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Structure and Conformation of Bis(methylthio)methane, $(MeS)_2CH_2$, Determined by Gas-Phase Electron Diffraction and ab Initio Methods

Elizabeth M. Page,*,† David A. Rice,*,† Kirsten Aarset,‡,§ Kolbjørn Hagen,‡ and Anthony R. J. Genge∥

Department of Chemistry, University of Reading, Whiteknights Park, Reading RG6 6AD, U.K.,
Department of Chemistry, Norwegian University of Science and Technology, N-7491, Trondheim, Norway, and
Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, U.K.

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The gas-phase structure and conformational properties of bis(methylthio)methane, $(MeS)_2CH_2$, have been determined by electron diffraction, augmented by results from ab initio molecular orbital calculations. The molecule was found to exist in the gas phase at ~100 °C, predominantly in the G^+G^+ form (70(18)%), where the CH_3 groups are on opposite sides of the SCS plane, with a smaller contribution from the GA form in the conformational mixture. The main conformer possesses C_2 symmetry with a dihedral angle ϕ(CSCS) of 54(6)°. The second conformer has C_1 symmetry with CSCS dihedral angles of 74° and 186° (ab initio values). Assuming entropy differences between the two conformers as obtained from MP2/6-311+G(d) calculations ($\Delta S = R \ln 2 + 2.72$ cal mol^{-1} K^{-1}), this composition corresponds to an enthalpy difference of $\Delta H = 2.2(6)$ kcal mol^{-1}. The corresponding ab initio/DFT enthalpy difference values at 373 K are 1.49 kcal mol^{-1} (HF), 2.38 kcal mol^{-1} (MP2), and 2.15 kcal mol^{-1} (B3LYP). The results for the main distances (r_g) and angles ($\angle_\alpha$) from the combined GED/ab initio (HF/6-311+G(d)) study of the G^+G^+ form of $(MeS)_2CH_2$ (with estimated 2σ uncertainties) are $r(C_{CH_3}-S) = 1.805(2)$ Å, $r(C_{CH_2}-S) = 1.806(2)$ Å, $r(C_{CH_3}-H) = 1.108(5)$ Å, $r(C_{CH_2}-H) = 1.098(5)$ Å, $\angle(C-S-C) = 102.8(24)°$, $\angle(S-C-S) = 115.9(3)°$, $\angle(H-C_{CH_2}-H) = 107.5°$ (ab initio), and $\angle(S-C_{CH_3}-H) = 108.9°$ (ab initio).

Introduction

Our interest in compounds of the type $CH_3YCH_2YCH_3$ (Y = S, Se, Te) stems from two different but complementary areas of research. The first area of interest involves the conformational properties of such molecules which have been the subject of much discussion among structural experimentalists[1−3] and theoreticians.[4−7] Molecules of the type $RYCH_2YR$ (R = H, CH_3, CF_3; Y = O, S, Se, Te) can display four different conformational arrangements with different symmetries depending upon the values of the dihedral angles around the C−Y bonds, as depicted in Figure 1. Ab initio molecular orbital calculations carried out on the compounds $CH_2(OH)_2$[5] and $CH_2(SH)_2$,[6] and on the methylated oxygen analogue $CH_3OCH_2OCH_3$[4] suggest that there is a preference for the G^+G^+ conformation with C_2 symmetry, as the G^+G^- (C_s) and the GA (C_1) forms are calculated to be of slightly higher energy. The preference for the G^+G^+ form of $CH_2(OH)_2$ was ascribed to the stabilizing effect in the molecule of an anomeric interaction. This stabilization effect, that favors the gauche form, is the delocalization of an oxygen lone pair from one oxygen atom into the σ^*(C−O) orbital formed by the adjacent oxygen atom ($p_y \rightarrow \sigma^*C$).[8] Although no structural measurements on $CH_2(OH)_2$ and $CH_2(SH)_2$ have been reported to support the conclusion drawn from ab initio calculations, gas-phase structural studies have been reported for $CH_3OCR_2OCH_3$ (R = H,[1] CH_3[9]), the results of which are in accord with the theoretical interpretation. More recently, the gas-phase structures of the molecules $CF_3SCH_2SCF_3$,[3] $PF_2S(CH_2)_3SPF_2$,[10] CH_3S_3H,[11] and $CH_3S_3CH_3$[2] have been determined and all were found to adopt the G^+G^+ conformation, indicating that it is the lowest energy form.

