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Calorimetric, Computational (G2(MP2) and G3) and Conceptual Study of the Energetics of the Isomeric 1,3- and 1,4-Dithianes[†]

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To understand the relative isomeric stabilities of 1,3- and 1,4-diheterocyclohexanes and the ultradiagonal strain energy of thiirane, the enthalpies of formation and sublimation of 1,4-dithiane have been measured. The enthalpy of formation for this compound in the solid state is −69.6 ± 2.3 kJ mol^{-1}, while for the gaseous state, the value is −6.9 ± 2.4 kJ mol. The value for the enthalpy of sublimation is 63.0 ± 0.6 kJ mol^{-1}. Ab initio molecular orbital calculations at the G2(MP2) and at G3 levels were performed, and the calculated enthalpies of formation are compared with the experimental data.

Introduction

Oxygen- and sulfur-containing heterocycles have occupied a fundamental position in chemistry for many years.[1] For example, synthetic organic chemists have found the simplest and strained three-membered heterocycloalkanes such as oxiranes[2a] and thiiranes[2b] to be excellent synthons for formal addition of "two-carbon" fragments[2a,b] and as starting materials for the formation of larger heterocyclic compounds.[2c] The relatively unstrained six-membered heterocycloalkanes[3] such as dioxanes and dithianes have been employed in a wide variety of organic reactions such as the controlled halogenation and sulfonation of alcohols and unsaturated species[4] and the addition of a functionalized single carbon unit onto both electrophiles[5a] and nucleophiles.[5b,c] However, there exist distinct differences in the reactivities of oxygen and sulfur synthons even within the same family of heterocycloalkanes. For example, while nucleophilic attack on a ring carbon is the most important reaction of oxiranes,[6a] nucleophilic attack on carbon and electrophilic attack on sulfur are both common reactions with thiiranes.[6b]

1,3-Dioxanes and 1,3-dithianes are convenient derivatives of aldehydes and ketones, masking the carbonyl group.[7a] 1,3-Dioxanes behave like acyclic acetals and ketals in being acid-labile, and as such have been exploited for the protection of aldehydes and ketones.[7b] On the other hand, the C−S bonds in 1,3-dithianes often require metal-induced hydrolysis necessary for the recovery of carbonyl compounds.[7c] In addition, there is a well-recognized ability by sulfur to stabilize adjacent carbanions. For example, 1,3-dithiane is easily deprotonated by *n*-butyllithium to give 2-lithio-1,3-dithiane,[8a] whereas 2-lithio-1,3-dioxane is much more difficult to prepare (Figure 1).[8b]

The difference in size, electronegativity, and bond polarities associated with oxygen and sulfur are reflected in contrasting structural, conformational, and reactivity behavior for the corresponding heterocycles. Thus, C−O−C bond angles are substantially larger (ca. 113°) than the corresponding C−S−C bond angles (ca. 97°), whereas C−O bonds are significantly shorter (ca. 1.43 Å) than typical C−S bonds (ca. 1.81 Å). Regarding conformational properties, O−C−C−O segments exhibit a preference for *gauche* arrangements ("attractive *gauche* effect" [9]), whereas S−C−C−S segments adopt largely *anti* conformations

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[†] Structural Effects on the Thermochemical Properties of Sulfur Compounds. Part 2.

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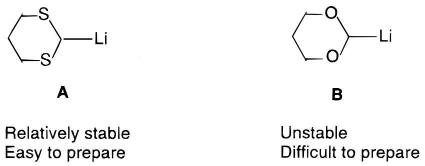

Figure 1.

("repulsive *gauche* effect").[9] In contrast, the anomeric effect[10] tends to be stronger in O−C−O relative to S−C−S segments.

Thermodynamic data such as the enthalpy of formation is often helpful in the understanding of contrasting structural and conformational properties and reactivity patterns exhibited by organic compounds such as the oxygen- and sulfur-containing compounds we are discussing. In particular, we report herein the enthalpies of combustion, sublimation, and formation of 1,4-dithiane, to accompany our recent study of its 1,3-isomer[11] and those data from literature studies[12] of the isomeric dioxanes and of thiirane and oxirane to derive the strain energies of these three-membered heterocycles.

Results

The results of combustion experiments for 1,4-dithiane are given in Table 1.

and correspond to the reaction:

$$C_4H_8S_2(c) + 9O_2(g) + 228\ H_2O(l) = 4\ CO_2(g) + 2[H_2SO_4{\cdot}115H_2O](l) \quad (1)$$

The symbols in this table have the same meaning as in ref 13, and the experimental values have also been derived as in ref 14. The massic energy of combustion of the compound is referred to the final temperature of the experiments of 298.15 K. Table 2 gives the standard molar energy and enthalpy of combustion for the crystalline state at $T = 298.15$ K.

The uncertainties of the standard molar energy and enthalpy of combustion are twice the final overall standard deviation of the mean and were estimated as outlined by Olofsson.[15] The values for the standard molar enthalpies of formation of $H_2O(l)$ and $CO_2(g)$ at $T = 298.15$ K, $-(285.830 \pm 0.042)$ kJ mol^{-1} and $-(393.51 \pm 0.13)$ kJ mol^{-1}, respectively, were taken from CODATA.[16] The value of the enthalpy of formation of $H_2SO_4{\cdot}115H_2O$, $-(887.811 \pm 0.040)$ kJ mol^{-1}, was taken from ref 17.

The results of our Knudsen-effusion experiments for 1,4-dithiane are summarized in Table 3.

The vapor pressures were calculated by means of the equation

$$p = \{(\Delta m/W_a\, at)\}(2\pi RT/M)^{1/2} \quad (2)$$

where p represents the vapor pressure, Δm the mass loss during the time t, W_a the Clausing coefficient of the Knudsen-cell orifice, a the area of the effusion orifice, R the gas constant, T the temperature (in Kelvin), and M the molar mass of the compound of interest.

An equation of the type

$$\log(p/\mathrm{Pa}) = -B(T/\mathrm{K})^{-1} + A \quad (3)$$

was fitted to the results of Table 3 by the method of least squares. The quantities $\delta p/p$ are the fractional deviations of the experimental vapor pressures from those computed using eq 3. The highest percentage error for the vapor pressure in Table 3 is 0.5. The parameters A and B for eq 3 are (12.1 ± 0.1) and $-(3312 \pm 30)$, respectively. The molar enthalpy of sublimation, corresponding to the mean temperature θ of its experimental range, $\Delta_{\mathrm{sub}}H_{\mathrm{m}} = (63.4 \pm 0.6)$ kJ mol^{-1}, has been calculated from the corresponding value of B. The uncertainties assigned to the values of $\Delta_{\mathrm{sub}}H_{\mathrm{m}}°$ are based on the standard deviation value of B.

