MOLECULAR MECHANICS (MM3) CALCULATIONS ON DISULFIDES

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An MM3 parameter set was developed for disulfides so as to permit the force field representation of these molecules with respect to geometries, including conformations, vibrational spectra and heats of formation.

INTRODUCTION

Disulfides are of particular interest because of their occurrence in proteins, where they have an important function in establishing structure, and also in other biologically active molecules. The MM2 force field† was parameterized for disulfides many years ago[1,2] and the present work is concerned with updating that parameterization to the MM3 force field.‡.

The disulfides are formally analogous to organic peroxides, although their chemical behavior is notably different in many respects. In the present study, we first examined the simple molecules hydrogen persulfide, methyl hydrosulfide, dimethyl disulfide and methyl ethyl disulfide. Comparisons were made between the structures calculated with MM3 and the experimental and *ab initio* data which are available. Vibrational spectra were used to ensure that the simple compounds were adequately described by the force field, and we then turned our attention to dithiane, tetrathiane and related compounds. The MM3 parameter set devised for these compounds is listed in Table 1.

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† The MM2 force field is summarized in Ref. 2. 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 commerical users from MDL (see next footnote).
‡ 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.

Table 1. MM3 parameter set for disulfide compounds[a]

A. Bond stretching parameter

Bond	ks (mdyn Å^{-1})	l_0 (Å)
15 15	2·62	2·019

B. Bending parameters

Angle	$k\theta$ (mdyn Å rad^{-2})	θ_0
15 15 44	0·773	92·2
1 15 15	1·000	101·8

C. Torsional parameters

Dihedral angle				V1	V2	V3
44	15	15	44	0·350	−6·450	0·350
1	15	15	44	0·850	−6·685	0·750
1	15	15	1	1·850	−7·555	2·340
5	1	15	15	0·300	0·000	0·600
1	1	15	15	−0·200	0·000	0·000
2	1	15	15	−0·300	0·000	0·100
15	1	15	15	0·200	0·000	0·100

D. Torsion–stretch parameter

	KTS
15 15	0·220

E. Electronegativity

Bond	End of bond	Atom type	Correction
15 15	15	44	0·023
1 15	15	15	0·010
15 44	15	15	−0·005

[a] Atom types are as in MM3.‡ Type 15 is sulfide or disulfide sulfur, 44 is a hydrogen attached to sulfur, and 1 and 5 are sp³ carbon and carbon attached hydrogen respectively. Parameters not given here (for hydrocarbons)[3] are incorporated into MM3 already.

Table 2. The vibrational spectra of simple disulfides

Hydrogen persulfide

Exp.[4]	MM3	Δ	Sym.	Assig.
2577	2591	14	A	S—H str.
2513	2590	77	B	S—H str.
886	888	2	A	S—S—H bend.
882	874	−8	B	S—S—H bend.
510	509	−1	A	S—S str.
416[a]	427	11	A	H—S—S—H tors.
RMS		32		

Methyl hydrodisulfide

Exp.[5]	MM3	Δ	Sym.	Assig.
3007	2982	−25	A	C—H str.
2995	2981	−14	A	C—H str.
2930	2875	−55	A	C—H str.
2535	2592	57	A	S—H str.
1437	1429	−8	A	CH₃ def.
1419	1415	−4	A	CH₃ def.
1313	1354	31	A	CH₃ def.
959	1016	57	A	CH₃ wag.
956	1013	57	A	CH₃ rock.
874	881	7	A	H—S—S bend.
697	702	5	A	S—C str.
512	512	0	A	S—S str.
314	321	7	A	C—S—S bend.
—	254	—	A	C—S—S—H tors.
—	191	—	A	H—C—S—S tors.
RMS		34		

Dimethyl disulfide

Exp.[6]	MM3	Δ	Sym.	Assig.
2997	2984	−13	A	Asym. CH₃ str.
2997	2983	−14	B	Asym. CH₃ str.
2997	2982	−15	A	Asym. CH₃ str.
2997	2982	−15	B	Asym. CH₃ str.
2927	2876	−51	A	Sym. CH₃ str.
2927	2876	−51	B	Sym. CH₃ str.
—	1432	—	A	Asym. CH₃ bend.
1441	1430	−11	B	Asym. CH₃ bend.
1422	1415	−7	B	Asym. CH₃ bend.
—	1414	—	A	Asym. CH₃ bend.
—	1356	—	A	Sym. CH₃ bend.
1309	1354	45	B	Sym. CH₃ bend.
959	1019	60	A	CH₃ rock.
—	1014	—	B	CH₃ rock.
959	1013	54	B	CH₃ rock.
—	1011	—	B	CH₃ rock.
694	703	9	A	S—C str.
694	701	7	B	S—C str.
514	514	0	A	S—S str.
272	279	7	B	S—S—C bend.
242	241	−1	A	S—S—C bend.
—	189	—	A	H—C—S—S tors.
—	184	—	B	H—C—S—S tors.
106	116	10	A	C—S—S—C tors.
RMS		30		

