

MOLECULAR MECHANICS (MM3) CALCULATIONS ON SULFIDES

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The structures of eleven sulfide compounds including methanethiol, ethanethiol, dimethyl sulfide, ethyl methyl sulfide, di-*tert*-butyl sulfide, thiacyclopentane, thiacyclobutane, 5-thiabicyclo [2.1.1] hexane and 7-thiabicyclo [2.2.1] heptane have been calculated to agree with experimental data, along with the vibrational spectra of the first three of these. The heats of formation of 24 sulfides (including mercaptans) have also been calculated to agree with experimental data. In general, the force field for sulfides seems to be similar in accuracy with that for hydrocarbons.

INTRODUCTION

Earlier papers have described the MM3 force field,[†] which has previously been used for calculations on hydrocarbons¹ and several kinds of functionalized molecules.²⁻⁵ The present work is concerned with the extension of these calculations to dialkyl sulfides, including mercaptans.

Over the years it has been shown⁶ that there are many errors, mostly small, built into the MM2 force field. Rather than trying to continue to patch these, it was decided to start again from the beginning, and develop a general new force field, which is called MM3. In addition to fitting the information previously in agreement with MM2,[‡] it was desirable to fit additional information, particularly including vibrational spectra.

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† The MM3 program is available to all users from the Technical Utilization Corporation Inc., 235 Glen Village Court, Powell, Ohio 43065, and to commercial users only from Molecular Design Ltd., 2132 Farallon Drive, San Leandro, California 94577. The current version is available to run on most types of computers, and interested parties should contact one of the distributors directly.

‡ The MM2 force field is summarized in Ref. 41. The original program (MM2(77)) is available from the Quantum Chemistry Program Exchange, Creative Arts Building 181, 840 State Highway 46 Bypass, Bloomington, Indiana 47405, Program 395. The latest version of MM2, referred to as MM2(87), is available to academic users from QCPE, and to commercial users from MDL (see previous footnote).

RESULTS AND DISCUSSION

The procedure used began with the MM2 force field as a starting point. Because of various changes in the potential functions and in the hydrocarbon parameters, preliminary structures were initially calculated using the MM3 force field but the MM2 parameters, and these were only fair. Systematic adjustments were then made to the various parameters so as to improve the structures. Additionally, the vibrational spectra were calculated for three simple model compounds – methylmercaptan, ethylmercaptan and dimethyl sulfide. After the parameter optimization had proceeded far enough to give good structures and acceptable vibrational spectra, the heats of formation for a set of sulfides were also fitted, and all of these things were optimized simultaneously. The optimization methods were mostly trial and error, although least squares methods were used in the heat of formation calculations. As noted previously,⁷ the more general use of least squares methods for optimizing the structural parameters (as introduced by Lifson and Warshel⁸) did not work very well unless things were adjusted by hand in addition, and such procedures require enormous amounts of computer time. They were consequently not used in the present work, except for the heats of formation. (Standard least squares methods work directly with homogeneous data sets, where all the elements consist of quantities measured in the same units, and only their relative weightings need to be decided. In the present instance one wants to optimize many different kinds of physical quantities, and one needs to decide the relative weights of these different kinds of quantities. While we did this

Table 1. MME force field parameters for sulfur¹

<i>Torsion</i>				V1	V2	V3	
Atom type nos							
15	1	1	15	1.250	-0.300	0.000	
15	1	15	1	0.000	-0.900	0.300	
15	1	1	15	1.250	-0.300	0.000	*5
15	1	15	15	0.000	-0.900	0.300	*5
1	1	1	15	0.000	0.200	0.400	
1	1	15	1	-0.440	-0.260	0.600	
5	1	1	15	0.000	0.000	0.540	
1	1	15	44	-0.500	0.000	0.267	
5	1	15	1	0.000	0.000	0.660	
5	1	15	44	0.000	0.000	0.400	
1	1	1	15	0.000	0.200	2.150	*5
1	1	15	1	-0.440	-0.260	1.450	*5
56	15	56	56	0.000	0.000	1.150	*4
15	56	56	56	0.000	0.000	1.150	*4
5	56	56	15	0.000	0.000	0.540	
56	15	56	5	0.000	0.000	0.660	
5	1	56	15	0.000	0.000	0.540	
56	1	1	56	0.000	0.000	1.160	*5
56	15	56	1	0.000	0.000	1.160	*5
56	1	56	1	0.000	0.000	1.160	*5
1	1	56	15	0.000	0.000	1.160	*5
2	1	15	44	0.000	0.000	0.270	
15	1	2	5	0.000	0.000	0.400	
15	1	2	2	0.000	0.000	-0.300	

<i>Torsion-stretch</i>			KTS
Atom type nos			
1	15		0.1700

<i>Bonds</i>				
Bond type		<i>k</i> (s)	<i>l</i> (0)	
15	44	3.87	1.3420	
1	15	3.00	1.8050	
1	15	3.00	1.8080	*5
15	56	3.00	1.8140	*4

