Structure and Conformation of Bis(trifluoromethylthio)methane, $CH_2(SCF_3)_2$

Monika Korn[a], Alois Haas[b], and Heinz Oberhammer*[a]

Institut für Physikalische und Theoretische Chemie der Universität Tübingen[a],
Auf der Morgenstelle 8, 72076 Tübingen, Germany

Lehrstuhl für Anorganische Chemie II der Ruhr-Universität Bochum[b],
Postfach 102148, 44780 Bochum, Germany

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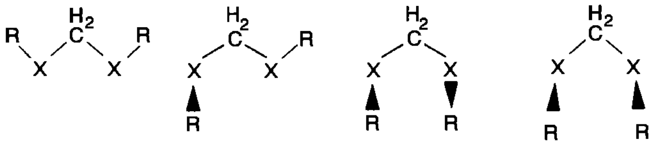
The geometric structure and conformational properties of bis(trifluoromethylthio)methane, $CH_2(SCF_3)_2$, were determined by gas electron diffraction. The main conformer (70 ± 15%) possesses C_2 symmetry with dihedral angles $\Phi(SCSC) = 79.1(10)°$. The second conformer possesses C_1 symmetry. The following skeletal geometric parameters (distances r_a [pm] and angles $\angle_\alpha$ [°] with 3-σ uncertainties) were obtained: C–S 183.6(3), S–CF_3 179.3(3), S–C–S 112.1(6), and C–S–C 98.2(10). The geometric structures and relative conformational stabilities were well reproduced by ab initio calculations at the HF/3-21G* level.

The conformational properties of compounds of the type $RX-CH_2-XR$, with X = O, R = H or Me have attracted considerable interest from experimentalists[1,2] and theoreticians[3–6]. Depending on the dihedral angles around the C–X bonds, these compounds can adopt four different conformations (ap, ap), (sc, ap), +sc, +sc), and (+sc, –sc).



(ap, ap) (sc, ap) (+ sc, + sc) (+ sc, – sc)

Extensive ab initio calculations for the parent compound $CH_2(OH)_2$ show the clear preference of the (+sc, +sc) conformation. (+sc, –sc) and (sc, ap) structures are predicted to be higher in energy by 3–5 kcal/mol, and the (ap, ap) form does not represent a stable conformation and is higher by 8–11 kcal/mol, depending on the computational method. The strong preference of the (+sc, +sc) conformation is rationalized by the generalized anomeric effect[7]. Hyperconjugative orbital interactions between the oxygen lone pair lp_O and the antibonding σ^* orbital of the opposite C–O bond favor the synclinal orientations of the O–R bonds. Gas-phase structural studies for dimethoxymethane, $CH_2(OMe)_2$, and 2,2-dimethoxypropane, $Me_2C(OMe)_2$, confirm these theoretical predictions[1,2]. Recently, the influence of the anomeric effect on the conformational properties of the analogous sulfur compound $CH_2(SH)_2$ has been investigated by ab initio methods[6,8]. Again, the (+sc, +sc) structure is predicted to be favored, but the relative energies of the other conformations are considerably lower than those in $CH_2(OH)_2$, 0.9–1.4 kcal/mol for (sc, ap), 1.1–1.3 kcal/mol for (+sc, –sc) and 2.8–4.1 kcal/mol for (ap, ap). To our knowledge, no experimental gas-phase structures of such dithiomethanes are known, which would confirm these theoretical predictions. In the present study we report on a gas electron diffraction (GED) investigation of the conformational properties and geometric structure of bis(trifluoromethylthio)methane. The experimental structure determination is supplemented by ab initio calculations.

Ab initio Calculations

Calculations for $CH_2(SH)_2$ using different ab initio methods[6,8] have been reported in the literature. The relative energies for conformations with C_2, C_s, C_1, and C_{2v} symmetry have been calculated by the HF method with Huzinaga's MINI-1*[8] and 6-31G**[6] basis sets and by the MP2/6-31G** method[6]. According to our calculations (see below) the C_{2v} structure corresponds to a maximum on the energy hyperface. The above calculations demonstrate that the conformational properties do not depend strongly on the calculational method. For this reason and because of the size of $CH_2(SCF_3)_2$, we performed calculations only at the HF/3-21G* level using the Gaussian 90 program[9]. Calculations for $CH_2(SH)_2$ with the HF/3-21G* method are included in this study to allow a direct comparison with the theoretical and experimental results for $CH_2(SCF_3)_2$. The vibrational frequencies were calculated for all fully optimized structures to ensure that the derived conformation corresponds to a minimum on the energy hyperface. For $CH_2(SH)_2$, the potential function for simultaneous rotation around both C–S bonds (C_2 symmetry) was calculated in steps of 30°, and full geometry optimizations were performed for the two minima. The global minimum occurs for the (+sc, +sc) conformation with $\Phi_1(SCSH) = \Phi_2(SCSH) = 57.7°$. The (ap, ap) conformer with C_{2v} symmetry ($\Phi_1 = \Phi_2 = 180°$)

