

and 1-bromoocetyne (0.945 g, 5 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 30 min at room temperature, and to the solution were added (*Z*)-1-hexenyldisiamylborane (8 mL of a 0.75 M solution in benzene, 6 mmol) and NaOMe in MeOH (7 mL of a 1 M solution). The reaction mixture was heated under reflux for 2 h and then treated with aqueous NaOH (1.8 mL of a 3 M solution) and H₂O₂ (1.8 mL of a 30% solution) for 1.5 h at room temperature to remove the unreacted alkenylborane. The product was extracted with hexane and dried over MgSO₄. Analysis of the extracts by means of GLC indicated that 2.65 mmol (53%) of (*5Z*)-tetradec-5-en-7-yne was formed together with 0.13 mmol (2.6%) of (*5E*)-enyne. After the removal of the solvent the enyne purified by distillation; bp 86–87 °C (1 torr). An analytically pure sample was obtained by preparative GLC: n_D^{20} 1.4620; IR (neat) 3020, 2200, 1610 cm⁻¹; ¹H NMR (CCl₄) δ 0.93 (t, 3 H), 1.15–1.65 (m, 12 H), 2.05–2.45 (m, 4 H), 5.40 (d, 1 H, *J* = 11 Hz), 5.80 (dt, 1 H, *J* = 7 and 11 Hz); MS, *m/e* (M⁺) 192.1880, for C₁₄H₂₄ obsd calcd 192.1878.

The enynes, prepared by the above procedure using 1 mol % of catalyst and 10% excess of 1-alkenyldisiamylborane, are as follows.

(*5E*)-Tetradec-5-en-7-yne: n_D^{20} 1.4641; IR (neat) 3020, 2220, 955 cm⁻¹; ¹H NMR (CCl₄) δ 0.91 (t, 6 H), 1.11–1.70 (m, 12 H), 1.92–2.34 (m, 4 H), 5.33 (d, 1 H, *J* = 16 Hz), 5.94 (dt, 1 H, *J* = 6.5 and 16 Hz). Anal. Calcd for C₁₄H₂₄: C, 87.42; H, 12.58. Found: C, 87.27; H, 12.59.

(*3E*)-1-Phenyl-3-en-1-yne: n_D^{20} 1.5619; IR (neat) 3020, 2200, 955 cm⁻¹; ¹H NMR (CCl₄) δ 0.93 (t, 3 H), 1.20–2.05 (m, 4 H), 2.15 (q, 2 H), 5.62 (d, 1 H, *J* = 16 Hz), 6.17 (dt, 1 H, *J* = 6.5 and 16 Hz), 7.24 (m, 5 H). Anal. Calcd for C₁₃H₁₆: C, 90.64; H, 9.36. Found: C, 90.47; H, 9.33.

(*3E*)-1-Phenylpent-3-en-1-yne: n_D^{23} 1.5948; IR (neat) 3020, 2215, 955 cm⁻¹; ¹H NMR (CCl₄) δ 1.82 (d, 3 H, *J* = 6.5 Hz), 5.55 (d, 1 H, *J* = 16 Hz), 6.09 (dq, 1 H, *J* = 6.5 and 16 Hz), 7.21 (m, 5 H); MS, *m/e* 142 (M⁺), 117, 103, 89. Anal. Calcd for C₁₁H₁₀: C, 92.91; H, 7.09. Found: C, 92.80; H, 7.05.

(*1E*)-1-Phenyldec-1-en-3-yne: n_D^{20} 1.5643; IR (neat) 3025, 2215, 955 cm⁻¹; ¹H NMR (CCl₄) δ 0.92 (t, 3 H), 1.16–1.79 (m, 8 H), 2.33 (m, 2 H), 6.06 (dt, 1 H, *J* = 2 and 16 Hz), 6.90 (d, 1 H, *J* = 16 Hz), 7.28 (m, 5 H); MS, *m/e* 212 (M⁺), 183, 169, 155, 141, 128, 115, 91. Anal. Calcd for C₁₆H₂₀: C, 90.50; H, 9.50. Found: C, 90.38; H, 9.47.

Reaction of 1-Hexenyl-1,3,2-benzodioxaborole with Allylic Compounds (Table VI). In a 25-mL flask was placed a mixture of Pd(PPh₃)₄ (0.058 g, 0.05 mmol), (*E*)-1-hexenyl-1,3,2-benzodioxaborole (0.222 g, 1.1 mmol), and allylic compounds (1 mmol) in 5 mL of dry benzene in an atmosphere of nitrogen. After the reaction mixture was heated under reflux for 2 h, the reaction mixture was analyzed directly by GLC on a

SE-30 column by comparison with the authentic sample.²⁷ The results are shown in Table VI.

Reaction of 1-Octenylboranes with Palladium Complexes (Table VII). In a 25-mL flask was placed palladium complexes (1.0 mmol) and dry THF under a nitrogen atmosphere. To this solution was added (*E*)-1-octenyl-1,3,2-benzodioxaborole (0.253 g, 1.1 mmol) or (*E*)-1-octenyldisiamylborane (1.1 mL of a solution in THF, 1.1 mmol) dropwise, and the solution was stirred at room temperature. To the solution was then added an appropriate amount of decane in the reaction using the π -allylpalladium complex or tridecane in the reaction using (trichlorovinyl)palladium complex, and the reaction mixture was analyzed directly by GLC on SE-30 column. The products were determined by comparison with authentic samples. Preparation of 1,4-undecadiene had been described elsewhere.⁵⁵ 1,1,2,2-Trichloro-1,3-decadiene was prepared by the following procedure.