<i>Electronegativity corrections to <i>l</i>₀</i>				
Bond type	End of bond		Atom type	Correction
1	15	15	44	0.020
1	1	1	15	-0.001
56	56	56	15	-0.010
2	1	1	15	-0.010

<i>Bond dipole moment</i>			
Bond type	Moment		
1	15	1.20	
15	44	-0.90	
15	56	-1.20	*4
1	15	1.20	*5

(continued)

Table 1. (Continued)

<i>Van der Waals</i>					
Atom type			Epsilon	Radius	
44			0.020	1.6200	
<i>Angles</i>					
Atom types			$k(b)$	Theta(0)	Ed. type
1	15	44	0.650	96.000	
1	1	15	0.740	108.000	1
1	1	15	0.740	109.500	2
1	1	15	0.740	110.100	3
1	15	1	0.840	95.900	
5	1	15	0.740	110.800	1
5	1	15	0.740	110.000	2
5	1	15	0.740	108.000	3
2	1	15	0.650	107.800	1
2	1	15	0.650	107.800	2
2	1	15	0.650	113.900	3
1	1	15	0.740	108.000	1
1	1	15	0.740	109.500	2
1	1	15	0.740	110.100	3
1	15	1	0.840	96.900	
15	56	56	0.500	100.500	0
56	15	56	0.470	94.300	
15	1	15	0.420	110.000	
15	1	15	0.420	110.000	
1	56	15	0.740	109.200	
5	56	15	0.740	111.500	
<i>Stretch-bend</i>					
7	-0.040	X-S-Y			
8	0.010	X-S-H			
16	0.290	X-S-Y		*4	
20	0.280	X-S-Y		*5	
<i>Hydrogen bonding</i>					
2....44	0.200	2.830			
15....44	0.200	2.550			

^a Atom type numbers are 1 for (sp³) carbon, 5 for hydrogen attached to carbon and 44 for hydrogen attached to sulfur. If the carbon is contained in a four-member ring, it is type 56. Parameters not given are defined in the program and published.¹ Bond lengths and angles are given in Å and degrees throughout this manuscript and otherwise CGS units are used. For further information, see the MM3 operations manual.

(Ref. 7) we found that it is expedient to simply adjust the parameters being optimized, rather than to very indirectly adjust the weighting scheme. The application of trial and error methods becomes increasingly difficult as the size of the data sets increase, however, and we may be close to the practical limit for the use of these methods at this point.)

The parameters required to define the force field for these compounds are given in Table 1. They must be added to those given previously for hydrocarbons² to obtain the full force field. These parameters supersede the preliminary set which was included in MM3(90),

and which were marked with ** to indicate that they were preliminary.

Infrared spectra for methanethiol, ethanethiol and dimethyl sulfide were used to optimize the bond stretching and angle bending constants in these molecules. Table 2 shows the experimental and calculated vibrational spectrum of each compound. The original experimental assignments of the methyl rocking frequencies of dimethyl sulfide were rather uncertain.⁹ From the other calculations and experimental spectra shown in Table 1, it seems unlikely that any of these frequencies could be above 1200 cm⁻¹. We have therefore revised

Table 2. Vibrational spectra (cm^{-1}) of some simple sulfur compounds

Methanethiol ¹⁰				Ethanethiol ¹¹				Dimethyl sulfide ⁹			
MM3	IR	Δ	Mode	MM3	IR	Δ	Mode	MM3	IR	Δ	Mode
2982	3000	-18	C—H	2930 _{av}	2950	-20	C—H	2947 _{av}	2924	+23	C—H
2980	2870	+10	C—H	2586	2575	+11	S—H	1434	1460	-26	CH ₃ def.
2875	—	—	C—H	1493	1450	+43	CH ₂ scis.	1426	—	—	CH ₃ def.
2585	2597	-12	S—H	1468	1450	+18	CH ₃ def.	1418	1420	-2	CH ₃ def.
1420	1475	-55	CH ₃ def.	1457	1385	+72	CH ₃ def.	1415	—	—	CH ₃ def.
1414	1430	-16	CH ₃ def.	1442	—	—	CH ₃ def.	1356	1325	-31	CH ₃ def.
1352	1335	+17	CH ₃ def.	1376	1309	+67	CH ₂ twist	1353	1304	+49	CH ₃ def.
1013	1060	-57	H—C—S	1269	1269	0	CH ₂ wag	1027	1040	-13	CH ₃ rock
1008	957	+61	H—C—S	1035	1097	-62	CH ₃ rock	1021	1026	-5	CH ₃ rock ^a
823	803	+20	C—S—H	1016	1049	-33	CH ₃ rock	1010	976	+34	CH ₃ rock ^a
695	704	-9	C—S	975	978	-3	C—C	1002	919	+83	CH ₃ rock
249	—	—	torsion	850	870	-20	C—S—H	702	704	-2	S—C asym.
rms	—	34	—	801	745	+56	CH ₂ rock	683	683	0	S—C sym.
				662	660	+2	S—C	285	285	0	C—S—C
				334	332	+2	C—C—S	219	—	—	torsion
				268	—	—	torsion	188	—	—	torsion
				205	—	—	torsion	rms	—	30	—
				rms	—	35	—	—	—	—	—