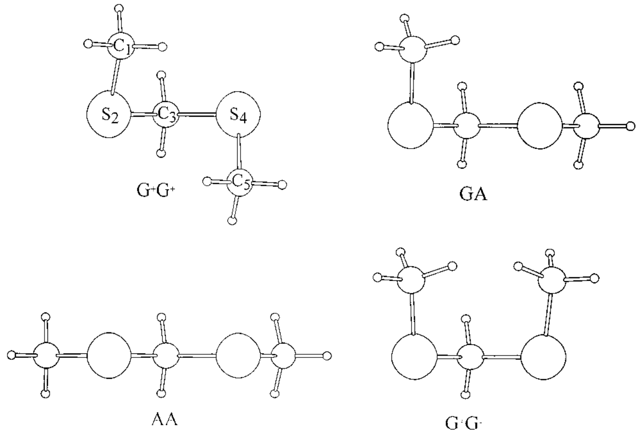

Figure 1. Diagrams of the four conformers of bis(methylthio)methane: G^+G^+ with C_2 symmetry, GA with C_1 symmetry, AA with C_{2v} symmetry, and G^+G^- with C_s symmetry.

The second research area concerning these molecules lies in their ability to display differing modes of chelation with d- and p-block ions. With Cu(I) and Ag(I), the methylene-bridged thio- and selenoethers yield three-dimensional networks incorporating channels which can host PF_6^- or BF_4^- anions.[12] As such, the

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* To whom correspondence should be addressed. E-mail: e.m.page@reading.ac.uk, d.a.rice@reading.ac.uk. Fax: +44 (0) 118 9316331.

† Department of Chemistry, University of Reading.

‡ Department of Chemistry, Norwegian University of Science and Technology.

§ Present address: Oslo College, Faculty of Engineering, N-0254 Oslo, Norway.

∥ Department of Chemistry, University of Southampton.

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structures are extended, three-dimensional arrays formed by ligand bridges between adjacent tetrahedrally-coordinated metal centers. In consideration of the strain angle, which would result from ligand chelation rather than bridging, this latter is expected to be the preferred mode of complexation. Thus, it was somewhat surprising to discover that reaction of $MeYCH_2YMe$ (Y = S, Se) with $SnCl_4$ yields mononuclear Sn(IV) species with the ligand chelated in a bidentate manner.[13] These compounds were the first structurally characterized examples of chelating methylene-bridged dithio- or diselenoethers. It is therefore of some relevance to understand the conformation and geometry of the parent ligands in order to appreciate their ability to complex in this seemingly strained fashion. We thus decided to undertake a combined electron diffraction and ab initio study of the chalcogenoethers $MeYCH_2YMe$ (Y = S, Se, Te), and the results for the thioether are presented here.

Experimental Section

Bis(methylthio)methane, $(MeS)_2CH_2$, Aldrich Chemical Co. (99%, bp 147 °C), was used without further purification to obtain electron diffraction data on the Reading gas diffraction apparatus fitted with an all-glass nozzle.[14] The sample was held at temperatures of 75−80 °C (long camera, LC) and 90−95 °C (short camera, SC) and the nozzle at temperatures between 90 and 95 °C (LC) and 100−105 °C (SC). The camera distances employed were 49.624 cm (LC) and 24.526 cm (SC), with an accelerating voltage of 42.02 kV. The electron wavelength (0.058 716 Å) was calibrated against diffraction patterns of benzene.[15] In the first experiment, the quality of the short camera data was not very good, and several new electron diffraction (ED) experiments were carried out to improve the data using a wider beam stop to reduce extraneous scattering. Three plates from the long camera and two plates from the short camera distances, scanned on the Agfa Arcus II scanner,[16] were deemed suitable for use in the final refinements. The data, covering the ranges $2.50 \leq s/\text{Å}^{-1} \leq 15.00$ and $7.00 \leq s/\text{Å}^{-1} \leq 28.00$ at intervals of $\Delta s = 0.25$ Å^{-1} (where $s = 4\pi\lambda^{-1} \sin\theta$ and 2θ is the scattering angle), were processed as previously described[17] using scattering amplitudes and phases taken from ref 18. The experimental intensity curves and the backgrounds are shown in Figure 2. Radial distribution (RD) curves were calculated in the usual way by Fourier transformation of the function $I'_m(s) = Z_C Z_S (A_C A_S)^{-1} sI_m(s) \exp(-0.002s^2)$, where $A = s^2F$ and F is the absolute value of the complex electron scattering amplitudes. Theoretical intensity data were used for $s \leq 2.25$ Å^{-1} in the experimental intensity curve before the experimental RD curve was calculated.