In a 50-mL flask was placed Pd(PPh₃)₄ (0.104 g, 0.09 mmol) in benzene (10 mL), tetrachloroethylene (0.51 mL, 5 mmol), (*E*)-1-octenyl-1,3,2-benzodioxaborole (0.758 g, 3.3 mmol), and NaOEt in EtOH (3 mL of a 2 M solution), and the reaction mixture was heated under reflux for 4 h. To the solution was then added aqueous NaOH (4 mL of a 3 M solution), and the mixture was stirred for 2 h at room temperature. After the usual workup, the diene was extracted with hexane and dried over MgSO₄. Distillation of the products gave 0.247 g (31%) of the corresponding diene: bp 142 °C (15 torr). An analytically pure specimen was obtained by preparative GLC: IR (neat) 1725, 1635, 1550, 955, 125 cm⁻¹; ¹H NMR (CCl₄) δ 0.89 (t, 3 H), 1.10–1.50 (m, 8 H), 1.0–2.4 (m, 2 H), 6.27 (dt, 1 H, *J* = 7 and 15 Hz), 6.59 (d, 1 H, *J* = 15 Hz); MS, *m/e* (M⁺) obsd for C₁₀H₁₅Cl₃ 240.0289, 242.0242, 244.0132, 246.0164, calcd 240.0239, 242.0210, 244.0178, 246.0151.

Reaction of Lithium 1-Hexenylmethylidisiamylborate with (*E*)- β -Styryl Bromide (Equation 13). A dried 25-mL flask was charged with Pd(PPh₃)₄ (0.0578 g, 0.05 mmol), dry THF (2 mL), and (*E*)- β -styryl bromide (0.183 g, 1 mmol). To this mixture was added lithium 1-hexenylmethylidisiamylborate⁵⁶ in THF (3 mL of a 0.45 M solution), and the mixture was then refluxed for 3 h. The remaining borane was then oxidized with aqueous NaOH (0.5 mL of a 3 M solution) and 30% H₂O₂ (0.5 mL) for 1 h at room temperature. Analysis of the organic phase by GLC showed the formation of 1-phenyl-1,3-octadiene (9%) together with small amounts of 1-phenyl-1-propene and 2,3-dimethyl-4-nonene.

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Trifluoroethylidynesulfur Trifluoride, CF₃C≡SF₃, and Its Dimer

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Abstract: CF₃C≡SF₃, the first species with a sulfur-carbon triple bond, has been prepared by dehydrofluorination of CF₃CH=SF₄ or CF₃CH₂SF₅. It is a colorless gas with mp -122.8 °C and an estimated bp -15 °C. Its molecular structure has been determined by a single-crystal X-ray investigation at -130 °C (space group *P*₂₁; *a* = 6.298 Å, *b* = 7.599 Å, *c* = 5.667 Å, β = 105.59°, *Z* = 2, 608 observed reflections, *R* = 0.05). The molecule exhibits a very short C≡S bond (1.394 Å) and an almost linear C—C≡S geometry (171.5°). The triple bond reacts with HF to form the starting materials. On warming up slowly to -30 °C dimerization is observed. The dimer has been analyzed by X-ray crystallography at -122 °C (space group *P*₂₁/*n*; *a* = 12.808 Å, *b* = 5.612 Å, *c* = 6.571 Å, β = 90.13°, *Z* = 2, 952 observed reflections, *R* = 0.045). The molecule is a butene CF₃(SF₃)C=C(CF₃)SF₃ with trans (*E*) configuration. This molecule is probably formed when CF₃C≡SF₃ is internally cleaved into a carbene CF₃-C̣-SF₃. NMR data and other physical measurements of these novel materials are given.

Introduction

CH₂=SF₄¹ and its derivatives CH₃C=SF₄,² CF₃CH=SF₄,³ and CF₃(CH₃)C=SF₄³ have strong, almost nonpolar carbon-sulfur double bonds within a very distinct geometry.^{4,5} Some of these alkylidene sulfur tetrafluorides turned out to be remarkably stable materials. Soon after the discovery of CH₂=SF₄ the

question arose if triple-bonded systems would be capable of existence. Early attempts to generate HC≡SF₃ by HF cleavage

(1) G. Kleemann and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, **17**, 516 (1978).

(2) B. Pötter and K. Seppelt, *Inorg. Chem.* **21**, 3147 (1982).

(3) B. Pötter, G. Kleemann, and K. Seppelt, *Chem. Ber.*, **117**, 3255 (1984).

(4) G. Kleemann and K. Seppelt, *Chem. Ber.* **116**, 645 (1983).

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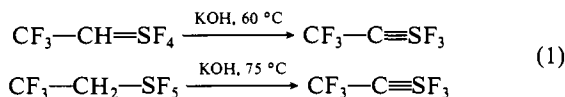
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from CH₂=SF₄ under various conditions were unsuccessful. The reaction cannot be terminated, and S=CF₂ or its hydrolysis product S=C=O is obtained. Single substitution, as in CH₃C-H=SF₄ and CF₃CH=SF₄, should prevent the second-step HF elimination. From CF₃CH=SF₄ the material CF₃C≡SF₃ has finally been isolated as described in a preliminary communication.⁶ In the meantime ab initio calculations on several X-C≡SF₃ derivatives have been undertaken.⁷

Results and Discussion

Chemical Reactions. CF₃C≡SF₃ has been obtained by two slightly different methods, by cleaving HF from CF₃CH=SF₄ and CF₃CH₂SF₅ (eq 1). The first reaction has the advantage

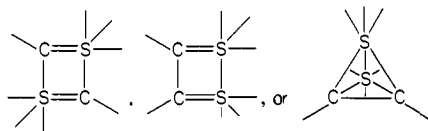


of yielding a pure material but the disadvantage of the complicated preparation of the starting material, which takes many steps including an isomer separation (CF₃CH=SF₄/CF₂=CHSF₅).³ The opposite is true for the second reaction, both to advantage and disadvantage of the reaction.

The compound CF₃C≡SF₃ is a colorless gas with a melting point of -122.8 °C and a boiling point of approximately -15 °C, rapidly decomposing at this temperature.

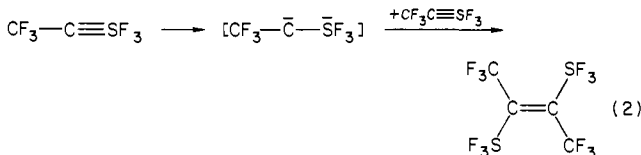
Anhydrous HF adds across the triple bond at low temperatures; CF₃CH=SF₄ and finally CF₃CH₂SF₅ are formed. Other attempts of addition reactions (HCl, XeF₂, inter alia) have not resulted in novel compounds. With AsF₅ a solid adduct of still unknown composition is formed.

