Calorimetric and Computational Study of 1,4-Dithiacyclohexane 1,1-Dioxide (1,4-Dithiane Sulfone)

María Victoria Roux,*,[†] Manuel Temprado,[†] Pilar Jiménez,[†] Rafael Notario,*,[†] Ramón Guzmán-Mejía,[‡] and Eusebio Juaristi*,[‡]

Instituto de Química Física "Rocasolano", CSIC, Serrano 119, 28006 Madrid, Spain, and Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, Apartado Postal 14-740, 07000 México D.F., Mexico

victoriaroux@iqfr.csic.es

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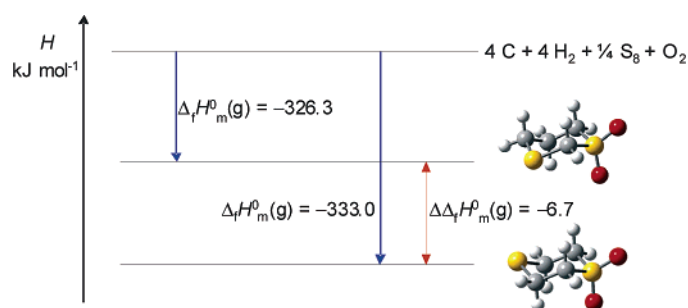
This work reports the enthalpies of formation in the condensed and gas state of 1,4-dithiacyclohexane 1,1-dioxide (1,4-dithiane sulfone, **5**), derived from the enthalpy of combustion in oxygen, measured by a rotating bomb calorimeter and the variation of vapor pressures with temperatures determined by the Knudsen effusion technique. The theoretically estimated enthalpy of formation was calculated from high-level ab initio molecular orbital calculations at the G2(MP2) level. The theoretical calculations appear to be in very good agreement with experiment. A comparison of the conversion of thiane sulfone **3** to 1,3-dithiane sulfone **4** and 1,4-dithiane sulfone **5** clearly shows the 1,3 isomer to be 6.7 kJ mol^{-1} less stable, probably owing to diminished electrostatic repulsion between the sulfur heteroatoms in 1,4-sulfone **5**.

Introduction

In recent years, thermochemical studies of sulfur-containing six-membered heterocycles have provided essential information on the relative importance of steric, electrostatic, and stereo-electronic interactions that are responsible of the enthalpies of formation of these type of compounds.[1]

In a particular example, comparison of the enthalpies of formation, symbolized $\Delta_f H°_m$, for thiane **1**, 1,3-dithiane **2**, thiane sulfone **3**, and 1,3-dithiane sulfone **4**, shows that the enthalpy of formation of 1,3-dithiane sulfone **4** is less exothermic than expected; that is, a destabilization worth 7.7 kJ mol^{-1} is evident (Figure 1).

Analysis of the charge distribution in the compounds of interest was carried out by means of the NBO method[3] and suggests that a repulsive electrostatic interaction between positively charged sulfur atoms is responsible for the observed difference in the enthalpy of formation of 1,3-dithiane sulfone **4** (Figure 2).

Comparison of the enthalpies of formation for isomeric compounds is particularly useful since it shows their relative stability.[1] In this regard, the determination of the enthalpy of formation of 1,4-dithiane sulfone **5**, where the sulfur atoms are not geminal, was deemed of interest. It can be anticipated that

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[†] Instituto de Quimica Fisica "Rocasolano".

[‡] Centro de Investigacion y de Estudios Avanzados del IPN.