^aThe lines at 1274 and 1243 cm^{-1} were assigned to these vibrations in Ref. 9. The two bands cited here were interpreted as combination bands.

two of these original assignments as shown in Table 2. The average rms error in the fit of the three compounds in Table 2 to the experimental spectra is 33 cm^{-1} , which is similar to the fit for hydrocarbons.¹⁻⁵

Dimethyl sulfide

A microwave study on this compound has been reported.¹² It was found to be in a C_{2v} conformation with both methyl groups staggered with respect to the adjacent C—S bond. The results of this study are shown in Table 3 and compared with the corresponding MM3 values.

Methanethiol

The structure of this compound and the barrier to internal rotation are known from microwave experiments.^{15,16} The results of these experiments are shown in Table 4 together with the corresponding MM3 values.

Ethanethiol

Three staggered molecular conformations are possible for ethanethiol, two enantiomers of C_1 point group symmetry and a single form of C_s symmetry. The

Table 3. The structure of dimethyl sulfide

Parameter	MW ¹² (r_s)	ED ¹³ (bond lengths r_b , bond angles r_{av})	MM3
C—S	1.802(2)	1.807(2)	1.808
C—S—C	98.87(17)	99.05(4)	98.1
S—C—H _a	110.75	—	109.8
S—C—H _b	106.6	—	109.2
Torsional barrier	2.3	2.1 ^b	2.25
I_A	28.376 ^b	28.519 ^c	29.009/2.03%
I_B	66.314 ^b	66.522 ^c	65.931/-0.58%
I_C	88.387 ^b	88.488 ^c	88.371/-0.02%

^aMW and ED are used throughout this manuscript to represent microwave and electron diffraction respectively, methods of structure determination.

^bReported in Ref. 14. The moments of inertia are the effective values for the ground vibrational state.

^cMoments of inertia for the zero-point average structure.

Table 4. Comparison of the calculated and observed structures of methanethiol

Parameter	MW ^{15,a} (r_0)	MW ^{16,a}	MM3 ^a
C—S	1·819(5)	1·8177(2)	1·825
S—H	1·335(10)	1·3291(40)	1·343
C—S—H	96·5(5)	100·27(17)	96·8
C—H	1·092(10)	1·1039(20)	1·112
H—C—H	109·75(5)	110·27(17)	109·4
Torsional barrier	1·27		1·28
I_A		0·493	0·838/—
I_B		6·502	6·559/0·87%
I_C		6·777	6·845/1·00%

^aThe structural parameters correspond to the staggered geometries.

Table 5. Observed and calculated structures of ethanethiol

Parameter	MW structure ²² (r_s)		MW structure ²¹ (R_s)		MM3	
	<i>gauche</i>	<i>trans</i>	<i>gauche</i>	<i>trans</i>	<i>gauche</i>	<i>trans</i>
C—C	1·528(7)	1·529(6)	1·530	1·530	1·534	1·533
C—S	1·814(9)	1·820(5)	1·829	1·829	1·833	1·833
<CCS	113·69°(48)	108·57°(32)	—	—	111·7	111·1
<CSH	96°(57)	96·22°(38)	95·23°	95·23°	97·0	96·7
S—H	1·336(10)	1·322(6)	1·328	1·328	1·343	1·343
ω_{CCSH}	61·75°(97)	180°	60°	180°	61·8	180·0
I_A	17·580	17·784			18·360/4·4%	17·512/—1·5%
I_B	95·448	92·124(2)			95·171/—0·3%	95·632/3·8%
I_C	104·283(3)	103·520(2)			104·528/0·2%	106·668/3·0%

spectra of ethanethiol in the amorphous solid (glass) and crystalline forms at low temperature led to the conclusion that the *gauche* form is more stable in the crystal,¹⁷ and, from calorimetric data, an enthalpy difference of 0·3 kcal mol⁻¹ was estimated. A number of microwave studies of the molecule have been reported.^{18–22} One of the more recent MW studies²¹ shows that the *gauche* conformer is more stable than the *trans* form by $0·41 \pm 0·04$ kcal mol⁻¹. The r_s structures for both the *gauche* and *trans* forms have been reported by Nakagawa *et al.*²² and r_s structures for both forms have also been proposed by Schmidt and Quade.²¹ The results of these MW studies are shown in Table 5 together with the corresponding MM3 values.

Table 6. Relative energies of different conformations of ethanethiol (kcal mol⁻¹)

Conformation	E_{rel} (obs.) ^{17,23}	E_{rel} (calc.)
C_1 (G)	0·0	0·0
C_2 (T)	0·30	0·29
<i>Ecl</i> (H—H)	1·42	1·25
<i>Ecl</i> (H—Me)		1·30
C_3 <i>Ecl</i> (Hs on C)		3·97
C_1 <i>Ecl</i> (Hs on c)	3·75	3·66

The relative energies of the different conformations of ethanethiol are shown in Table 6 and compared with the experimental values which are available.

