

The thermochemistry of alkanethiols and thioethers. Estimation of the enthalpies of formation of 1,3-dithiapropane and 1,3,5-trithiapentane

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Dedicated to Professor Eusebio Juaristi on his 55th birthday
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Abstract

We have carried out a study on the thermochemistry of alkanethiols and thioethers. Relationships between the enthalpies of formation of alkanes, alkanethiols, and thioethers are discussed with the purpose of deriving different group interconversion contributions that permit the estimation of unknown $\Delta_f H_m^0(g)$ values for alkanethiols and thioethers from known values of alkanes. We have also carried out a theoretical study at the G2(MP2), G2, and G3 levels, calculating the enthalpies of formation of two compounds, 1,3-dithiapropane and 1,3,5-trithiapentane, and comparing them with the values previously estimated.

Keywords: Alkanethiols, thioethers, 1,3-dithiapropane, 1,3,5-trithiapentane, enthalpies of formation, Gaussian-n calculations

Introduction

The structure and energetics of molecules are fundamental concepts in Chemistry, the energy associated with a particular structure being related to the constituent atoms, and the corresponding bonds and angles that form the molecular framework.¹ Thermodynamic data such as the enthalpies of formation are often helpful in the understanding of the conformational and reactivity trends exhibited by the molecules. One of the purposes of thermochemistry is to derive the enthalpies of formation of compounds from their elements, and to relate them to structure and chemical binding.¹⁻³

Several empirical methods have been applied to the calculation of enthalpies of formation of hydrocarbons and alkane derivatives. The simplest procedures for calculating values for standard enthalpies of formation assume that enthalpies of atomization of compounds may be represented by a sum of contributions from the constituent bonds. Sophisticated procedures

require a large number of parameters and so less elaborate, more generally applicable, procedures are required. The three most commonly used are those due to Laidler,⁴ Allen^{5,6} and Benson.^{7,8} In the Laidler bond additivity approach,⁴ values for some bond energies are allowed to depend on the environments of the bonds. The Allen group increment method^{5,6} assumes constant values for bond energies, but also includes contributions from molecular fragments. The Benson group additivity scheme^{7,8} does not use bond energies and instead assumes that enthalpies of formation or atomization can be represented by contributions from different types of molecular fragments. The unified scheme of Cox and Pilcher,² which consolidates the Allen, Benson and Laidler methods, is more sophisticated and has been applied almost exclusively to simple hydrocarbons.

More recently, the Pedley method⁹ that allows bond-energy terms to vary among a number of specific environments, and the additive bond-energy scheme of Smith^{10,11} that includes geminal H–H terms have been developed.

In this work we have carried out a study on the thermochemistry of alkanethiols and thioethers. Relationships between the enthalpies of formation of alkanes, alkanethiols, and thioethers are discussed with the purpose of deriving different group interconversion contributions that permit the estimation of unknown $\Delta_f H_m^0(\text{g})$ values for alkanethiols and thioethers from known values of alkanes. We have also carried out a theoretical study at the G2(MP2), G2, and G3 levels, calculating the enthalpies of formation of two compounds, 1,3-dithiopropane and 1,3,5-trithiapentane, and comparing them with the values previously estimated.

Results and Discussion

The known enthalpies of formation⁹ in the gas phase, $\Delta_f H_m^0(\text{g})$, of alkanes, alkanethiols and thioethers, have been collected in Table 1. As it is well known,^{2,12-17} the values of the thermodynamic properties of a homologous series, $\text{Y}-(\text{CH}_2)_m-\text{H}$, show a monotonic, often linear, dependence on m . Prosen, Johnson and Rossini,¹³ proposed the general relation:

$$\Delta_f H_m^0[\text{Y}-(\text{CH}_2)_m-\text{H},(\text{g})]/\text{kJ mol}^{-1} = A + Bm + \delta \quad (1)$$