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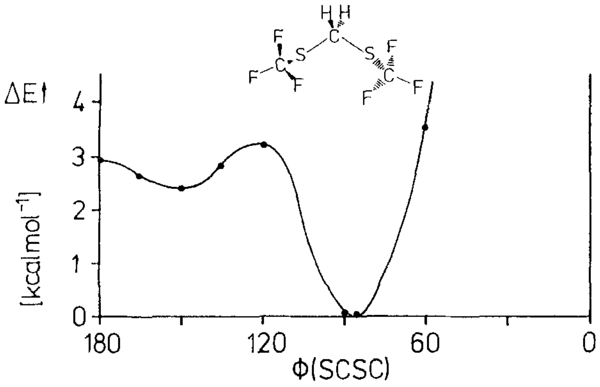
does not correspond to a stable structure, but to a transition state between two equivalent (ap, ap) conformations with $\Phi_1 = \Phi_2 = 154.9°$[10]. This stable structure is 2.9 kcal/mol higher in energy than the (+sc, +sc) conformer. In addition to these two conformations with C_2 symmetry, structures with C_s symmetry ($\Phi_1 = -\Phi_2 = 66.6°$, $\Delta E = 1.5$ kcal/mol) and C_1 symmetry ($\Phi_1 = 65.6°$, $\Phi_2 = 189.4°$, $\Delta E = 1.0$ kcal/mol) correspond to minima on the energy hyperface. In the C_1 conformer both S−H bonds lie on the same side of the SCS plane. An analogous search for stable conformers was performed for $CH_2(SCF_3)_2$. The potential function for structures with C_2 symmetry is shown in Figure 1. For small dihedral angles unreasonably short F···F contacts between the two CF_3 groups occur, and no structure optimizations were performed for $\Phi = 0°$ and 30°. The general shape of this potential function correspond to that for $CH_2(SH)_2$, but the global minimum for the (+sc, +sc) conformer is shifted from the dihedral angle of 57.7° in $CH_2(SH)_2$ to 86.0° in $CH_2(SCF_3)_2$. This increase is due to steric repulsions between sulfur and fluorine atoms of the opposite CF_3 group. For a dihedral angle of 60° the shortest S···F contact (ca. 280 pm) is considerably shorter than the respective van der Waals distance (320 pm). F···F contacts between the two CF_3 groups are longer than the respective van der Waals distance of 270 pm. The second stable structure with C_2 symmetry and dihedral angle of 152.0° (ap, ap) is predicted to be higher in energy by 2.4 kcal/mol. As may be expected from the two minima in the potential curve for C_2 conformers, a structure with C_1 symmetry and dihedral angles around 90 and 150° corresponds also to a minimum in the energy surface. Full geometry optimization of this (sc, ap) conformer leads to an energy of 0.7 kcal/mol relative to the (+sc, +sc) structure, and to dihedral angles $\Phi_1 = 76.7°$ and $\Phi_2 = 154.2°$. In this C_1 conformer of $CH_2(SCF_3)_2$ the two CF_3 groups lie on opposite sides of the SCS plane, in contrast to the result for $CH_2(SH)_2$, where both SH groups are predicted to be on the same side of this plane. (+sc, −sc) conformers with C_s symmetry do not form stable structures because of unreasonably close contacts between the two CF_3 groups. The calculated geometric parameters of the (+sc, +sc) and (sc, ap) conformers are included in Table 1.

Figure 1. Potential curve for C_2 symmetry ($\Phi_1 = \Phi_2$) of $CH_2(SCF_3)_2$