The enthalpy of sublimation at $T = 298.15$ K has been computed using the same equation as in ref 18. The $C^0_{\mathrm{p,m}}(\mathrm{cr})$ values have been determined by DSC, and $C^0_{\mathrm{p,m}}(\mathrm{g})$ values were calculated using the values given by Dorofeeva.[19] The standard molar enthalpies of sublimation and formation for both crystalline and gaseous states of 1,4-dithiane at $T = 298.15$ K are given in Table 4.

No combustion enthalpy for 1,4-dithiane has been found for comparison with our results. The enthalpy of sublimation of 1,4-dithiane was determined previously by De Wit[20] and Azandegbe.[21] The enthalpy of sublimation at $T = 267.91$ K given by De Wit, corrected to $T = 298.15$ K, is 71.9 kJ mol^{-1} and that determined by Azandegbe by gas−liquid chromatography was 68.9 ± 0.5 kJ mol. Morawetz[22] determined the enthalpy of sublimation of one dithiane isomer, but it is not clear which species he studied.

Geometries of 1,3-dithiane, **1**, and 1,4-dithiane, **2**, optimized at the MP2(FULL)/6-31G(d) level, are presented in Tables 5 and 6.

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Table 1. Results of Combustion Experiments of 1,4-Dithiane at T = 298.15 K[a]

m'(compound) /g[b]	0.97498	1.00287	1.02609	0.99391	1.05334	1.01707
m''(polyethene) /g[b]	0.08293	0.07226	0.08457	0.08307	0.07452	0.07821
m''''(fuse) /g[b]	0.00231	0.00247	0.00229	0.00235	0.00229	0.00238
ΔT_c/K = $(T_f - T_i + \Delta T_{corr})$/K	1.2097	1.2233	1.2699	1.2308	1.2828	1.2499
ϵ(calor) $(-\Delta T_c)$/kJ[c]	−34.9682	−35.3602	−36.7072	−35.5789	−37.0802	−36.1295
ϵ(cont.) $(-\Delta T_c)$/kJ[d]	−0.0571	−0.0579	−0.0605	−0.0583	−0.0612	−0.0594
ΔU_{ign}/kJ[e]	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004
$\Delta U_{diln}(H_2SO_4)$/kJ[f]	−0.0195	−0.0207	−0.0217	−0.0203	−0.0230	−0.0214
$\Delta U_{dec}(HNO_3)$/kJ[h]	0.0309	0.0318	0.0325	0.0315	0.0334	0.0322
ΔU(corr. to std. states)/kJ[i]	0.0107	0.0105	0.0110	0.0108	0.0109	0.0108
$-m''''\Delta_c u^o$(fuse)/kJ	0.0403	0.0430	0.0399	0.0410	0.0400	0.0415
$-m''\Delta_c u^o$(polyethene)/kJ	3.8455	3.3507	3.9216	3.8519	3.4554	3.6267
$\Delta_c u^o$(compound)/kJ g^{-1}	−31.9157	−31.9108	−31.9502	−31.9163	−31.9214	−31.9532
$\langle \Delta_c u^o$(298.15 K)$\rangle$/kJ g^{-1}	−31.9279 ± 0.0076					

[a] For a definition of the symbols, see refs 13 and 14. T_{th} = 298.15 K; V_{bomb} = 0.260 dm^3; p^i_{gas} = 2.03 MPa; m^i_{water} = 10.00 g. [b] Masses obtained from apparent mass. [c] ϵ(calor), energy equivalent of the whole system less the content of the bomb. [d] ϵ(cont.), energy equivalent of the contents of the bomb $\epsilon(\text{cont.})(-\Delta T_c) = \epsilon^i(\text{cont.})(T_i - 298.15\ \text{K}) + \epsilon^i(\text{cont.})(298.15\ \text{K} - T_f + \Delta T_{corr.})$. [e] Experimental energy of ignition. [f] Experimental energy of formation of sulfuric acid. [h] Experimental energy of formation of nitric acid. [i] ΔU(corr. to std. states) is the sum of items 81−85, 87−90, 93, and 94 in ref 14.

Table 2. Standard Molar Energy of Combustion and Enthalpies of Combustion and Formation at T = 298.15 K

compound	$\Delta_c U^o{}_m$, kJ mol^{-1}	$\Delta_c H^o{}_m$, kJ mol^{-1}	$\Delta_f H^o{}_m$, kJ mol^{-1}
1,3-dithiane	−3843.3 ± 2.0[11]	−3855.7 ± 2.0[11]	−65.6 ± 2.2[11]
1,4-dithiane	−3839.0 ± 2.2	−3851.4 ± 2.2	−69.9 ± 2.3

Table 3. Vapor Pressures, *P*, of 1,4-Dithiane

T/K	t/s[a]	Δm/mg[b]	p/Pa[c]	$10^2(\delta p/p)$[d]
269.00	19980	1.62	0.663	2.63
271.02	23580	4.07	0.774	−3.35
277.06	21600	7.07	1.49	−0.28
279.52	22080	9.36	1.93	0.96
283.46	19260	6.45	2.81	−0.037
284.75	15420	10.91	3.25	2.14
286.12	14640	6.15	3.54	−2.35
287.65	11700	10.62	4.19	0.066

[a] Time for the experiment. [b] Mass of sublimed substance. [c] Vapor pressure. [d] δp denotes deviation of the experimental vapor pressures from the values computed using eq 4.

Table 4. Standard Molar Enthalpies at T = 298.15 K

compound	$\Delta_f H^o{}_m$(cr), kJ mol^{-1}	$\Delta_{sub} H^o{}_m$, kJ mol^{-1}	$\Delta_f H_m{}^o$(g), kJ mol^{-1}
1,3-dithiane	−65.6 ± 2.2[11]	62.9 ± 0.7[11]	−2.7 ± 2.3[11]
1,4-dithiane	−69.9 ± 2.3	63.0 ± 0.6	−6.9 ± 2.4

Table 5. Experimental and Calculated Structure of 1,3-Dithiane (Bond Lengths in Angstroms and Bond Angles in Degrees)

	exp[a]	calc[b]
C−C	1.533	1.52
C−S	1.812	1.81
C−H	1.116	1.10
SCS	115.0 (114.1)[c]	115.4
CSC	98.1 (98.7)[c]	97.6
SCC	114.9 (113.2)[c]	114.0
HCH	104	107
SCSC	61.4	61.8

[a] Gas-phase electron diffraction data taken from ref 23. [b] Geometry optimized at MP2(FULL)/6-31G(d) level. [c] Microwave data taken from ref 24.

The most stable form for both species has the chair conformation with symmetries C_s and C_{2h} for 1,3-dithiane and 1,4-dithiane, respectively (see Figure 2).