where A is a constant peculiar to the end group Y ; B is a constant for all normal alkyl series, independent of Y ; and δ is a term which has a small finite value for lower members, being largest for $m = 0$, and becomes zero for higher members, beginning near $m = 4$. B values of -20.71 , -20.62 and -20.53 kJ mol^{-1} have been obtained by us for n -alkanes, 1-alkenes and 1-alkynes, respectively, using the experimental data available in the literature.⁹ However, for 1-alkanols, B has a value of -20.13 kJ mol^{-1} . The reason for the different methylene increment in 1-alkanols is not well understood.¹¹ In 1-alkanethiols a B value of $-(20.80 \pm 0.18)$ kJ mol^{-1} is obtained, indicating that their behavior is similar to that generally observed, but different to that

of 1-alkanols. A value of $-4.95 \text{ kcal mol}^{-1}$ ($-20.71 \text{ kJ mol}^{-1}$) was obtained by Good and DePrater¹⁸ using the data between 1-butanethiol and 1-decanethiol.

An interesting way in which data may be examined is via calculations of energies for converting one group, such as methyl or methylene, to another. Group interconversion is more satisfactory that replacement of a hydrogen by a functional group since nonbonded interactions will cancel to some extent in the former case but not in the latter.¹⁶

Following the ideas of Stull et al.,¹⁹ Wiberg et al.,¹⁵ and Slayden and Liebman,¹² we can describe the energetics of alkanethiols and thioethers defining the quantities:

$$\Delta\Delta_f H_m^0[\text{CH}_3 \rightarrow \text{SH},(\text{g})] = \Delta_f H_m^0[\text{R-SH},(\text{g})] - \Delta_f H_m^0[\text{R-CH}_3,(\text{g})] \quad (2)$$

$$\Delta\Delta_f H_m^0[\text{CH}_2 \rightarrow \text{S},(\text{g})] = \Delta_f H_m^0[\text{R-S-R}',(\text{g})] - \Delta_f H_m^0[\text{R-CH}_2\text{-R}',(\text{g})] \quad (3)$$

The variation of the $\Delta\Delta_f H_m^0$ values for alkanethiols is small. Not taking into account the conversion from ethane to methanethiol, where a CH_3 group attached to another CH_3 group is converted to SH, we obtain a mean value of $57.8 \pm 1.1 \text{ kJ mol}^{-1}$, using 18 data points. In the case of thioethers, the $\Delta\Delta_f H_m^0$ values present a wider range of values and the four compounds with higher deviations have not been taken into account in the calculation of the mean value, $63.2 \pm 2.3 \text{ kJ mol}^{-1}$ (obtained using 13 data points)

Table 1. Experimental enthalpies of formation^a of alkanes, alkanethiols and thioethers, used in this work, and calculated $\Delta\Delta_f H_m^\circ[\text{CH}_3 \rightarrow \text{SH}_m(\text{g})]$ and $\Delta\Delta_f H_m^\circ[\text{CH}_2 \rightarrow \text{S}_m(\text{g})]$ values, for alkanethiols and thioethers, respectively. All values in kJ mol^{-1}