Ethyl methyl sulfide

The bond distances (r_g) and angles (θ_a) in ethyl methyl sulfide have been determined by gas electron diffraction.²⁴ The two C—S bond lengths have been estimated independently with the aid of the rotational constants for the *trans* conformer reported by Imaishi and Hayashi.²⁵ The dihedral angle for the *gauche* conformer was found to be $66 \pm 9^\circ$ and the fraction of the *trans* conformer in the gas phase at 20 °C is reported to be $N_t/(N_t + N_g) = 0·25 \pm 0·15$. If there is 25% of the *trans* form at 20 °C the enthalpy difference (ΔH) is $\cong 0·25$ kcal mol⁻¹, favoring the *gauche* form. However, if there is 40% of the *trans* form at 20 °C ΔH is $\cong 0·16$ kcal mol⁻¹, favoring the *trans* form. Spectroscopic experiments have found that the two conformers have nearly the same energy in the gas phase,²⁶ the *gauche* conformer being 30 ± 50 cal mol⁻¹ more stable.²⁷ The MME calculations give an enthalpy difference of 0·13 kcal mol⁻¹, favoring the *trans* form. Table 7 shows the results of the electron diffraction study together with the corresponding MM3 values.

Table 7. The observed and calculated structures of ethyl methyl sulfide

Parameter	Gas ED structure (r_g) ^a	MM3		
		<i>gauche</i>	<i>anti</i>	av.
C—C	1.536(8)	1.534	1.533	1.534
C—H	1.111(8)	1.113	1.113	1.113
C—S(methyl)	1.806(27) ^b	1.810	1.808	1.809
C—S(methylene)	1.818(27) ^b	1.820	1.816	1.818
C—S(av)	1.813(4)	1.815	1.812	1.814
<CSC	97.1(1.1)	99.6	98.1	98.9
<SCC	114.0(0.5)	112.5	111.0	111.8
<HCH	109.6(1.4)	107.9	108.1	108.0
ω_{CSC} (<i>gauche</i>)	66(9)	72.3		
I_A	5.252 ^c		5.375/2.34%	
I_B	26.458 ^c		26.558/0.38%	
I_C	30.099 ^c		30.304/0.68%	

^a Seems to be weighted *trans* and *gauche* parameters.

^b These distances were determined separately by a joint analysis of ED and MW data. The rest of the parameters obtained by the joint analysis were essentially equal to the ED values given in this table.

^c Moments of inertia obtained from the best-fit rotational constants corresponding to the r_a structure of the *trans* conformer derived from the combined analysis of ED and MW data. The r_a values for all the bond lengths (except C—H) are 0.002 Å smaller than the r_g values given in Table 7. The r_g value of C—H is 1.096 Å. Our calculated moments of inertia should be ca 0–1% larger than the experimental ones, here and in general.

Di-*tert*-butyl sulfide

The molecular structure of di-*tert*-butyl sulfide has been investigated by gas electron diffraction.²⁸ The molecule has C_2 symmetry. The structure of this molecule is very strained due to steric hindrance between the two bulky *tert*-butyl groups. Experimentally (ED)²⁸ it is found that the *tert*-butyl groups evade each other by tilting away by 7(2)° and by torsionally displacing by 12(8)° from the staggered geometry. The experimental value for the C—S—C angle is found to be larger in this molecule than in dimethyl sulfide and methyl ethyl sulfide by about 14°, and the S—C bond length (r_g) is longer by about 0.04 Å than in the other molecules. The MM3 calculations show the torsional displacement to be about 10°, the C—S—C angle to be wider by 15° and

the C—S bond length longer by about 0.04 Å than in the other compounds. Table 8 compares the structures of di-*tert*-butyl sulfide obtained from ED study and MM3 calculations.

Thiacycloalkanes

Some of the parameters for four- and five-membered ring sulfides were taken to be different from the parameters for open-chain compounds. The four-membered ring parameters were based on electron diffraction data for thiacyclobutane²⁹ and 5-thiabicyclo[2.1.1]hexane.³⁰ The parameterization of the five-membered rings was based on electron diffraction data for thiacyclopentane³¹ and 7-thiabicyclo[2.2.1]heptane.³⁰

Thiacyclobutane

The structure of thiacyclobutane has been determined from a combination of electron diffraction and microwave spectroscopy.^{29,32} A nematic NMR structure of this molecule is also known.³³ The ring is puckered like cyclobutane (contrary to oxetane) and the potential function is found to have a double minimum with a barrier of 0.73 kcal mol⁻¹ at the planar configuration.³² The frequency of the ring-puckering motion obtained from precise microwave intensity measurements is reported³² to be 140 cm⁻¹. The MM3 force field gives a barrier of 0.73 kcal mol⁻¹ and the frequency of the ring puckering motion is calculated to be 166 cm⁻¹. Table 9 shows the results of the experimental

