Molecular Structure of Hexakis(trifluoromethylthio)ethane

By **Heinz Oberhammer**,* Institut für Physikalische und Theoretische Chemie der Universität Tübingen, 7400 Tübingen 1, Germany
A. Haas and **K. Schlosser**, Lehrstuhl II für Anorganische Chemie, Ruhn Universität Bochum, Germany

The molecular structure of $C_2(SCF_3)_6$ has been investigated by electron-diffraction studies on the vapour. The best agreement between experiment and model is obtained with local C_1 symmetry for the $C(SCF_3)_3$ groups and C_i overall symmetry for the molecule. The following geometric parameters for the C_2S_6 skeleton have been determined (r_g values): C–C 1.624(37), C–S 1.839(12) Å, S–C–S 113.9(0.3)°, where the error limits are three times the standard deviations. Other geometric parameters and vibrational amplitudes are given. The most striking result of this investigation is the long C–C bond.

HEXAKIS(TRIFLUOROMETHYLTHIO)ETHANE, which is formed during the photolysis of $(CF_3)_2C{=}S$, at <20 °C shows homolytic cleavage of the central C–C bond as follows:[1]

$$(CF_3S)_3C{-}C(SCF_3)_3 \rightleftharpoons 2C(SCF_3)_3^{\bullet}$$

An electron-diffraction investigation has been performed to provide geometric parameters for this molecule and which may allow an explanation for the spontaneous dissociation.

EXPERIMENTAL

Hexakis(trifluoromethylthio)ethane was obtained by irradiating a boiling solution of $(CF_3)_2C{=}S$ in hexane at 300 nm. After irradiation for 10 h the reaction mixture was cooled to −60 °C; the precipitate obtained was filtered off and crystallized from diethyl ether; m.p. 124—130 °C (in a sealed tube), ^{19}F n.m.r. spectrum in 90% CCl_3F, $\delta(CF_3)$ = 36.9 p.p.m.

Electron-diffraction intensities were recorded on 13 × 18 cm Kodak Electron Image plates with a Balzers KD-G2 unit.[2] The accelerating voltage was 60 kV. Details of the experiment are summarized in Table 1.† The pressure of sublimation at *ca.* 75 °C together with the large nozzle diameter was just sufficient to record diffraction patterns. At higher temperatures decomposition of the compound may occur. The electron wavelength was determined from ZnO diffraction patterns. Two plates for each camera distance were selected and reduced separately. Details of the data-reduction procedures are described elsewhere.[3]

TABLE 1

Experimental conditions

Nozzle–plate distance/cm	50	25
Sample temperature/°C	75	75
Nozzle temperature/°C	70	70
Camera pressure/Torr	10^{-6}	10^{-6}
Exposure time/min	0.5—2	1—2.5
Nozzle diameter/mm	0.5	0.5
Electron wavelength/Å	0.049 25(1)	0.049 27(1)
s range/$Å^{-1}$	1.4—1.5	8—30