Alkanes	Alkanethiols	Thioethers
$\Delta_f H_m^\circ(\text{g})$	$\Delta_f H_m^\circ(\text{g})$	$\Delta_f H_m^\circ(\text{g})$
	$\Delta\Delta_f H_m^\circ[\text{CH}_3 \rightarrow \text{SH}_m(\text{g})]$	$\Delta\Delta_f H_m^\circ[\text{CH}_2 \rightarrow \text{S}_m(\text{g})]$
CH_3CH_3	CH_3SH	CH_3SCH_3
$\text{CH}_3\text{CH}_2\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{SH}$	$\text{CH}_3\text{SCH}_2\text{CH}_3$
$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	$\text{CH}_3(\text{CH}_2)_2\text{SH}$	$\text{CH}_3\text{S}(\text{CH}_2)_2\text{CH}_3$
$\text{CH}_3\text{CH}(\text{CH}_3)_2$	$(\text{CH}_3)_2\text{CHSH}$	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	$\text{CH}_3(\text{CH}_2)_3\text{SH}$	$(\text{CH}_3)_3\text{CHSCH}_3$
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$	$(\text{CH}_3)_2\text{CHCH}_2\text{SH}$	$\text{CH}_3\text{S}(\text{CH}_2)_3\text{CH}_3$
$(\text{CH}_3)_3\text{CCH}_3$	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{SH}$	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_3$
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	$(\text{CH}_3)_3\text{CSH}$	$(\text{CH}_3)_2\text{CHSCH}_2\text{CH}_2\text{CH}_3$
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	$\text{CH}_3(\text{CH}_2)_4\text{SH}$	$(\text{CH}_3)_3\text{CSCH}_3$
$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SH}$	$\text{CH}_3\text{S}(\text{CH}_2)_4\text{CH}_3$
$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{SH}$	$\text{CH}_3(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{CH}_3$
$(\text{CH}_3)_3\text{CCH}_2\text{CH}_3$	$(\text{CH}_3)_3\text{CCH}_2\text{SH}$	$\text{CH}_3\text{CH}_2\text{S}(\text{CH}_2)_3\text{CH}_3$
$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{SH}$	$(\text{CH}_3)_2\text{CHSCH}(\text{CH}_3)_2$
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_3(\text{CH}_2)_5\text{SH}$	$(\text{CH}_3)_3\text{CSCH}_2\text{CH}_3$
$(\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2$	$(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2\text{SH}$	$\text{CH}_3(\text{CH}_2)_3\text{S}(\text{CH}_2)_3\text{CH}_3$
$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$	$\text{CH}_3(\text{CH}_2)_2\text{C}(\text{CH}_3)_2\text{SH}$	$\text{CH}_3(\text{CH}_2)_2\text{SCH}(\text{CH}_3)_3$
$(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_3$	$\text{CH}_3(\text{CH}_2)_6\text{SH}$	$(\text{CH}_3)_3\text{CSCH}_2\text{CH}_2\text{CH}_3$
$(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{CH}_3)_3$	$\text{CH}_3(\text{CH}_2)_7\text{SH}$	$\text{CH}_3(\text{CH}_2)_3\text{S}(\text{CH}_2)_3\text{CH}_3$
$(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_3$	$\text{CH}_3(\text{CH}_2)_8\text{SH}$	$(\text{CH}_3)_3\text{CSCH}(\text{CH}_3)_3$
$(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{CH}_3)_3$	$\text{CH}_3(\text{CH}_2)_9\text{SH}$	$\text{CH}_3(\text{CH}_2)_4\text{S}(\text{CH}_2)_4\text{CH}_3$

^a Values taken from ref 9.

Table 2. Calculated $\Delta_f H_m^0(\text{g})$ values for alkanethiols and thioethers, using the $\Delta\Delta_f H_m^0[\text{CH}_3 \rightarrow \text{SH},(\text{g})]$ and $\Delta\Delta_f H_m^0[\text{CH}_2 \rightarrow \text{S},(\text{g})]$ values obtained in this work. All values in kJ mol^{-1} ^a