Molecular Orbital Calculations. It is not realistic to expect the electron diffraction method to be able to determine completely the structures of the different possible rotational conformers of bis(methylthio)methane, because the bonded distances and the valence angles of the different conformers will have only slightly different values. With the ED method it is only possible, in most cases, to determine the averages of these values and not the differences between them. These differences, however, are quantities which can be determined with confidence by ab initio molecular orbital calculations. Such calculations have also been shown to produce good starting values for the force constants needed to calculate the vibrational amplitudes and perpendicular amplitude corrections used in the analysis of the ED data and to give approximate values for the relative enthalpies and energies of the different conformers. Ab initio calculations (HF/6-311+G(d) and MP2/6-311+G(d)) were performed using the program GAUSSIAN 94[19] for the conformers G^+G^+ [$C_1-S_2-C_3-S_4$ (ϕ_1) and $C_5-S_4-C_3-S_2$ (ϕ_2) torsion angles $\phi_1 = \phi_2 \approx 60°$, C_2 symmetry], GA [$\phi_1 \approx 60°$, $\phi_2 \approx 180°$, C_1 symmetry], AA [$\phi_1 = \phi_2 = 180°$, C_{2v} symmetry], and G^+G^- [$\phi_1 = -\phi_2 \approx 60°$, C_s symmetry] of bis(methylthio)methane. DFT calculations (B3LYP/6-311+G(d)) were also made for the G^+G^+ and the GA conformers. In all calculations, the G^+G^+ form was found to be the lowest energy form, with the GA conformer 1.4−2.3 kcal mol^{-1} higher in energy and the AA and G^+G^- conformers higher again in energy. Cartesian force fields were calculated (MP2/6-311+G(d)) for the four different conformers. These calculations also provided theoretical values for enthalpy and entropy differences between conformers at the temperature where the experimental data were obtained. Results for torsion angles and relative conformational enthalpies are shown in Table 1.

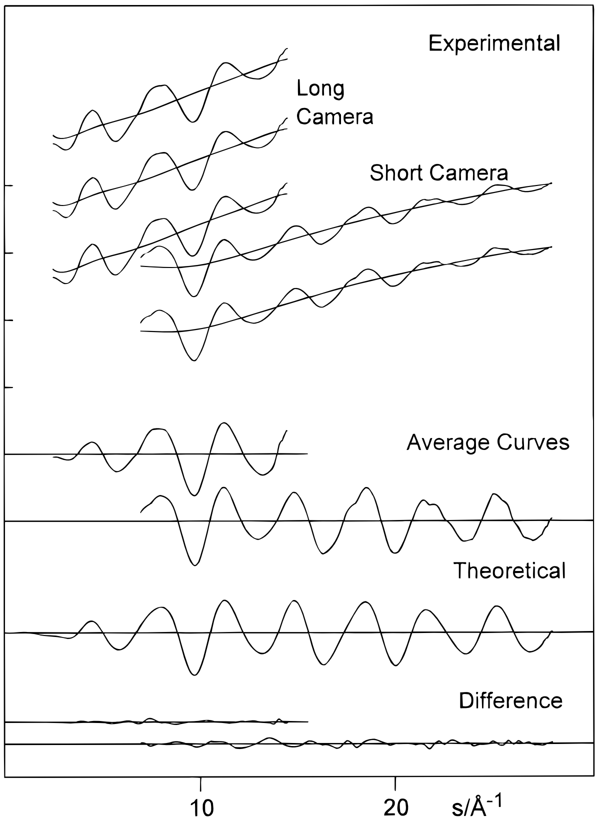

Figure 2. Intensity curves for bis(methylthio)methane. Long camera and short camera curves are magnified four times relative to the backgrounds on which they are superimposed. Average curves are in the form $sI_m(s)$. The theoretical curve is calculated from the final model shown in Table 2. Difference curves are experimental minus theoretical.

