J. Am. Chem. Soc. 1990, 112, 6839-6841 6839

((Pentafluorothio)methylidyne)sulfur Trifluoride, $F_5SC{\equiv}SF_3$. A Nonclassical Molecular Structure?

Ilse Weiss,[1a] Heinz Oberhammer,*,[1a] Rolf Gerhardt,[1b] and Konrad Seppelt[1b]

Contribution from the Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 7400 Tübingen, West Germany, and Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, 1000 Berlin, West Germany. *Received April 9, 1990*

Abstract: A gas electron diffraction study of $F_5SC{\equiv}SF_3$ based on a rigid model yields a structure with a bent $S{-}C{\equiv}S$ chain and the following geometric parameters (r_a values and 3σ uncertainties): $(S{-}F)_{\mathrm{mean}} = 1.559\ (2)$ Å, $S{\equiv}C = 1.401\ (9)$ Å, $S{-}C = 1.699\ (12)$ Å, $S{-}C{\equiv}S = 159\ (3)°$, FSF ($SF_5$) = 88.6 (3)° and FSF ($SF_3$) = 93.9 (6)°. Analysis of the data imposing linearity of the chain results in abnormally large vibrational amplitudes for some nonbonded distances and in an increase of the agreement factor by ca. 30%. The electron diffraction experiment does not provide conclusive information about the dynamic properties of this molecule. Structural models with large amplitude motions for internal rotation of the SF_5 group or for the $S{-}C{\equiv}S$ bending vibration (with a double-minimum potential) do not improve the fit of the experimental intensities. The potential barrier for the linear structure cannot be determined. The similar electronic properties of SF_5 and CF_3 groups and the experimentally and theoretically established structure for $F_3CC{\equiv}SF_3$ ($C{-}C{\equiv}S$ = 155 (3)° and 155°, respectively) suggest that the "effective" (i.e., thermal average) $S{-}C{\equiv}S$ angle of 159 (3)° results from a nonclassical distortion of the equilibrium structure of $F_5SC{\equiv}SF_3$.

Introduction

During the past decades chemists have developed bonding models that are very successful in rationalizing experimentally determined structures of molecules and in predicting such structures for new compounds. The concepts of hybridization or VSEPR[2] allow qualitively correct predictions for bond angles in all but very few cases. The exceptions, where the actual structure does not conform with these concepts, have been termed "nonclassical" structures or structures with "nonclassical distortions".[3] Such distortions can lead to nonplanarity of pseudo-olefins of the type $R_2X{=}XR_2$, to nonlinearity of cumulated double bonds or to nonlinearity of triple-bond systems $R{-}X{\equiv}Y{-}R'$. Experimentally observed examples of nonplanar pseudo-olefins are distannene, $R_2Sn{=}SnR_2$,[4] and digermene, $R_2Ge{=}GeR_2$,[5] examples for nonlinear cumulenones are propadienone $H_2C{=}C{=}C{=}O$[6,7] and carbon suboxide.[8] Nonlinear triple-bond systems have been predicted theoretically for $H{-}Si{\equiv}Si{-}H$[9] and the first experimental example is $CF_3C{\equiv}SF_3$, where a $C{-}C{\equiv}S$ angle of 155 (3)° has been determined for the gas-phase structure.[10]

Trinquier and Malrieu[3] have rationalized these nonclassical distortions in a simple valence bond model, which relates the occurrence and extent of such distortions to the singlet-triplet separation of the diradicals R_2X that form the double bond or to the doublet-quartet separation of the triradicals RX that form the triple bond. Only if this energy separation is larger than the delocalization energy of the $\sigma + \pi$ double or $\sigma + \pi_x + \pi_y$ triple bond, a nonclassical distortion occurs. Thus, such distortions depend on a very subtle energy balance between large contributions and the net effect may be very small. This shows up in ab initio calculations, where results can depend very crucially on the computational level and correlation effects may be very prominent. It also shows up in experiments where the geometric deviation from the classical structure and the energy difference between classical and nonclassical structures may be small. In the solid state such distortions may be obscured by packing effects in either direction, i.e., a distortion can be caused by intermolecular interactions or it may be compensated for, depending on the packing in the crystal. Therefore, only structural studies in the gas phase allow for unambiguous information about such nonclassical distortions.