As can be seen in Tables 5 and 6, the calculated structural parameters are in good agreement with the experimental ones.

Table 6. Experimental and Calculated Structure of 1,4-Dithiane (Bond Lengths in Angstroms and Bond Angles in Degrees)

	exp[a]	calc[b]
C−C	1.49	1.52
C−S	1.81	1.81
C−H	1.09	1.09
CSC	99.0	99.0
CCS	126.3	113.5
HCH		108.0
SCCS		68.1

[a] X-ray data taken from ref 25. [b] Geometry optimized at MP2(FULL)/6-31G(d) level.

1 (C_s) **2** (C_{2h})

Figure 2. Conformations of 1,3-dithiane **1** and 1,4-dithiane **2**.

G2(MP2)-[26] and G3-calculated[27] energies, at 0 K, for 1,3-dithiane and 1,4-dithiane, as well as the reference compounds thiirane, **3**, oxirane, **4**, cyclopropane, **5**, tetrahydro-2*H*-thiopyran, **6**, tetrahydro-2*H*-pyran, **7**, cyclohexane, **8**, 1,3-dioxane, **9**, and 1,4-dioxane **10**, are given in Table 7 (see Figure 3).

To calculate enthalpy values at T = 298 K, the difference between the enthalpy at temperature T and 0 K can be evaluated according to standard thermodynamics.[29] The thermal correction in Gaussian-n (Gn) theories is made using scaled (0.8929) HF/6-31G(d) frequencies for the vibrations in the harmonic approximation[30] (the classical approximation for translation ($^3/_2RT$) and rotation ($^3/_2RT$ for nonlinear molecules, and RT for linear molecules) and an additional RT for converting energy to enthalpy (the PV term).

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Table 7. G2(MP2)- and G3-calculated Energies, at 0 K, and Enthalpies, at 298 K (All Values in hartrees)

compound	G2(MP2) E_0	G2(MP2) H_{298}	G3 E_0	G3 H_{298}
1,3-dithiane **1**	−952.37064	−952.36321	−953.18091	−953.17348
1,4-dithiane, **2**	−952.37202	−952.36460	−953.18228	−953.17487
thiirane, **3**	−476.15702	−476.15267	−476.56146[a]	−476.55711[a]
oxirane, **4**	−153.52931	−153.52521	−153.67058[a]	−153.66647[a]
cyclopropane, **5**	−117.62885[b]	−117.62448[b]	−117.76761[a]	−117.76324[a]
tetrahydro-2*H*-thiopyran, **6**	−593.85914	−593.85199	−594.40322	−594.39607
tetrahydro-2*H*-pyran, **7**	−271.24179	−271.23521	−271.52312	−271.51654
cyclohexane, **8**	−235.34438	−235.33749	−235.62287	−235.61598
1,3-dioxane, **9**	−307.14556	−307.13933	−307.42980	−307.42356
1,4-dioxane **10**	−307.13700	−307.13072	−307.42086	−307.41458

[a] Value taken from ref 27. [b] Value taken from ref 28.

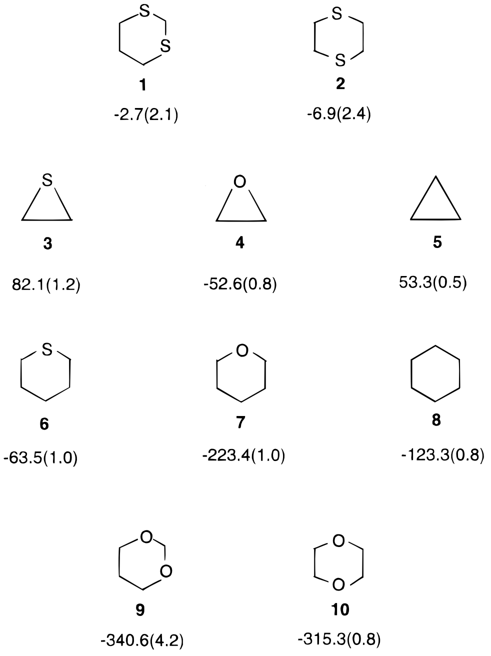

Figure 3. Experimental enthalpies of formation in the gas state in kJ mol^{-1}. Values in parentheses are the intervals of uncertainty.

G2(MP2) and G3 enthalpies at 298 K, for all the studied compounds, are collected in Table 7.

Discussion

1. Theoretical Enthalpies of Formation. To confirm the reliability of the measured enthalpies of formation of 1,3- and 1,4-dithiane, we have obtained theoretical values evaluated at the G2(MP2)[26] and G3[27] levels of theory.

G2(MP2) corresponds 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.

It has been reported[31−34] that the G2 family of computational methods (notably G2(MP2)[26] and G2[35] itself) allows the reliable estimation of the standard enthalpies of formation in the gas phase for a variety of compounds and structural types. In many cases, the computed magnitudes agree with the experimental data within 7.5 kJ mol.[33]

The standard procedure to obtain enthalpies of formation in G2 theory is through atomization reactions (see Experimental Section), but there has been some evidence in recent years that there is an accumulation of errors in the application of G2 theory (and of related, and derived, approaches) to larger molecules.[31,33,36,37] Glukhotsev and Laiter[36] have shown that more accurate heats of formation for benzene and 1,3-butadiene can be derived using isodesmic or homodesmotic reactions instead of atomization energies as in standard G2 theory. The cancellation of errors for such cases involving similar chemical bonds obviously improves the agreement with experiment. More recently, Nicolaides and Radom[31] have shown that the heats of formation for benzene and other hydrocarbons can be improved significantly by the use of isodesmic and isogyric reactions involving these species.

As Raghavachari et al.[34] have pointed out, one of the deficiencies of the isodesmic reaction approach is that many different isodesmic reactions can be set up for the same molecule yielding different results. These authors have very recently proposed to use simpler, but better defined, reactions to assess the performance of theoretical methods in a more systematic manner. A standard set of isodesmic reactions is "bond separation reactions",[38] where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages. They demonstrated[34] that the combination of such bond separation reactions with G2 theory generally leads to a significant improvement in the accuracy of theoretically evaluated heats of formation.

Very recently, Curtiss et al.[27] set forth Gaussian-3 theory (or G3 theory) for the calculation of molecular energies of compounds containing first- and second-row atoms. This new theoretical procedure modifies G2 theory[35] in several ways including a new sequence of single-point energy calculations using different basis sets, a new formulation of the higher-level correction, a spin−orbit correction for atoms, and a correction for core correlation. G3 theory was assessed[27] using the G2/97 test

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(32) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460.

(33) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(34) Raghavachari, K.; Stefanov, B. B.: Curtiss, L. A. *J. Chem. Phys.* **1997**, *106*, 6764.