The above-mentioned decomposition of CF₃C≡SF₃ occurs, though rather slowly, at -50 °C. At a yield of more than 70%, the dimer is formed as a colorless solid, which decomposes under melting above -20 °C. The nature of the other, minor decomposition products of CF₃C≡SF₃ has not yet been identified. Again, the dimer is thermally unstable. It rapidly decomposes above the melting point, and, when kept at -30 °C for prolonged times, CF₃C=CCF₃ is observed as the major product. The results of the crystal-structure investigation of the dimer is somewhat surprising. It turns out to be a 2-butene derivative CF₃(SF₃)₂C=C(CF₃)SF₃. Cyclic systems such as

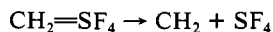


could have been possible alternatives. The 2-butene structure might have formed by S-S bond cleavage from the ring system as well as the tetrahedron derivative.

We rather assume a nonsymmetric dimerization reaction, according to eq 2 (Figure 3a,b). The formation of a carbene in-



termediate would be a parallel to the intermediate carbene formation in many decomposition reactions of CH₂=SF₄.



The overall decomposition of CF₃C≡SF₃ can be described as a strange case of alkyne metathesis, where the intermediate is now known. The nature of the sulfur-containing products of the re-

Table I. Bond Lengths and Bond Angles for CF₃C≡SF₃ (standard deviations in parentheses)

	this work		ab initio calculation ^c
	a	b	
C-S	1.398 (5)	1.420	1.404
C-C	1.418 (7)	1.439	1.434
S-F(11)	1.527 (11)	1.568	1.551
S-F(12)	1.536 (3)	1.568	1.551
S-F(13)	1.550 (10)	1.568	1.557
S-F(21)	1.304 (19)	1.354	1.360
S-F(22)	1.332 (7)	1.378	1.360
S-F(23)	1.335 (18)	1.362	1.360
C-C-S	171.5 (2.0)		179.9
C-S-F(11)	119.7 (1.1)		123.3
C-S-F(12)	124.9 (0.3)		123.3
C-S-F(13)	124.6 (1.1)		123.3
C-S-F(21)	108.8 (1.5)		111.9
C-S-F(22)	111.8 (0.5)		111.9
C-S-F(23)	115.6 (1.4)		111.9

^a Calculated with parameters of Table IV. ^b Corrected for anisotropic thermal vibrations. ^c Since the molecule in the crystal has nearly an eclipsed conformation, the calculated values for the eclipsed conformer are given. The values for the staggered conformer are almost identical.⁷

Table II. Bond Lengths and Bond Angles for CF₃(SF₃)C=C(CF₃)SF₃ (standard deviations in parentheses)

S-C(1)	1.821 (3)	F(11)-S-F(12)	87.2 (1)
C-C(1)	1.319 (6)	F(11)-S-F(13)	169.9 (1)
C(1)-C(2)	1.537 (5)	F(12)-S-F(13)	88.0 (1)
C(2)-F(21)	1.319 (4)	F(11)-S-C(1)	85.9 (1)
C(2)-F(22)	1.333 (4)	F(12)-S-C(1)	102.6 (1)
C(2)-F(23)	1.325 (4)	F(13)-S-C(1)	86.5 (1)
S-F(11)	1.683 (2)	S-C(1)-C(2)	112.7 (2)
S-F(12)	1.554 (2)	C(2)-C(1)-C	125.4 (4)
S-F(13)	1.672 (2)	C(1)-C(2)-F(21)	112.0 (3)
S-C(1)-C	1.219 (3)	C(1)-C(2)-F(22)	111.0 (3)
		C(1)-C(2)-F(23)	109.4 (3)
		F(21)-C(2)-F(22)	107.4 (3)
		F(21)-C(2)-F(23)	109.7 (3)
		F(22)-C(2)-F(23)	107.3 (3)

action 2CF₃C≡SF₃ → 2CF₃C=CF₃ remains unknown, however.

The structural characterization of CF₃C≡SF₃ and its dimer presents experimental difficulties, which are only partly due to their low melting temperatures of -122 and -20 °C, respectively, but mainly due to the thermal instability of both compounds. The usual procedure of in situ crystal growth using a miniaturized Bridgman technique,⁸ as in the case of SF₄=CH₂,⁵ is not possible. But, fortunately, the system offers the possibility to use its chemistry for growing crystals of both the monomer and dimer from one sample. It seems worthwhile to discuss the principle of the experimental approach here, as it should be widely applicable to quite different structural problems.

As crystals of the pure dimer deposit from CF₃C≡SF₃ when it is warmed up, the conclusion can be drawn that the phase relationship between both compounds is of the eutectic type. Such a system allows solution growth for one of the components, which one depending upon the composition of the sample. Following this idea, crystals of CF₃C≡SF₃ are first grown from a sample which contains a small amount of the dimer. Then the dimerization of the sample is performed at elevated temperature, but terminated early enough to yield a concentrated solution of the dimer in CF₃C≡SF₃. Crystals of the dimer are grown from this solution. It is a fascinating aspect of such a procedure to perform chemical reactions in a capillary and probe the products by single-crystal techniques.

Crystal Structure. Figure 1 presents stereographic views of the crystallographic unit cells of CF₃C≡SF₃ (a) and CF₃(SF₃)C=C(CF₃)SF₃ (b). The molecular structures are shown in Figure

(6) B. Pötter and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, **23**, 150 (1984).