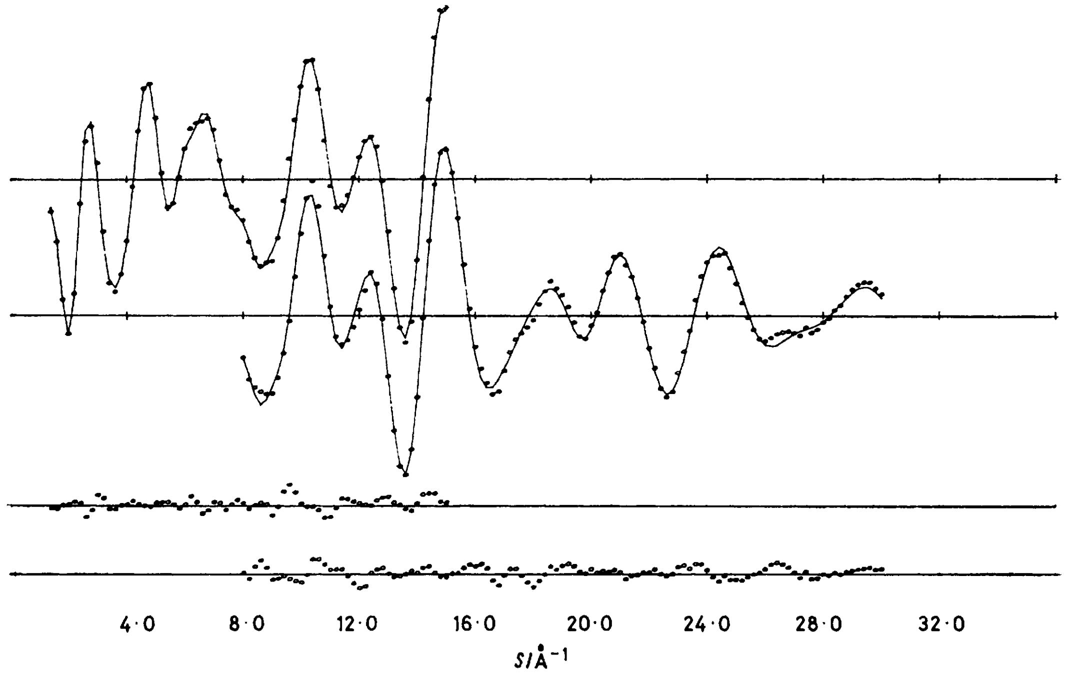

FIGURE 1 Experimental (○) and theoretical (—) molecular intensities and differences

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† Throughout this paper: 1 Å = 100 pm; 1 Torr = (101 325/760) Pa; 1 cal = 4.184 J.

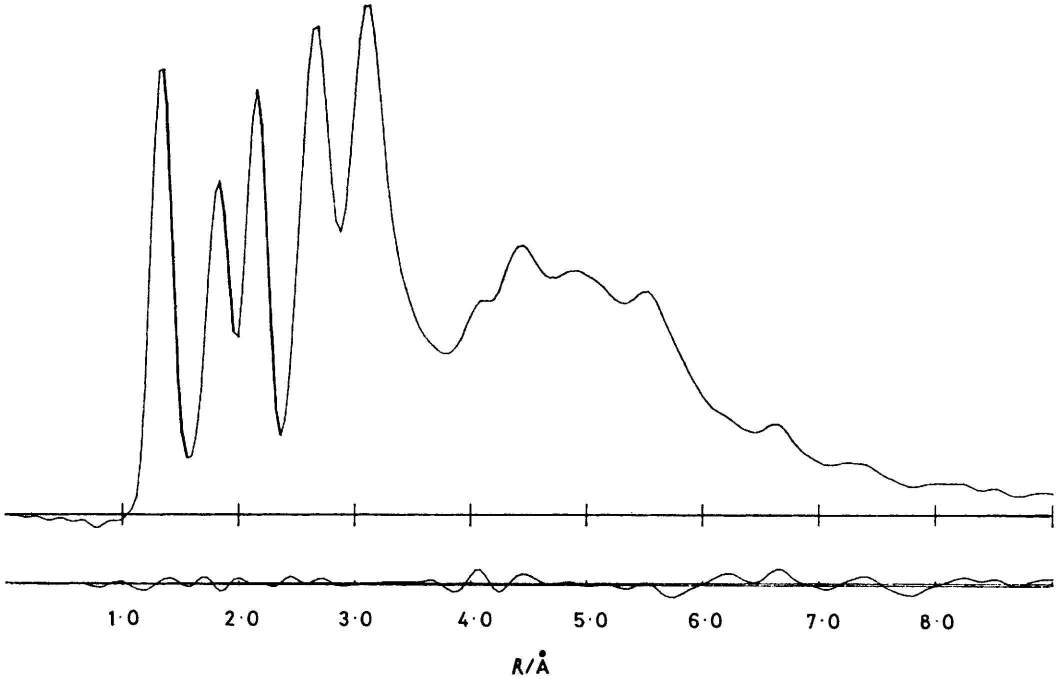

FIGURE 2 Radial distribution function

The averaged molecular intensities for the two camera distances and the theoretical molecular-intensity function for the final model are shown in Figure 1. Scattering amplitudes and phase shifts of Haase [4] were used.