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(36) Glukhovtsev, M. N.; Laiter, S. *Theor. Chim. Acta* **1995**, *92*, 327.

(37) Raghavachari, K.; Stefanov, B. B.: Curtiss, L. *Mol. Phys.* **1997**, *91*, 555.

(38) Hehre, W. J.; Radom. L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

Table 8. G2(MP2)- and G3-Calculated Heats of Formation, at 298.15 K, in kJ mol^{-1}, Obtained from Atomization and Bond Separation Energy Reactions

compound	G2(MP2) atom.	G2(MP2) BSE	G3 atom.	G3 BSE	exp[a]
1,3-dithiane **1**	−1.3	−1.5	2.1	−2.1	−2.7 ± 2.1[b]
1,4-dithiane, **2**	−4.9	−5.1	−1.5	−5.8	−6.9 ± 2.4[c]
thiirane, **3**	75.4	75.2	78.9	76.7	82.1 ± 1.2
oxirane, **4**	−59.7	−51.5	−52.6	−51.4	−52.6 ± 0.8
cyclopropane, **5**	59.5	55.4	56.1	57.3	53.3 ± 0.5
tetrahydro-2*H*-thiopyran, **6**	−61.6	−65.8	−63.8	−64.8	−63.5 ± 1.0
tetrahydro-2*H*-pyran, **7**	−224.8	−220.6	−224.4	−222.1	−223.4 ± 1.0
cyclohexane, **8**	−113.4	−121.5	−122.7	−120.4	−123.3 ± 0.8
1,3-dioxane, **9**	−352.9	−336.4	−343.2	−340.7	−340.6 ± 4.2
1,4-dioxane **10**	−330.3	−313.8	−319.6	−317.2	−315.3 ± 0.8

[a] Values taken from ref 12. [b] Value taken from ref 11. [c] This work.

set, including enthalpies of formation, and the new procedure corrects many of the deficiencies of G2 theory.

We now present the calculated enthalpies of formation for dithianes and a series of reference compounds.

1.a. Heats of Formation Calculated from Atomization Reactions. As shown in Table 8, $\Delta_f H_m°$ values calculated from G2(MP2) energies using an atomization reaction scheme (see Experimental Section) are in good agreement with the experimental values, but in some cases the differences between experimental and theoretical values are high, 12.3 kJ mol^{-1} for 1,3-dioxane and 15.0 kJ mol^{-1} for 1,4-dioxane.

If we plot theoretical versus experimental $\Delta_f H_m°$ values, the following correlation equation (eq 4) is obtained:

$$\Delta_f H_m°[\text{G2(MP2), atom}] = (0.9 \pm 2.7) + (1.030 \pm 0.016)\ \Delta_f H_m°(\text{exp})\ (\text{kJ mol}^{-1});\ n = 10;\ r = 0.9991;\ \text{sd} = 7.1\ \text{kJ mol}^{-1} \quad (4)$$

The use of G3 theory clearly improves the results. As shown in Table 8, these theoretical $\Delta_f H_m°$ values are very close to the experimental ones, the largest difference between both values being 5.4 kJ mol^{-1} in the case of 1,4-dithiane. Correlation eq 5 is now obtained:

$$\Delta_f H_m°(\text{G3, atom}) = (1.5 \pm 1.1) + (1.012 \pm 0.006)\ \Delta_f H_m°(\text{exp})\ (\text{kJ mol}^{-1});\ n = 10;\ r = 0.9998;\ \text{sd} = 2.9\ \text{kJ mol}^{-1} \quad (5)$$

It has to be noted that the standard deviation of the correlation line decreases from 7.1 to 2.9 kJ mol^{-1} from the G2(MP2) to the G3 level.

1.b. Heats of Formation Calculated from Bond Separation Isodesmic Reactions. When the bond separation isodesmic reaction scheme (see Experimental Section) is used to calculate the heats of formation of the studied molecules, the comparison of the calculated $\Delta_f H_m°$ values, both at the G2(MP2) and the G3 levels, with the experimental values is very good. As is shown in Table 8, the higher discrepancies between theoretical and experimental values occur in the case of thiirane, 6.9 kJ mol^{-1} at the G2(MP2) level and 5.4 kJ mol^{-1} at the G3 level. In both cases, the standard deviations of the correlation lines between theoretical and experimental $\Delta_f H_m°$ values are very low, 2.7 and 2.8 kJ mol^{-1}, at the G2(MP2) and G3 levels, respectively.

As an example of the correlations, Figure 4 is the plot of the $\Delta_f H_m°$ values obtained at the G3 level using bond separation isodesmic reactions versus the experimental $\Delta_f H_m°$ values. It should be noted that, at this level, the equation $\Delta_f H_m°(\text{G3, BSE}) = \Delta_f H_m°(\text{exp})$ remains essentially within the confidence limits of the equation indicated in Figure 4.

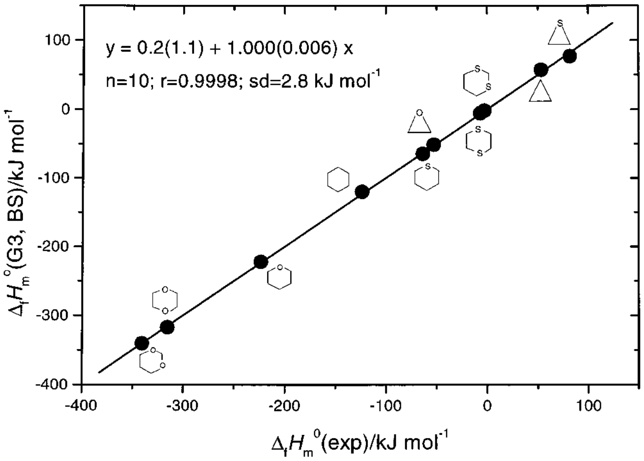

Figure 4. $\Delta_f H_m°$ values obtained at G3 level using bond separation isodesmic reactions versus the experimental $\Delta_f H_m°$ values.

In conclusion, if we want to obtain reliable theoretical enthalpies of formation of heterocyclic compounds such as the ones studied in this work, we have to use G3 energies if we obtain $\Delta_f H_m°$ values through atomization reactions. However, if we calculate $\Delta_f H°$ values through bond separation isodesmic reactions, both theoretical levels, G2(MP2) and G3, permit us to obtain very reliable theoretical enthalpies of formation.

2. Relative Isomeric Stabilities of 1,3- and 1,4-Diderivatized Cyclohexanes. The reliable thermochemical data reported in this paper for 1,4-dithiane, **2**, provide valuable information pertaining to the fundamental differences between oxygen- and sulfur-containing heterocycles. A proper rationalization is facilitated by comparison with the corresponding data for the oxygen analogue, 1,4-dioxane, **10**, as well as those for related systems containing only one heteroatom, or no heteroatom at all. Figure 3 summarizes the gas-phase enthalpies of formation for the organic compounds of interest.