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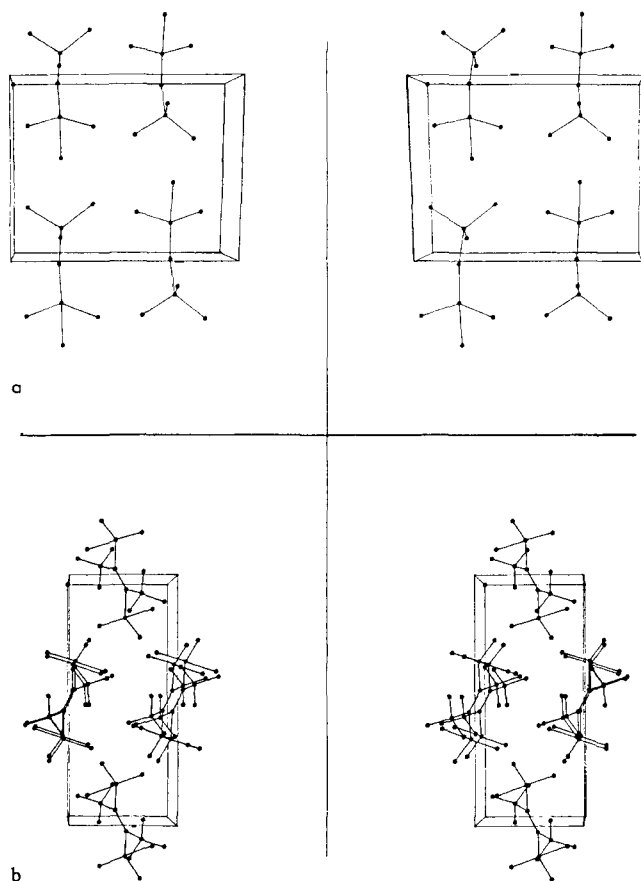


Figure 1. Molecular packing of the molecules in the structure of (a) $\text{CF}_3\text{C}\equiv\text{SF}_3$ and (b) $\text{CF}_3(\text{SF}_3)\text{C}=\text{C}(\text{CF}_3)\text{SF}_3$ viewed down the crystallographic c axes. The b axes are horizontal.

2. Tables I and II summarize bond distances and selected angles.

$\text{CF}_3\text{C}\equiv\text{SF}_3$. In Table I the results of the *ab initio* calculation are included. According to this calculation $\text{CF}_3\text{C}\equiv\text{SF}_3$ should have a linear $\text{C}-\text{C}\equiv\text{S}$ frame, a freely rotating CF_3 group, a short $\text{C}\equiv\text{S}$ trip bond, but also a shortened $\text{C}-\text{C}$ single bond. The molecule in the crystal deviates only little from these predictions:

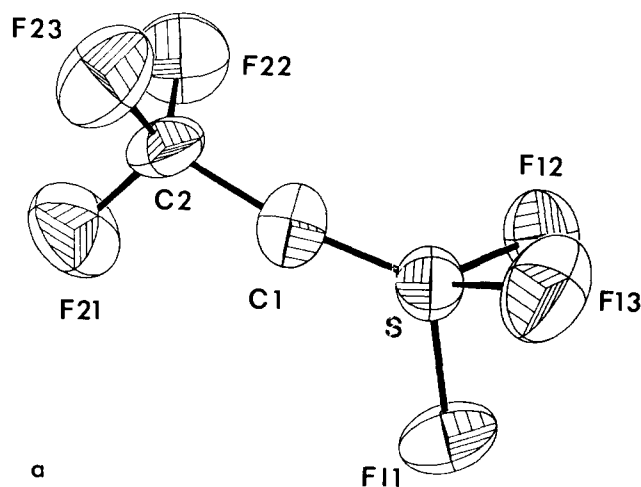
(1) All bond lengths are 0.006 to 0.06 Å shorter than predicted. Obviously a correction for vibration would give a better agreement, as can be concluded from the fact that the observed bond lengths of the terminal $\text{C}-\text{F}$ bonds differ the most, the central bonds the least from the calculated values. The bond length calculated in the usual way from the distances of the centers of thermal ellipsoids were therefore recalculated with the aid of *ORFFE*,⁹ taking into account the anisotropic thermal vibrations of the atoms. Assuming one atom (S) fixed, the vibrations of the others are calculated. As indicated in Table I our corrected bond lengths differ only by 0.002 to 0.015 Å from the *ab initio* calculated distances.

(2) The $\text{C}-\text{C}\equiv\text{S}$ frame is not completely linear, but an angle of 171.5° is observed.

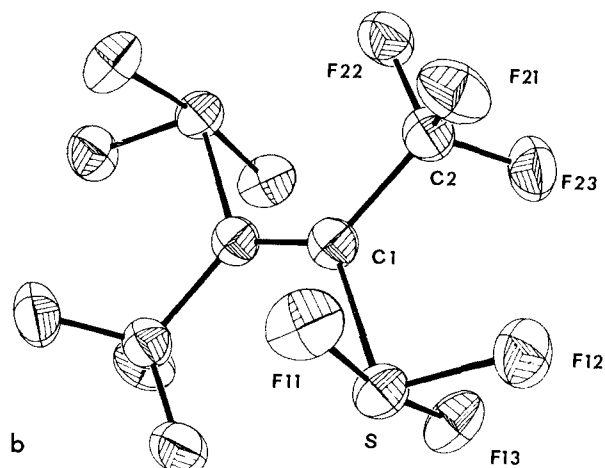
It is notable that the *ab initio* calculation did not predict this small deviation from linearity. In fact, the predicted linear structure of the molecule is in agreement with measurement in solution. The ^{19}F NMR spectra even at low temperatures show the fluorine on sulfur and those on carbon, respectively, to be equal. This means virtually free rotation of the CF_3 groups and also equilibration of any differences in the SF bonds which would be a result of the slight nonlinearity.

It is commonly known that linear systems of multiple bonds have a very small force constant for bending the system out of linearity. The slight deviation of the molecule from linearity in the crystal structure might therefore be due to packing problems.

(9) W. R. Busing, K. O. Martin, and H. A. Levy, *ORFFE*, ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1971.



a



b

Figure 2. Molecular structures: (a) $\text{CF}_3\text{C}\equiv\text{SF}_3$ and (b) $\text{CF}_3(\text{SF}_3)\text{C}=\text{C}(\text{CF}_3)\text{SF}_3$. The atoms are represented by thermal ellipsoids at the 50% probability level.

Analysis of the packing, however, does not substantiate this assumption. The molecules form (rather distorted) close-packed layers in the a, b plane, which are arranged in a stacking sequence according to cubic close packing. The (isolated) molecules show no close interactions with each other. The shortest intermolecular atomic contacts are those between F atoms. They are above 3 Å, i.e., roughly 50% longer than the intramolecular F-F distances and well above the sum of van der Waals radii. It remains to be seen what the structure of the gaseous molecules will be.