Structure Analysis.—The experimental radial distribution function (Figure 2) was calculated with a damping factor of $\exp(-0.002\,5s^2)$. A great number (*ca.* 80) of theoretical radial distribution functions was calculated, varying the S–C–S, C–S–C angles and the conformation of the $C(SCF_3)_3$ groups systematically to obtain a preliminary molecular model. The determination of the rotational positions of the individual SCF_3 groups around the C–S bonds, *i.e.* the dihedral angles τ_i between the CCS_i and CS_iC planes (see Figure 3), was difficult. Several molecular models with C_3 ($\tau_1 = \tau_2 = \tau_3$), C_s ($\tau_1 = 0$, $\tau_2 = -\tau_3$), and C_1 symmetry ($\tau_1 = 0$, $\tau_2 = \tau_3$) for the $C(SCF_3)_3$ groups were investigated during the course of this work. These calculations indicated clearly that the prevailing conformation could only be C_1. Small contributions from other conformations, however, cannot be excluded definitely. For the overall symmetry of the molecule we considered C_2 and C_i. The agreement between experiment and model was better for C_i symmetry; the radial distribution function, however, is not very sensitive to this overall symmetry. Furthermore, i.r. and Raman spectra and a preliminary *X*-ray diffraction investigation [5] indicate a centre of symmetry for this molecule in the solid phase. Therefore, for the gas phase as well only C_i symmetry was considered in the further structure analysis. The CF_3 groups were assumed to be staggered exactly about the C(0)–S bonds. Deviations from the staggered position by more than 10° made the fit between experiment and model definitely worse.

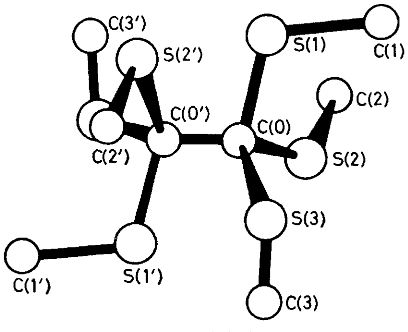

FIGURE 3 Molecular model (without fluorine atoms)

The preliminary molecular model obtained by the analysis of the radial distribution function was then refined by a least-squares procedure based on the experimental molecular scattering curves. A diagonal weight matrix was employed with elements increasing exponentially for $1.4 \leqslant s \leqslant 4$ and $8 \leqslant s \leqslant 9$ Å^{-1} for the 50 and 25 cm data respectively and decreasing exponentially for $14 \leqslant s \leqslant 15$ and $25 \leqslant s \leqslant 30$ Å^{-1}. The remaining elements were chosen to be unity. An interval of $\Delta s = 0.2$ Å^{-1} was used for the experimental molecular scattering curves.

The following assumptions for the geometry of the molecule were made: (*i*) C_i overall symmetry; (*ii*) D_{3d} symmetry for the C_2S_6 skeleton; (*iii*) C_{3v} symmetry for the CF_3 groups with the C_3 axis collinear with the S–C bonds, *i.e.* no tilt angle was introduced; (*iv*) C_1 symmetry for the $C(SCF_3)_3$ groups with $\tau_2 = \tau_3$. τ_1 was allowed to be different from zero, but it converged towards zero from either positive or negative values. Equating both C–S distances in this molecule resulted in a rather large value for the respective vibrational amplitude [l(C–S) 0.062 ± 0.005 Å]. When this amplitude was constrained to the more realistic value of 0.055 Å a difference of 0.014 Å between the two C–S distances was obtained, the C(0)–S distances being longer. This difference, however, is smaller than the respective error limits.