That C−S bonds are weaker than C−O bonds is evidenced by the less negative enthalpy of formation of tetrahydro-2*H*-thiopyran, **6**, relative to tetrahydro-2*H*-pyran, **7**, −63.5 and −223.4 kJ mol^{-1}, respectively. (By comparison, the enthalpy of formation of cyclohexane, **8**, is −123.3 kJ mol^{-1}.) As discussed by Wiberg and coworkers,[39] the lower electronegativity of sulfur relative to oxygen results in diminished Coulombic attraction between carbon and the heteroatom, and thus weaker C−S bonds.

Interestingly, introduction of a second heteroatom has quite contrasting consequences in the oxygen and sulfur heterocycles. Thus, conversion of tetrahydro-2*H*-pyran, **7**, into 1,3-dioxane, **9**, is a highly exothermic process, $\Delta\Delta_f H^\circ = -117.2$ kJ mol^{-1},[40] whereas conversion of tetrahydro-2*H*-thiopyran, **6**, into 1,3-dithiane, **1**, is strongly endothermic, $\Delta\Delta_f H^\circ = +60.8$ kJ mol^{-1}.[11] For the oxygen-containing system, exothermicity in the **7** to **9** transformation is reminiscent of the "*gem* effect",[9,41] where a carbon bound to more than one fluorine atom benefits from "double bond−no bond" stereoelectronic interactions and/or Coulombic attraction between carbon and the electronegative substituents. By contrast, the lack of this *gem* effect in the sulfur series can be explained in terms of the lower electronegativity of sulfur (nearly the same as carbon) relative to oxygen (lower atomic charges) and the concomitant reduction of Coulombic attraction.[39c] Also, the nonbonding orbitals at sulfur are less efficient in double bond−no bond $n_S \rightarrow \sigma^*_{C-S}$ stereoelectronic interactions.

Examination of the experimental enthalpies of formation for the 1,4-diheterocyclohexanes provides support for the previous interpretation in terms of the *gem* effect. Indeed, loss of this stabilizing interaction during 1,3-dioxane, **9**, to 1,4-dioxane **10**, isomerization is shown to be substantially endothermic, $\Delta\Delta_f H^\circ = +25.3$ kJ mol^{-1}. In contrast, conversion of 1,3-dithiane **1**, where no *gem* effect is apparent, to its 1,4-analogue, **2**, is actually slightly exothermic, $\Delta\Delta_f H^\circ = -4.2$ kJ mol^{-1}.

Ignoring experimental measurement derived uncertainties, we see that 1,4-dithiane is ca. 4 kJ mol^{-1} less stable than its 1,3-isomer: inclusion of the measured error bars allows for the possibility that the thermodynamic stability order may be slightly reversed. What is found for the isomeric stabilities of the other pairs of 1,3- and 1,4-diderivatized cyclohexanes? The currently found near equality of the enthalpies of formation of the isomeric dithianes is also found for the archival[12] 1,3- and 1,4- dimethylcyclohexanes (Ia and Ib) and for 1,3- and 1,4- cyclohexanediones[42] (IIa and IIb), while a significantly higher thermodynamic stability of the 1,3- over the 1,4-isomer is found for the isomeric sets of dioxanes[12] (IIIa and IIIb) and dimethylenecyclohexanes[43] (IVa and IVb) (see Figure 5).

The relative stabilities of the dioxanes are compatible with anomeric effect reasoning,[10] overriding any electrostatic effects that regulated the relative stability of the diones and dimethylene species.[44] We did not expect any particular steric or electronic effects in either the 1,3- or the 1,4-dimethyl species,[45] and none was found.[46]

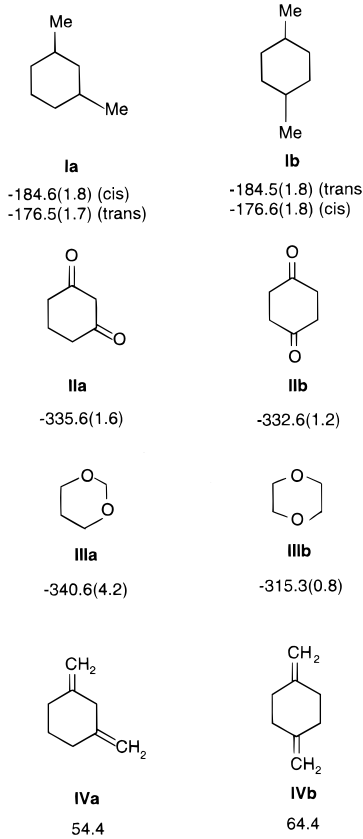

Figure 5. Experimental enthalpies of formation in the gas state in kJ mol^{-1}. Values in parentheses are the intervals of uncertainty.

While "dithia derivatization" of cyclohexane to result in either dithiols or exocyclic dithioethers remains unstudied, the small, nearly identical effects of forming the isomeric dithianes is entirely plausible. Unlike oxygen replacement of an internal CH_2 in an alkane to form an ether, there is very little site dependence on the resulting enthalpy of formation change on formation of a thioether.[47] For example, we find from archival sources that the enthalpies of formation of 2- and 3-oxapentane differ by some 14 kJ mol^{-1} while those of 2- and 3-thiapentane are the same within experimental error. This correctly suggests that the gas-phase sulfur reaction 6 is essentially thermoneutral for either the 1,3- or 1,4-dithiane isomer

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(39) (a) Wiberg, K. B.; Hada, C. M.; Rablen, P.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644. (b) Wiberg, K. G.; Nakaji, D. *J. Am. Chem. Soc.* **1993**, *115*, 10658. (c) Wiberg, K. B.; Rablen, P. *J. Am. Chem. Soc.* **1995**, *117*, 7, 2201.

(40) Månsson. M. *J. Chem. Thermodyn.* **1974**, *6*, 1153.

(41) (a) Ignacio, E, W.; Schlegel, H. B. *J. Phys. Chem.* **1992**, *96*, 5830 and references therein. (b) Juaristi, E.; Cuevas, G. *The Anomeric Effect*; CRC Press: Boca Raton, FL, 1995; pp 25 and 26.

(42) Pilcher, G.; Parchment, O. G.; Hillier, I. H.; Heatley, F.; Fletcher, D.; Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Monte, M. J. S.; Jiye, F. *J. Phys. Chem.* **1993**, *97*, 243. Note, this conclusion is relevant only for gas-phase species because solid 1,3-cyclohexanedione is, in fact, the β-hydroxyenone (β-ketoenol) tautomer and not the β-diketone that the name denotes.

