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Conformational Analysis. CVIII. The Calculation of the Structures and Energies of Alkanethiols and Thiaalkanes by the Molecular Mechanics Method[1,2]

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Abstract: The molecular mechanics method has been extended to include thiols and thioethers. Compounds studied include simple alkane derivatives, cyclic compounds, and bicyclic compounds, including rather strained ones. Bond lengths, bond angles, dihedral angles, rotational barriers, and heats of formation are all calculated and, in general, the agreement with the available experimental evidence is good.

The molecular mechanics or force field method is a semiempirical method for use in the calculation of geometries and energies of molecules.[3,4] The method has been shown to be a very fast, efficient way of determining these quantities, usually with good accuracy. It has been extensively applied by us in a consistent way to hydrocarbons[5,6] and less extensively to a few other classes of compounds including alkenes,[7] ketones,[8] silanes,[9] and conjugated systems.[10] The present work is an extension to simple sulfur compounds.

The force field developed herein is that described earlier,[5] with appropriate additions to deal with the sulfur atom. The necessary constants are given in Table IX. A few points are worth further discussion here.

As was discussed earlier with hydrocarbons,[5] it was advantageous to parameterize the force field so that rotational barriers calculated by minimization of the energies at both the minimum and maximum points on the rotational curve come out to be slightly lower than the experimental values. This is because the normal coordinate corresponding to the rotation which is measured experimentally does not allow for bond stretching and angle bending, which will occur when the energy is minimized. The stretching and bending force constants used were initially taken from the literature. In order to fit available structural information, it was necessary to reduce the bending constant by about 50%, for reasons previously described.

On the whole, the C–X stretching constants are about ¾ as large as the corresponding S–X constants, while the bending constants involving sulfur are somewhat larger than those corresponding ones in hydrocarbons. The sulfur compounds therefore tend to stretch more and bend less than do the corresponding hydrocarbons.

The van der Waals properties used for sulfur require comment. Since there are lone pairs of electrons on sulfur,

Table I. Comparison of the Calculated and Observed Structures of Thiaalkanes and Alkanethiols Used to Define Parameter Set

	Bond length, Å, or bond angle, deg			
		Obsd		
	Calcd	MW[12]	MW[13]	
Methanethiol[a]				
C_{sp^3}–S	1.821	1.825 ± 0.005	1.8237 ± 0.0002	
S–H	1.350	1.340 ± 0.010	1.3291 ± 0.0040	
C–S–H	96.7	96.5 ± 0.5	100.27 ± 0.17	
Ethanethiol (C_s)[a]		MW[14]	MW[15]	MW[16]
C_{sp^3}–S	1.828	1.835	1.835	1.835
S–H	1.348	1.345	1.350	1.350
C–C–S	110.5	108.5	108.43	108.3
C–S–H	97.1	97.17	96.43	96.43
Dimethyl sulfide[a]		MW[16a]		
C_{sp^3}–S	1.817	1.808 ± 0.002		
C–S–C	98.5	98.87 ± 0.17		
S–C–H_a	109.2	110.75		
S–C–H_s	107.3	106.6		
Thiacyclopentane		ED[17]		
(C_2 half-chair)				
C_{sp^3}–S	1.823	1.839 ± 0.002		
C–S–C	93.7	93.4 ± 0.5		
C–C–S	106.4	106.1 ± 0.4		
ω (S_1–C_2)[b]	14.7	14.8 ± 0.5		
ω (C_2–C_3)	39.7	40.5 ± 1.2		
ω (C_3–C_4)	51.3	52.5 ± 1.6		
5-Thiabicyclo[2.1.1]hexane		ED[18]		
C_{sp^3}–S	1.861	1.865 ± 0.004		
C–S–C	68.5	69.7 ± 0.5		
7-Thiabicyclo[2.2.1]heptane		ED[18]		
C_{sp^3}–S	1.837	1.837 ± 0.006		
C–S–C	79.8	80.1 ± 0.8		

[a] 0.006 Å has been added to reported bond lengths between all atoms except hydrogen (see text). [b] ω indicates the dihedral angle about the central bond.

Table II. Energy Calculations of Alkanethiols (kcal/mol)

Compd	ΔE, calcd	ΔE, obsd
Methanethiol		
Stg	0.00	0.00[12]
Ecl	1.14	1.27
Ethanethiol		
C_1 (G)	0.00	0.00[19,20]
C_s (T)	0.21	0.30
Ecl (H–H)	1.32	1.42
Ecl (H–Me)	1.25	
C_s Ecl (H's on C)	4.31	
C_1 Ecl (H's on C)	3.97	3.75
1-Propanethiol[a]		
T–G	0.00	0.00[21,22]
T–T	0.20	
G–G	0.30	0.40
G–T	0.63	
G–G'	0.67	
Ecl G (H–S)	4.11	
Ecl T (H–S)	4.30	
Ecl G (C–S)	5.31	
Ecl T (C–S)	5.67	
2-Propanethiol		
C_s	0.00	0.00[19]
C_1	0.26	0.00
2-Butanethiol[a]		
T–G	0.00	0.00[23]
T–T	0.33	
T–G'	0.66	
G–G	0.28	0.00
G–T	0.61	
G–G'	0.61	
G'–T	0.92	1.00
G'–G'	0.89	
G'–G	0.93	
2-Methyl-1-propanethiol[a]		
C_1–G	0.00	0.00[24]
C_1–T	0.27	
C_1–G'	0.37	
C_s–T	0.60	Small
C_s–G	0.56	
2-Methyl-2-propanethiol		
Stg	0.00	0.00[25]
Ecl	1.43	1.36
2-Methyl-2-butanethiol[a]		
C_1–G	0.00	0.00[26]
C_1–T	0.04	
C_1–G'	0.46	
C_s–G	0.24	0.25
C_s–T	0.35	
Ecl	5.24	
Cyclohexanethiol chair		
C_s–eq	0.00	
C_1–eq	0.21	0.00[27,28]
C_1–ax	1.10	
C_s–ax	1.92	0.9,[27] 1.1[28]

[a] See text for discussion. Experimental value refers to C–C–C–S frame and does not consider C–C–S–H conformations.

the electron density about the nucleus is unsymmetrical. We have chosen, however, to represent the sulfur atom as spherical and ignore the lone pairs. This is not necessarily the best approach, but it is the most simple approach and the one that we will use until when and if it is found to be inadequate. The van der Waals radius of sulfur was arrived at by means of the following considerations. As one begins with the rare gases and goes left across the periodic table, the electron cloud becomes larger, as a result of the decreasing nuclear charge. One might suppose that the van der Waals radius of the atom should similarly become larger. If one looks at contact distances as determined by X-ray crystallography, indeed they become larger by about 0.05 Å for each column of leftward movement across the table,[11] and hence one must add to the argon radius approximately 0.1 Å. As discussed earlier, the contact distances obtained from crystallography are considerably smaller than the van der Waals radii that are actually desired. If the Hill equation is used[5] for the van der Waals function, fixing the van der Waals radius fixes one of the parameters needed. The remaining parameter was fixed by keeping the polarizability of the sulfur atom the same as it is for argon.