Normal Coordinate Calculations. The theoretical force field from the MP2 calculations was used as input to the program ASYM40,[20] together with the appropriate **U**-matrixes, to obtain a symmetry force field. A set of scale constants for the nonredundant set of internal force constants was then refined to fit the observed vibrational frequencies.[21] These force fields were used to calculate the vibrational amplitudes (l), perpendicular amplitude corrections (K), and centrifugal distortion constants (δr) used subsequently in the least-squares refinements described below. Four scale constants were refined: C−H stretch, 0.88; C−S stretch, 0.89; S−C−H/H−C−H bends, 0.89; and C−S−C/S−C−S bends, 1.01. The scale constants for the torsional force constants were kept constant at 1.00. Using these four scale constants, the experimental frequencies were fitted with an average deviation of $\Delta\nu = 7$ cm^{-1}.

TABLE 1: Calculated Torsion Angle Values and Enthalpy Differences between Conformers for Bis(methylthio)methane[a]

	HF/6-311 + G(d)				MP2/6-311 + G(d)				B3LYP/6-311 + G(d)	
	G^+G^+	GA	AA	G^+G^-	G^+G^+	GA	AA	G^+G^-	G^+G^+	GA
$\phi(C_1-S_2-C_3-S_4)$	67.52	74.14	179.54	83.83	67.69	74.08	158.59	82.84	67.26	73.64
$\phi(C_5-S_4-C_3-S_2)$	67.52	186.48	179.54	−83.83	67.69	191.48	158.59	−82.84	67.26	191.06
ΔH	0.00	1.49	3.45	3.65	0.00	2.38	5.13	3.02	0.00	2.15

[a] Torsion angles (ϕ) in degrees, relative enthalpies in kcal mol^{-1}.

TABLE 2: Parameter Values for the G^+G^+ Conformer of Bis(methylthio)methane from Electron Diffraction and Theoretical Calculations

parameter[a]	ED, $r_\alpha/\angle_\alpha$	ED, r_g	l	HF[b]	B3LYP[b]	MP2[b]
$\langle r(C-S)\rangle$	1.802(2)	1.806(2)		1.811	1.827	1.807
$\Delta r(C-S)$	[0.003]			0.003	0.006	0.006
$\langle r(C-H)\rangle$	1.080(5)	1.106(5)	0.079[d]	1.081	1.091	1.092
$\angle C_1-S_2-C_3$	102.8(24)			101.0	100.1	98.6
$\angle S_2-C_3-S_4$	115.9(3)			117.7	118.0	117.2
$\langle\angle S-C_5-H\rangle$	[108.9]			108.9	108.5	109.1
$\angle H-C_3-H$	[107.5]			107.5	107.8	107.5
$\phi(C_1-S_2-C_3-S_4)$	54(6)			67.5	67.3	67.7
$\%G^+G^+$	70(18)					
ΔH	2.2(6)			1.49	2.15	2.38
R^c	0.096					
			Dependent Distances			
$r(C_3-S_4)$	1.801(2)	1.805	0.048(3)[e]	1.809	1.824	1.804
$r(C_5-S_4)$	1.804(2)	1.806	0.050(3)[e]	1.812	1.830	1.810
$\langle r(S\cdots H)\rangle$	2.380(4)	2.393	0.130(15)	2.390	2.410	2.397
$r(C\cdots C)$	2.816(48)	2.819	0.133(32)	2.795	2.800	2.741
$r(S\cdots S)$	3.058(6)	3.058	0.066(11)	3.103	3.136	3.090
$r(C\cdots S)$	3.361(55)	3.362	0.186(32)	3.544	3.554	3.472

[a] Distances (r) are in angstroms, angles ($\angle$) are in degrees, enthalpy differences (ΔH) are in kcal mol^{-1}. Values in parentheses are 2σ plus corrections for uncertainties in the voltage, camera distances, etc. [b] Basis set used is 6-311+G(d). [c] $R = [\sum_i w_i \Delta_i^2 / \sum_i w_i (s_i I_i(\text{obsd}))^2]^{1/2}$, where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$. [d] Not refined. [e] Refined as a group.