(43) (a) 1,3-Dimethylenecyclohexane: Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H. W.; Boesse, R. *Chem. Ber.* **1991**, *124*, 2499. (b) 1,4-Dimethylenecyclohexane: Roth, W. R.; Klärner, F. BG.; Lennartz, H. W. *Chem. Ber.* **1980**, *113*, 1818.

(44) Liebman, J. F. In *The Chemistry of Functional Groups, Supplement A2: The Chemistry of Dienes and Polyenes*; Rappoport, Z. Ed.; Wiley: Chicherter, 1997. Slayden, S. W.; Liebman, J. F. In *The Chemistry of Functional Groups Supplement A3: The Chemistry of Doubly-Bonded Functional Groups*; Patai, S., Rappoport, Z., Ed.; Wiley: Chichester, 1997.

(45) We explicitly chose the conformers in which both methyl groups were equatorial.

(46) Interesting comparisons would have been between the isomeric pair of bis(trifluoromethyl)cyclohexanes and between the cyclohexanedicarbonitriles, but there are no relevant thermochemical data available for any of these species.

(47) For example, see the analysis found in the following: Slayden, S. W.; Liebman J. F. In *The Chemistry of Functional Groups Supplement E2: The Chemistry of Hydroxyl, Ether and Peroxide Groups*; Patai, S. Ed.; Wiley: Chichester, 1993. Liebman J. F.; Crawford, K. S. K.; Slayden, S. W. In *The Chemistry of Functional Groups Supplement S: The Chemistry of Sulphur-containing Functional Groups*; Patai, S., Rappoport, Z., Ed.; Wiley: Chichester, 1993.

$$2\ cyclo\text{-}(CH_2)_5S \rightarrow 1,3\text{- or }1,4\text{-}cyclo\text{-}(CH_2)_4S_2 + cyclo\text{-}(CH_2)_6 \quad (6)$$

while the corresponding oxygen reactions of either dioxane are not thermoneutral

$$2\ cyclo\text{-}(CH_2)_5O \rightarrow 1,3\text{- or }1,4\text{-}cyclo\text{-}(CH_2)_4O_2 + cyclo\text{-}(CH_2)_6 \quad (7)$$

Using our enthalpy of formation values for the dithianes and those from ref 4 for the other species, the predicted thermoneutrality for reaction 6 is confirmed within experimental error for both isomers. Reaction 7 is exothermic by ca. 20 kJ mol^{-1} for the 1,3-dioxane isomer and endothermic by ca. 8 kJ mol^{-1} for its 1,4-isomer.

3. The Ultradiagonal Strain Energy of Thiirane. Furthermore, now that we have a measured enthalpy of formation for 1,4-dithiane, we can derive the "ultradiagonal" strain energy,[48] UDSE, of thiirane. Recall, this is defined by halving the formal enthalpy of homodesmic reaction 8:

$$1,4\text{-}cyclo\text{-}(CH_2)_4S_2 \rightarrow 2\ cyclo\text{-}(CH_2)_2S \quad (8)$$

$$\mathrm{UDSE}[cyclo\text{-}(CH_2)_2S, g] = \Delta_f H_m°[cyclo\text{-}(CH_2)_2S, g] - {}^1/_2\ \Delta_f H_m°[cyclo\text{-}(CH_2)_4S_2, g] \quad (9)$$

Using solely experimentally measured enthalpies of formation, the strain energy result is 85.6 ± 1.7 kJ mol^{-1}, entirely compatible with that suggested earlier[49] and significantly less than the values of 115.0 and 105.1 kJ mol^{-1} found for cyclopropane and oxirane,[50] respectively. As shown in Table 9, these conclusions are confirmed by G2(MP2) and G3 theories.

Table 9. "Ultradiagonal" Strain Energies,[a] Calculated from Experimental and Theoretical $\Delta_f H°$ Values, for Thiirane, Oxirane, and Cyclopropane[b]

compound	exp.	G2(MP2)	G3
thiirane, **3**	82.1 ± 1.3	77.8	79.6
oxirane, **4**	105.1 ± 0.9	105.4	107.2
cyclopropane, **5**	115.0 ± 0.6	116.2	117.5

[a] Defined in ref 48. [b] All values in kJ mol^{-1}.

Experimental Section

Materials. 1,4-Dithiane, purity > 99%, was supplied by Lancaster. The sample was carefully dried under vacuum. Determination of purity, assessed by DSC by the fractional fusion technique,[51] indicated that the mole fraction of impurities in the compound was less than 0.001. No impurities (≥0.001%) could be detected by GC. The sample was studied by DSC in the temperature range between $T = 258$ K and $T = 301$ K, and no transition in the solid state was observed.

Procedure for Thermochemical Measurements. An isoperibol calorimeter equipped with a rotary bomb and an isothermal water jacket was used for the measurements of the energy of combustion. The apparatus has been described in ref 11. The rotating mechanism allows simultaneous axial and end-over-end rotation of the bomb. The combustion bomb has an internal volume of 0.260 dm^3, and it is lined with platinum. All the internal fittings, electrodes, gimbal, and crucible are also fabricated from platinum. The bomb is initially in the inverted position, so that the combustion gases come into contact only with platinum and with the water that covers the valves and gaskets.

Calorimeter temperatures were measured to $\pm 10^{-4}$ K with a platinum resistance thermometer of 100 Ω at time intervals of 15 s using a calibrated resistance bridge (Model F26, Automatic System Laboratories Ltd.) interfaced to a microcomputer programmed to calculate the adiabatic temperature change.[52] The electrical energy for ignition was determined from the change in potential difference across a 4700 μF capacitor previously charged to 13.5 V upon partial discharge, through a platinum wire of 0.05 mm diameter to which a cotton thread had been tied. The initial and final voltages across the condenser were recorded. The initial temperature of the combustion experiments was chosen so that the final calorimeter temperature would be near 298.15 K, and the energy of reaction was always referred to the final temperature of 298.15 K.