Stretch-bend and torsion-bend functions were found to be important in trying to fit the geometries of small ring hydrocarbons.[5] The same functions were used as before,[5b] with the stretch-bend constant being chosen to fit the structures of 5-thiabicyclo[2.1.1]hexane and 7-thiabicyclo[2.2.1]heptane. The energy minimization scheme has been described previously.[5a]

Results

We have based the structural parameterization of our model on methanethiol, ethanethiol, dimethyl sulfide, thiacyclopentane, 5-thiabicyclo[2.1.1]hexane, and 7-thiabicyclo[2.2.1]heptane. We want our calculated geometries to be the same as the corresponding X-ray structures so the first three compounds, which had their structures determined from microwave spectra, need to be corrected. Fortunately, the corrections are small, at least for hydrocarbons, and we have followed the same procedure of adding 0.006 Å to bond lengths obtained by microwave methods to convert them to the corresponding X-ray values.[5] The values in

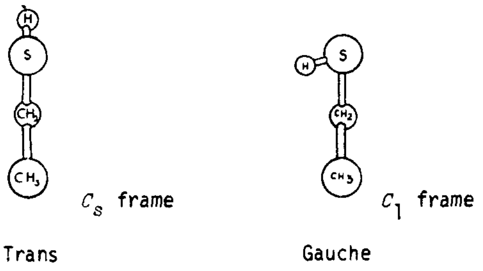


Figure 1. Ethanethiol.

Table I are the X-ray values (or corrected microwave values). The force field parameters were then chosen to fit the compounds in Table I, and they are given in Tables IX and X.

Alkylthiols. Using the parameters thus developed, the calculations were carried out on compounds given in Table II. The conformations are generally simple staggered ones, and they will be discussed here in some detail, as considerable experimental data concerning them are available. Their calculated relative energies are given in Table II and compared with the experimental values which are available.

The simplest alkanethiol, methanethiol, exists in a staggered conformation and has a barrier to internal rotation of about 1.3 kcal/mol, a value much smaller than that observed for ethane. In contrast to ethane, however, the van der Waals interaction in methanethiol differs but little (0.3 kcal/mol) between the two forms, and the torsional energy accounts for most of the energy difference.

Three staggered molecular conformations are possible for ethanethiol, two enantiomers of C_1 point group symmetry and a single form of C_s symmetry (see Figure 1). The 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[19] and, from calorimetric data, an enthalpy difference of 0.3 kcal/mol was estimated. We calculate the gauche conformer to be 0.21 kcal/mol lower in enthalpy than the trans form. Allowing for the fact that the C_1 form exists as a *dl* pair, this would amount to a free energy difference of 0.62 kcal/mol at room temperature, favoring the gauche conformer.

The main difference in steric energy between the two forms of ethanethiol occurs in the van der Waals energy component and is largely due to the interactions between the thiol hydrogen and the two adjacent methylene hydrogens.

In considering the conformations of higher alkanethiols, the problem becomes more complex, for it is necessary to consider the conformation about both the C-C and C-S bonds. For example, in a molecule as simple as 1-propanethiol, there are five conformations, four of which are *dl* pairs, T-T, T-G, G-T, G-G, and G-G′. Here the first symbol refers to a trans (T) or gauche (G) conformation about the C-C bond and the second symbol to the molecular form about the C-S bond, where G and G′ refer to the two nonequivalent gauche conformations (see Figure 2). Their energies are given in Table II.

From vibrational spectra, Hayashi[21] and coworkers concluded that, in the gaseous and liquid states, T-T form and G-T molecular forms are present, with the T-T form having the lower energy. They were unable to observe the other isomers. In general, spectroscopic observations lead to conformational conclusions regarding the main frame only; the conformation of hydrogen on sulfur is not determined. Calorimetric studies indicated that, in the gaseous state, the trans S-C-C-C skeletal frame has an enthalpy 0.40 kcal/mol lower than the gauche.[22] We calculate 0.37 kcal/mol for the enthalpy difference between the T-G and G-G conformations and 0.43 kcal/mol for the difference between the T-T and G-T forms. Considering both of the conformations having the trans skeleton, T-T and T-G, and the three forms possessing the gauche frame, G-G, G-T, and G-G′, and allowing for the additional entropy due to the mixing of *dl* pairs, we calculate a free energy difference of 0.11 kcal/mol favoring the trans over the gauche.

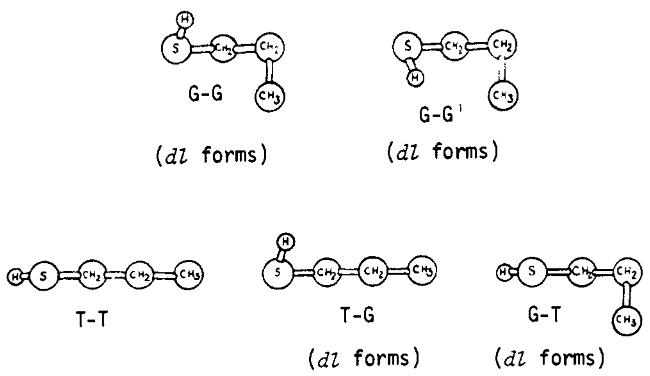


Figure 2. 1-Propanethiol.

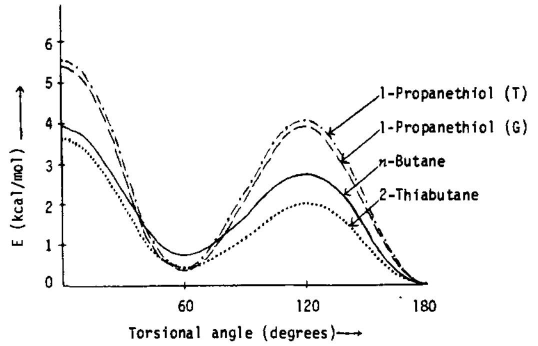


Figure 3. A comparison of the rotational barrier about the central bond of *n*-butane, 2-thiabutane, and 1-propanethiol.

The conformation about the C-C-S-H portion has not been determined experimentally, but we predict the gauche conformation to be lower in enthalpy than the trans form by about 0.2 kcal/mol, in both the trans and gauche C-C-C-S conformers. We calculate the G-G′ conformation to be of highest enthalpy because of the close approach of the terminal methyl group and the hydrogen atom of the thiol group.

In Figure 3 is shown a comparison of the rotational barriers about the central bands in 1-propanethiol and in butane. The results show that the torsional barrier of the 1-propanethiol is considerably higher than the corresponding barrier in *n*-butane. This is mainly due to the higher torsional energy in the eclipsed conformation of 1-propanethiol.

The enthalpy difference between the C_s and C_1 forms of 2-propanethiol has been estimated to be zero,[19] and we calculate a difference of 0.26 kcal/mol, with the C_s conformer being lower.

For 2-butanethiol (Figure 4), there are nine distinct conformations. In the designations, the first letter indicates whether the C-C-C-C portion has the trans (T) or one of the two nonequivalent gauche (G or G′) conformations, and the second letter has the same significance for the CH_2-CH_2-S-H chain. Each conformation is optically active. Their energies are given in Table II.

Thermodynamic and spectroscopic[23] results show that 2-butanethiol exists as a mixture of three distinct conformations with respect to the C-C-C frame. At room temperature, the concentration of molecules with either the T or G

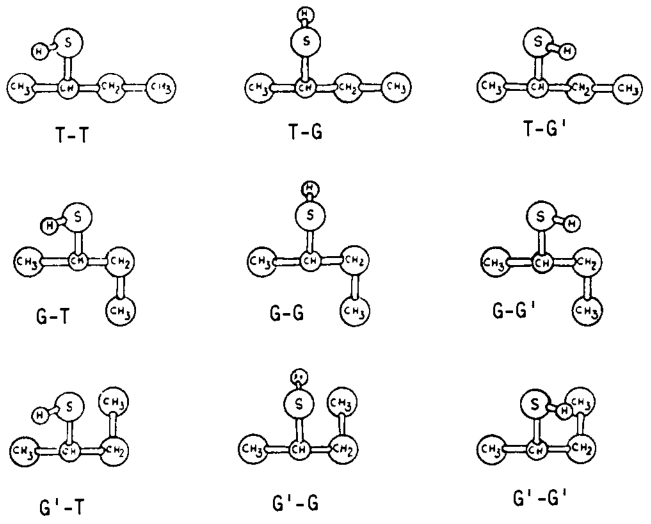


Figure 4. 2-Butanethiol.