Structure Analysis. Using the average values for the C−H bond distances and the S−C−H valence angles, the structure of each of the conformers of bis(methylthio)methane can be described by three distance and four angle parameters, in addition to the four torsion angles for the C−S bonds. The parameters chosen for the low-energy C_2 conformer are $\langle r(C-S)\rangle = {}^1/_2[r(C_1-S_2) + r(C_3-S_2)]$, $\Delta r(C-S) = [r(C_3-S_2) - r(C_1-S_2)]$, $r(C-H)$, $\angle S-C-S$, $\angle C-S-C$, $\angle S-C_3-H$, $\angle H-C_3-H$, and the four C−S torsion angles. C_{3v} symmetry was assumed for the two CH_3 groups. A trial structure was constructed from the appearance of the experimental radial distribution curve and from the ab initio and ASYM40 results. Refinements of this structure by the method of least-squares[22] using the electron diffraction data were carried out by adjusting a theoretical $sI_m(s)$ curve simultaneously to the experimental data sets using a unit weight matrix. Upon calculating theoretical radial distribution curves (see Figure 2) for the different possible conformers, it was clear that the majority of the molecules had a G^+G^+ conformation (C_2 symmetry). However, a minor amount of a second form had to be included in order to achieve the best fit to the experimental data. In dimethyltrisulfane ($CH_3-S-S-S-CH_3$), this minor form was found to be the G^+G^- conformer with C_s symmetry,[2] while, in bis(trifluoromethylthio)methane ($CF_3SCH_2SCF_3$), the minor form found was the GA conformer with C_1 symmetry.[3] Least-squares refinements of our data showed that, in bis(dimethylthio)methane, the best fit was obtained with the GA conformer as the minor form. This is supported by the results of the ab initio/DFT calculations. Including a third conformer in the molecular model did not improve the agreement with the experimental data. None of the torsion angles for the GA form or the H−C−S−C torsion angles for the G^+G^+ conformer could be well determined from the experimental data, and these parameters were therefore also kept constant at the ab initio values. The differences in bond distances and valence angles between the different conformers as well as the differences between the different types of C−H distances in the same conformer were kept constant at the values obtained from HF/6-311+G(d). The parameters $\Delta r(C-S)$, $\angle S-C_3-H$, and $\angle H-C_3-H$ could not be well determined from the experimental data, and these parameters were therefore kept constant at the ab initio values in the final refinement. In the preliminary refinements, a simple dynamic model was also tested but no improvement in the fit to the experimental data was obtained. Certain vibrational amplitude parameters constructed by grouping individual amplitudes were refined, as can be seen in the table of the final results (Table 2). Those vibrational amplitudes which could not be determined experimentally were kept constant at the ASYM40 values. In the final least-squares refinement, two distance, three angle, and five amplitude parameters and the conformational mixture were refined simultaneously. The most important results from the least-squares refinements are shown in Table 2 together with some of the parameter values obtained by the theoretical calculations. Table 3 contains the correlation matrix for the refined parameters. Intensity curves for the final model are shown in Figure 2, and the corresponding radial distribution curves are shown in Figure 3, where theoretical and difference curves for the G^+G^+ and the GA conformers are also shown.