Ironically the structure of the first metal carbyne complex $t\text{-IW}(\text{CO})_4\equiv\text{CC}_6\text{H}_5$ resulted in a $\text{W}\equiv\text{C}-\text{C}$ angle of $162(4)^\circ$,¹⁰ whereas later structures of such complexes gave linear systems ($t\text{-ICr}(\text{CO})_4\equiv\text{CH}_3$).¹¹ The first nonionic carbyne complex in the tantalum series, $(\text{C}_5\text{H}_5)_2(\text{PMe})_2\text{ClTa}\equiv\text{CC}_6\text{H}_5$, has a $\text{Ta}\equiv\text{C}-\text{C}$ angle of $171.5(5)^\circ$.¹² The deviations from linearity in these systems are not all clear.

If it were not for reasons of packing problems, a very small polar (ylidic) character of the triple bond could account for the nonlinearity of the $\text{CF}_3\text{C}\equiv\text{SF}_3$ molecule. In a simplified model a full charge on carbon and sulfur should result in a $\text{C}-\text{C}-\text{S}$ angle of 120° . It is noteworthy that the nonlinearity of the molecule

(10) E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner, and H. Lorentz, *Angew. Chem., Int. Ed. Engl.*, **12**, 564 (1973).

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(12) M. R. Churchill and W. J. Youngs, *Inorg. Chem.*, **18**, 171 (1979).

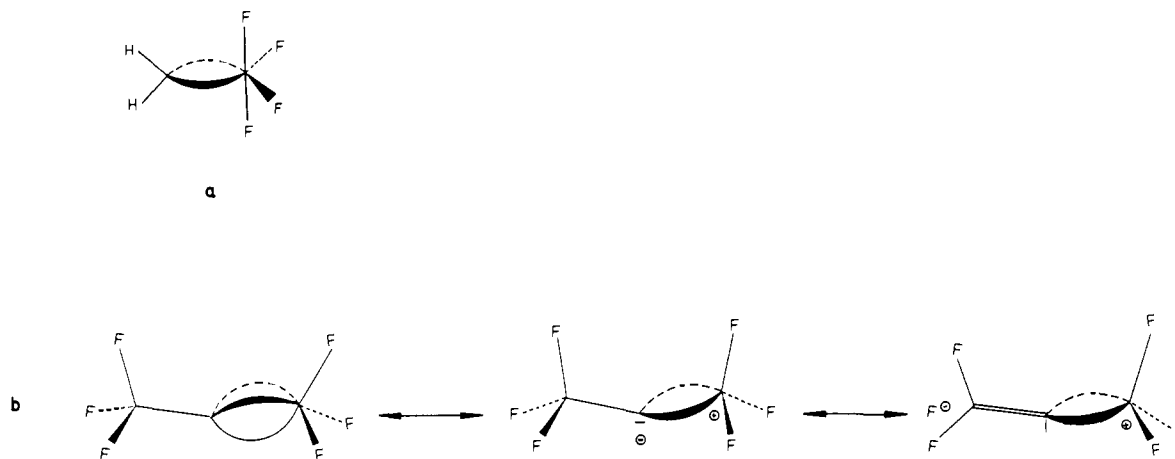


Figure 3. (a) Structure of CH₂=SF₄; the double bond is symbolized by two bent single bonds. As predicted, the protons are located in the axial plane; the F_{ax}-S-F_{ax} angle (found 170°) is close to 180° and the F_{eq}-S-F_{eq} angle (found 96.4°) is close to 90°. (b) Structure of CF₃C≡SF₃; the triple bond is symbolized by three bent single bonds, thus giving a linear configuration and F-S-F angles of 90° (found 90.9–94.3°). The small derivation from linearity is explained by allowing a resonance form of the ylidic type. The very short C-C bond is explained by allowing a resonance form of another ylidic type commonly called hyperconjugation. The influence of both resonances forms is thought to be small, however.

corresponds to small asymmetries in the bond angles and distances within the SF₃ group. This becomes evident from Figure 2a, which shows the molecule with the C—C≡S unit in the plane of the drawing together with the values given in Table I. The C-S-F(11) angle involving the in-plane F atom is significantly smaller than the angles involving the out-of-plane F atoms. The C-C-F angles, though at the limits of accuracy, show an opposite behavior.

The C≡S bond distance (1.398 Å) is even shorter than the bond distance in N≡SF₃ (1.416 (3) Å)¹³ and significantly shorter than the double bonds in CS₂ (1.559 (2) Å),¹⁴ F₂C=S (1.589 (10) Å),¹⁵ H₂C=SF₄ (1.554 (4) Å),^{4,5} and matrix-isolated CS (1.568 (7) Å).¹⁶ It is interesting to calculate the expected distance of a C≡S triple bond using the bond-length–bond-order concept,^{17,18} which assumes the ratio of bond order *s* to be an exponential function of bonds lengths *d*. Referring to the single-bond distance *d*(1) (=1.82 Å for the C-S bond), the relation is $s = (d/d(1))^{1/N}$. The exponent is fixed at N = 4.5 by introducing the value *d* = 1.56 Å for *s* = 2.^{19,20} For *s* = 3 a C≡S distance *d* = 1.43 Å is calculated in rather good agreement with the observed value. The description of the C≡S bond in CF₃C≡SF₃ as a true triple bond seems justified. The F₃C—C≡ single bond is also very short (1.418 (7) Å). It is a well-known effect that single bonds adjacent to multiple bonds are shorter than normal, but the corresponding bonds in CF₃C≡CCF₃ are 1.478 (4) Å.²¹ The remaining discrepancy can be explained by hyperconjugation; see Figure 3b.