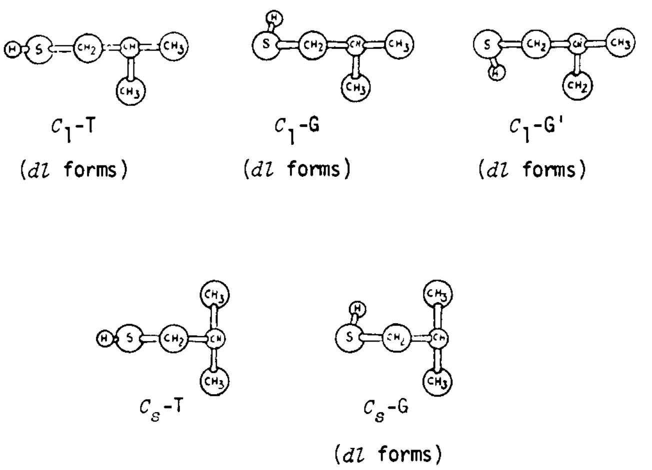


Figure 5. 2-Methyl-1-propanethiol.

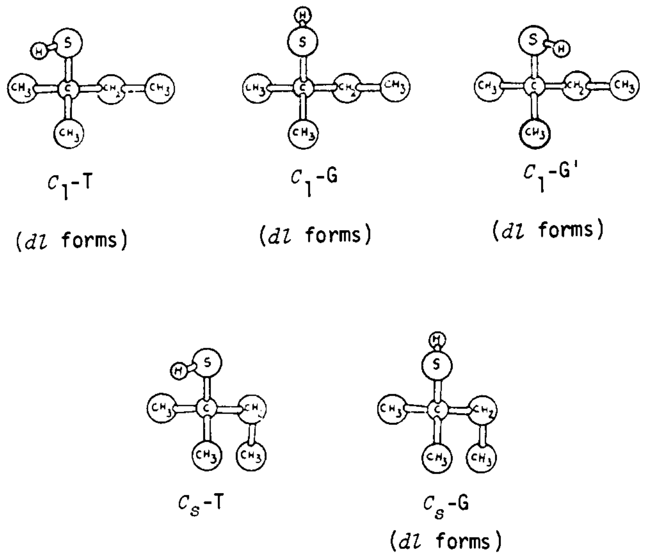


Figure 6. 2-Methyl-2-butanethiol.

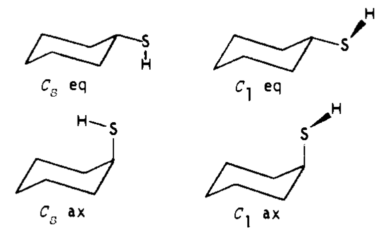


Figure 7. Cyclohexanethiol.

frame was calculated by McCullough and coworkers[23] to be 91%, and that of molecules with the G′ conformation 9%, which would correspond to a free energy difference of 1.37 kcal/mol. This value is in reasonable agreement with the value for the free energy that we calculate (from data in Table II) of 1.03 kcal/mol. No experimental data are available concerning the conformation about the CH_2-CH-S-H portions, but we calculate the gauche conformation to be lower in enthalpy by 0.33 kcal/mol.

The five distinct conformations of 2-methyl-1-propanethiol are shown in Figure 5.

The conformation of the $(C)_2$-C-C-S frame is referred to as either C_1 or C_s, while the T or G refers to a trans or gauche conformation about the C-C-S-H portion of the molecule.

Based on the calculated results for the parent 1-propanethiol where the T-G frame was found to be of lower enthalpy, we would expect that of the three conformations of 2-methyl-1-propanethiol having C_1 symmetry, the C_1-G conformation would be lowest in enthalpy, which is found (Table II). In the C_s-T conformation, the van der Waals energy is higher than that found in the C_s-G conformer, but the bending energy of the latter is higher by about the same amount, and the two conformations have about the same enthalpy.

Thermodynamic and spectroscopic results are consistent in indicating that the enthalpy difference between C_1 and C_s forms of 2-methyl-1-propanethiol is small,[24] with both conformations present in the liquid at room temperature, and the C_1 frame is preponderant.[29] We calculate the enthalpy and free energy to be lower for the C_1 frame by 0.40 and 0.79 kcal/mol, respectively.

As shown in Figure 6, 2-methyl-2-butanethiol has five conformations, three having a molecular frame with C_1 symmetry and two having C_s symmetry.

The C_1 frame of 2-methyl-2-butanethiol involves one gauche *n*-butane interaction and one gauche C-C-C-S interaction, whereas the C_s frame involves two gauche *n*-butane interactions. A rough approximation to the enthalpy difference between these is the difference between the sum of the two gauche *n*-butane interactions (1.6 kcal/mol) and the sum of the one gauche *n*-butane (0.8 kcal/mol) and one gauche C-C-C-S interaction (0.4 kcal/mol) or (0.4 kcal/mol). We calculate the C_1-T conformation to be 0.31 kcal/mol lower in enthalpy than the C_s-T form, while the difference between the C_1-G and C_s-G conformers is 0.24 kcal/mol, the former being of lower enthalpy. If we consider the enthalpy difference between the C_s and C_1 molecular frames, we calculate the latter to be 0.2 kcal/mol lower, in good agreement with the spectroscopic value[26] of 0.25 ± 0.25 kcal/mol. This gives a free energy difference of 0.7 kcal/mol at room temperature, favoring the C_1 form.

For cyclohexanethiol, there are a large number of possible conformations which arise from the equatorial-axial equilibrium of the frame and different orientations of the thiol groups. We considered only the chair forms of the ring (Figure 7) since it is the form observed at room temperature.[28]

Both the equatorial and axial chair forms of cyclohexanethiol may exist in conformations of C_s and C_1 symmetry. We calculate the C_s equatorial form to be 0.21 kcal/mol lower in energy than the C_1 equatorial conformation (Table II). Eliel and Thill[27] report the equatorial conforma-

Table III. Energy Calculations of Acyclic Thiaalkanes (kcal/mol)

Compd	ΔE, calcd	ΔE, obsd
2-Thiapropane		
Stg	0.00	0.00^{16a}
Ecl	1.95	2.13
2-Thiabutane		
C_S	0.00	$0.00^{30,31}$
C_1	0.29	0.00
Ecl (H–C)	1.87	1.97
Ecl (C–C)	2.77	
3-Thiapentane		
C_{2v} T–T	0.00	$0.00^{29,32,33}$
C_1 T–G	0.35	
C_2 G–G	0.67	
C_S	1.26	
3-Methyl-2-thiabutane		
C_1	0.00	0.00^{34}
"C_S"	0.24	
3,3-Dimethyl-2-thiabutane		
Stg	0.00	0.00^{35}
Ecl	1.97	2.00
2-Methyl-3-thiapentane		
C_1–T	0.00	
"C_S–T"	0.24	
C_1–G	0.36	
C_1–G'	0.85	
"C_S–G"	1.51	
2,2-Dimethyl-3-thiapentane		
"C_S"	0.00	
C_1	0.86	
C_1	1.46	
2,4-Dimethyl-3-thiapentane		
C_2	0.00	0.00^{28}
C_1	0.29	
"C_S"	0.59	
C_1	1.43	
C_{2v}	2.62	
2,2,4-Trimethyl-3-thiapentane		
"C_S (1)	0.00	
C_1	0.84	
"C_S" (2)	2.38	

tion to be 0.9 kcal/mol more stable in the liquid state. Thermodynamic work[28] gives an enthalpy difference of 1.1 kcal/mol in the gas. Our calculated value for free energy difference is 1.14 kcal/mol at 25°.