The only other compound besides $F_3CC{\equiv}SF_3$ containing a $C{\equiv}SF_3$ entity, that has been synthesized so far is $F_5SC{\equiv}SF_3$.[11] The crystal structure,[11] which was determined at −168 °C, shows a linear $S{-}C{\equiv}S$ skeleton, in contrast to $F_3C{-}C{\equiv}SF_3$, where the skeleton is bent in the crystal [CCS = 171 (2)°][12] as it is in the gas phase. In the latter compound for which the nonclassical distortion from linearity is larger in the gas phase [CCS = 155 (3)°], packing effects compensate this distortion partially. In the case of $F_5SC{\equiv}SF_3$, it cannot be decided whether the exact linear conformation in the crystal is caused by the substitution of CF_3 by SF_5 or by packing effects. In an attempt to answer this question, we performed a structural analysis in the gas phase by electron diffraction.

Structure Analysis

The experimental radial distribution function is shown in Figure 1. Model calculations demonstrate that for a linear structure two prominent peaks should occur around 3.5 Å corresponding to the $S_1{\cdots}F_e$ distances (F_e = equatorial fluorines of the SF_5 group) and around 4.1 Å corresponding to the $S_2{\cdots}F$ distances (F = fluorines of the SF_3 group). The absence of such peaks in this region indicates a nonlinear skeleton or abnormally large vibrational amplitudes for these nonbonded distances. In the least-squares analysis a diagonal weight matrix[13] was applied to the molecular intensities and scattering amplitudes and phases of Haase[14] were used for calculating the theoretical intensities. Local

---

(1) (a) Tübingen. (b) Berlin.

(2) Gillespie, R. J. *Angew. Chem.* **1967**, *79*, 885; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 819.

(3) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303-5315.

(4) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

(5) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387.

(6) Brown, R. D.; Champion, R.; Elmes, P. S.; Godfrey, P. *J. Am. Chem. Soc.* **1985**, *107*, 4109.

(7) Brown, R. D.; Dittmann, R. D. *Chem. Phys.* **1984**, *83*, 77.

(8) Ohshima, Y.; Yamamoto, S.; Kuchitsu, K. *Acta Chem. Scand.* **1988**, *A42*, 307-317.

(9) Lischka, H.; Köhler, H. J. *J. Am. Chem. Soc.* **1983**, *105*, 6646. Brinkley, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 603. Kawei, F.; Noro, T.; Murakami, A.; Ohomo, K. *Chem. Phys. Lett.* **1982**, *92*, 479. Kalcher, J.; Sax, A.; Olbrich, G. *Int. J. Quantum Chem.* **1984**, *24*, 543.

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

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

(12) Pötter, B.; Seppelt, K.; Simon, A.; Peters, E.-M.; Hettich, B. *J. Am. Chem. Soc.* **1985**, *107*, 980-985.

(13) Oberhammer, H.; Willner, H.; Gambler, W. *J. Mol. Struct.* **1981**, *70*, 273.

0002-7863/90/1512-6839$02.50/0

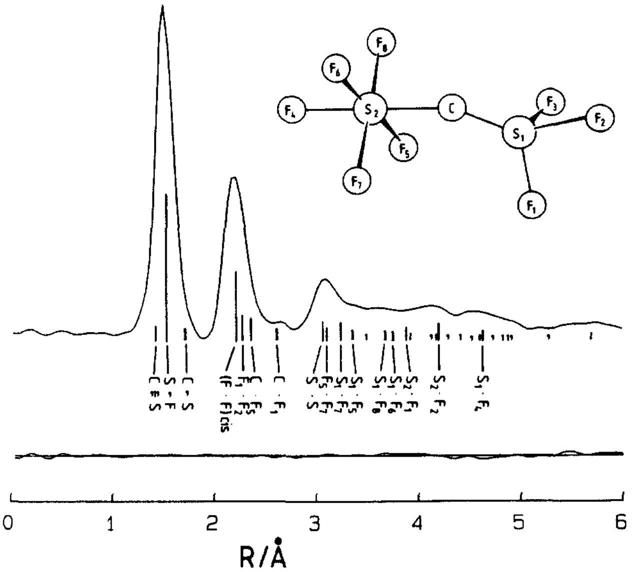

Figure 1. Experimental radial distribution function and difference curve. The bars indicate the positions of the interatomic distances. Bars without label correspond to distances between fluorines of the SF_5 and SF_3 groups.