(continued)

Table 2. *(Continued)*

Ethyl methyl disulfide

(a) *Trans* conformation

Exp.[7]	MM3	Δ	Sym.	Assign.
3030	2983	−47	A	Asym. CH₃(—S) str.
3030	2982	−48	A	Asym. CH₃(—S) str.
2962	2964	2	A	Asym. CH₃(—C) str.
2962	2963	1	A	Asym. CH₃(—C) str.
2907	2950	43	A	Sym. CH₂ str.
2907	2899	8	A	Asym. CH₂ str.
2865	2876	11	A	Sym. CH₃(—C) str.
2865	2869	4	A	Asym. CH₃(—C) str.
1418	1488	70	A	CH₂ def.
1453	1466	13	A	Asym. CH₃(—C) def.
1453	1457	4	A	Asym. CH₃(—C) def.
1453	1441	−12	A	Asym. CH₃(—C) def.
1437	1431	−6	A	Asym. CH₃(—S) def.
1437	1415	−22	A	Asym. CH₃(—S) def.
1380	1375	−5	A	Sym. CH₃(—C) def.
1307	1355	48	A	Sym. CH₃(—S) def.
1255	1278	23	A	CH₂ twist.
1050	1032	18	A	CH₃(—C) def.
1050	1018	32	A	CH₃(—C) def.
1030	1016	−14	A	CH₃(—S) def.
1030	1012	−18	A	CH₃(—S) def.
969	979	10	A	C—C str.
775	841	66	A	CH2 rock.
698	702	4	A	C—S str. (Me)
641	676	35	A	C—S str. (Et)
522	537	15	A	S—S str.
—	320	—	A	S—C—C— bend.
—	267	—	A	H—C—C—S tors.
—	250	—	A	S—S—C bend. (Me)
—	212	—	A	S—S—C bend. (Et)
—	175	—	A	H—C—S—S tors.
—	109	—	A	C—S—S—C tors.
—	58	—	A	C—C—S—S tors.
RMS		30		

(b) *Gauche* conformation

Exp.[7]	MM3	Δ	Sym.	Assign.
3030	2983	−47	A	Asym. CH₃(—S) str.
3030	2982	−48	A	Asym. CH₃(—S) str.
2962	2968	6	A	Asym. CH₃(—C) str.
2962	2963	1	A	Asym. CH₃(—C) str.
2907	2951	44	A	Asym. CH₂(—C) str.
2907	2901	−6	A	Sym. CH₂ str.
2865	2876	11	A	Sym. CH₃(—C) str.
2865	2872	7	A	Sym. CH₃(—C) str.
1418	1501	83	A	CH₂ def.
1453	1471	18	A	Asym. CH₃(—C) def.
1453	1459	6	A	Asym. CH₃(—C) def.
1453	1447	−6	A	Asym. CH₃(—C) def.
1437	1431	6	A	Asym. CH₃(—S) def.
1437	1415	−22	A	Asym. CH₃(—S) def.
1380	1382	2	A	Sym. CH₃(—C) def.
1307	1355	48	A	Sym. CH₃(—S) def.
1255	1274	19	A	CH₂ twist.

(continued)

Table 2. (Continued)

1050	1033	−17	A	CH$_3$(—C) def.
1050	1016	−34	A	CH$_3$(—C) def.
1030	1016	−14	A	CH$_3$(—S) def.
1030	1012	−18	A	CH$_3$(—S) def.
969	973	4	A	C—C str.
775	841	66	A	CH$_2$ rock.
698	703	5	A	C—S str. (Me)
668	660	−8	A	C—S str. (Et)
507	511	4	A	S—S str.
—	355	—	A	S—C—C bend.
—	290	—	A	H—C—C—S tors.
—	247	—	A	S—S—C bend. (Me)
—	208	—	A	S—S—C bend. (Et)
—	182	—	A	H—C—S—S tors.
—	112	—	A	C—S—S—C tors.
—	62	—	A	C—C—S—S tors.
RMS		30		

a Cited in Ref. 8.