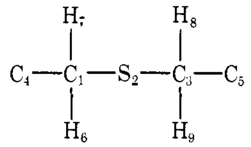
Thiaalkanes. We have summarized the results of energy calculations to a wide variety of thiaalkanes in Table III. The simplest of the thiaalkanes, 2-thiapropane, exists in a C_{2v} conformation with both methyl groups staggered with respect to the adjacent C–S bond[16a] (see Figure 8).

In 2-thiabutane, there are three conformations, one of C_s point group symmetry and a pair of C_1 *dl* forms (Figure 9). Raman and IR studies[30] of 2-thiabutane led to the conclusion that both exist in the gas and liquid states, of which only the trans persists in the crystal. Spectroscopic and thermodynamic data[31] indicate that these two rotational isomers have nearly the same enthalpy.

We calculate the C_s isomer of 2-thiabutane to be 0.29 kcal/mol lower in enthalpy than the C_1 conformation (Table III), which leads to a lower free energy for the C_1 conformer by 0.11 kcal/mol.

The rotational barriers are lower here than in butane (Figure 3), and this can be mainly attributed to the longer C–S bond lengths, which reduce the van der Waals repulsions in the eclipsed forms. The same effect has also been observed in the corresponding silanes.[9]

Table IV. Dihedral Angles (deg) of the Conformations of 3-Thiapentane



Dihedral angle	C_{2v} T–T	C_1 T–G	C_2 G–G	"C_S"
1–2–3–5	180.0	73.1	58.6	102.1
1–2–3–8	59.1	52.7	67.7	25.5
1–2–3–9		166.9	178.6	139.0
3–2–1–4		174.0	58.7	63.6
3–2–1–6		65.5	178.7	175.9
3–2–1–7		53.7	67.6	61.5

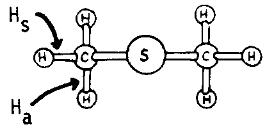


Figure 8. Staggered conformation of 2-thiapropane.

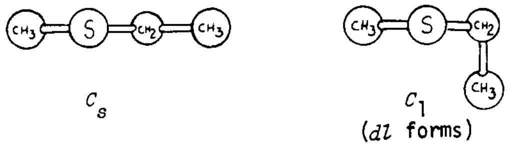


Figure 9. 2-Thiabutane.

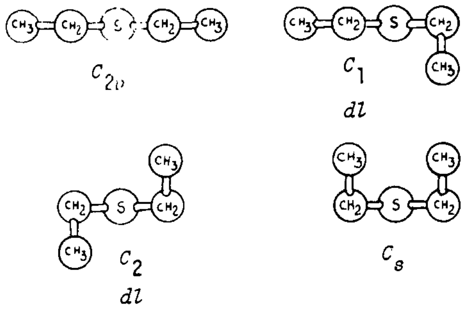


Figure 10. 3-Thiapentane.

Different trans and gauche conformations of the two ethyl groups in 3-thiapentane result in four spectroscopically distinct isomers (Figure 10).

By analogy with 2-thiabutane, the C_{2v} (T–T) conformation of 3-thiapentane would be expected to be lower in enthalpy than the C_1 (T–G) conformation, and the calculations indicate that it is by 0.35 kcal/mol. From spectral studies,[29] it was concluded that the C_{2v} and C_1 conformations of 3-thiapentane are more stable than the C_2 form, as we calculate (Table III), and that the C_{2v} form was found in the crystal.[33]

The C_2 conformation involves steric interactions of the two terminal methyl groups and is 0.67 kcal/mol higher in enthalpy than the C_{2v} conformation. In the C_2 conformation, the C–S–C angle increases to 103.6°, and the S–C–C angles increase to 114.0°, in an attempt to alleviate the repulsions of the two methyl groups.

In the C_s conformation, there is a serious steric interaction between the two methyl groups. We started with a C_s geometry but found that, in an attempt to relieve the steric crowding, the molecular frame twisted in such a way that the resulting minimum energy conformation is no longer of C_s symmetry. The resulting conformation is 0.9 kcal/mol higher in torsional energy than the other three conformations. We have summarized the dihedral angles of this conformation, designated "C_s", as well as those of the other minimum energy conformers of 3-thiapentane in Table IV.

The rotational isomers of 3-methyl-2-thiabutane (Figure

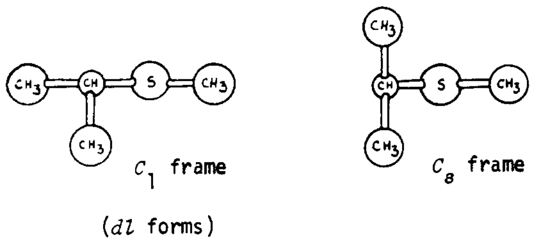
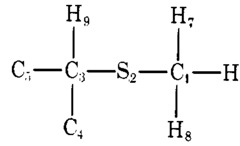


Figure 11. 3-Methyl-2-thiabutane.

Table V. Dihedral Angles (deg) of the Conformations of 3-Methyl-2-thiabutane



$$\begin{array}{ccccccccc} & & H_9 & & & & H_7 & & \\ & & | & & & & | & & \\ C_5 & — & C_3 & — & S_2 & — & C_1 & — & H_6 \\ & & | & & & & | & & \\ & & C_4 & & & & H_8 & & \end{array}$$

Dihedral angle	C_1	"C_s"
1-2-3-4	68.2	77.3
1-2-3-5	168.4	51.5
1-2-3-9	52.4	167.3
3-2-1-6	169.8	170.7
3-2-1-7	75.6	72.0
3-2-1-8	52.1	53.1

11) consist of three conformations, one of C_s symmetry and a C_1 *dl* pair. The molecular spectral data cited by McCullough et al.[34] suggested that both conformations contribute to the observed spectra, while Scott and El-Sabban[29] attributed the observed spectra solely to the C_1 conformation.

In studying 3-methyl-2-thiabutane, we started with the perfectly idealized C_1 and (C_s) conformations. These two conformations minimized normally to give the dihedral angles summarized in Table V. In addition, we started with two other conformations of 3-methyl-2-thiabutane, one in which the isopropyl group was eclipsed and the C_1 methyl group staggered, and one in which the isopropyl group was staggered and the methyl group eclipsed. In preliminary calculations with a slightly different force field, both of these conformations minimized to give a "C_s" form, which is of slightly lower energy than (C_s) and slightly distorted from C_s symmetry. In an attempt to determine whether both the "C_s" and (C_s) conformations, which are very close in geometry and energy, are really true minima, we rotated one methyl group, C_4, about the C_3-C_4 bond in 2° increments for a range of about 10° on each side of the minimized dihedral angle. All of the rotated "C_s" forms reverted to the same geometry and energy as the starting "C_s" conformation, thereby establishing the latter as a true minimum on the potential energy surface. When the same procedure was followed for the (C_s) conformation, all of the rotated forms minimized to the lower energy "C_s" conformation. This (C_s) form, then, is not a true minimum energy conformation but represents a saddle point on the energy surface. (The minimization scheme used does not find only minima, it finds places on the potential surface where all the first derivatives of the energy with respect to the coordinates are zero and, hence, saddle points are also located.) In all of the cases that follow, similar testing for saddle points was done in all questionable cases, and only true minima are reported.

We calculate the enthalpy difference between the "C_s" and C_1 conformations to be 0.24 kcal/mol, the C_1 conformer being of lower enthalpy.

The question arises as to whether the conformation which we designate as "C_s" should be treated as a *dl* pair since the conformation does not possess a plane of symmetry, as would a true C_s conformation, and is therefore optically active. We decided not to consider the "C_s" conformation as a *dl* pair, however, since the barrier height separating the *d* and *l* forms is only about 0.2 kcal/mol and less than RT at room temperature.