Table 8. The observed and calculated structures of di-*tert*-butyl sulfide

Parameter	ED (bond lengths r_g , bond angles r_a)	MM3
S—C	1.854(5)	1.852
C—C	1.539(3)	1.540
C—H	1.127(4)	1.112
<CSC	113.2(12)	113.9
<SC ² C ³	102.2(9)	106.2
<CCC	109.6(5)	109.2
<CCH	111.2(11)	111.9
Tilt ^a	7.1(20)	3.7

^a The tilt angle of the *tert*-butyl groups is the angle between the C—S bond and the line from the carbon to the point in the plane containing the three attached methyls which is equidistant from all of them.

Table 9. The observed and calculated structures of thiacyclobutane

Parameter	ED ²⁹ (bond lengths r_g , bond angles r_{av})	NMR ³³	MM3
C—C	1.549(3) ^b	1.550	1.550
C—S	1.847(2) ^b	1.845	1.844
C—S—C	76.8(3) ^a	76.7	76.8
C—C—C	95.6(4) ^a	95.2	95.3
C—C—S	90.6(3) ^a	90.9	90.5
$\langle C^2SC^4-C^2C^3C^4 \rangle$	26(2) ^a		27.7
I_A^c	8.301		8.394/1.12%
I_B^c	12.575		12.666/0.73%
I_C^c	18.897		18.914/0.09%

^a Derived from a joint analysis of diffraction intensities and rotational constants.

^b Derived from the r_{av} structure.

^c Calculated from the effective rotational constants for the ground vibrational state determined by MW spectroscopy.^{29,32}

Table 10. The observed and calculated structures of thiacyclopentane

Parameter	ED ³¹ (r_g, C_2)	MM3	
		C_2	C_s
C—S	1.839(2)	1.840	1.823
C—C	1.536(2)	1.537	1.548
$\langle CSC \rangle$	93.4(5)	93.3	88.7
$\langle CCS \rangle$	106.1(0.4)	106.6	105.2
$\langle CCC \rangle$	105.0(0.5)	105.5	108.7
$\omega(S^1-C^2)^a$	14.8(0.5)	14.2	43.0
$\omega(C^2-C^3)$	40.5(1.2)	39.0	31.0
$\omega(C^3-C^4)$	52.5(1.6)	50.4	0.0

^a ω indicates the dihedral angle about the central bond.

studies and the MM3 calculations on the geometry of this compound.

Table 9 shows that the parameters fit quite well. I_A deviates more than 1% from the experimental value, but the overall fit seems to be good.

Thiacyclopentane

Some evidence exists that the pseudo-rotation of the ring in thiacyclopentane is restricted and that the conformation possessing C_2 symmetry is preferred.³¹ Pitzer and Donath³⁴ estimated this C_2 conformation to be about 3 kcal mol⁻¹ more stable than the C_s , and the value was later determined³⁵ to be 2.8 kcal mol⁻¹. Such a high barrier to pseudo-rotation is to be contrasted with that in cyclopentane (zero). This experimental value was determined using a heat capacity method and may contain considerable error. The MM3 value is only 1.78 kcal mol⁻¹ and seems to be too low. However, in order to fit the structure and the heat of formation, this is the best we can do with the barrier. Table 10 shows the results of the ED study together with the corresponding MM3 values.

5-Thiabicyclo[2.1.1]hexane and 7-thiabicyclo[2.2.1]heptane

The structures of both of these compounds have been determined by gas electron diffraction by Fukuyama *et al.*³⁰ In case of 7-thiabicyclo(2.2.1)heptane, the rotational constants obtained by Irie *et al.*³⁶ by microwave spectroscopy were also taken into account. This made it possible to determine the two non-equivalent C—C bond lengths in this molecule independently. The calculated and experimental structures for these molecules are given in Tables 11 and 12.

Table 11. The observed and calculated structures of 5-thiabicyclo[2.1.1]hexane

Parameter	ED ³⁰ (bond lengths r_g , bond angles, r_α)	MME
$(C^1-C^2, C^2-C^3)_{av}$	1.539(16)	1.546
C^1-C^6	1.564(24)	1.552
C—S	1.865(4)	1.870
C—C _{av}	1.549	1.549
$\langle CSC \rangle$	69.5(6)	68.0

Table 12. The observed and calculated structures of 7-thiabicyclo[2.2.1]heptane

Parameter	ED ³⁰ (r_{av})	ED ³⁰ (r_g bond lengths, θ_{av} bond angles)	MM3
C ₁ —C ₂	1.535	1.538(6)	1.545
C ₂ —C ₃	1.557	1.561(15)	1.559
C—S	1.834	1.837(4)	1.836
<CSC	80.2	80.2(8)	81.1
I_A	30.5253 ^a		30.8020/0.91%
I_B	31.7485 ^a		31.8787/0.41%
I_C	34.3937 ^a		34.5151/0.35%

^a The moments of inertia were obtained from the combined analysis of ED and MW data.