Vibrational analysis

The calculated and experimental vibrational frequencies related to the disulfide parameterization are summarized in Table 2.

RESULTS

Hydrogen persulfide

Both microwave[9,10] and gas phase electron diffraction[11] studies on this molecule have been reported. It was found to be in a C_2 conformation with a dihedral angle of approximately 90° with respect to the S—S bond. There is an *ab initio* calculation[12,13] with a 3-21G* basis set available in the literature for the energy barrier. We also calculated the moments of inertia of this compound, which were in fairly good agreement with microwave data. The experimental and *ab initio* results and the corresponding MM3 structures are shown in Table 3.

Methyl hydrodisulfide

The structure of this compound was determined by the microwave (MW) method.[14] Again, the energies were fit to the *ab initio* calculation with a 3-21G* basis set. The MM3 and experimental results are listed in Table 4.

Dimethyl disulfide

Both MW[15] and gas phase electron diffraction (ED)[16,17] structural data are available for this compound. The experimental and MM3 results are shown in Table 5. The exact barrier about the S—S bond is uncertain. However, all studies agree that the conformation with an approximately 90° dihedral angle (*gauche* form) is

Table 3. The structure of hydrogen persulfide[a]

	MW (r_e)	ED (r_α)	MM3
S—S	2·055(1)	2·055(1)	2·0614 (90)
			2·0728 (ecl·)
			2·0570 (*anti*)
S—H	1·327(3)	1·352(10)	1·3371 (90)
			1·3372 (ecl.)
			1·3366 (*anti*)
SSH	91·33(50)	91·95(50)	92·16 (90)
			94·02 (ecl.)
			91·94 (*anti*)
HSSH	90·60(5)	90·62(5)	90·6 (90)
			0·0 (ecl.)
			180·0 (*anti*)

Moments of Inertia

	MW[b]	MM3	Error (%)
I_x	0·5714	0·5781	1·17
I_y	12·0396	11·9668	−0·60
I_z	12·0443	11·9721	−0·60

Energy

	Ab initio (3-21G*)[12]	MM3
90	0·00	0·00
anti	5·67	5·85
ecl.	8·18	7·97

Dipole moment

Exp.[13]	MM3
1·17	1·265

a Bond lengths in Å; angles in deg.; moments of inertia in $10^{**}(−39)GM^*CM^{**}2$; energy in kcal mol^{-1}; dipole moments in D; MW = Microwave; ED = electron diffraction.
b $A = 146,858·170(32)$MHz, $B = 6970·430(3)$MHz, $C = 6967·689(3)$MHz.

the most stable. One of the recent *ab initio* studies with a 3-21G* basis set shows[12] that the *gauche* conformer is more stable than the *anti* and eclipsed forms by 5·55 and 11·66 kcal mol^{-1}, respectively, compared with the MM3 results of 5·53 and 11·84 kcal mol^{-1}.

Ethyl methyl disulfide

Experimental infrared (IR), Raman and ED studies of this molecule have been reported. A number of theoretical calculations have also been carried out to study the conformational properties of this molecule. The optimized geometries are summarized in Table 6, together with those observed.

There is no report of the rotational barrier height about the S—S bond for this molecule. MM3 calculations show that the *gauche* form is more stable

Table 4. The structure of methyl hydrodisulfide[a]

	MW[14]	MM3
S—S	2·038	2·0502 (90)
		2·0620 (ecl.)
		2·0465 (anti)
S—C	1·823	1·8166 (90)
		1·8198 (ecl.)
		1·8160 (anti)
S—H	1·339	1·3369 (90)
		1·3357 (ecl.)
		1·3367 (anti)
SSH	98·3	92·02 (90)
		93·77 (ecl.)
		91·93 (anti)
SSC	102·5	102·89 (90)
		104·92 (ecl.)
		102·73 (anti)
SCH	—	109·61 (90)
		109·63 (ecl.)
		109·61 (anti)
CSSH	88·9	88·6 (90)
		0·0 (ecl.)
		180·0 (anti)

Moments of Inertia

	MW[b]	MM3	Error (%)
I_x	4·9759	4·9772	0·03
I_y	18·8921	19·0660	0·92
I_z	22·8024	22·9124	0·48

Energy

	Ab initio (3-21G*)[12]	MM3
90	0·00	0·00
anti	5·79	5·76
ecl.	8·60	8·61

Dipole moment

	Exp.	MM3
—		1·511

[a] Units as in Table 3.
[b] $A = 16865·3758(71)$MHz, $B = 4442·1185(18)$MHz,
$C = 3680·3640(16)$MHz.