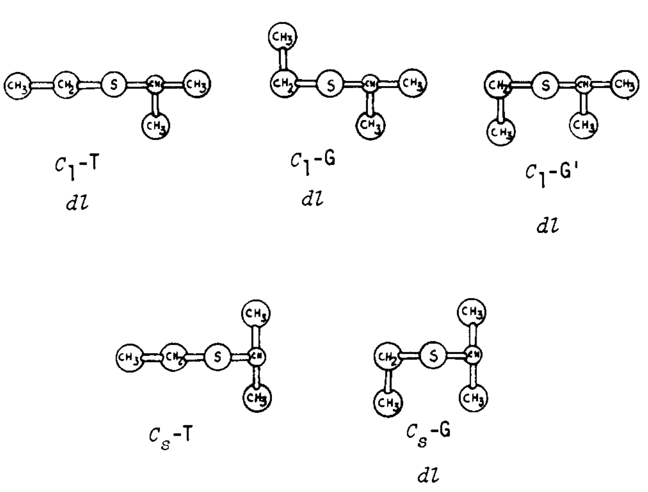


Figure 12. 2-Methyl-3-thiapentane.

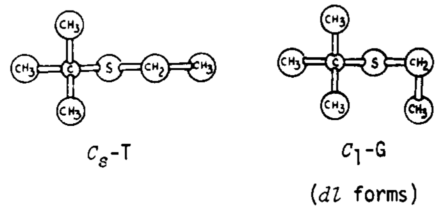


Figure 13. 2,2-Dimethyl-3-thiapentane.

In Figure 12 are shown the five distinct conformations of 2-methyl-3-thiapentane, four of which exist as *dl* forms. The C_1 or C_s refers to the $(CH_3)_2$-C-S frame, and the T, G, or G′ refers to the conformation about the C-S-CH_2 portion, T, G, or G′, trans or one of the nonequivalent gauche conformations. We calculate the C_1 form to be of lower enthalpy than the C_s frame. The C_1 form is calculated to be 0.24 kcal/mol lower in steric energy than the "C_s-T" conformer. This is similar to 3-methyl-2-thiabutane, where the C_1 form was also calculated to be 0.24 kcal/mol of lower enthalpy than the C_s.

The bending energy component is higher in the "C_s-T" conformer and mainly accounts for the higher energy of the C_s form.

In considering the entropy difference between the C_1 and C_s conformations, we did not treat the "C_s-T" conformation as a *dl* pair because of the low barrier (0.10 kcal/mol) separating them. It will be noted from the dihedral angles that conformation C_1-G′ is twisted considerably in an attempt to relieve the severe methyl-methyl repulsions.

The C_s and C_1 conformations of 2,2-dimethyl-3-thiapentane are shown in Figure 13.

The conformation that we calculate to be of lowest enthalpy is the "C_s" conformation (actually a *dl* pair separated by an 0.1-kcal barrier). There are two different C_1 conformations.

There are four distinct conformations of 2,4-dimethyl-3-thiapentane, C_{2v}, C_1, C_s, and C_2, pictured in Figure 14.

Molecular spectral data[28] indicated that only the C_2 conformation was present in the liquid state. Later work[29] suggested the possibility of the C_s form also being present. Our calculations indicate that the C_2 form is of lowest enthalpy. The C_1 and C_s conformations each involve a steric interaction between methyl groups on different isopropyl groups

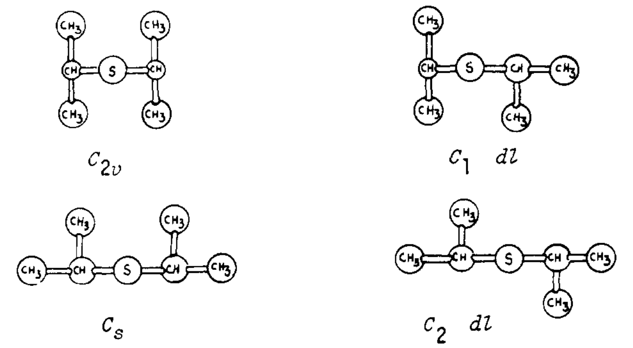


Figure 14. 2,4-Dimethyl-3-thiapentane.

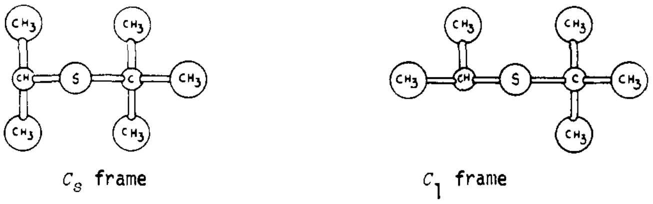


Figure 15. 2,2,4-Trimethyl-3-thiapentane.

which is absent in the C_2 form, and the C_{2v} conformation involves two such interactions. In all but the C_2 conformation, there is a twisting about the C-S bonds in an attempt to alleviate the steric repulsion of the methyl groups which destroys the symmetry.

There are expected two energetically distinct staggered conformations for 2,2,4-trimethyl-3-thiapentane, C_s and C_1, as shown in Figure 15.

The C_s conformation, which involves two severe methyl repulsions, would be expected to have a higher enthalpy. The "C_s" conformation twisted considerably to relieve the steric interactions and is no longer of C_s symmetry. The conformation calculated to be of lowest enthalpy, designated "C_s" (I), has the *tert*-butyl group staggered and the isopropyl group almost eclipsed in a C_s manner.

There appears to be only one spectroscopically distinct staggered conformation of 2,2,4,4-tetramethyl-3-thiapentane of C_2 point group symmetry. Various conformations all minimized this conformation. It has a C_2 axis perpendicular to the C_1-S_2C_3 plane passing through the sulfur atom.

Thiacycloalkanes. Thiacyclobutane proved to be an important compound in fixing the bending constants for sulfides, as did cyclobutane for hydrocarbons. Spectroscopic bending constants gave a heat of formation that was much too positive. When the bending constants were reduced (they were all maintained proportional to the spectroscopic values) to approximately fit this quantity (see later), they were found to be satisfactory for all of the other studies herein.

Our calculated structure is given in Table VI. The ring is puckered like cyclobutane (contrary to oxetane). At the time these calculations were done, the only available experimental structure was in poor agreement with ours.[36a] Subsequently a good electron diffraction structure has been reported,[36b] and also a nematic NMR structure[36c] (Table VI). The agreement of these with our structure is quite good.

Thiacyclopentane was studied next. Some evidence exists that the pseudorotation of the ring in thiacyclopentane is restricted, and that the conformation possessing C_2 symmetry is preferred. Pitzer and Donath[37] estimated this C_2 conformation to be about 3 kcal/mol more stable than the C_s, and the value was later determined[38] to be 2.8 kcal/mol. Such a high barrier to pseudorotation is to be contrasted with that in cyclopentane (zero). The energies of six conformations ranging from C_2 to C_s symmetry were calculated (see Figure 16) and show the C_2 conformation to be more stable than the C_s by 2.09 kcal/mol. All of the other conformations minimized to either this C_2 conformer or to the C_s conformer, indicating that only these two conformations correspond to energy minima. The calculations show that all interactions (van der Waals, stretching, bending, and torsional) are larger in the C_s than in the C_2 form.

Table VI. Thiacyclobutane Structures

Parameter	Calcd	Elec diff	NMR	Microwave
C-C	1.545	1.550 ± 0.003	1.550	1.549
C-S	1.842	1.847 ± 0.002	1.845	1.819
C-S-C	76.4	77.0 ± 0.5	76.7	
C-C-C	95.0	95.8	95.2	84.5
C-C-S	91.8	90.5	90.9	
	17	26 ± 4	26.5	40

Figure 16. Thiacyclopentane.