Table 13. The structure of ethane-1,2-dithiol

Parameter	ED (r_g)	MM3		
		tGg'	$g'Gg$	Average
C—H	1.118(11)	1.114	1.114	1.114
S—H	1.373(15)	1.343	1.343	1.343
C—C	1.537(6)	1.539	1.539	1.539
C—S	1.824(2)	1.835(av.)	1.835	1.835
<CCS	113.1(4)	112.1	112.4	112.2
<HCH	103.7(57)	106.3(av.)	106.1	106.2
<CCH	111.1(13)	109.3(av.)	109.3	109.3
<SCH	108.8(13)	109.9(av.)	109.8	109.8
τ_{SCCS}	69.0(15)	68.6	68.1	68.4
I_A	9.031 ^a	9.169	9.365	
I_B	37.478 ^a	37.517	37.224	
I_C	43.358 ^a	43.621	43.154	
S...H	~2.70	2.797	2.791	2.794
S...S	~3.50	3.492	3.499	3.495

^a Moments of inertia were obtained from rotational constants reported in Ref. 39.

Ethane-1,2-dithiol

Two electron diffraction studies have been reported on this molecule. Shultz and Hargittai³⁷ report a ΔH of 0.8 kcal mol⁻¹, favoring the *anti* form, at 70 °C. Barkowski *et al.*³⁸ report $\Delta E^0 = E_G^0 - E_A^0 = 0.41$ (86) kcal mol⁻¹ and $\Delta S^0 = S_G^0 - S_A^0 - R \ln 2 = -1.0$ (22) cal deg⁻¹ mol⁻¹. The MM3 calculations give a ΔH of 0.83 kcal/mol favoring the $g'Tg'$ over the $g'Gg$ form. Barkowski *et al.* also report the structure of this molecule. The MM3 calculations show that the tGt' and $g'Gg$ forms are present in about the same amount as the tGg' form is less stable than the $g'Gg$ form by only 0.04 kcal mol⁻¹. Therefore, the average structure of the two conformers (tGg' and $g'Gg$) (i.e. the bond lengths and angles averaged over the two structures) obtained from the MM3 calculations should be compared with the geometry reported in the ED study. The tGg' structure was the only one seen in the microwave spectrum. The average structures of the molecule obtained in the ED study and from the MM3 calculations are shown in Table 13.

Allylmercaptan

The molecular structure of allylmercaptan has been studied by microwave spectroscopy.⁴⁰ There are two

Table 14. The structure of allylmercaptan

	MW ⁴⁰	MM3	Error (%)
C=C	1.354	1.339	
C—C	1.486	1.495	
C—S	1.819	1.829	
S—H	1.335	1.343	
<C=C—C	121.6	124.4	
<CCS	110.9	113.2	
<CSH	96.5	96.6	
ω_{CCS}	124(3)	118.1	
ω_{CCSH}	50	58.1	
I_x^a	25.2163	25.4742	1.23
I_y^a	180.7681	1.10	1.10
I_z^a	187.1004	188.9775	1.00
Dipole moment	1.331	1.238	

^a In atomic units.

Table 15. Heat of formation input data

	Wt	$H_f(0)$	SUMH*	Steric	POP	TORS	T/R	Compound
1	1	-5.47	-13.77	0.35	0.00	-0.42	2.40	Methanethiol
2	10	-11.07	-19.46	1.23	0.06	0.00	2.40	Ethanethiol
3	10	-8.96	-27.54	0.76	0.00	0.00	2.40	Dimethyl sulfide
4	8	-16.23	-26.20	2.30	0.28	0.42	2.40	1-Thiabutane
5	6	-14.24	-33.23	1.95	0.10	0.42	2.40	2-Thiabutane
6	7	-19.96	-38.92	3.10	0.22	0.84	2.40	3-Thiapentane
7	9	-18.21	-25.15	2.71	0.13	0.00	2.40	2-Propanethiol
8	7	-21.63	-38.92	3.63	0.21	0.42	2.40	3-Methyl-2-thiabutane
9	7	-45.15	-61.67	14.81	0.00	0.84	2.40	Di- <i>tert</i> -butyl sulfide
10	7	-8.15	-34.89	11.22	0.16	0.42	2.40	Thiacyclopentane
11	6	-15.18	-36.11	5.15	0.00	0.00	2.40	Thiacyclohexane
12	8	-22.97	-35.81	8.66	0.20	0.00	2.40	Cyclohexanethiol
13	7	-24.43	-46.70	4.05	0.60	1.26	2.40	2-Thiahexane
14	3	14.51	-24.42	19.98	0.00	0.42	2.40	Thiacyclobutane
15	7	-28.99	-44.61	5.86	0.00	0.42	2.40	3,3-Dimethyl-2-thiabutane
16	7	-23.26	-34.51	4.62	0.25	0.42	2.40	2-Methyl-1-propanethiol
17	7	-26.20	-30.84	3.96	0.00	0.00	2.40	2-Methyl-2-propanethiol
18	5	-30.38	-37.57	6.95	0.17	0.42	2.40	2-Methyl-2-butanethiol
19	3	-28.01	-44.61	4.77	0.14	0.84	2.40	2-Methyl-3-thiapentane
20	4	-35.37	-50.29	6.97	0.00	0.84	2.40	2,2-Dimethyl-3-thiapentane
21	4	-33.91	-50.29	6.46	0.19	0.84	2.40	2,4-Dimethyl-3-thiapentane
22	5	-11.42	-34.58	18.17	0.16	0.42	2.40	Cyclopentanethiol
23	5	-16.34	-40.58	12.16	0.16	0.42	2.40	2-Methylthiacyclopentane
24	5	-2.32	-15.91	2.23	0.33	0.42	2.40	Ethane-1,2-dithiol