Table I. Results of Electron Diffraction Analysis[a]

(a) Geometric Parameters

$(S—F)_{mean}$	1.559 (2)	CS_1F_1	122.4 (6)
S≡C	1.401 (9)	$F_1S_1F_2$[b]	93.9 (6)
S—C	1.699 (12)	$F_4S_2F_5$	88.6 (3)
S—C≡S	159 (3)	$\tau(SF_5)$[c]	24 (14)

(b) Interatomic Distances and Vibrational Amplitudes

S≡C	1.40	0.051 (13) (l_1)	$S_1\cdots F_7$	3.24	0.15 (5) (l_7)
S—F	1.56	0.047 (2) (l_2)	$S_1\cdots F_5$	3.35	
S-C	1.70	0.063 (22) (l_3)	$S_1\cdots F_6$	3.54	
$F_4\cdots F_5$	2.17	0.063 (6) (l_4)	$S_1\cdots F_8$	3.65	
$F_5\cdots F_7$	2.29		$S_1\cdots F_4$	4.58	0.090[d]
$F_1\cdots F_2$	2.27		$S_2\cdots F_1$	3.88	0.14 (5) (l_8)
$C\cdots F_5$	2.33	0.070[d]	$S_2\cdots F_2$	4.18	
$C\cdots F_1$	2.59	0.128 (27) (l_5)	$F\cdots F$[e]	3.46–4.86	0.20 (4) (l_9)
$S\cdots S$	3.04	0.090 (16) (l_6)	$F_1\cdots F_4$	5.27	0.12[d]
$F_5\cdots F_6$	3.11	0.060[d]	$F_2\cdots F_4$	5.69	
$C\cdots F_4$	3.25				

(c) Agreement Factors[f]

$R_{50} = 0.036$ $R_{25} = 0.063$

[a] r_a values in angstroms and degrees. Error limits are 3σ values and include a possible scale error of 0.1% for bond lengths. For atom numbering see Figure 1. [b] Dependent parameter. [c] Effective torsional angle of SF_5 group. For $\tau = 0$, $S_1—F_1$ eclipses $S_2—F_7$. [d] Not refined. [e] Distances between fluorines of SF_5 and SF_3 groups. [f] $R = [\sum w_i\Delta_i^2/\sum(s_iM_i(\exp))^2]^{1/2}$, $\Delta_i = s_iM_i(\exp) - s_iM_i(\text{calc})$.

C_{3v} and C_{4v} symmetries were assumed for the SF_3 and SF_5 groups and all SF distances in the SF_5 group were set equal. The difference between the SF bond lengths in the SF_5 and those in the SF_3 group [$\Delta SF = SF(SF_5) - SF(SF_3)$] is badly determined by the electron diffraction experiment, because of high correlations with the SF vibrational amplitude. Since the estimated uncertainty (3σ value) for ΔSF is larger than the value itself [0.015 (24) Å], all SF bond lengths were set equal in the further analyses. Vibrational amplitudes were collected in groups according to their distances (see Table I). With the above assumptions seven geometric parameters and nine vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than |0.6|: $SCS/l_9 = -0.77$, $CS_1F_1/l_4 = 0.83$, $F_4SF_5/l_4 = 0.72$, $\tau(SF_5)/l_8 = 0.65$, $l_1/l_2 = 0.67$, $l_2/l_3 = 0.77$, $l_8/l_9 = -0.61$ (see Figure 1 for atom labeling and Table I for numbering of vibrational amplitudes).

The results of this analysis, which is based on a rigid model (i.e., no large-amplitude motions), are summarized in Table I. The SCS moiety is bent with an SCS angle of 159 (3)°. Refinements with the SCS chain constrained to linearity result in rather large vibrational amplitudes for the nonbonded S···F distances [0.24 (2) Å] and lead to an increase of the agreement factor for the long camera distance data, R_{50}, by ca. 30%. If the amplitudes are fixed at the values derived for the bent structure (see Table I), R_{50} increases by more than 100%.

Since internal rotation of the SF_5 group is expected to be free or nearly free, a large-amplitude model may be more adequate for the analysis of the electron diffraction intensities. Furthermore, the small deviation of the skeleton from linearity of only 20° may lead to a large-amplitude SCS bending motion. Therefore, several least-squares analyses based on various large-amplitude models were performed. For a large-amplitude model with free internal rotation of the SF_5 group, the fit of the experimental intensities does not improve relative to the rigid model with an effective torsional angle for the SF_5 group. For the bending motion a double-minimum potential of the form

$$V = V_0[(\Phi/\Phi_0)^2 - 1]^2$$

was assumed where V_0 is the barrier to linearity, Φ is the deviation from linearity (180 – SCS), and Φ_0 corresponds to the potential minimum. Because of large correlations between V_0, Φ_0, and some vibrational amplitudes, the two parameters for the bending potential could not be refined simultaneously. Refinements with various but fixed V_0 values demonstrate that the electron diffraction intensities are rather insensitive to this barrier. For high barriers ($V_0 > 1$ kcal/mol) geometric parameters and vibrational amplitudes are equivalent to those derived for the rigid model. For low barriers only some vibrational amplitudes for nonbonded S···F and F···F distances vary, but do not become "unrealistic". In all these analyses the fit of the experimental intensities does not improve relative to the rigid model and the geometric parameters, including the average value for SCS, correspond to those in Table I. If a very flat single-minimum harmonic potential is assumed for the bending motion, the agreement factor R_{50} increases by ca. 30%.