Alkanethiols			Thioethers		
	Calculated	δ^a		Calculated	δ^a
$\text{CH}_3\text{CH}_2\text{SH}$	-46.9 ± 1.2	0.8	$\text{CH}_3\text{SCH}_2\text{CH}_3$	-62.5 ± 2.4	2.7
$\text{CH}_3(\text{CH}_2)_2\text{SH}$	-67.9 ± 1.3	0.1	$\text{CH}_3\text{S}(\text{CH}_2)_2\text{CH}_3$	-83.7 ± 2.4	1.5
$(\text{CH}_3)_2\text{CHSH}$	-76.4 ± 1.3	0.2	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$	-83.7 ± 2.4	0.2
$\text{CH}_3(\text{CH}_2)_3\text{SH}$	-88.2 ± 1.4	0.2	$(\text{CH}_3)_2\text{CHSCH}_3$	-90.4 ± 2.5	-0.1
$(\text{CH}_3)_2\text{CHCH}_2\text{SH}$	-95.8 ± 1.4	-1.5	$\text{CH}_3\text{S}(\text{CH}_2)_3\text{CH}_3$	-103.7 ± 2.4	1.3
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{SH}$	-95.8 ± 1.4	-1.1	$\text{CH}_3\text{CH}_2\text{S}(\text{CH}_2)_2\text{CH}_3$	-103.7 ± 2.4	-1.1
$(\text{CH}_3)_3\text{CSH}$	-110.2 ± 1.4	0.6	$(\text{CH}_3)_3\text{CSCH}_3$	-122.7 ± 2.5	1.6
$\text{CH}_3(\text{CH}_2)_4\text{SH}$	-109.1 ± 1.4	-0.9	$\text{CH}_3\text{S}(\text{CH}_2)_4\text{CH}_3$	-124.4 ± 2.6	2.6
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SH}$	-114.1 ± 1.4	-0.8	$\text{CH}_3(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{CH}_3$	-124.4 ± 2.6	-1.3
$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{SH}$	-116.8 ± 1.4	-1.5	$(\text{CH}_3)_2\text{CHSCH}(\text{CH}_3)_2$	-138.4 ± 2.5	-3.6
$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{SH}$	-120.3 ± 1.4	-1.0	$\text{CH}_3\text{CH}_2\text{S}(\text{CH}_2)_3\text{CH}_3$	-124.4 ± 2.6	-3.4
$(\text{CH}_3)_3\text{CCH}_2\text{SH}$	-128.1 ± 1.4	-0.9	$\text{CH}_3(\text{CH}_2)_3\text{S}(\text{CH}_2)_3\text{CH}_3$	-165.0 ± 2.4	-2.7
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{SH}$	-128.1 ± 1.4	1.0	$\text{CH}_3(\text{CH}_2)_4\text{S}(\text{CH}_2)_4\text{CH}_3$	-207.6 ± 3.4	2.7
$\text{CH}_3(\text{CH}_2)_5\text{SH}$	-129.8 ± 1.7	-0.1			
$(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2\text{SH}$	-146.6 ± 1.7	-1.3			
$\text{CH}_3(\text{CH}_2)_2\text{C}(\text{CH}_3)_2\text{SH}$	-147.9 ± 1.9	-0.4			
$\text{CH}_3(\text{CH}_2)_6\text{SH}$	-150.7 ± 1.7	0.8			
$\text{CH}_3(\text{CH}_2)_9\text{SH}$	-213.0 ± 2.7	-2.0			

$$^a \delta = \Delta_f H_m^0(\text{exp}) - \Delta_f H_m^0(\text{calc}).$$

With the $\Delta\Delta_f H_m^0[\text{CH}_3 \rightarrow \text{SH},(\text{g})]$ and $\Delta\Delta_f H_m^0[\text{CH}_2 \rightarrow \text{S},(\text{g})]$ values calculated above, it is now possible to estimate the enthalpies of formation of different alkanethiols or thioethers. We have first applied this method to the calculation of $\Delta_f H_m^0(\text{g})$ for the alkanethiols and thioethers used in the derivation of the $\Delta\Delta_f H_m^0$ values. The results are collected in Table 2. The average deviation is 0.8 kJ mol^{-1} for alkanethiols, and 1.9 kJ mol^{-1} for thioethers.

A further step in the process of proving the validity of our predictions is to calculate $\Delta_f H_m^0(\text{g})$ values for a series of compounds containing the sulfide and/or thiol groups, and not used in the derivation of the $\Delta\Delta_f H_m^0$ values. Nine compounds have been found in the literature: cyclopentanethiol, cyclohexanethiol, cyclopentyl methyl sulfide, 3,5-dithiaheptane, 3,6-dithiaoctane, and four alkanedithiols: 1,4-dithiabutane, 1,5-dithiapentane, 1,6-dithiahexane, and 1,7-dithiaheptane. The calculated $\Delta_f H_m^0(\text{g})$ values for all of these compounds are collected in Table 3. As it can be seen, a very good agreement is obtained between the experimental and calculated $\Delta_f H_m^0(\text{g})$ values.