GED Analysis for $CH_2(SCF_3)_2$

The radial distribution function (RDF) is obtained by Fourier transformation of the molecular intensities. Figure 2 compares the experimental curve with calculated RDFs for the (+sc, +sc) conformer (C_2 symmetry) and for the (sc, ap) conformer (C_1 symmetry) which were obtained with the final structural data of Tables 1 and 2. The function for the (ap, ap) structural model (not shown in Figure 3) differs strongly from the experimental curve in the range $r > 280$ pm, and this conformation can be excluded. The curves for C_1 and C_2 models do not differ drastically, and the C_2 model is in better agreement with the experimental RDF. The fit of the experimental cuve is improved for mixtures of C_2 and C_1 conformers in a ratio of about 2:1. The preliminary geometric parameters derived from the RDF were refined by a least-squares analysis. The intensities were multiplied by a diagonal wight matrix, and known scattering amplitudes and phases were used[11]. Local C_{3v} symmetry was assumed for the CF_3 groups. This constraint is justified by the ab initio calculations which predict a tilt angle of less than 1°. The torsional angle $\tau(CF_3)$ describes the deviation of the CF_3 groups from the exact staggered orientation $[\tau(CF_3) = 0°]$. The experimental value is an "effective" angle due to the large-amplitude torsional vibrations. Only a mean value for the two C−S distances, $(C{-}S)_{mean}$, could be derived from the GED intensities, and the difference between these two bond lengths was set equal to the ab initio value. Furthermore, the calculated value was used for the HCH bond angle. The geometric parameters for the C_1 conformer were set equal to those of the C_2 structure, except for the dihedral angles and the SCS angle. The ab initio calculations predict a decrease of 2.7 for this latter parameter in the C_1 form. This difference was incorporated in the least-squares analysis. The dihedral angles for this minor conformer could not be determined in the GED experiment and were set equal to the ab initio values. Variations of these angles by ±10° had no effect on the fit of the experimental intensities. Vibrational amplitudes were collected in groups according to their distances, and amplitudes with low contributions were fixed in the least-squares analysis (see Table 2). With these assumptions seven geometric parameters and eleven vibrational amplitudes were refined simultaneously. Least-squares analyses were performed for various conformational mixtures. The best fit of the experimental intensities was obtained for a ratio of 70:30 with an estimated uncertainty of ±15%. The final results are listed in Table 1 (geometric parameters) and Table 2 (vibrational amplitudes).

Discussion

It the different multiplicities of the two conformers [2 for (+sc, +sc) and 4 for (sc, ap)] are taken into account and if entropy differences are neglected, the experimental conformational ratio [70(15)% (+sc, +sc) and 30(15)% (sc, ap)] corresponds to an enthalpy difference $\Delta H^0 = 0.9(5)$ kcal/mol. This value is indistinguishable from the ab initio value, $\Delta E = 0.7$ kcal/mol. Although this energy difference be-

Figure 2. Calculated radial distribution functions for C_1 and C_2 symmetry and experimental curve. The difference curve (bottom) corresponds to RDF(exp) − RDF(calc) for 70% C_2 and 30% C_1 conformers

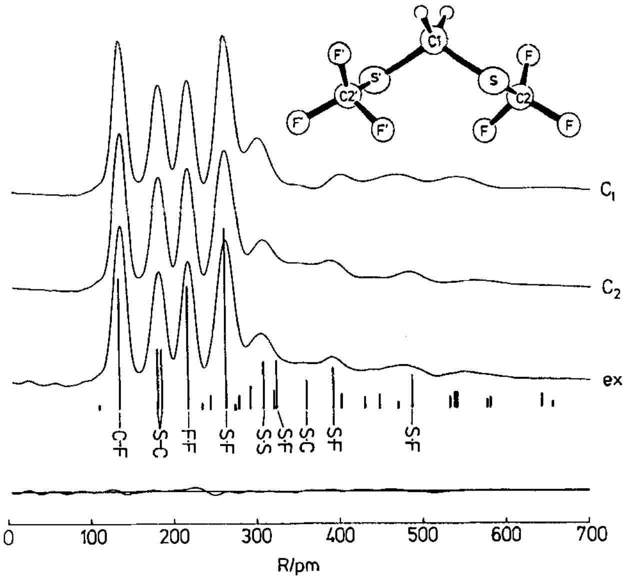


Table 1. Geometric parameters of $CH_2(SCF_3)_2$ from GED and ab initio calculations (C_2 and C_1 symmetry)

	GED[a] (+sc, +sc)	HF/3-21G* (+sc, +sc)	HF/3-21G* (sc, ap)
$(C–S)_{mean}$	181.4(3)	179.3	179.5
Δ(C–S) = (C1–S) – (S–C2)	4.3[b]	4.3	4.6
C1–S	183.6(3)	181.4	181.8
S–C2	179.3(3)	177.1	177.2
C–F	134.2(2)	134.9[c]	134.8[c]
C–H	109.5[d]	107.9	107.8
S–C–S	112.1(6)	115.8	113.1
C–S–C	98.2(10)	96.2	96.4
F–C–F	107.3(1)	108.4	108.4
H–C–H	107.6[b]	107.6	109.0
Φ_1 (SC1SC2)	79.1(10)	86.0	76.7
Φ_2 (SC1SC2')	79.1(10)	86.0	154.2
τ (CF_3)	12.8(12)	0.0	1.5
% (+sc, +sc)	70(15)	–	–
ΔE (kcal / mol)	–	0.0	0.7

