about 2:1. Volatile monomer was pumped off in vacuo at −78 °C. NMR measurements were done in CH_3F solution at −90 °C to freeze out all possible inter- and intramolecular exchange reactions: ^{19}F NMR (−90 °C) δ 68.2, 64.9, 63.1 (SF_{2ax}), −41.0, −49.5, −51.4 (SF_{eq}), −56.5, −57.1, −58.0 (CF_3); ^{19}F NMR (−30 °C, CF_2Cl_2) δ 68.2, 64.0 (SF_{2ax}), −41.0, 50.5 (SF_{eq}); ^{13}C NMR (−90 °C, CD_2Cl_2) δ 147.4, 143.5, 142.8 (mult, CF_3), 119.3, 119.1, 118.6 (J_{CF} = 280 Hz, q).

Preparation of $CF_3N{=}CFC(CF_3){=}SF_2$. $CF_3C{\equiv}SF_3$ (0.34 g, 2 mmol), 2.8 g of $CFCl_3$, 2 mmol of CF_3NC, and a little CD_2Cl_2 were subsequently condensed into a 9-mm NMR tube. Reaction occurred between −80 and −60 °C, along with some polymerization of CF_3NC. After the end of reaction, as controlled by ^{19}F NMR, the tube was opened, and the dark yellow contents were pumped through −78 and −196 °C cold traps. The −78 °C trap contained a yellow, wax-type solid that melts at −25 °C. The compound decomposed at room temperature. $CF_3N{=}CFC(CF_3){=}SF_2$: $Z{:}E$ = 2:1; ^{19}F NMR δ −7.2, −9.2 (A, SF_2), −22.3, −16.0 (B, CF), −54.9, −54.6 (C), −52.8, −53.4 (D, NCF_3); J_{AB} = 2.4, 8.5, J_{AC} = 15.0, 16.2, J_{AD} = 3.6, 2.4, J_{BC} = 10.1, 10.4, J_{BC} = 12.8, 13.1 Hz (CCF_3).

Preparation of $C_6F_5N{=}CFC(CF_3){=}SF_2$. C_6F_5NC (0.3 g, 1.6 mmol), 3.5 g of $CFCl_3$, and 0.6 g (3.5 mmol) of $CF_3C{=}SF_3$ were condensed into a trap. The mixture was left at −78 °C for 1 h. While the mixture was warmed to −10 °C, all volatile material was pumped off, leaving behind a yellow, viscous liquid that solidified at −78 °C. Sublimation in vacuo from room temperature to a −70 °C cold finger yielded a yellow, wax-type material which melts at room temperature to a yellow liquid. $C_6F_5N{=}CFC(CF_3){=}SF_2$: $Z{:}E$ = 1.35:1; ^{19}F NMR δ −7.3, −9.4 (A, SF_2), −29.5, −23.4 (B, CF), −57.2, −57.0 (C, CF_3), −150.8, −150.2 (D, *m*-PhF), −161.9, −161.8 (E, *p*-PhF), 165.3, 165.4 (F, *σ*-PhF), J_{AB} = 3.1, 8.1, J_{AC} = 15.6, 17.1, J_{BC} = 9.8, 10.1, J_{BF} = 12.8, 13.4, $J_{DD'}$ = 2.5, 2.5, J_{DE} = 21.4, 21.3, J_{DF} = 21.9, 21.9, $J_{DF'}$ = −6.6, −6.6, $J_{FF'}$ = 2.5, 2.5 Hz; MS m/z = 363 ($C_8HF_8NS^+$, 0.7), 344 ($C_8HF_7NS^+$, 0.1), 295 ($C_7H_2F_5NS^+$, 8), 276 ($C_7H_2F_4NS^+$, 3), 251 ($C_6H_2F_4NS^+$, 36), 193 ($C_7F_5N^+$, 21), 101 (CF_3S^+, 100), 85 ($CH_2F_3N^+$, 99) 64 (CF_2N^+, 55), 44 (CS^+, 71); IR ν 3396 (w), 2964 (w), 2656 (w), 2447 (w), 2272 (w), 2086 (w), 2016 (w), 1706 (s), 1651 (m), 1635 (m), 1589 (m), 1506 (s), 1451 (m), 1340 (s), 1316 (s), 1288 (s), 1160 (s), 1081 (m), 1034 (s), 994 (s), 947 (s), 947 (s), 824 (m), 778 (s), 778 (s), 724 (s), 707 (s), 678 (m), 635 (m), 619 (m) cm^{-1}; Raman (fl.) ν 2497, 2098, 1698, 1484, 1371, 781, 456 cm^{-1}.

Preparation of $C_6F_5N{=}CFC(SF_5){=}SF_2$. C_6F_5NC (0.7 g, 3.6 mmol) and 7.4 g of $CFCl_3$ were condensed into a cold trap. After dissolution of C_6F_4NC at −78 °C, 0.93 g (4.1 mmol) of $F_5SC{\equiv}SF_3$ was condensed in, and the mixture was warmed until reaction occurred, which is obvious by a yellow coloration. The mixture was cooled again to −78 °C, all volatile material was pumped off, and recrystallization from $CFCl_3$ at −78 °C afforded large, rectangular crystals. $C_6F_5N{=}CFC(SF_5){=}SF_2$ (*Z* isomer): ^{19}F NMR (CD_2Cl_2) δ −0.6 (A, SF_2), −17.3 (B, CF), 80.8 (C, SF_{ax}), 74.4 (D, SF_{eq}), −148.8 (E, *m*-PhF), −148.8 (F, *p*-PhF), −162.9 (G, PhF), J_{AB} = 14.6, J_{AD} = 19.5, J_{BD} = 14.6, J_{BG} = 14.6, J_{CD} = 143.2, J_{EF} = 19.5 Hz.

A suitable single crystal was mounted on an Enraf Nonius CAD 4 four-cycle diffractometer with the help of a special device.[39,40] The structure was solved by the program SHELXS86 and refined with the program SHELSX76.[41] Full-matrix refinement of 217 parameters resulted in an agreement function of R = 0.073 and wR = 0.071. For further details and results, see Tables I and II.

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Supplementary Material Available: Tables of atomic positional parameters, anisotropic thermal parameters, and bond lengths and angles (10 pages); tables of observed and calculated structure factors (65 pages). Ordering information is given on any current masthead page.

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[33] Dietrich, H.; Dierks, H. *Messtechnik* (*Braunschweig*) **1970**, *78*, 184–186.

[34] Buschmann, J.; Koritsanszky, T.; Kuschel, R.; Luger, P.; Seppelt, K. *J. Am. Chem. Soc.* **1991**, *113*, 233.

[35] Luger, P. *Kapkor, An endless cylindrical column correction program.* Freie Universität Berlin: Berlin, 1984.

[36] Hall, S. R., Stewart, J. M., Eds. *XTAL 2.2 User's Manual*; University of Western Australia, Nedlands, Australia, and University of Maryland, College Park, MD, 1987.

[37] *International Tables for X-Ray Crystallography IV*; Ibers, J. A., Hamilton, W. C., Eds.; The Kynoch Press: Birmingham, England, 1974; p 148.

[38] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[39] Veith, H.; Bärnighausen, H. *Z. Kristallogr.* **1985**, *170*, 5.

[40] Schumann, H.; Genthe, W.; Hahn, E.; Hossein, M. B.; Helm, D. v. d. *J. Organomet. Chem.* **1986**, *29*, 67.

[41] Sheldrick, G. M. *SHELX76, Crystal structure refinement program*; University of Cambridge: Cambridge, England, 1976.