TABLE 3: Correlation Matrix (×100) for Parameters of Bis(methylthio)methane

		σ_{LS}[a]	r_1	r_2	$\angle_3$	$\angle_4$	$\angle_5$	l_6	l_7	l_8	l_9	l_{10}	%
1	$\langle r(C-S)\rangle$	0.0003	100										
2	$\langle r(C-H)\rangle$	0.0018	−3	100									
3	$\angle S-C-S$	0.1215	−31	8	100								
4	$\angle C-S-C$	0.8602	−25	−1	52	100							
5	$\phi(C-S-C-S)$	2.1245	27	2	−21	−71	100						
6	$l(C-S)$	0.0005	3	−6	−4	−4	5	100					
7	$l(S\cdots H)$	0.0032	−1	−12	11	49	−35	17	100				
8	$l(C\cdots C)$	0.0113	−22	−21	18	39	−22	−5	21	100			
9	$l(S\cdots S)$	0.0037	37	7	−30	−61	63	10	−23	−43	100		
10	$l(C\cdots S)$	0.0112	−23	−2	11	26	−30	−6	10	37	−43	100	
11	$\% G^+G^+$	4.10	40	8	−32	−69	66	4	−30	−59	91	−56	100

[a] σ_{LS} is the standard deviation from least-squares refinements.

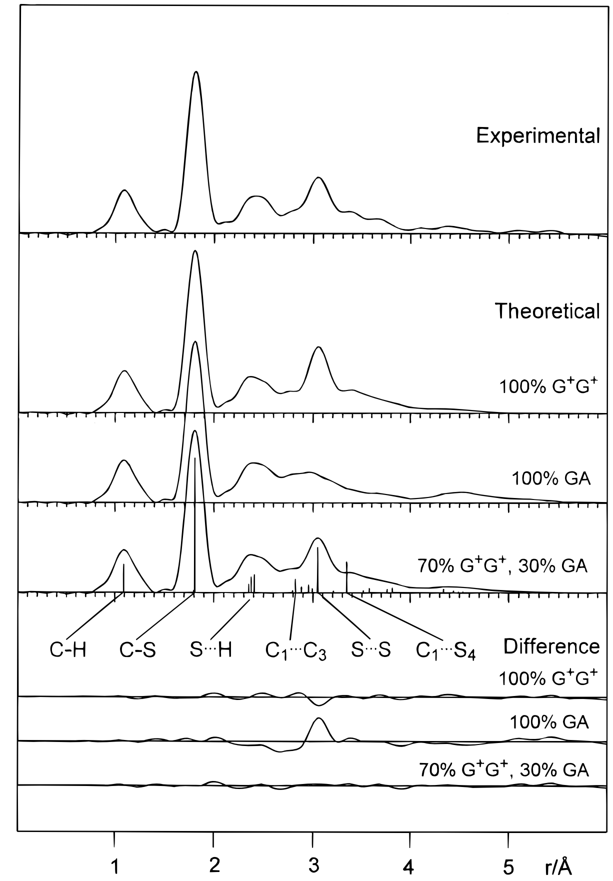

Figure 3. Radial distribution curves for bis(methylthio)methane. The experimental curve is calculated from the average intensity curve with theoretical data for $s \leq 2.25$ Å^{-1} and with convergence factor $B = 0.002$ Å^2. Vertical bars indicate interatomic distances in the molecule; the lengths of the bars are proportional to the weights of the terms.

Discussion

All theoretical calculations showed the G^+G^+ conformer, with C_2 symmetry, to be the most stable of the four possible conformers for the molecule $(CH_3S)_2CH_2$. The G^+G^+ conformer was calculated to be lower in energy than the second most stable (GA) conformer. Least-squares refinements, carried out on the electron diffraction data, showed that a model consisting of mainly the G^+G^+ conformer (70(18)%) with a smaller percentage of the GA conformer (30(18)%) gave the best fit to the experimental data. Thus, this conformational mixture was used to calculate the structural parameters and theoretical intensity and RD curves for $(CH_3S)_2CH_2$ shown in Table 2 and Figures 2 and 3, respectively. It may seem surprising that a second conformer (GA) is present when the calculated enthalpy difference between the GA and G^+G^+ forms is considered. However, in this study the importance of entropy factors is apparent. Allowing for the difference in multiplicity of the conformers (two for the G^+G^+ conformer and four for the GA conformer) and using the ab initio entropy differences from the MP2 frequency calculations ($\Delta S_{tot} = R \ln 2 + 2.72$ cal mol^{-1} K^{-1}), the experimental conformational ratio obtained corresponds to an enthalpy difference of 2.2(6) kcal mol^{-1}, which is larger than the value obtained in HF calculations but quite close to those obtained in MP2 and B3LYP calculations. The larger enthalpy differences between the G^+G^+ conformer and the other two less stable conformers (G^+G^-, 3.02 kcal mol^{-1}; AA, 5.13 kcal mol^{-1}; MP2 values) and the smaller total entropy differences (G^+G^-, 1.37 cal mol^{-1} K^{-1}; AA, 1.92 cal mol^{-1} K^{-1}) also justify the exclusion of both forms from the model used to determine the structure of $(CH_3S)_2CH_2$.