*SUMH is the contribution of the hydrocarbon portion of the molecule to the heat of formation.

Table 16. Heat of formation input

Compound	C—S	S—H	- <i>sec</i>	- <i>tert</i>	S—Me	SCCS	S-56
1 Methanethiol	1	1	0	0	1	0	0
2 Ethanethiol	1	1	0	0	0	0	0
3 Dimethyl sulfide	2	0	0	0	2	0	0
4 1-Thiabutane	1	1	0	0	0	0	0
5 2-Thiabutane	2	0	0	0	1	0	0
6 3-Thiapentane	2	0	0	0	0	0	0
7 2-Propanethiol	1	1	1	0	0	0	0
8 3-Methyl-2-thiabutane	2	0	1	0	1	0	0
9 Di- <i>tert</i> -butyl sulfide	2	0	0	2	0	0	0
10 Thiacyclopentane	2	0	0	0	0	0	0
11 Thiacyclohexane	2	0	0	0	0	0	0
12 Cyclohexanethiol	1	1	1	0	0	0	0
13 2-Thiahexane	2	0	0	0	1	0	0
14 Thiacyclobutane	0	0	0	0	0	0	2
15 3,3-Dimethyl-2-thiabutane	2	0	0	1	1	0	0
16 2-Methyl-1-propanethiol	1	1	0	0	0	0	0
17 2-Methyl-2-propanethiol	1	1	0	1	0	0	0
18 2-Methyl-2-butanethiol	1	1	0	1	0	0	0
19 2-Methyl-3-thiapentane	2	0	1	0	0	0	0
20 2,2-Dimethyl-3-thiapentane	2	0	0	1	0	0	0
21 2,4-Dimethyl-3-thiapentane	2	0	2	0	0	0	0
22 Cyclopentanethiol	1	1	1	0	0	0	0
23 2-Methylthiacyclopentane	2	0	1	0	0	0	0
24 Ethane-1,2-dithiol	2	2	0	0	0	1	0

Table 17. Heat of formation output data^a

Best values					
C—S =	6.173	S—H =	-1.610		
-sec =	-2.956	-tert =	-6.902		
S—Me =	1.529	SCCS =	-0.919		
S-56 =	8.065				
Wt	$H_f(0)$ Calc.	$H_f(0)$ Exp.	Difference (calc. - exp.)	Compound	
1	1	-5.35	-5.48	0.12	Methanethiol
2	10	-11.20	-11.07	-0.13	Ethanethiol
3	10	-8.97	-8.96	-0.01	Dimethyl sulfide
4	8	-16.23	-16.23	0.00	1-Thiabutane
5	6	-14.49	-14.24	-0.25	2-Thiabutane
6	7	-20.01	-19.96	-0.05	3-Thiapentane
7	9	-18.30	-18.21	-0.09	2-Propanethiol
8	7	-21.34	-21.63	0.29	3-Methyl-2-Thiabutane
9	7	-45.08	-45.15	0.07	Di-tert-butyl sulfide
10	7	-8.35	-8.15	-0.20	Thiacyclopentane
11	6	-16.21	-15.18	-1.03	Thiacyclohexane
12	8	-22.95	-22.97	0.02	Cyclohexanethiol
13	7	-24.51	-24.43	-0.08	2-Thiahexane
14	3	14.51	14.51	0.00	Thiacyclobutane
15	7	-28.96	-28.99	0.03	3,3-Dimethyl-2-thiabutane
16	7	-22.25	-23.26	1.01	2-Methyl-1-propanethiol
17	7	-26.82	-26.20	-0.62	2-Methyl-2-propanethiol
18	5	-29.97	-30.38	0.41	2-Methyl-2-butanethiol
19	3	-27.07	-28.01	0.94	2-Methyl-3-thiapentane
20	4	-34.64	-35.37	0.73	2,2-Dimethyl-3-thiapentane
21	4	-33.96	-33.91	-0.05	2,4-Dimethyl-3-thiapentane
22	5	-11.82	-11.42	-0.40	Cyclopentanethiol
23	5	-16.05	-16.34	0.29	2-Methylthiacyclopentane
24	5	-2.32	-2.32	0.00	Ethane-1,2-dithiol

^aStandard deviation = 0.44.