In making up a very simple bond model for CF₃C≡SF₃, it is very important that the bond angles between the fluorine on sulfur are all close to 90° (as predicted). We therefore suggest a bonding description by three bent single bonds (see Figure 3), in other words, the interconnection of the octahedron of sulfur with the tetrahedron of carbon through a common triangular face. The analogous description has successfully been used for the C=S double bond in CH₂=SF₄ (see Figure 3a) and may be a physical reality: electron density calculations on the still unknown FC≡SF₃ show three distinct maxima 0.396 Å away from the C-S axis in

Table III. Crystal and Refinement Data for CF₃C≡SF₃ (I) and CF₃(SF₃)C=C(CF₃)SF₃ (II) (standard deviations in parentheses)

	I	II
space group	P2 ₁ (no. 4)	P2 ₁ /n (no. 14)
<i>a</i> (Å)	6.298 (7)	12.808 (8)
<i>b</i> (Å)	7.599 (8)	5.612 (2)
<i>c</i> (Å)	5.667 (7)	6.571 (4)
β (deg)	105.59 (9)	90.13 (5)
<i>Z</i>	2	2
<i>V</i> (Å ³)	261.24	471.26
ρ (g cm ⁻³) (calcd)	2.16	2.40
no. of observations with intensities <i>I</i> > 2σ(<i>I</i>)	608	952
no. of variables	82	82
<i>R</i>	0.05	0.045
<i>R_w</i>	0.052	0.045

the symmetrical directions staggering the S-F bonds! Unfortunately, from the preciseness of the X-ray analysis of CF₃C≡SF₃ one cannot hope such details to show up in electron density maps. In difference Fourier maps the height of the structure in the region between S and C atom is similar to that in other (irrelevant) parts of the unit cell.

A more sophisticated view has to take into account that the angle C—C≡S deviates from 180°, which shows a slight reduction of the C≡S bond order from 3 and, together with the shortened C-C distance, a slight increase of the C-C bond order. Starting with a linear triple bond situation, a little share of ylidic resonance forms with the negative charge on carbon and (C)–fluorine would explain the nonlinearity and the very short C-C bond, respectively (Figure 3b).

A comparison of ¹³C NMR measurements of the series CH₃-CH₂SF₅, CF₃CH≡SF₄, and CF₃C≡SF₃ throws some further light on the chemical bonding in the latter molecule. The CF₃ group is easily identified and has a rather constant chemical shift; see Table V. The central C atom, which has single, double, and triple bonds, shows the complicated fine structures due to the coupling with protons and different fluorine atoms. But more important, they show a stepwise shift to higher field (higher shielding). This again is an indication for the bond model as described above and in Figure 3. Classical multiple bonds should result in a chemical shift of opposite direction. Also small but increasing polar character of the ylidic type in the sequence CF₃CH₂SF₅, CF₃CH=SF₂, and CF₃C≡SF₃ could account for this abnormality.

CF₃(SF₃)C=C(CF₃)SF₃. Again the crystal structure is composed of isolated molecules. The 2-butene appears in trans (*E*) configuration. The C=C double bond has a normal distance (1.311 Å); also the -CF₃ configuration is normal. Besides the rather unexpected formation of the molecule discussed earlier, the most remarkable features are the single-bonded SF₃ groups.

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(19) The value *N* = 4.5 is rather surprising. It is near the value for the multiple bonds between C, N, O, and smaller than the value for multiple bonds between elements of the higher periods.²⁰

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Table IV. Atomic Coordinates and Isotropic Thermal Parameters (standard deviations in parentheses)

	x	y	z	U ^a
CF ₃ C≡SF ₃ (I)				
S	0.8009 (2)	0.7180	0.6280 (2)	50 (1)
F(11)	0.7454 (14)	0.5720 (15)	0.4360 (19)	85 (3)
F(12)	0.5685 (4)	0.7226 (22)	0.6662 (7)	81 (2)
F(13)	0.7405 (12)	0.8688 (14)	0.4375 (18)	75 (3)
C	0.9966 (9)	0.7092 (40)	0.8161 (11)	71 (3)
C(2)	1.1812 (8)	0.7198 (23)	1.0241 (9)	50 (2)
F(21)	1.2967 (17)	0.5759 (16)	1.0379 (19)	89 (4)
F(22)	1.1214 (7)	0.7172 (27)	1.2323 (5)	90 (2)
F(23)	1.3151 (15)	0.8566 (16)	1.0281 (16)	77 (3)
CF ₃ (SF ₃)C=C(CF ₃)SF ₃ (II)				
S	0.8447 (1)	0.4463 (2)	0.6478 (1)	33 (1)
F(11)	0.8858 (2)	0.1737 (4)	0.7207 (3)	45 (1)
F(12)	0.7596 (2)	0.3170 (4)	0.5198 (3)	44 (1)
F(13)	0.8090 (2)	0.7009 (4)	0.5340 (3)	44 (1)
C	0.9559 (2)	0.4463 (6)	0.4761 (5)	30 (1)
C(2)	0.9333 (3)	0.3171 (6)	0.2739 (5)	35 (1)
F(21)	0.9027 (2)	0.0949 (4)	0.3030 (3)	46 (1)
F(22)	1.0180 (2)	0.3098 (4)	0.1568 (3)	42 (1)
F(23)	0.8609 (2)	0.4360 (4)	0.1715 (3)	47 (1)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Table V. ¹³C NMR Data for CF₃CH₂SF₅, CF₃CH=SF₄, and CF₃C≡SF₃ (ppm vs. Me₄Si, and Hz, respectively)^a

	δ _{CF₃}	δ _C	¹ J _{CF}	¹ J _{CH}	² J _{CCF}	² J _{CSF}	² J _{CCH}	³ J _{CCSF}
CF ₃ CH ₂ SF ₅	122.6	67.5	275.3	142.2	35.1	20.3 e	6.9	4.4 e
CF ₃ CH=SF ₄	121.9	55.6	265.6	192.8	9.9	1.7 a 42.0 a 47.7 a 48.5 e	28.4	<0.5 a 4.9, 2 × a 2.4 e
CF ₃ C≡SF ₃	118.2	30.4	259.1		11.1	61.6		7.4

^a For ¹⁹F and ¹H spectra, see Experimental Section and ref 3. a = axial fluorine atom, e = equatorial fluorine atom.

They have a typical pseudo-trigonal-bipyramidal configuration with two longer axial SF bonds (1.686, 1.667 Å), one shorter equatorial S-F bond (1.556 Å), and an equatorial S-C bond.

The equatorially nonbonding electron pair is visible by its repulsion of the other ligands: the S(F_{ax})₂ angle is 170.1° (instead of 180°); the C-S-F_{eq} angle is 102.6° (instead of 120°).