With these assumptions, nine geometric parameters, *i.e.* four bond distances, three bond angles, and two dihedral angles, are required to define the geometry of the molecule. Amplitudes of vibration were refined for the principal bonded and 1,3 non-bonded distances. Amplitudes for 1,4, 1,5, and longer distances were grouped together, independent of the actual distances (see Table 2). The amplitudes of all C · · · C distances, which contribute little to the molecular intensities, were fixed in the least-squares analysis.

TABLE 2

Structural parameters and vibrational amplitudes for $C_2(SCF_3)_6$

(*a*) Bond distances and vibrational amplitudes (Å)

	r_g	l
C–F	1.340(3)	0.048(3)
C–C	1.624(37)	0.055(ass)
$(S–C)_{av.}$	1.832(4)	0.062(5)
S(1)–C(0)	1.839(12)	0.055(ass)
S(1)–C(1)	1.825(14)	0.055(ass)

(*b*) Bond and dihedral angles (°)

F–C–F	107.3(0.2)	C–S–C	110.6(1.2)
S–C–S	113.9(0.3)	τ_1	0.7(4.8)
C–C–S [a]	104.5(0.3)	$\tau_2 = \tau_3$	89.0(1.4)

(*c*) Vibrational amplitudes for non-bonded distances which were refined in the least-squares analysis

F · · · F 1,3	0.053(4)	S · · · S 1,3	0.099(22)
S · · · F 1,3	0.097(6)	C · · · S 1,3	0.069(19)
C · · · F 1,4	0.169(53)	$(S \cdots S)_{gauche}$	0.135(42)
S · · · C 1,4 S · · · C 1,5	0.257(125)	$(S \cdots S)_{trans}$ S · · · F 1,5	0.122(43) 0.380(129)
C · · · F 1,5	0.191(124)	S · · · F 1,6	0.202(29)
C · · · F 1,6	0.351(222)	C · · · F 1,7	0.248(206)
F · · · F 1,8	0.225(100)		

(*d*) Agreement factors (%) [b]

R_{50}	8.4	R_{25}	9.7

[a] Dependent parameter. [b] $R = [\Sigma W_i \Delta_i^2 / \Sigma W_i I_i^2(\text{expt.})]^{\frac{1}{2}}$ with $\Delta_i = I_i$ (expt.) $- I_i$ (calc.) and W_i is the weighting function. ass = Assumed.

The following correlation coefficients had values larger than 0.6; [r(C–C), S–C–S] = 0.88, [r(C–F), F–C–F] = 0.72, and [r(C–C), l(S · · · F) 1,3] = 0.68. The results of the final least-squares procedure are summarised in Table 2. The error limits quoted are 3σ and include uncertainties due to correlation between data points and geometric assumptions. The error limits, however, do not include the neglect of shrinkage effects. The great number of large-amplitude torsional vibrations in this molecule will have a considerable effect on the dihedral angles. Thus, the results in Table 2 have to be interpreted as 'effective' values. Several tests have indicated that the agreement between experiment and model could be improved further by relaxing some of the geometric constraints and above all by using a larger number of mean-square amplitudes. This, however, does not seem to be worthwhile, since further high correlations between parameters are introduced without changing the results of Table 2 by more than the respective σ values. Since it is impossible to refine vibrational amplitudes for each distinct distance in a molecule of this size, the use of more amplitudes would only improve the fit of the experimental intensities, and not lead to greater physical significance for these values.