The anomeric effect is the explanation generally cited to explain the preference for the G^+G^+ conformation in molecules of the type $(RY)_2CH_2$ and $(RY)_2Y$.[8] Indeed for most of the examples studied experimentally ($CH_3OCH_2OCH_3$,[1] $CF_3SCH_2SCF_3$,[3] and CH_3SSSCH_3[2]), the C_2 conformation is the prevalent form. Contributions from structures with the anti arrangement of R groups are destabilized by lone pair−lone pair interactions, which are expected to decrease as the electronegativity and π-donor ability of Y decreases.[5,23] Thus, anomeric effects of $CH_2(YH)_2$ compounds are smaller for Y = S, Se, and Te than for Y = O, as shown by the observation that $CH_3OCH_2OCH_3$[1] exists solely in the G^+G^+ form whereas the sulfur analogue is a mixture of G^+G^+ and GA forms. The smaller anomeric effects shown by molecules containing the lower-row elements are attributed to non-hyperconjugative (steric and electrostatic) contributions and reduced orbital interactions which increasingly favor the anti structures on going down the group. The G^+G^- form having C_s symmetry is destabilized by steric repulsions between the now adjacent R groups and would be expected to be found only in molecules where R is small (R = H or CH_3) or Y is large.

Although the conformation adopted by $MeSCH_2SMe$ is not surprising, the size of the dihedral angle $\phi(C_1S_2C_3S_4)$ (54(6)°) is somewhat smaller than expected from ab initio calculations (68°) and by comparison with the equivalent angle found in similar compounds (see Table 4). It is smaller even than the value calculated for the thiol $(SH)_2CH_2$ (ϕ(SCSH) = 57.7° [6]), although there are no experimental data here for comparison. Using a dynamic model did not change this experimental value, and restricting the torsion angle to 68° gave a significantly poorer fit between experimental and theoretical RD curves. As the importance of anomeric interactions upon the conformational properties of $RYCH_2YR$ compounds is predicted to decrease strongly as the group 16 atom increases in size, a smaller

TABLE 4: Comparison of Structural Parameters for $CH_3SCH_2SCH_3$ and Related Molecules[a]

parameter type	HSMe	MeSMe r_g, $\angle_\alpha$	MeSSMe r_g, $\angle_\alpha$	$MeSCH_2SMe$ r_g, $\angle_\alpha$	$MeOCH_2OMe$ r_a, $\angle_\alpha$	$CF_3SCH_2SCF_3$ r_a, $\angle_\alpha$	MeSSSMe r_g, $\angle_\alpha$	$SnCl_4(MeSCH_2SMe)$ r, $\angle$
$r(C_{CH_3}-Y)$[c]	1.814(5)	1.807(2)	1.816(1)	1.805(2)	1.432(4)	1.793(3)	1.817(2)	1.809(6), 1.801(6)
$r(Y-C_{CH_2})$				1.806(2)	1.382(4)	1.836(3)		1.807(6), 1.818(6)
$\angle C-Y-X$[c]	96.5(5)			102.8(24)	114.6(5)	98.2(10)	103.1(5)	103.4(3), 102.7(3)
$\angle C-Y-C$		99.05(4)						
$\angle C-Y-S$			103.2(2)					
$\angle Y-C-Y$				115.9(3)	114.3(7)	112.1(6)		111.1(3)
ϕ(CSCS)				54(6)	63.3(9)	79.1(10)	79(5)	88.4(4), 132.2(3)
method[b]	MW	ED/MW	ED	ED	ED	ED	ED	X-ray
ref	27	25	26	this work	1	3	2	13