Experimental Section

General NMR spectra were taken on a JEOL 90 multinuclear instrument; chemical shifts are vs. Me₄Si and CFC₃, according to IUPAC convention. IR spectra were taken on a Beckmann Acculab 10 instrument, mass spectra on a Varian CH 5 instrument, 70-eV excitation energy.

CF₃CH=SF₄³ and HOOCCH₂SF₅²² were prepared according to literature methods. SF₄ was purchased from Air Products and used without further purification.

2,2,2-Trifluoroethylsulfur Pentafluoride. To HOOCCH₂SF₅ (18.6 g, 0.1 mol), in a 100-mL stainless steel autoclave, 1 g of water was added. SF₄ was condensed into the -196 °C cooled autoclave with the help of a glass vacuum line. The autoclave was heated to 110 °C for 48 h.

The contents of the autoclave was very slowly pumped through 1 L of dilute NaOH solution, and the remaining gases were trapped at -78 °C. The mixture of product and SOF₂ was distilled with a 30-cm spinning-band column to give 15 g of CF₃CH₂SF₅ as a colorless, stable liquid (68%), bp 40 °C, ¹H NMR δ 5.85; ¹⁹F NMR δ -67.7 (CF₃), 67.6 (SF₃), = 73.7 (SF_a) ppm; J_{F_a-F_e} = 152, J_{F_e-CF₃} = 10.1, J_{F_e-CF₃} = 10.1, J_{F_e-H} = 5.1, J_{CF₃-H} = 10.0 Hz; ¹³C NMR, see Table V.

The material was shown to be identical with the one described by De Marco and Fox,²³ so further identification was omitted.

Trifluoroethylidynesulfur Trifluoride. (a) **From CF₃CH=SF₄.** A 60-cm long Pyrex or quartz tube was filled with powdered KOH. The particle size of the powder should be about 1 mm at the entrance and much finer at the outlet. The tube was thoroughly dried at 100 °C in vacuo for 0.5-1 h. CF₃CH=SF₄ (3 g) was slowly pumped at 55-60 °C in vacuo through the horizontal tube, and the resulting gases were trapped at -196 °C. If the starting material CF₃CH=SF₄ was pure, the

CF₃C≡SF₃ was also pure. Otherwise, the impurities (CF₂=CHSF₅ or hydrocarbons) were found in the product.

The reaction is exothermic, and too rapid dehydrofluorination will result in melting of the KOH/KF/HF solid. The yields varied. In 10 runs the maximum yield was found to be 80%, with a typical yield of about 50%. In one case no product was obtained for unknown reasons. CF₃C≡SF₃ is colorless as gas, liquid, and solid, mp -122.8 °C, bp -15 °C (estd): ¹⁹F NMR δ 65.7 [(S)F] -43.9 [(C)F] ppm, J_{F-F} = 19.5 Hz; ¹³C NMR, see Table V; IR 1740, 1225, 1168, 862, 795, and 730 cm⁻¹. Mass spectrum: molecular peak at 169.962 71, 13.2% (calcd: 169.962 50), and numerous smaller fragments.

(b) **From CF₃CH₂SF₅.** The product was the same as described above, except the best reaction temperature was found to be 75 °C. The main product was CF₂=CHSF₅; CF₃C≡SF₃ amounted only to a few per cent. This product cannot be separated completely from CF₂=CHSF₅. The yields are low (2-8%).

Dimer: CF₃(SF₃)C=C(CF₃)SF₃. A sample of CF₃C≡SF₃ was held at -30 °C for 12 h. This procedure was possible with impure samples also. After evaporation of all volatile materials, colorless crystals of the dimer were obtained (about 80%). A small amount of CF₃C≡SF₃ always remained as the monomer. The material is pure if freshly prepared, as shown by ¹⁹F NMR. The material, after being sublimed at -20 °C under high vacuum, showed decreased purity. Melting of the material from -20 to 0 °C results in partial decomposition.

¹⁹F NMR: Three complicated multiplets at δ 75.8 (SF_{ax}), -48.1 (SF_{eq}), and -51.8 (CF₃), ²J_{F_{ax}-F_{eq}} = 90 Hz. The mass spectra gave *m/z* 251 as the highest peak (M⁺ - SF₃). On warming to room temperature, or even at -40 °C, the dimer decomposes to give CF₃C≡CCF₃ as the major product, detected by its ¹⁹F NMR spectrum, δ -54.9 ppm.

Reaction of CF₃C≡SF₃ with HF. CF₃C≡SF₃ was condensed into a 5-mm o.d. FEP NMR tube, and anhydrous HF was added to it on a metal vacuum line. The tube was sealed and kept at -78 °C. At this temperature no reaction was observed by NMR spectroscopy. At -40 °C the CF₃C≡SF₃ was slowly consumed, CF₃CH=SF₄ was found, and, after some hours, this was converted to CF₃CH₂SF₅.

Reaction of CF₃C≡SF₃ with HCl. A similar reaction in a glass NMR tube again led to CF₃CH=SF₄ and CF₃CH₂SF₅ only, along with some chlorine. Probably some HF is formed from the HCl by decomposition, and HF reacts further as described above.

Reaction of CF₃C≡SF₃ with XeF₂. In a glass NMR tube a few crystals of XeF₂ were dissolved in dry CFC₃ and an equimolar amount of CF₃C≡SF₃ was added by condensation. At -30 °C no reaction was observed. Warming to room temperature for a few minutes again yielded

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$\text{CF}_3\text{CH}=\text{SF}_4$ and CF_3CHSF_5 , probably as a result of HF formation due to a hydrocarbon impurity.

Crystal Growth. An X-ray capillary (0.2 mm) was attached to the trap and after evacuation to 10^{-4} torr $\text{CF}_3\text{C}=\text{SF}_3$ was evaporated and condensed into the capillary by cooling with liquid nitrogen. In order to guarantee good control of crystal growth, the capillary was thoroughly cleaned with 2% HF and detergent in water. Then it was sealed under 1 atm of argon and transferred to the diffractometer in a stream of nitrogen at -160°C .