Discussion

The electron diffraction analysis results in a bent structure for $F_5S—C≡SF_3$ with an "effective" (i.e., thermal average) SCS angle of 159 (3)°. However, no conclusive information about the dynamic properties of this molecule can be derived from these data. Unfortunately, such information is not provided by available vibrational data, either. With a typical force constant for —C≡ bending of 0.25 mdyn·Å, the SCS bending vibration is predicted at 80 cm^{-1}. In the gas-phase FIR spectrum, which was recorded down to 50 cm^{-1}, no absorption was observed below 200 cm^{-1}. The Raman spectrum of the liquid (at 173 K) shows a very weak signal at 190 cm^{-1}, which would correspond to an unrealistically high SCS force constant of more than 2.0 mdyn·Å. In the slope of the Rayleigh scattering, weak protuberances at 40 cm^{-1} and even weaker at 80 cm^{-1} probably indicate the presence of transitions. If these are assigned to the fundamental and overtone of the bending vibration, an SCS force constant of 0.08 mdyn·Å is obtained in the normal coordinate analysis.[15] With the assumption of a double-minimum potential this force constant leads, together with the effective bending angle of 159 (3)°, to a barrier for the linear structure of $V_0 = 0.2$ kcal/mol. For a very flat harmonic single-minimum potential the effective SCS angle of 159 (3)° would correspond to a bending force constant of 0.008 mdyn·Å with a bending frequency of 15 cm^{-1}. As mentioned above, such a linear structure with a very large amplitude bending vibration is rather unlikely in the electron diffraction analysis (increase of R_{50} by 30%).

For $F_3CC≡SF_3$ the experimental data (electron diffraction and microwave spectroscopy) were conclusive about a bent equilibrium structure with an effective bending angle of 155 (3)°.[10] The barrier to linearity was estimated to be ≥0.5 kcal/mol. For this

---

(14) Haase, J. Z. Naturforsch. A 1970, 25A, 936.

(15) Christen, D. J. Mol. Struct. 1978, 48, 101.

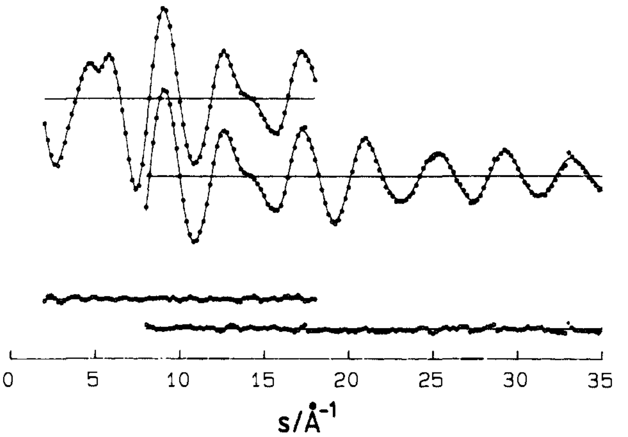

Figure 2. Experimental (dots) and calculated (full line) molecular intensities and differences.

molecule the nonclassical distortion at the "sp-hybridized" carbon atom (—C≡) is confirmed by theory, if electron correlation effects are included in the ab initio calculations.[10] The amount of bending and the barrier to linearity depend strongly on the computational procedure (MP3, MP4SD, MP4SDQ). The highest level of theory that could be afforded with the available computing power, MP4DSQ/3-21G*//HF/3-21G*, predicts an equilibrium bending angle of 155° and a barrier of 0.2 kcal/mol.[16] The presently available computing resources do not allow for equivalent calculations for $F_5SC{\equiv}SF_3$. Since electronic properties of CF_3 and SF_5 groups are similar, the derived structure of $F_3CC{\equiv}SF_3$ can be considered as an additional support of the present electron diffraction interpretation for $F_5SC{\equiv}SF_3$, which highly favors the presence of a nonclassical distortion in this molecule. The energy difference between a bent and a linear structure is estimated to be well below 1 kcal/mol. The apparent contradiction between gas-phase and solid-state structures can be rationalized by implying packing effects in the crystal. A similar difference between gas-phase and solid-state structures was observed for $F_3CC{\equiv}SF_3$ [CCS = 155 (3)° and 171 (2)°, respectively]. An extensive comparison between gas-phase and solid-state structures of ortho-substituted biphenyls[17] reveals systematic structural differences in the two phases. On the average, the dihedral angle between the two phenyl groups is about 20° smaller in the solid phase relative to the gas phase. The energy necessary for this structural change is in the order of 1 kcal/mol. This comparison between solid-state and gas-phase structures demonstrates that structural differences involving energies up to 1 kcal/mol can easily be caused by packing effects. Thus, the X-ray study for $F_5SC{\equiv}SF_3$, which results in a perfectly linear S—C≡S chain, does not contradict the experimental result for the gas phase.