DISCUSSION

The configuration of the ethane carbon atoms deviates considerably from tetrahedral. It can be regarded as intermediate between the configuration of an sp^3-hybridized carbon atom and the planar sp^2 configuration of the $C(SCF_3)_3$ radicals, which follows from analysis of the e.s.r. spectra. The large S–C–S angle (113.9 ± 0.3°) can be explained by the 'B-strain' effect of the SCF_3 groups bonded to the same carbon atom. Further increase of this angle, however, would be sterically unfavourable. The non-bonded S(1) · · · S(2′) distance (3.10 Å) is almost as short as the S(1) · · · S(2) distance (3.08 Å). Consequently, strong interaction between the *gauche* substituents, *i.e.* a significant 'F-strain' effect. results in lengthening of the central C–C bond. The value for this single bond (1.624 ± 0.037 Å) is the most striking result of this structure investigation. Due to the very small contribution of this bond to the molecular scattering intensities, this parameter can be determined only indirectly from the bonded C–S and non-bonded S · · · S and C · · · S distances of the C_2S_6 skeleton. For this reason the error limit is very large. This long C–C bond is in agreement with the very low dissociation energy for which a preliminary value of 10—12 kcal mol^{-1} is obtained. We assume the barrier to internal rotation around the C–C bond to be higher than this dissociation energy.

The S(1)–C(1) bond length (1.823 ± 0.014 Å) agrees very well with the corresponding values for $S(CF_3)_2$ (1.830 ± 0.015 Å) [6] and $N(SCF_3)_3$ (1.825 ± 0.006 Å).[7] The C(0)–S(1) bond distance (1.839 ± 0.012 Å) is slightly longer than the S(1)–C(1) bond, but the difference is smaller than the corresponding error limits. For the C–S bond in ethane-1,2-dithiol [8] a value of 1.819 ± 0.002 Å was determined. The C–S–C bond angles in $C_2(SCF_3)_6$ are considerably larger (110.6 ± 1.2°) than the corresponding values obtained for SMe_2 (98.9 ± 0.2°) [9] or $S(CF_3)_2$ (105.6 ± 3.0).[6] This may be a consequence of steric repulsions between the CF_3 groups.

The geometry of the CF_3 groups in this molecule follows the general trends that have been observed for the very simple $X–CF_3$ type molecules (X = F, Cl, Br, or I).[3b] The relatively long C–F bond (1.340 ± 0.003 Å) is in agreement with the low electronegativity of sulphur. The small F–C–F bond angle (107.3 ± 0.2°) can be regarded as a consequence of the long C–F bond, since the non-bonded F · · · F distances in most CF_3 groups are remarkably constant. This value is 2.158 ± 0.005 Å for $C_2(SCF_3)_6$, whereas an average F · · · F distance (r_g value) of 2.157 ± 0.003 Å was observed for trifluoromethyl halides.

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REFERENCES

[1] A. Haas and K. Schlosser, *Tetrahedron Letters*, 1976, 4631.

[2] W. Zeil, J. Haase, and L. Wegmann, *Z. Intrumentenk.*, 1966, **74**, 84; H. Oberhammer, 'Developments in the Apparatus used in Europe including U.S.S.R. for Studies of Electron Diffraction in Vapours,' in 'Molecular Structures by Diffraction Methods,' The Chemical Society, London, 1976, vol. 4.

[3] (*a*) H. Oberhammer and J. Strahle, *Z. Naturforsch.*, 1975, **A30**, 296; (*b*) V. Typke, M. Dakkouri, and H. Oberhammer, *J. Mol. Struct.*, 1978, **44**, 85.

[4] J. Haase, *Z. Naturforsch.*, 1970, **A25**, 936.

[5] C. Krüger, personal communication.

[6] H. J. M. Bowen, *Trans. Faraday Soc.*, 1954, **50**, 452.

[7] C. J. Marsden and L. S. Bartell, *J.C.S. Dalton*, 1977, 1582.

[8] J. Hargittai and G. Schultz, *J.C.S. Chem. Comm.*, 1972, 323.

[9] L. Pierce and M. Hayasaki, *J. Chem. Phys.*, 1961, **35**, 479.