The bomb, which initially contains air at atmospheric pressure, is assembled and charged with oxygen to a total pressure of 3.04 MPa at $T = 298.15$ K (Air Liquid, N-50) without previous flushing as is usual in combustion experiments with compounds containing sulfur. The procedure for determining the energy of combustion of sulfur compounds was recently reported.[11] The initial amount of water on the bomb was 10.00 cm^3, and the air at atmospheric pressure was left in the bomb before charging it with oxygen. The energy of combustion of thiocamphor was determined by burning the solid sample in pellet form. Because of the relatively high vapor pressure of thiocamphor, the pelleted compound was enclosed in polyethene bags. Under these conditions no carbon or CO was found. The energy equivalent of the calorimeter, ϵ(calor), was determined in the same conditions under which the experiments were done: with rotation, 10 cm^3 of water added to the bomb and a pressure of oxygen of 3.04 MPa, using the combustion of benzoic acid, NIST standard reference sample 39j, having a massic energy of combustion under the conditions specified in the certificate of −(26434 ± 3) J g^{-1}, hence $\Delta_c u° = -(26414 \pm 4)$ J g^{-1}. From 10 calibration experiments the value of the energy equivalent was determined and used in computing the results of the combustion experiments: $\epsilon(\mathrm{calor}) = (28.9084 \pm 0.0024)$ kJ K^{-1}. Frequent calibration experiments were made throughout the series of combustion experiments. The empirical formula and massic energy of combustion of our polyethene,[53] $C_{0.960}H_{2.000}$ and −(46371 ± 4) J g^{-1}, and cotton-thread fuse, $C_{1.000}H_{1.740}O_{0.871}$ and (17410 ± 37) J g^{-1}, were determined in our laboratory. After disassembly of the calorimeter the bomb gases were slowly let out and the absence of CO and SO_2 was checked with Dräger tubes (sensitivity level. 1 and 0.1 ppm, respectively). The liquid phase in the bomb was quantitatively transferred to a volumetric flask together with the washing water, boiled to remove the carbon dioxide dissolved and diluted to 100 cm^3. To determine the chemical composition at the end of the reaction of the liquid phase in the bomb, aliquots of the diluted bomb solutions were titrated with standard alkali to determine the total acid. Some titrations were made before carbon dioxide is removed, or after the solution has been boiled to remove carbon dioxide. No difference is found in cases which the bomb washings are titrated in both conditions.

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(48) (a) Skancke, A.; Van Vechten, D.; Liebman, J. F.; Skancke, P. N. *J. Mol. Struct.* **1996**, *376*, 461 (b) Skancke, A.; Liebman, J. F. *J. Org. Chem.* **1999**, *64*, 6361.

(49) See, for example: Pihlaja, K.; Taskinen, E. In *Physical Methods in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1974; Vol. 6, p 199.

(50) This is not a trivial interrow comparison. It is interesting that the replacement of oxygen in oxirane by its third-row counterpart, sulfur, to form thiirane results in a significant decrease of strain energy of the three-membered ring, as does the replacement of nitrogen in diazirines by its third-row counterpart, phosphorus, to form diphosphirnes (see ref 48b). However, replacement of a carbon in cyclopropane by silicon to form silirane (see ref 48a) significantly increases the strain energy.

(51) Marti, E. E. *Thermochim. Acta* **1973**, *5*, 173.

(52) Roux, M. V.; Jiménez, P.; Dávalos, J. Z.; Abboud, J.-L. M; Molina, M. T. *J. Chem. Thermodyn.* **1996**, *28*, 1029.

(53) Jiménez, P.; Roux, M. V.; Turrión, C.; Gomis, F. *J. Chem. Thermodyn.* **1987**, *19*, 985.

Table 10. Physical properties at $T = 298.15$ K

compound	M, g mol^{-1}	ρ, g cm^{-3}	$(\delta V/\delta T)_P \times 10^{-7}$, dm^3 g^{-1} K^{-1}	c_P, J K^{-1} g^{-1}
polyethene	13.558	0.918	7.65	2.0
cotton	27.700	1.5	9.69[54]	1.48
1,4 -dithiane	120.2395	1.378[25]	(3.35)	1.07

[a] The value in parentheses was estimated.

The analyses of the products were made immediately after the combustion experiments. The absence of $SO_3^{=}$ and NO_2^- was checked by calibrated ionic chromatography. The quantity of nitric acid was taken as the difference between the total acid and the theoretical quantity of sulfuric acid calculated from the mass of the sample. The corrections for nitric acid were based on the value of −59.7 kJ mol^{-1} for the molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2(g), O_2(g), and H_2O(l). All weighings were performed with a Mettler AT-21 microbalance. For the correction of apparent mass to mass, conversion of the energy of the actual bomb process to that of the isothermal process, and the correction to standard states, we have used the values of density, ρ, massic heat capacity, c_p, and $(\delta V/\delta T)_p$, respectively, given in Table 10. Heat capacities were determined by DSC.

Correction to standard states was made as described by Hubbard, Scott, and Waddington.[14]

The energy of solution of carbon dioxide in water at 298.15 K, $\Delta_{sol}U(CO_2)$, was taken as 7.09 kJ mol^{-1}, and the solubility constant, $K(CO_2)$, as 0.03440 mol DM^{-3} atm^{-1} at 298.15 K.[55] The atomic weights of the elements were those recommended by APACE in 1996.[56]

The accuracy of the calorimetric combustion experiment was checked by measuring the energy of combustion of thianthrene, as has been recommended by Head and Sabbah.[57] The standard molar enthalpy obtained, $\Delta_c H_m° = -7252.1 \pm 3.0$ kJ mol^{-1}, is in good agreement with the values obtained by other authors.[11]

A differential scanning calorimeter (Perkin-Elmer DSC-2C), connected to a Model 3600 Data Station and provided with an Intracooler-2-unit, was used in this research. Its temperature scale was calibrated by measuring the melting point of the recommended high-purity reference materials: *n*-octadecane, octadecanoic acid, benzoic acid, tin, and indium.[58] The power scale was calibrated using high-purity indium (mole fraction: >0.99999) as reference material.[58] The vapor pressures for 1,4-dithiane were measured by the Knudsen-effusion method as previously described.[59] The apparatus consisted, essentially, of a stainless steel sublimation chamber immersed in a jacket and connected to a high-vacuum system (1×10^{-4} Pa). The temperature of the jacket was maintained constant to within ± 0.005 K for each vapor-pressure experiment and was measured with a calibrated platinum resistance thermometer. The enthalpy of sublimation was computed from the relation between pressure and temperature. The effusion orifice area, a, and the Clausing coefficient,[60] W_a, were $a = (4.44 \pm 0.02) \times 10^{-4}$ cm^2 and $W_a = (0.943 \pm 0.012)$.

Computational Details. Standard ab initio molecular orbital calculations[38] were performed with the Gaussian94 series of programs.[61]

Energies of 1,3-dithiane, **1**, and 1,4-dithiane, **2**, thiirane, **3**, oxirane, **4**, cyclopropane, **5**, tetrahydro-2*H*-thiopyran, **6**, tetrahydro-2*H*-pyran, **7**, cyclohexane, **8**, 1,3-dioxane, **9**, and 1,4-dioxane **10**, as reference compounds, were calculated using Gaussian-*n* theories, at the G2(MP2),[26] and the very recently proposed[27] G3 levels.

Theoretical Determination of Heats of Formation. (a) From Atomization Reactions. In standard Gaussian-*n* theories, theoretical enthalpies of formation at 0 K are calculated through atomization reactions.