Thiacyclohexane may exist in a chair form or in boat or twist conformation, analogous to cyclohexane. When no restrictions were placed on the molecule, the nonsymmetrical twist form minimized to a symmetrical conformation. As with cyclohexane, the chair form is the conformation of lowest enthalpy, with the twist-boat conformation being 4.03 kcal/mol higher. No experimental value is available for the chair-twist energy difference, but it has been estimated[39] to be 4.02 kcal/mol.

No experimental conformational free energies for substituted thiacyclohexanes have been reported. We calculate the free energy difference between the axial and equatorial forms of 2-, 3-, and 4-methylthiacyclohexane to be 0.99, 1.10, and 1.59 kcal/mol, respectively, in favor of the equatorial conformation in each case. The value for the 4-methyl compound is close to that found for methylcyclohexane, and the interactions leading to the observed energy differences are similar in the two cases; about half of the energy difference is due to the vicinal interaction of the tertiary hydrogen with four neighbors when equatorial vs. two neighbors when axial. About one-fourth of the energy difference is due to the interaction of this tertiary hydrogen with the methyl hydrogens, and the remaining fourth is due to the interaction of the methyl hydrogen with the syn-axial hydrogens.

In the 2-methyl compound, the tertiary hydrogen has vicinal hydrogens on one side only, so we expect and find that the half of the energy due to these interactions will be reduced by about half. The axial 3-methyl group faces one syn-axial hydrogen and, by a slight rotation, it can be largely avoided so the energy here is also reduced, for a very different reason, however.

Thiabicycloalkanes. We next considered the cis and trans forms of 2-thiabicyclo[3.3.0]octane and the 3-thia isomer (Table VII).

For 3-thiabicyclo[3.3.0]octane, we calculate that the difference between the cis and trans isomers is 2.41 kcal/mol, a value considerably less than that in the 2-thia compound (4.57 kcal/mol) or in bicyclo[3.3.0]octane (5.52 kcal/mol). The larger cis-trans energy difference of the 2- relative to the 3-isomer is due largely to increased bending energy (at

Table VII. Energy Calculations of Thiacycloalkanes (kcal/mol)

Compd	ΔE, calcd
Thiacyclopentane	
Half-chair (C_2)	0.00
Envelope (C_S)	2.09
Thiacyclohexane	
Chair	0.00
Twist-boat (C_S)	4.03
2-Methylthiacyclohexane	
Equatorial	0.00
Axial	0.99
3-Methylthiacyclohexane	
Equatorial	0.00
Axial	1.10
4-Methylthiacyclohexane	
Equatorial	0.00
Axial	1.59
2-Thiabicyclo[3.3.0]octane	
Cis	0.00
Trans	4.57
3-Thiabicyclo[3.3.0]octane	
Cis	0.00
Trans	2.41
2-Thiadecalin	
Trans	0.00
Cis (S ax) (A)	1.59
(S eq) (B)	1.91
3-Thiadecalin	
Trans	0.00
Cis (S adj eq) (C)	2.03
Cis (S adj ax) (D)	2.37
8-Thiabicyclo[3.2.1]octane (IX)	
Chair	0.00
Boat	6.46
9-Thiabicyclo[3.3.1]nonane (XIII)	
Chair	0.00
Boat-chair	2.93

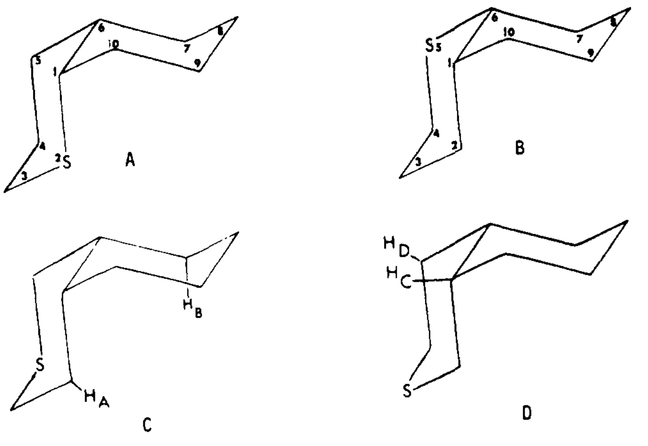


Figure 17. Conformations of 2-thiadecalin (A and B) and 3-thiadecalin (C and D).

the inter-ring angle) in the trans conformation when the sulfur is in the 2-position. The large cis-trans enthalpy difference in the hydrocarbons is due mainly to torsion and to the fact that all of the endocyclic ring angles are reduced to very low values. The small natural C-S-C angle stabilizes the trans isomer in the three thia compounds.

The cis and trans conformations of 2-thiadecalin and 3-thiadecalin are shown in Figure 17. For 2-thiadecalin, there are two cis conformations each of which exists as a *dl* pair.

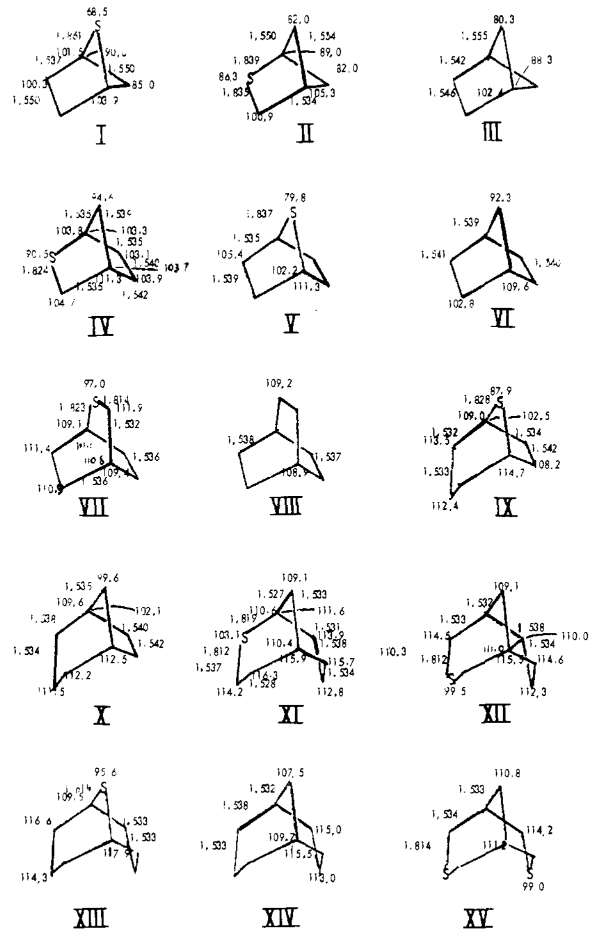


Figure 18.

We calculate that the cis conformation in which the sulfur atom is axial (Figure 17A) is of lower enthalpy than the one in which the sulfur atom is equatorial (Figure 17B) by 0.32 kcal/mol, largely because of the increased bending energy associated with the C_4-C_5-C_6, C_1-C_6-C_5, and S_5-C_6-C_7 angles in the conformation in which the sulfur atom is equatorial.

For 2-thiadecalin, the trans is calculated to be of lower enthalpy than the cis by 1.70 kcal/mol. The entropy of mixing of the two cis *dl* pairs amounts to 3.00 eu, while that of *dl* trans is 1.38 eu. A free energy difference is predicted favoring *trans*- over *cis*-2-thiadecalin by 1.21 kcal/mol at 25°.