Finally, we have calculated the enthalpies of formation of two compounds with unknown $\Delta_f H_m^0(\text{g})$ value: a dithiol, 1,3-dithiopropane [or methanedithiol], HSCH_2SH , and a compound

with –S– and –SH groups in the same molecule, 1,3,5-trithiapentane [or bis(mercaptomethyl)sulfide], HSCH₂SCH₂SH. The values obtained are shown in Table 3.

Table 3. Calculated $\Delta_f H_m^0(g)$ values for a series of sulfur compounds, using the $\Delta\Delta_f H_m^0[CH_3 \rightarrow SH, (g)]$ and $\Delta\Delta_f H_m^0[CH_2 \rightarrow S, (g)]$ values calculated in this work. All values in kJ mol⁻¹

Compound	$\Delta_f H_m^0(g)$	
	Calculated	Experimental ^a
c-C ₅ H ₉ SH	-48.4 ± 1.3	-48.1 ± 0.9
c-C ₆ H ₁₁ SH	-96.8 ± 1.5	-96.2 ± 0.9
c-C ₅ H ₉ SCH ₃	-63.7 ± 2.5	-64.7 ± 1.0
CH ₃ CH ₂ SCH ₂ SCH ₂ CH ₃	-61.2 ± 3.5	-65.2 ± 1.5 ^b
CH ₃ CH ₂ S(CH ₂) ₂ SCH ₂ CH ₃	-82.1 ± 3.5	-83.0 ± 1.5 ^b
HS(CH ₂) ₂ SH	-10.1 ± 1.7	-9.7 ± 1.2
HS(CH ₂) ₃ SH	-31.3 ± 1.7	-29.8 ± 1.2
HS(CH ₂) ₄ SH	-51.3 ± 1.7	-50.6 ± 1.8
HS(CH ₂) ₅ SH	-72.0 ± 2.0	-71.0 ± 1.4
HSCH ₂ SH	10.9 ± 1.6	-----
HSCH ₂ SCH ₂ SH	31.9 ± 2.9	-----

^a Values taken from ref 9, unless otherwise noted ^b Value taken from ref 20.

With the purpose of checking the accuracy of the estimated enthalpies of formation of the above mentioned two compounds, we have also carried out a theoretical study, calculating their enthalpies of formation at the G2(MP2), G2 and G3 levels. These methods have been previously used by us²¹⁻²⁹ for the calculation of the enthalpies of formation of different compounds containing S atoms: thiirane,²¹ thiane,^{21,22} 1,3- and 1,4-dithiane,²¹ 1,3,5-trithiane,²² 2- and 3-thiophenecarboxylic acids,²³ thiane sulfoxide and thiane sulfone,²⁴ 1,3-dithiane sulfone,²⁶ and 1,3-dithiane sulfoxide.²⁷ In all the cases, a good agreement between experimental and theoretical results was obtained.

The most stable conformers of both studied compounds are in gauche, gauche conformation (anomeric effect) as it is well known^{30,31} in the case of HSCH₂SH. To our knowledge, there is not any conformational study in the literature for HSCH₂SCH₂SH. The MP2(FULL)/6-31G(d)-optimized structures are drawn in Figure 1.

Calculated energies at 0 K, and enthalpies at 298 K, for 1,3-dithiopropane and 1,3,5-trithiapentane are given in Table 4.

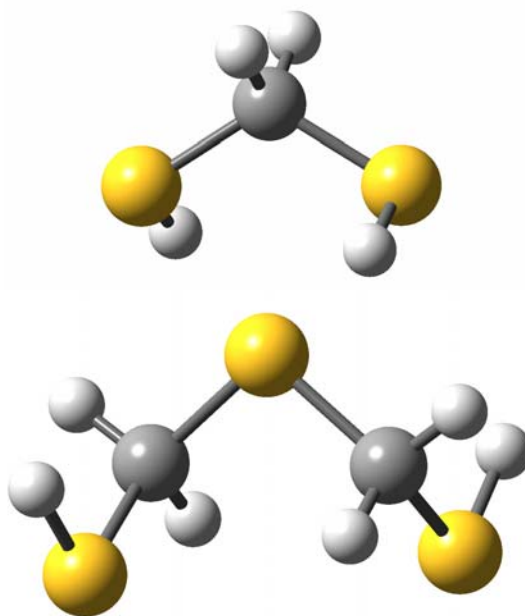
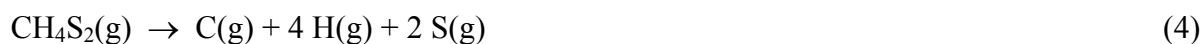