[a] Distances (r) are in angstroms, angles (∠) are in degrees. Values in parentheses are estimated uncertainties and may have different definitions in the different publications; see references. [b] ED = electron diffraction. MW = microwave. [c] Y = O, S. X = S, CH_2.

dihedral angle is expected in $(MeS)_2CH_2$ than in the equivalent oxygen compound, and this is found to be the case (ϕ(COCO) = 63.3(9)° in $MeOCH_2OMe$). Calculations at the HF/6-31G(d) level resulted in a ϕ(COCO) torsion angle of 67° for this molecule, which is close to the value obtained experimentally.[1] Steric interactions of the methyl groups would be expected to increase the dihedral angle. This is supported by the observation that when the methyl group of $MeSCH_2SMe$ is replaced by the more bulky CF_3 group in $CF_3SCH_2SCF_3$,[3] the torsion angle was found to increase to 79(1)°, which was assumed to be due to steric interactions between the CF_3 groups and the opposite sulfur atoms.

The C−S bond length in $MeSCH_2SMe$ (r_g = 1.805(2), 1.806(2) Å) was refined as an average of the two nonequivalent C−S distances with a fixed difference from the ab initio calculations. The value obtained is in excellent agreement with that found for dimethyl sulfide (r_g = 1.807(2) Å)[25] and compares well with the ab initio values.

The valence angle at the central sulfur atom in $(MeS)_2CH_2$ ($\angle$C−S−C = 102.8 (24)°) is considerably smaller than that in the equivalent oxygen compound ($\angle$C−O−C = 114.6(5)°), which would be expected from a consideration of increased steric interactions around the smaller atom. The value found for $MeSCH_2SMe$ compares well with that calculated from the ab initio calculations of 101°. The experimentally determined angle at the central carbon atom in $MeSCH_2SMe$, $\angle$S−C−S = 115.9(3)°, is also fairly close to the calculated value of 117.7° and to that in dimethoxymethane (114.3(7)°).

In the X-ray crystal structure of the complex $[SnCl_4(MeSCH_2SMe)]$, the dithioether was found to be bidentately coordinated to the metal atom to give a highly-strained four-membered CSSnS ring.[13] The dithioether maintains an approximate G^+G^+ configuration with the Me groups directed on opposite sides of the SnS_2Cl_2 plane. A consideration of the structural parameters in $[SnCl_4(MeSCH_2SMe)]$ shows that the terminal C−S bonds of the ligand and the valence angles at the central sulfur atoms ($\angle$C−S−C) are virtually unchanged upon coordination to the metal atom, as can be seen from Table 4. The central $\angle$S−C−S angle contracts only slightly on coordination to the metal atom in $[SnCl_4(MeSCH_2SMe)]$ ($\angle$S−C−S = 115.9(3)° in $MeSCH_2SMe$; $\angle$S−C−S = 111.1(3)° in $[SnCl_4(MeSCH_2SMe)]$). It seems that complexation of $MeSCH_2SMe$ has little effect on the terminal C−S bonds or angles but that the strain is relieved by an increase in the dihedral angles and by a ring pucker such that C_3 is lifted out of the plane of the S_2SnS_3 atoms. That the ring is still relatively strained can be seen in the acute angle of 67.82(5)° subtended by the chelating S atoms at the Sn atom. The major conformational change upon coordination to the metal atom is seen in the values of the dihedral (CSCS) angles, which increase from 54(6)° in the free ligand to 88.4(4)° and 132.2(3)° in the complex as the molecule twists to form the four-membered chelate ring.

Conclusions

The molecule $(MeS)_2CH_2$ was shown to exist predominantly in the G^+G^+ form, having C_2 symmetry. This form is also predicted to be the most stable by ab initio/DFT calculations, and it is the conformation generally assumed by molecules of the type CH_3YXYCH_3 (X = S, CH_2; Y = O, S, Se). The experimentally determined geometrical parameters of the C_2 form of $CH_3SCH_2SCH_3$ are similar to those obtained for other molecules of this type, the only anomaly being the relatively small dihedral angle. A comparison of the parameters in the free molecule with those of chelated $CH_3SCH_2SCH_3$ reveals that the methyl groups twist further out of the SCS plane upon coordination, but there are few other significant structural changes.

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