[a] Distances r_a [pm] and angles $\angle_\alpha$ [°]; error limits are 3-σ values and include a possible scale error of 0.1%; for atom numbering see Figure 2. – [b] Ab initio value. – [c] Mean values are given for parameters which are not unique. – [d] Not refined.

tween the (+sc, +sc) and the (sc, ap) conformation is considerably lower in the sulfur compound relative to that in dihydroxymethane (ΔE = 3–5 kcal/mol), the anomeric effect still influences the conformational properties of $CH_2(SCF_3)_2$. This finding is in qualitative agreement with the theoretical calculations[6,8] which predict that anomeric interactions affect the conformational properties of $HX{-}CH_2{-}XH$ compounds. Their importance, however, decreases strongly for X = S, Se, Te, compared to X = O. Considering only steric interactions, the (ap, ap) conformation is expected to be the most stable structure. The dihedral angle Φ(SCSC) = 79.1(10)° in $CH_2(SCF_3)_2$ is larger than Φ(OCOC) angles in dimethoxymethane [63.3(9)°[11]] and 2,2-dimethoxypropane [52.0(12)°[21]]. A small dihedral angle Φ(SCSC) = 57.7° is predicted for $CH_2(SH)_2$, and this indicates that the increase of Φ in the SCF_3 compound is not due to stereoelectronic effects but rather due to steric interactions between the CF_3 groups with the opposite sulfur atoms.

Table 2. Interatomic distances [pm] and vibrational amplitudes [pm] for $CH_2(SCF_3)_2$ from GED[a]

C-H	110	7.1[b]		C1··C2	274	10.3(11)	a_6
C-F	134	4.4(1)	a_1	S··S'	304		
H··H	179	11.0[b]		S··C2'	356	13.7(32)	a_7
S-C2	179	4.9(2)	a_2	S··F'	387	14.7(20)	a_8
C1-S	184			C1··F	392		
F··F	216	5.5(2)	a_3	F··F'	427	12.1(35)	a_9
S··H	241	10.0[b]		C2··F'	444		
X[c]··H	233-481	20.0[b]		C2··C2'	466	16.2(23)	a_{10}
S··F	261	8.9(3)	a_4	S··F'	483		
Y[d]··F	288-322	22.0(30)	a_5	X[c]··F'	526-534	30.0[b]	
				X[c]··F'	571-688	25.5(81)	a_{11}

[a] Error limits are 3-σ values; for atom numbering see Figure 2. – [b] Not refined. – [c] X = C2 or F. – [d] Y = S or C1.

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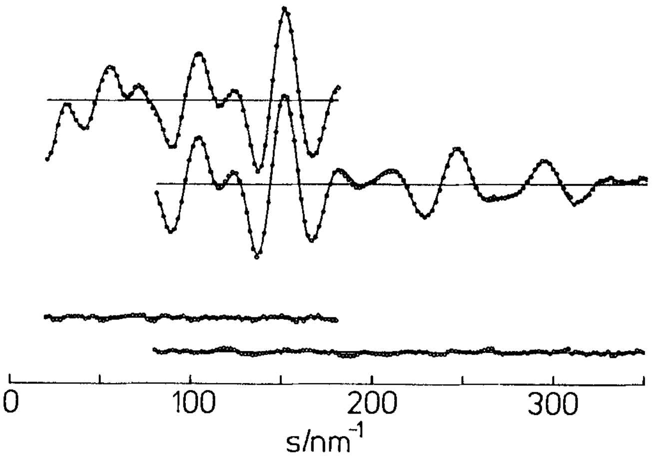
Experimental

$CH_2(SCF_3)_2$ was prepared from CH_2I_2 and $Hg(SCF_3)_2$ in 73% yield according to literature methods[12]; b.p. 78°C (ref.[12] 78°C). – The electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[13] at camera distances (nozzle-to-plate distance) of 25 and 50 cm and with an accelerating voltage of ca. 60 kV. The electron wavelength was determined from ZnO powder patterns. The sample reservoir was cooled to −40°C and the inlet system and nozzle were kept at room temperature. The photographic plates were analyzed by standard procedures[14], and averaged molecular intensities in the *s* ranges 20–180 and 80–350 nm^{-1} in steps of $\Delta s = 2\ nm^{-1}$ are presented in Figure 3.

Figure 3. Experimental (dots) and calculated (full line) molecular intensities and differences for $CH_2(SCF_3)_2$



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