Figure 1. MP2(FULL)/6-31G(d)-optimized structures of 1,3-dithiapropane and 1,3,5-trithiapentane.

Table 4. G2(MP2), G2 and G3 total energies at 0 K, and enthalpies at 298 K, for 1,3-dithiapropane and 1,3,5-trithiapentane. All values in Hartrees

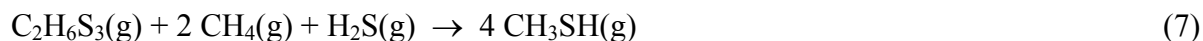
Compound	G2(MP2)		G2		G3	
	E_0	H_{298}	E_0	H_{298}	E_0	H_{298}
1,3-dithiapropane	-	-	-	-	-	-
	835.87847	835.87276	835.89167	835.88595	836.55170	836.54598
1,3,5-trithiapentane	-	-	-	-	-	-
	1272.8435	1272.8349	1272.8632	1272.8547	1273.8756	1273.8671
	0	8	8	6	6	4

In standard Gaussian-n theories, theoretical enthalpies of formation are calculated through atomization reactions (5) and (6). We have detailed this method in previous studies.^{32,33}



Raghavachari et al.³⁴ have proposed to use a standard set of isodesmic reactions, the "bond separation reactions",³⁵ to derive the theoretical enthalpies of formation. This method has been detailed in previous studies.^{32,33}

The bond separation reactions for 1,3-dithiapropene and 1,3,5-trithiapentane are, respectively:



The $\Delta_f H_m^0$ calculated values, at the G2(MP2), G2 and G3 levels, using both atomization and isodesmic bond separation reactions, are shown in Table 5. The averages of the values calculated at the different Gn levels from atomization and bond separation isodesmic reactions, 16.3 and 27.7 kJ mol⁻¹, for 1,3-dithiapropene and 1,3,5-trithiapentane, respectively, are in reasonable agreement with the values previously estimated in this work, 10.9 and 31.9 kJ mol⁻¹, respectively, within the uncertainties associated to Gaussian-n methods.

Table 5. Calculated enthalpies of formation for the studied compound at the G2(MP2), G2 and G3 levels using both atomization and bond separation isodesmic reactions. All values in kJ mol⁻¹

Compound	G2(MP2)		G2		G3	
	atomization	Bond separation	atomization	bond separation	atomization	bond separation
1,3-dithiapropene	11.0 (17.0) ^a	15.4	19.2 (17.3) ^a	15.4	18.5	14.3
1,3,5-trithiapentane	19.9 (30.3) ^a	25.6	33.0 (30.9) ^a	25.7	30.1	23.4

^a Value obtained from atomization reaction including spin-orbit and bond additivity corrections.

This method has been detailed in ref 24

Computational Details

Standard ab initio molecular orbital calculations³⁵ were performed with the Gaussian03 series of programs.³⁶ The energies of the studied compounds were calculated using Gaussian-n theories, at the G2(MP2),³⁷ G2³⁸ and G3³⁹ levels.

G2(MP2) and G2 correspond effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d)-optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies and a so-called higher-level correction to accommodate remaining deficiencies.

The scheme of G3 theory is similar to that of G2, but the MP2 single-point energy calculation is performed with a new basis set, referred to as G3large that includes core correlation. So, G3 is effectively at the QCISD(T,full)/G3large level, making certain

assumptions about the additivity of the calculations. It also includes a spin-orbit correction for atomic species only. The higher-level empirical correction is now different for atoms and for molecules.

Acknowledgements

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