Table 5. The structure of dimethyl disulfide[a]

	MW (r_0,θ_0)[15]	ED (r_g,θ_0)[17]	MM3
S—S	2·038(20)	2·029(3)	2·0312 (90)
			2·0509 (ecl.)
			2·0275 (anti)
S—C	1·810(10)	1·816(3)	1·8170 (90)
			1·8194 (ecl.)
			1·8163 (anti)
SSC	102·8(15)	103·2(2)	103·10 (90)
			107·02 (ecl.)
			102·78 (anti)
SCH	108·9(20)	111·3(6)	109·64 (90)
			109·70 (ecl.)
			109·61 (anti)
CSSC	84·7(30)	85·3(37)	83·9 (90)
			0·0 (ecl.)
			180·0 (anti)

Moments of Inertia

	MW[b]	MM3	Error (%)
I_x	10·2798	10·3705	0·88
I_y	29·7970	29·8316	0·12
I_z	32·6494	32·8611	0·65

Energy

	Ab initio (3-21G*)[12]	MM3
90	0·00	0·00
anti	5·55	5·53
ecl.	11·66	11·84

Dipole moment

Exp.[18]	MM3
1·90 ± 0·02	1·739

[a] Units as in Table 3.
[b] $A = 8163·64$ MHz, $B = 2816·42$ MHz, $C = 2570·37$ MHz.

than the *trans* and *cis* conformations by 5·56 and 12·88 kcal mol^{-1}, respectively. For rotation of the ethyl group about the C—S bond, we investigated six conformations, the *trans* (T), the *gauche* (G, G'), the skew (S, S') and the *cis* (C) conformers. Several CNDO/2 and *ab initio* calculations have previously been used to study the conformational stability here. A recent *ab initio* MO calculation for this molecule with a 3-21G + (C, S) basis set is available.[21] An MP2 perturbation calculation was also performed to include electron correlation. All calculations agree that the

most stable conformer is the G form, except the CNDO/2 calculation which gives the T form instead. The order of the total energies by MM3 is $G > T > G'$. The order of the T and G' forms is reversed by the large basis set MP2 calculation (Table 7), but the overall agreement is reasonable.

Di- and tetra-thianes

Having the necessary parameters to deal with disulfides, we turned our attention to compounds containing the S—S linkage in the skeleton. We first looked at 1,2-dithiane, 1,2,4,5-tetrathiane and their derivatives. We examined three conformations for 1,2-dithiane – the chair form (C_2 symmetry), the twist form (C_2 symmetry) and the boat form (C_s symmetry). The chair form is more stable than the twist and boat forms by

Table 6. The structure of ethyl methyl disulfide

	ED[17,19,20]	MM3
S—S	2.031(3)	2.0323 (G)
		2.0359 (G')
		2.0308 (T)
(S—C)av	1.813(4)	1.8221 (G)
		1.8235 (G')
		1.8210 (T)
C—C	1.540(7)	1.5340 (G)
		1.5331 (G')
		1.5332 (T)
(SSC)av	103.2(3)	103.46 (G)
		104.20 (G')
		103.07 (T)
SCC	112.4(16)	112.12 (G)
		113.18 (G')
		110.97 (T)
CSSC	84.4(69)	83.7 (G)
		94.2 (G')
		83.8 (T)
CCSS	66.8(76)	69.9 (G)
		−70.2 (G')
		179.1 (T)

Table 7. Energies (kcal mol^{-1}) of methyl ethyl disulfide conformations

	Ab initio		
	STO-3G	(3-21G + d(C, S)/MP2)[21]	MM3
G	0·00	0·00	0·00 (C—S)
G'	0·58	0·64	0·70 (C—S)
T	0·06	0·77	0·05 (C—S)
S	1·26	—	1·15 (C—S)
S'	1·38	—	1·23 (C—S)
C	2·12	—	2·92 (C—S)
trans-	—	—	5·56 (S—S)
cis	—	—	12·88 (S—S)

4·44 and 11·96 kcal mol^{-1}, respectively. Similar calculations on 3,3,6,6-tetramethyl-1,1-dithiane showed similar results, with calculated energies of 2·04 and 21·64 kcal mol^{-1}, respectively. The results are summarized in Table 8.