For 3-thiadecalin, we calculate that the cis conformation with the sulfur atom adjacent to an equatorial methylene carbon attached to the ring (Figure 17C) is 0.34 kcal/mol more stable than that in which the sulfur atom is adjacent to an axial methylene, mostly because of increased van der Waals repulsions. In particular, the S-H_C and S-H_D van der Waals interactions (Figure 17D) raise the van der Waals energy by 0.92 kcal/mol compared with 0.60 kcal/mol for the two repulsions between the sulfur atom and H_A and H_B (Figure 17C). The difference between the S-H interactions of the two conformations, 0.32 kcal/mol, is close to the total energy difference (0.34 kcal/mol).

The enthalpy difference between *cis*- and *trans*-3-thiadecalin is calculated to be 2.15 kcal/mol. Both of the cis conformations of 3-thiadecalin, as well as the trans isomer, exist as *dl* pairs. The entropy of mixing of the cis conformations amounts to 3.00 kcal/mol compared with 1.38 kcal/mol for the trans. These values give a lower free energy for the trans by 1.66 kcal/mol (at 25°).

Table VIII. Heats of Formation (kcal/mol)

				ΔH				
	Wt	Torsion energy	Conf energy	Calcd	Exptl	Calcd − exptl[41]	Exptl error	Calcd strain
Methanethiol	1	−0.3	0.00	−4.93	−5.40	0.47	0.144	−0.25
Ethanethiol	10	0.0	0.06	−11.18	−11.00	−0.18	0.11	0.00
1-Propanethiol	8	0.3	0.28	−16.19	−16.14	−0.05	0.16	0.58
2-Propanethiol	9	0.0	0.13	−18.20	−18.14	−0.06	0.16	0.13
2-Butanethiol	6	0.2	0.40	−22.92	−23.09	0.17	0.20	1.11
2-Methyl-1-propanethiol	6	0.2	0.25	−22.71	−23.17	0.46	0.20	0.96
2-Methyl-2-propanethiol	6	0.0	0.00	−26.28	−26.12	−0.16	0.21	0.01
2-Methyl-2-butanethiol	6	0.1	0.17	−30.08	−30.34	0.22	0.22	1.80
Cyclohexanethiol	8	0.0	0.20	−23.01	−22.90	−0.11	0.20	1.24
Chain series								
2-Thiapropane	10	0.0	0.00	−8.79	−8.89	0.10	0.13	−0.05
2-Thiabutane	6	0.3	0.22	−14.49	−14.17	−0.32	0.28	0.57
3-Thiapentane	7	0.6	0.42	−20.58	−19.89	−0.69	0.19	1.17
3-Methyl-2-thiabutane	7	0.2	0.21	−21.40	−21.55	0.15	0.18	1.26
3,3-Dimethyl-2-thiabutane	7	0.0	0.00	−28.70	−28.91	0.21	0.18	1.51
2-Methyl-3-thiapentane	2	0.5	0.31	−27.15	−28.00	0.85	0.60	1.85
2,2-Dimethyl-3-thiapentane		0.4	0.30	−34.35	−35.30		0.60	2.42
2,4-Dimethyl-3-thiapentane	5	0.4	0.19	−33.96	−33.73	0.17	0.24	2.60
2,2,4-Trimethyl-3-thiapentane		0.3	0.13	−40.50				3.52
2,2,4,4-Tetramethyl-3-thiapentane	1	0.0	0.00	−45.52	−4.60	−0.92	0.7	6.43
Ring series								
Thiacyclobutane	4	0.3	0.00	14.49	14.58	0.09	0.27	19.72
Thiacyclopentane	7	0.0	0.00	−6.71	−8.07	1.36	0.25	4.11
Thiacyclohexane	6	0.0	0.00	−15.79	−15.12	−0.67	0.18	0.61
2-Methylthiacyclohexane		0.0	0.23	−22.51				1.13
3-Methylthiacyclohexane		0.0	0.25	−22.42				0.87
4-Methylthiacyclohexane		0.0	0.08	−22.65				0.64
3,3-Dimethylthiacyclohexane		0.0	0.00	−29.98				2.18
Fused ring series								
cis-2-Thiabicyclo[3.3.0] octane		0.0	0.00	−8.39				11.22
trans-2-Thiabicyclo[3.3.0] octane		0.0	0.00	−3.81				15.79
cis-3-Thiabicyclo[3.3.0] octane		0.0	0.00	−7.93				11.33
trans-3-Thiabicyclo[3.3.0] octane		0.0	0.00	−5.52				13.74
trans-2-Thiadecalin		0.0	0.00	−28.96				1.82
cis-2-Thiadecalin		0.0	0.16	−27.21				3.57
trans-3-Thiadecalin		0.0	0.00	−29.05				1.37
cis-3-Thiadecalin		0.0	0.14	−26.88				3.55
Polycyclic series								
2-Thia[2.1.1] hexane (II)		0.0	0.00	28.16				36.60
5-Thia[2.1.1] hexane (I)		0.0	0.00	23.67				32.45
2-Thia[2.2.1] heptane (IV)		0.0	0.00	−2.33				11.70
7-Thia[2.2.1] heptane (V)		0.0	0.00	−3.35				11.02
2-Thia[2.2.2] octane (VII)		0.0	0.00	11.28				8.33
2-Thiabicyclo[3.3.1] nonane (XI)		0.0	0.00	−16.84				8.35
3-Thiabicyclo[3.3.1] nonane (XII)		0.0	0.00	−18.24				6.60
8-Thiabicyclo[3.2.1] octane (IX)		0.0	0.00	−11.50				8.46
9-Thiabicyclo[3.3.1] nonane (XIII)		0.0	0.00	−16.54				9.00
3,7-Dithiabicyclo[3.3.1] nonane (XV)		0.0	0.00	−3.67				6.46

The calculated cis–trans enthalpy differences of 1.21 and 1.66 kcal/mol in 2-thiadecalin and 3-thiadecalin, respectively, are both smaller than for decalin, 2.77 kcal/mol. The repulsion of the two nearest inter-ring hydrogens, and the deformations which occur to relieve it, yields a large part of the enthalpy difference in decalin. In the stable forms of *cis*-2-thiadecalin (Figure 17A) and *cis*-3-thiadecalin (Figure 17C), there are no hydrogens on sulfur, and there is one less H_A–H_B repulsion than in decalin, and hence there is a smaller cis–trans energy difference than for decalin.

After investigating the fused five- and six-membered rings, we expanded our study to include a number of additional small bicyclic thiaalkanes. The calculated geometries for 5-thiabicyclo[2.1.1]hexane (I) and 7-thiabicyclo[2.2.1]heptane (V) (Table II) are in good agreement with the experimentally known structures since they were used in the parameterization of the force field. The geometries of the rest of the thia compounds, summarized in Figure 18, are predictions. The calculated structures of the corresponding hydrocarbons are included for comparison.

Several of the compounds studied (I, V, IX, and XIII) contain a single sulfur bridge between two other rings. The angle between the two bridging carbons, the C–S–C angle, indicates the progression from the highly strained 5-thiabicyclo[2.1.1]hexane (I) (68.5°) to the less strained 9-thiabicyclo[3.3.1]nonane (XIII) (95.6°). A similar progression occurs in the corresponding hydrocarbons, with the corresponding C–C–C angle about 12° larger in each case.

It has been suggested that the large bridgehead angle (115.5°) in bicyclo[3.3.1]nonane (XIV) is due to the nonbonded repulsions of the two endo hydrogens at C_3 and C_7.[5] In 3-thiabicyclo[3.3.1]nonane (XII) where there are no endo hydrogens at the 3-position, we calculate the corresponding angle to be 115.5°. In XII, it appears that the S–H_{endo} repulsion is responsible for widening the tertiary bridge angle relative to the hydrocarbon. This interaction results in 1.34 kcal/mol of van der Waals energy, while the H_{endo}–H_{endo} repulsion in the hydrocarbon (XIV) results in

1.31 kcal/mol of van der Waals energy. Thus there is a similar tendency for the sulfur compound to open out this angle in order to avoid the S–H$_{endo}$ interaction.