Growing of suitable single crystals was performed on a four-circle diffractometer $P2_1$, which carries a specially designed low-temperature device.²⁴

$\text{CF}_3\text{C}=\text{SF}_3$ (I) The sample, which was partly solid at -126°C , was annealed at this temperature for 15 h, yielding several monomer crystals with sizes below 1 mm. At -124°C a few crystals remained suspended in liquid. Their sizes were increased by oscillating the temperature between -124 and -126°C monitoring the diffraction intensity of a suitable reflection. A specimen of approximately 2 mm length oriented along [010] in the capillary axis was chosen for the data collection at -130°C . The crystal nearly filled the diameter of the capillary but was still surrounded by some melt and slightly changed its position during the data collection. A further reduction of the temperature was not feasible as the scattering intensity of the polycrystalline eutectic was significant.

$\text{CF}_3(\text{SF}_3)\text{C}=\text{C}(\text{CF}_3)\text{SF}_3$ (II). After the completion of the data collection for I the sample was warmed, kept at -20°C for approximately 5 min, and cooled to -133°C again. During this cooling process the dimer which had formed first separated in supercooled droplets before crystallizing. At -80°C approximately 50% of the sample consisted of solid II, besides solution. With the exception of a few crystals all the solid was dissolved again at -45°C . The sizes of these crystals were slowly increased by carefully lowering the temperature in steps of 1° until a suitable needle-shaped crystal of approximately 2-mm length resulted, which again was oriented along [010] in the capillary axis. Data collection was performed at -122°C .

Data Collection and Structure Solutions. Measurements were performed with Mo $K\alpha$ radiation using a graphite monochromator. The lattice constants of I and II resulted from a least-squares refinement of the positions of 15 reflections measured at -130 and -122°C , respectively, in the range $8^\circ \leq 2\theta \leq 28^\circ$. Scattering intensities were measured in the ω - 2θ scan mode in the range $3^\circ \leq 2\theta \leq 55^\circ$, with a scan width

of 1° and equal times for scan and total background measurements. The scan rate varied between 1 and 29 deg/min. The data were corrected for absorption by using the semiempirical ϕ -scan technique. No further corrections except the usual polarization and Lorentz corrections were applied. The structures were solved by direct methods and refined by least-squares methods using the program system SHELXTL (version 3.0, 1981) on a Data General Eclipse computer. Final full-matrix least-squares refinements converged to the values of $R = \Sigma\Delta F/\Sigma F_0$ and $R_w = [\Sigma w(\Delta F)^2/wF^2]$ listed in Table III; the atomic parameters are summarized in Table IV (see paragraph at the end of the paper regarding supplementary material).

$\text{CF}_3\text{C}=\text{SF}_3$ (I). Data were collected in the sector $0 \leq h \leq 8$, $0 \leq k \leq 9$, and $-7 \leq l \leq 7$ resulting in a total of 698 reflections out of which 608 had an intensity $I > 2\sigma(I)$. The only observed systematic absences were $0k0$ for $k = 2n + 1$, indicating $P2_1$ or $P2_1/m$, out of which the noncentrosymmetric space group had to be chosen. The atomic positions came out from an E -map and were refined to an isotropic value $R = 0.16$. Anisotropic refinement led to the final value $R = 0.05$.

$\text{CF}_3(\text{SF}_3)\text{C}=\text{C}(\text{CF}_3)\text{SF}_3$ (II). Diffraction data were collected within the range $0 \leq h \leq 16$, $0 \leq k \leq 7$, $-8 \leq l \leq 8$. Out of 1258 measured reflections 952 had intensities larger than $I = 2\sigma(I)$ and were used for solving the phase problem and for refinement. The observed systematic absences were $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ leading to the space group $P2_1/n$. All atomic positions came out from an E -map and least-squares refinement with isotropic temperature factors led to a reliability factor $R = 0.09$. The anisotropic refinement converged to $R = 0.045$.

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Registry No. $\text{CF}_3\text{CH}_2\text{SF}_5$, 65227-29-4; $\text{HO}_2\text{CCH}_2\text{SF}_5$, 762-59-4; SF_4 , 7783-60-0; $\text{CF}_3\text{C}=\text{SF}_3$, 88476-03-3; $\text{CF}_3\text{CH}=\text{SF}_4$, 88476-02-2; $\text{CF}_2=\text{CHSF}_5$, 58636-78-5; (E)- $\text{CF}_3\text{C}(\text{SF}_3)=\text{C}(\text{CF}_3)\text{SF}_3$, 94203-25-5; $\text{CF}_3\text{C}=\text{CCF}_3$, 692-50-2; HF, 7664-39-3; HCl, 7647-01-0; XeF_2 , 13709-36-9.

Supplementary Material Available: Tables of structure factors, atomic positional parameters, and anisotropic thermal parameters (12 pages). Ordering information is given on any current masthead page.

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Comparative Study of Nucleophilic Addition to Free and Metal-Coordinated Carbocations

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Abstract: A kinetic study in acetone is prepared for phosphorus and nitrogen donor nucleophile addition to three carbocations: (*p*-(dimethylamino)triphenyl)methyl (1), pyronin (2), and (*p*-(dimethylamino)phenyl)tropylium (3). In the absence of steric effects, the Ritchie N_+ correlation is obeyed by the reactions; i.e., relative nucleophilic reactivity is electrophile independent. More significantly, the relative reactivities of phosphorus and nitrogen donors toward free carbocations are the same as that observed for addition to metal-coordinated cyclic π -hydrocarbons even though the latter reactions involve metal-carbon bond cleavage. Both types of reactions have similar transition states.

The addition of nucleophiles to free carbocations is a fundamental reaction in organic chemistry. Ritchie et al.¹ have shown that oxygen and nitrogen donor nucleophiles add to a wide range of stabilized carbocations according to eq 1, in which k is the second-order rate constant for the electrophile-nucleophile com-

bination, k_0 is the rate constant for a reference nucleophile, and N_+ is a parameter dependent only on the nucleophile and reaction conditions.

$$\log(k/k_0) = N_+ \quad (1)$$

This relationship means that relative nucleophilic reactivity is electrophile independent. It follows that selectivity is constant and hence does not correlate with reactivity as would be required

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