We then looked at the conformational characteristics of 1,2,4,5-tetrathiane and its tetramethyl derivative.

Table 8. Conformations and energies of 1,2-dithiane and 3,3,6,6-tetramethyl-1,2,-dithiane

Compound	Chair(C_2)	Twist(C_2)	Boat(C_s)
Parent	0·00	4·44	11·96
Tetramethyl	0·00	2·04	21·64

These molecules are of interest because of the unusual characteristics of the cyclohexane ring system known experimentally. Cyclohexane has a chair conformer that is more stable than the next most stable form, the twist conformer with D_2 symmetry, by 5–6 kcal mol^{-1}. 1,1,4,4-tetramethylcyclohexane has a similar, but smaller, energy difference of about 3 kcal mol^{-1}. The lower energy difference in the tetramethyl derivative comes from the unfavorable axial methyl repulsions in the chair form, but not for the twist conformation. The most stable conformation for 1,2,4,5-tetrathiane is the chair form, which is 3·64 kcal mol^{-1} below the twist form. This energy difference is somewhat larger than our previous MM2 calculated value of 1·1 kcal mol^{-1}. On the contrary, the tetramethyl derivative has the twist conformation about 0·4–0·8 kcal mol^{-1} lower in energy than the chair (from the NMR study by Bushweller[22]). Our present calculation gives 1·09 kcal mol^{-1}.

Dithiocins

5H,8H-Dibenzo[d, f] [1,2]dithiocin is another disulfide compound of interest whose X-ray structure has been determined.[25] This molecule has a central eight-membered ring which contains the disulfide linkage. Possible ring conformations are the chair and the tub forms. Our MM3 calculation shows that the chair conformation is more stable than the tub by 0·70 kcal mol^{-1}, which is in aggrement with experiment[22-24] and with earlier molecular mechanics calculations.[1] The MM3 results are summarized together with the observed structure in Table 10.

Di-*tert*-adamantyl disulfide

Next we examined the strained disulfide compound, di-*tert*-adamantyl disulfide (DTA). Usually, the S—S

Table 9. Conformations and energies of 1,2,4,5-tetrathiane and 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane

Compound	Chair(C_{2h})	Twist(D_2)	Boat(C_{2v})	Boat(C_2)	Half-chair[a](C_2)
Parent	0·00	3·64	21·05	6·70	17·00
Tetramethyl	1·09	0·00	31·42	3·83	15·20

[a] Transition state (only one imaginary vibrational frequency).

Table 10. The structure of
5H,8H-dibenzo[d,f][1,2]dithiocin[a]

Bond/angle	Chair	Tub	X-ray (chair)
S—S	2·0235	2·0312	2·035(1)
C—S	1·8327	1·8440	1·835(3)
SSC	103·09	104·69	104·3(1)
CSSC	61·7	83·5	56·4(2)

[a] Bond lengths in Å, angles in deg.

Table 11. The structure of di-tert-adamantyl disulfide (DTA)

	X-ray[26,a]	X-ray[b]	MM3
S—S	2·048(7)	2·041	2·0454
C—S	1·84(2)	1·840	1·8467
< SSC	106·8(13)	107·0	106·69
ωcssc	110·5(9)	110·4	112·1
ωsscc	70·0(9)	−69·8	−66·1
ωsscc	−56·0(9)	56·3	55·8
ωsscc	−171·0(9)	171·0	175·6
ωsscc	53·0(9)	53·1	55·8
ωsscc	−69·0(9)	−68·5	−66·1
ωsscc	173·0(9)	173·0	175·6

[a] These are the data given in Ref. 26. The signs obtained for the torsion
angles from the fractional coordinates are different in part, and we
believe the latter to be correct.
[b] The values were converted from X-ray fractional coordinates given in
Ref. 26.

bond in an unstrained disulfide has a dihedral angle of 80–90°. A room-temperature X-ray diffraction study has been reported for DTA.[26] The X-ray structure is given in Table 11 and compared with the MM3 results. The MM3 torsional angle CSSC is 112·1°, which agrees with the observed value of 110·5°(9).