With the exception of the SCS angle, the geometric parameters derived for the gas phase are in good agreement with the crystal values. The C≡S bond lengths of 1.401 (9) Å [1.392 (4) Å in the crystal] is even shorter than this bond in $F_3CC{\equiv}SF_3$ [1.434 (14) Å and 1.420 (5) Å for gas and solid, respectively]. The C—S bond [1.699 (12) Å in the gas and 1.682 (4) Å in the solid] is considerably shorter than the C(sp)—SF_5 single bond in F_5S—C≡CH [1.736 (6) Å[18] or 1.727 (5) Å[19]]. Due to disorder of the SF_5 group in the crystal the geometric parameters of this group could not be determined in the X-ray analysis. In the solid state, the SF bonds in the SF_3 group [1.534 (3) Å] are shorter than these bonds in F_3C—C≡SF_3 (1.568 Å). In the gas electron diffraction analysis only a mean value for all SF bonds could be derived [$(SF)_{mean}$ = 1.559 (2) Å], and the difference is badly determined [ΔSF = 0.015 (24) Å]. Thus, a strict comparison between the two studies is not possible. The FSF angle in the SF_3 group [93.9 (6)° for the gas and 93.5 (2)° for the solid] is typical for such angles in X≡SF_3 compounds [93.92 (16)° in N≡SF_3,[20] 93.2 (9)° in F_3C—C≡SF_3].

Experimental Section

$F_5SC{\equiv}SF_3$ was synthesized as described in the literature,[11] and purified by repeated fractional condensation. Small amounts of the precursor $(SF_5)_2CH_2$ (~2%) were observed in the NMR spectrum. This impurity could not be detected in the structure analysis. The sample was transferred from Berlin to Tübingen in liquid nitrogen. The electron diffraction intensities were recorded with the Balzers Gasdiffractograph[21] at two camera distances (25 and 50 cm). The electron wavelength (ca. 60 kV accelerating voltage) was calibrated with ZnO diffraction patterns. The sample reservoir was kept at −60 °C and the inlet system and nozzle were at room temperature. The camera pressure during the experiment did not exceed 10^{-5} Torr. Two plates for each camera distance were analyzed by the usual procedures of this laboratory.[13] Numerical values for the total intensities in the s range 2–18 and 8–35 Å^{-1} in steps of Δs = 0.2 Å^{-1} are deposited as supplementary material. The averaged molecular intensities are presented in Figure 2.

Acknowledgment. We thank Dr. G. Pawelke, Universität Wuppertal, for recording gas-phase FIR and liquid-phase Raman spectra. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is acknowledged.

Note Added in Proof. After submission of this paper, ab initio calculations for F_5S—C≡SF_3 were performed at the MP2/6-31G*//HF/6-31G* level (Dr. Detlef Labrenz, Cray Research GmbH, München, FRG). These calculations result in a nonclassical distortion with a shallow energy minimum for S—C≡S near 150° and thus support the interpretation of the electron diffraction data. A communication to this journal with these results and computational details is planned.

Supplementary Material Available: Numerical values for total electron diffraction intensities (2 pages). Ordering information is given on any current masthead page.

---

[16] The values for the bending angles (180 - CCS) given in the theoretical part and in the Note Added in Proof of ref 10 are in error by a factor of 2. Thus, the equilibrium CCS angle obtained by the MP4SDQ method is 155° (instead of 130°), which is in very good agreement with the effective angle of 155 (3)° derived from the experiment. See Correction and Addition to ref 10: *J. Am. Chem. Soc.* **1990**, *112*, 5388.

[17] Pratt Brock, C.; Minton, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 4586–4593.

[18] Zylka, P. Dissertation, Tübingen, 1988.

[19] Császár, A.; Hedberg, K.; Terjeson, R. J.; Gard, L. *Inorg. Chem.* **1987**, *26*, 955–958.

[20] Small, C. E.; Smith, J. G. *Mol. Phys.* **1979**, *37*, 665.

[21] Oberhammer, H. *Molecular Structure by Diffraction Methods*; The Chemical Society: Burlington House: London, 1976; Vol. 4, p 24.