Table 18. Heat of formation data for strain energy calculations

Wt	$H_f(0)$	SUMH	Steric	POP	TORS	T/R	Compound	
1	10	-5.35	-13.77	0.00	0.00	-0.42	2.40	Methanethiol
2	10	-11.20	-18.44	0.00	0.06	0.00	2.40	Ethanethiol
3	10	-8.97	-27.54	0.00	0.00	0.00	2.40	Dimethyl sulfide
4	10	-14.49	-32.21	0.00	0.10	0.42	2.40	2-Thiabutane
5	10	-18.30	-23.12	0.00	0.13	0.00	2.40	2-Propanethiol
6	10	-26.82	-27.80	0.00	0.00	0.00	2.40	2-Methyl-2-propanethiol
7	10	-16.23	-24.12	0.00	0.28	0.42	2.40	1-Thiabutane
8	10	-9.48	-42.39	0.00	0.34	1.26	2.40	2,5-Dithiahexane

Compound	C—S	S—H	-sec	-ter	S—Me	SCCS
1 Methanethiol	1	1	0	0	1	0
2 Ethanethiol	1	1	0	0	0	0
3 Dimethyl sulfide	2	0	0	0	2	0
4 2-Thiabutane	2	0	0	0	1	0
5 2-Propanethiol	1	1	1	0	0	0
6 2-Methyl-2-propanethiol	1	1	0	1	0	0
7 1-Thiabutane	1	1	0	0	0	0
8 2,5-Dithiahexane	4	0	0	0	2	1

Table 19. Heat of formation output data for strainless compounds^a

Best values					
C—S =	6.593	S—H =	-1.767		
- <i>sec</i> =	-2.536	- <i>tert</i> =	-6.246		
S-Me =	1.533	SCCS =	-0.527		
	Wt	$H_f(0)$ Calc.	$H_f(0)$ Exp.	Difference (calc. - exp.)	Compound
1	10	-5.43	-5.35	-0.08	Methanethiol
2	10	-11.15	-11.20	0.05	Ethanethiol
3	10	-8.89	-8.97	0.08	Dimethyl sulfide
4	10	-14.57	-14.49	-0.08	2-Thiabutane
5	10	-18.30	-18.30	0.00	2-Propanethiol
6	10	-26.82	-26.82	0.00	2-Methyl-2-propanethiol
7	10	-16.19	-16.23	0.04	1-Thiabutane
8	10	-9.48	-9.48	0.00	2,5-Dithiahexane

^aStandard deviation = 0.054.

stable isomers, *cis* and *gauche*, with respect to the C=C—C—S dihedral angle. The *gauche* conformer was found to be more stable by MM3 calculation, which agrees with experiment (Table 14).

Heats of formation

These can be calculated in the usual way using the bond increment method.⁴¹ The experimental data were taken from Refs. 42–44 and are summarized in Table 15. The parameters required for simple sulfides and mercaptans are the C—S and C—H bond parameters, and structural parameters for secondary tertiary and methyl groups attached to sulfur. To fit the cyclobutyl derivative, a parameter is needed for the sulfur–cyclobutane carbon, which one would expect to be similar to, but not identical with, the ordinary C—S bond. Additionally, a parameter is required to fit a vicinal disulfide. Table 16 shows the number of times each parameter appears in each compound. The least squares fitting to the data gives the parameters and results shown in Table 17. The standard deviation is 0.44 kcal mol⁻¹, which is similar to the value found for hydrocarbons, and also similar to the experimental errors from the combustion data. Strainless heats of formation may also be calculated as in Tables 18 and 19. The actual heat of formation calculated for a molecule, minus this strainless value, is a measure of the strain energy of the compound.

CONCLUSIONS

Structures, energies (conformational, and heats of formation) and a few other properties have been examined for 24 sulfides (including mercaptans), and in general the data can be well reproduced. Additionally, the vibrational spectra for three simple molecules have been well reproduced. For these, the average rms error is

33 cm⁻¹. This error could presumably be reduced by adding more cross-terms into the spectroscopic calculation.

There is one notable systematic error in the structures which will have to be addressed later. This concerns the bond angle C—C—S in molecules in which this angle is present. The angle opens out much wider in the *gauche* conformation than it is in the *anti*, and while MM3 calculates some opening, the approximate experimental opening (4°) is a good deal larger than the approximate calculated value (1°). For the present, the error has been averaged out, but still appears as an error between 1° and 2° in bond angles of this type in many compounds. A torsion–bend interaction for this kind of angle is necessary in order to reduce this error. A similar error has been found with the corresponding oxygen compounds, the amines and the phosphines.^{1–3} There seems to be no doubt now that the error is in fact quite general for compounds of the type C—C—X. Since this type of interaction was not explicitly included in earlier studies with other kinds of functional groups, it is similarly omitted here, but will eventually need to be included in all of these kinds of structures.

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