Consider the molecule $C_mH_nX_p$ in the gas phase. $\Delta_f H_m°$(0 K) for this compound is calculated from the Gaussian-*n* (G3 or G2(MP2), in our case) energies at 0 K for the atomization reaction 10, $\Delta H°_a$, and the experimental heats of formation of C(g), H(g), and X(g).

$$C_mH_nX_p(g) \rightarrow mC(g) + nH(g) + pX(g) \qquad \Delta H°_a \quad (10)$$

Combining the next two equations:

$$\Delta H°_a = mG3(C, 0\ K) + nG3(H, 0\ K) + pG3(X, 0\ K) - G3(C_mH_nX_p, 0\ K) \quad (11)$$

$$\Delta H°_a = m\ \Delta_f H°_{m,exp}(C, 0\ K) + n\ \Delta_f H°_{m,exp}(H, 0\ K) + p\ \Delta_f H°_{m,exp}(X, 0\ K) - \Delta_f H°_m(C_mH_nX_p, 0\ K) \quad (12)$$

the heat of formation of $C_mH_nX_p$ is given by:

$$\Delta_f H°_m(C_mH_nX_p, 0\ K) = G3(C_mH_nX_p, 0\ K) - mG3(C, 0\ K) - nG3(H, 0\ K) - pG3(X, 0\ K) + m\ \Delta_f H°_{m,exp}(C, 0\ K) + n\ \Delta_f H°_{m,exp}(H, 0\ K) + p\ \Delta_f H°_{m,exp}(X, 0\ K) \quad (13)$$

where G3 (0 K) are the G3 [or G2(MP2)] total energies at 0 K and $\Delta_f H°_{m,exp}$ are the experimental enthalpies of formation, at 0 K, of the isolated atoms in the gas phase.[62]

In the case of 1,3- or 1,4-dithiane, $C_4H_8S_2$, the theoretical enthalpy of formation at 298 K is calculated by correcting $\Delta_f H°_m$(0 K) as follows:[32]

$$\Delta_f H°_m(C_4H_8S_2, 298\ K) = \Delta_f H°(C_4H_8S_2, 0\ K) + \Delta H_T^{calc}(C_4H_8S_2) - 4\ \Delta H_T^{exp}[C(s)] - 4\ \Delta H_T^{exp}[H_2(g)] - 2\ \Delta H_T^{exp}[S(s)] \quad (14)$$

where $\Delta H_T^{calc}(C_4H_8S_2)$, the difference between the enthalpy at temperature T and 0 K, is evaluated as indicated above and ΔH_T^{exp} for the elements refers to their standard states at 298 K.[64]

In the case of 1,3- or 1,4-dioxane, $C_4H_8O_2$, the theoretical enthalpy of formation at 298 K is calculated as follows:

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(62) We have used the JANAF values[63] 711.2, 216.04, 246.8, and 274.7 kJ mol^{-1} for the experimental enthalpies of formation, at 0 K, of C(g), H(g), O(g), and S(g), respectively.

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(64) Values are taken from ref 63: 1.050, 8.468, 8.680, and 4.410 kJ mol^{-1}, for C(s), H_2(g), O_2(g), and S(s), respectively.

(65) Experimental heats of formation for methane, ethane, hydrogen sulfide, methanethiol, water, and methanol are −74.87, −83.85, −20.50, −22.8, −241.83, and −201.1 kJ mol^{-1}, respectively.

$$\Delta_f H^\circ_m(C_4H_8O_2, 298\ K) = \Delta_f H^\circ(C_4H_8O_2, 0\ K) + \Delta H_T^{calc}(C_4H_8O_2) - 4\ \Delta H_T^{exp}[C(s)] - 4\ \Delta H_T^{exp}[H_2(g)] - \Delta H_T^{exp}[O_2(g)] \quad (15)$$

Related equations have been used in the case of the other studied compounds. G2(MP2)- and G3-calculated heats of formation, at $T = 298$ K, for compounds **1**−1**0**, using atomization reactions, are given in Table 8.

(b) From Bond Separation Isodesmic Reactions. As indicated above, there has been some evidence in recent years that there is an accumulation of errors in the application of G2 theory (or similar approaches) to larger molecules. Raghavachari et al.[34] have very recently proposed the use of simpler but better defined reactions to assess the performance of theoretical methods in a more systematic manner. A standard set of isodesmic reactions is "bond separation reactions",[38] where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages.

In the case of dithianes **1** or **2**, the bond separation reaction using its effective valence bond structure, is

$$C_4H_8S_2(g) + 4CH_4(g) + 2H_2S(g) \rightarrow 2CH_3CH_3(g) + 4CH_3SH(g) \qquad \Delta H^\circ_{BS} \quad (16)$$

The bond separation reaction energies are then evaluated at G3, or G2(MP2), levels of theory:

$$\Delta H^\circ_{BS} = 2\ G3(CH_3CH_3, 298\ K) + 4\ G3(CH_3SH, 298\ K) - 4\ G3(CH_4, 298\ K) - 2\ G3(H_2S, 298\ K) - G3(C_4H_8S_2, 298\ K) \quad (17)$$

and using the experimentally known heats of formation for the reference molecules, as given in ref 12:[65]

$$\Delta_f H^\circ_m(C_4H_8S_2, 298\ K) = G3(C_4H_8S_2, 298\ K) + 4\ G3(CH_4, 298\ K) + 2\ G3(H_2S, 298\ K) - 2\ G3(CH_3CH_3, 298\ K) - 4\ G3(CH_3SH, 298\ K) - 4\ \Delta_f H^\circ_{m,exp}(CH_4, 298\ K) - 2\ \Delta_f H^\circ_{m,exp}(H_2S, 298\ K) + 2\ \Delta_f H^\circ_{m,exp}(CH_3CH_3, 298\ K) + 4\ \Delta_f H^\circ_{m,exp}(CH_3SH, 298\ K) \quad (18)$$

In the cases of dioxanes, **9** or **10**, the process is similar, using the corresponding bond separation reaction

$$C_4H_8O_2(g) + 4CH_4(g) + 2H_2O(g) \rightarrow 2CH_3CH_3(g) + 4CH_3OH(g) \quad (19)$$

Related equations have been used in the case of the other studied compounds.

G2(MP2)- and G3-calculated heats of formation, at 298 K, for compounds **1**−**10**, using bond separation reactions, are collected in Table 8.

Conclusion

Calorimetric measurements (enthalpies of combustion and of sublimation) and G2(MP2) and G3 quantum chemical calculations show that the isomeric 1,3- and 1,4-dithianes have very nearly the same enthalpy of formation, unlike that for the related dioxanes.

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