In 3,7-dithiabicyclo[3.3.1]nonane (XV), there are no endo hydrogens, but there is an almost identical S–S van der Waals repulsion amounting to 1.39 kcal/mol. To minimize this interaction, the bridgehead angle opens similarly to a value of 115.7°.

In 8-thiabicyclo[3.2.1]octane (IX), we calculate the conformer having a chair form of the cyclohexane ring to be more stable than the comformer containing the boat form by 6.46 kcal/mol (Table VII). In bicyclo[3.2.1]octane (X), we calculate this difference to be a very similar 6.43 kcal/mol.

In 9-thiabicyclo[3.3.1]nonane (XIII), we calculate the energy of the double chair form to be lower than that of the chair-boat form by 2.93 kcal/mol compared with 1.24 kcal/mol calculated for the same difference in the hydrocarbon bicyclo[3.3.1]nonane (XIV). The increased energy of the boat-chair form is mostly due to torsional energy.

Heat of Formation Calculations

Our second major objective was to calculate the heats of formation for sulfur compounds. The approach was as follows. A set of 21 compounds was selected (listed in Table VIII with an experimental heat of formation) which includes simple thiaalkanes and alkanethiols, some of which are highly branched. Because of the difficulty one encounters in comparing experimental heats of combustion from one worker to another, the tabulation by Cox and Pilcher[40] was used for heat of formation data.

The necessary heat of formation parameters include the C–S and S–H bond energies and correction terms for branching [for attachments other than primary (excluding methyl)] to the total bond energy in addition to the hydrocarbon parameters. The S parameters were optimized simultaneously by the least-squares method. The gas-phase heat of formation at 25° is calculated according to

$$\Delta H_f = \Delta H_{steric} + \Delta H_{conf} + \Delta H_{bond} + \Delta H_{iso} + \Delta H_{neo} + \Delta H_{methyl} + PFC$$

where ΔH_{steric} is the energy of the molecule calculated by the program as previously described, ΔH_{conf} is the conformational enthalpy contributions from other conformations coexisting at 25°, ΔH_{bond} is the sum of the enthalpy contributions by C–C, S–C, C–H, and S–H bonds within the molecule, and ΔH_{sec}, ΔH_{tert}, and ΔH_{methyl} are correction terms for sulfur or carbon atoms attached to isopropyl (or secondary carbon), *tert*-butyl (or tertiary carbon), and methyl groups, respectively. The last term, PFC (partition function contributions), refers to the additional enthalpy which results from torsional contributions and from translation and rotation terms. For the molecules we have studied, there are three degrees of rotational freedom and three degrees of translational freedom. Since the classical limit for the average energy of each degree of freedom is equal to ½ *RT*, the translational-rotational energy contribution would amount of 3*RT*. We have added an additional *RT* term since we are concerned with the gaseous state at constant pressure rather than constant volume. The value of 4*RT* (2.4 kcal/mol) has therefore been added for all of the compounds listed in Table VIII.

We also included torsional contributions where appropriate and have shown these in Table VIII. These come about because torsional barriers in alkanes are usually so low, especially between methylene groups, the levels are rather closely spaced. This means that a larger percentage of the molecules are in excited torsional states than would be in excited vibrational states in a more rigid molecule. We estimate that about 0.3 kcal/torsional degree of freedom will be contributed to the heat of formation from this cause, and so it is therefore added to our calculated heats of formation as appropriate. Note that the amount is not added when one end of the unit is a methyl, as the methyl parameter would include that amount already. The heat of formation parameters are listed in Table X.

The experimental and calculated heats of formation are given in Table VIII. The most serious discrepancy between the calculated and experimental heats of formation occurs in thiacyclopentane where the difference is 1.36 kcal/mol. The standard deviation between the calculated and experimental values for the 20 compounds with nonzero weights in Table VIII is 0.53 kcal/mol. This is slightly, but not significantly, better than was done with the hydrocarbons themselves (0.60 kcal/mol). The average experimental error for the 20 thia compounds is 0.24 kcal/mol. We can therefore calculate the heats of formation with an average accuracy almost competitive with that obtainable by experiment. Unfortunately, almost no experimental data are available for small rings, strained bicyclics, etc. so our calculations cannot now be well tested in these interesting cases. These calculations provide the first estimates of the heats of formation for these compounds. A set of strainless heat of formation parameters was deduced for this group as a whole as was done for the hydrocarbons, taking the simple

Table IX. Force Field Parameters for Alkanethiols and Thiaalkanes[a]

Atom	r^*, Å	ϵ, kcal/mol
van der Waals Parameters for the Hill Equation		
S	2.00	0.184

Natural Bond Lengths and Stretching Force Constants

Bond	l_0 (Å)	k_1, mdyn/Å	Bond moment, D
C_{sp^3}–S	1.186	3.21	1.20
S–H	1.346	3.80	0.00

Natural Bond Angles and Bending Force Constants

Angle	θ_0 (deg)	k_θ, mdyn Å/rad^2
S–C_{sp^3}–C_{sp^3}	107.8	0.42
C_{sp^3}–S–C_{sp^3}	94.3	0.50
H–C_{sp^3}–S	108.2	0.30
C_{sp^3}–S–H	94.0	0.40

Stretch–Bend Constants

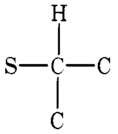
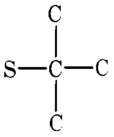
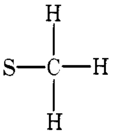
Angle	$k_{1\theta}$, mdyn/rad
C_{sp^3}–S–C_{sp^3}	0.16
C_{sp^3}–S–H	0.02

Torsional Parameters

Dihedral angle	Torsional constant, kcal/mol
C_{sp^3}–C_{sp^3}–C_{sp^3}–S	1.45
H–S–C_{sp^3}–C_{sp^3}	0.80
H–C_{sp^3}–C_{sp^3}–S	1.45
C_{sp^3}–C_{sp^3}–S–C_{sp^3}	1.45
H–C_{sp^3}–S–C_{sp^3}	1.45
H–C_{sp^3}–S–H	0.80

[a] The hydrocarbon parameters are those given in ref 5b.

Table X. Parameters for Heats of Formation Calculation (kcal/mol)

	C—S	S—H	 $S-\underset{C}{\overset{H}{C}}-C$	 $S-\underset{C}{\overset{C}{C}}-C$	 $S-\underset{H}{\overset{H}{C}}-H$
General	6.542	−1.724	−2.672	−5.628	3.044
Strainless	6.847	−1.533	−3.555	−7.635	2.800

compounds as strainless (Table VIII). For any saturated thiaalkane or alkanethiol, the corresponding "strainless" heat of formation is readily calculated from these strainless values. The calculated heat of formation is then compared with that for a strainless compound containing an equal number of C–C, C–H, S–C, and S–H bonds and primary, secondary, tertiary, and quaternary carbons attached to either a carbon or sulfur atom. The resulting differences between the calculated heats of formation and the strainless heats of formation, which are the strain energies, are also listed in Table VIII. As one would expect, the simple noncyclic compounds have low strain energies. The strain energy increases in members where there is branching and is usually quite high in the strained thiabicyclic compounds.

Conclusions

Calculations on a large variety of thiols and thiaalkanes have been carried out and found to be in reasonable agreement with the available experimental geometries and energy data. We can therefore add these classes of compounds to the growing list for which molecular mechanics calculations offer an easy alternative method for obtaining these kinds of data.

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