Heats of formation

The heat of formation of a compound is one of its fundamental properties. As part of this work, we developed a set of parameters to allow the calculation of the heats formation of disulfides, based on the experimental data[27,28] available. For a set of seven compounds with experimental errors in the range 0·3–0·6 kcal mol^{-1}, MM3 calculates the heat of formation with an average deviation of 0·20 kcal mol^{-1}. The agreement for this class of compunds is good, but this is in part due to the fact that the number of data fit is small.

The seven compounds used for this work are hydrogen disulfide, dimethyl disulfide, diethyl disulfide, dipropyl disulfide, dibutyl disulfide, diisobutyl disulfide and di-tert-butyl disulfide. We found that the contribution to the heat of formation of an alkyl group attached to a disulfide sulfur was different from that of the same group attached to an isolated sulfur. Therefore, we have to use different structural feature parameters to fit the experimental data. One difficulty is that no experimental heat of formation data are available to determine the value for an iso group

Table 12. The heats of formation for disulfide compounds[a]

		Best values					
		S—S = 6·430			S—S—tert = −7·550		
		S—S—Me = 1·945			S—S—H = 1·880		
		Fixed values					
		S—S—sec = −2·850			S—S—C = 0·000 (assumed)		

Wt	POP	TOR	T/R	Exp.	MM3	Diff. (MM3 − exp.)	Compound
10	0·00	0·42	2·40	3·90	3·90	0·00	Hydrogen persulfide
10	0·00	0·42	2·40	−5·64	−5·64	0·00	Dimethyl disulfide
10	0·20	1·26	2·40	−17·70	−17·77	−0·07	Diethyl disulfide
10	0·72	2·10	2·40	−27·88	−27·70	0·18	Dipropyl disulfide
8	1·02	2·94	2·40	−37·69	−38·12	−0·43	Dibutyl disulfide
8	0·74	2·10	2·40	−40·69	−40·43	0·26	Diisobutyl disulfide
8	0·00	1·26	2·40	−47·13	−47·13	0·00	Di-tert-butyl disulfide

[a] Standard deviation = 0·204.
[b] S—S = Bond increment of type 15–15.
S—S—Me = Structural feature in which the α-carbon is a methyl group.
S—S—sec = Structural feature in which two alkyl groups are attached to an α-carbon.
S—S—tert = Structural feature in which three alkyl groups are attached to an α-carbon.
S—S—H = Structural feature in which hydrogen is attached to an S—S bond.
S—S—C = Structural feature in which carbon is attached to an S—S bond.

Table 13. The heats of formation of disulfide compounds (strainless)[a]

Best values								
S—S	=	4·610			S—S-tert	= −5·950		
S—S—Me	=	2·270			S—S—H	= 0·000		
S—S—sec	=	−4·260			S—S—C	= −1·630		

Wt	POP	TOR	T/R	Exp.[b]	MM3	Diff. (MM3 − exp.)	Compound
10	0·00	0·42	2·40	3·90	3·90	0·00	Hydrogen persulfide
10	0·00	0·42	2·40	−5·64	−5·64	0·00	Dimethyl disulfide
10	0·03	0·84	2·40	−7·08	−7·08	0·00	Ethyl hydrodisulfide
10	0·04	0·84	2·40	−16·30	−16·30	0·00	Iso-propyl hydrodisulfide
10	0·00	0·84	2·40	−22·72	−22·72	0·00	tert-Butyl hydrodisulfide

[a] Standard deviation = 0·000.
[b] Calculated MM3 values.

attached to a disulfide sulfur. Since we know that the values for tertiary and methyl groups in this case are similar to neo and methyl groups attached to alkane compounds, we can estimate a reasonable structural feature parameter value for the iso group. The values of the neo, methyl and iso structural features for alkanes are $-6·641$, $1·045$ and $-2·627$ kcal mol^{-1}. The calculated values for tertiary and methyl groups attached to disulfide are $-7·550$ and $1·945$ kcal mol^{-1}. The estimated value for an iso group in a disulfide is $-2·850$ kcal mol^{-1}. There are two terms added to calculate H_f that will be further explained.[2] First, we add one TOR increment ($0·42$ kcal mol^{-1}) for an S—S bond because the lower rotational barrier is lower than $7·0$ kcal mol^{-1}. Second, the POP terms used in the H_f calculation were exactly calculated over all stable conformers for monosubstituted disulfides. Summaries of the heat of formation calculations for both strained and strainless compounds are shown in Tables 12 and 13. The C—S and S—H bond energy terms were carried over from earlier studies on sulfides,[29] and hydrocarbon terms were carried over from earlier studies on hydrocarbons.[3]

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