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

parameter	value				
m' (compound)[b]/g	0.629826	0.653014	0.639994	0.640914	0.651844
m'' (polyethene)[b]/g	0.081226	0.077427	0.075284	0.075163	0.083317
m''' (vaseline)[b]/g	0.354866	0.386496	0.399791	0.372781	0.403356
m'''' (fuse)[b]/g	0.002435	0.002312	0.002205	0.002477	0.002392
$\Delta T_c/K = (T_f - T_i + \Delta T_{corr})/K$	1.1969	1.2600	1.2664	1.2248	1.2944
ϵ (calor) $(-\Delta T_c)^c$/kJ	−34.5544	−36.3781	−36.5626	−35.3609	−37.3701
ϵ (cont.) $(-\Delta T_c)^d$/kJ	−0.0604	−0.0640	−0.0644	−0.0620	−0.0625
$\Delta U_{ign}{}^e$/kJ	0.0004	0.0004	0.0005	0.0005	0.0005
ΔU_{dec} (HNO$_3$)^f/kJ	0.0402	0.0512	0.0362	0.0435	0.0327
ΔU_{diln} (H$_2$SO$_4$)^g/kJ	−0.00409	−0.00451	−0.00425	−0.00429	−0.00446
ΔU(corr. to std states)^h/kJ	0.0221	0.0232	0.0238	0.0226	0.0243
$-m'' \Delta_c u°$ (polyethene)/kJ	3.7666	3.5904	3.4911	3.4854	3.8636
$-m''' \Delta_c u°$ (Vaseline)/kJ	16.3547	17.8125	18.4252	17.1804	18.5895
$-m'''' \Delta_c u°$ (fuse)/kJ	0.0424	0.0403	0.0384	0.0432	0.0417
$\Delta_c u°$ (compound)/kJ g^{-1}	−22.8515	−22.8611	−22.8378	−22.8605	−22.8349
$<\Delta_c u°$ (298.15 K)$>$/kJ g^{-1}			−22.8491 ± 0.0055		

[a] For a definition of the symbols see refs 4 and 5. [b] Masses obtained from apparent mass. [c] ϵ (calor), energy equivalent of the whole system but the content of the bomb. [d] ϵ (cont), energy equivalent of the contents of the bomb. [e] Experimental energy of ignition. [f] Experimental energy of formation of nitric acid. [g] Experimental energy of formation of sulfuric acid. [h] Energetic correction to standard states.
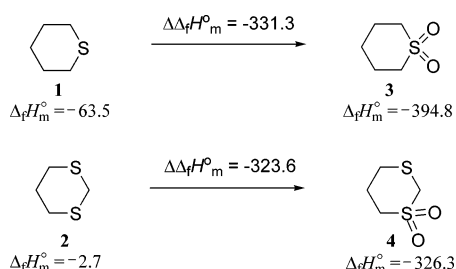
FIGURE 1. Differences in the enthalpy of formation ($\Delta\Delta_f H°_m$, in kJ mol^{-1}) for the conversions **1** into **3** and **2** into **4**.[2]

FIGURE 2. NBO charges [MP2(FULL)/6-31G(d) level] at selected heavy atoms in sulfones **3** and **4**.

electrostatic interaction between the sulfur heteroatoms would be less significant.

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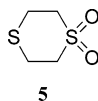
Results and Discussion

Experimental Determination of the Enthalpy of Formation in the Gas Phase. The enthalpy of formation in the gas state of 1,4-dithiane sulfone at $T = 298.15$ K, $\Delta_f H°_m$(g, 298.15 K), was determined from the experimental values of the standard enthalpy of formation in the crystalline state, $\Delta_f H°_m$(cr), and the standard enthalpy of sublimation, $\Delta_{sub} H°_m$, both referenced to $T = 298.15$ K.

From combustion experiments given in Table 1 corresponding to the reaction

$$C_4H_8O_2S_2(cr) + 8O_2(g) + 228H_2O(l) =$$
$$4CO_2(g) + 2[H_2SO_4 \cdot 115H_2O](l) \quad (1)$$
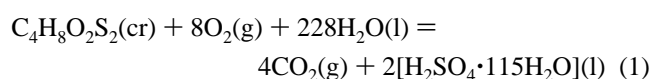
the experimental value for the enthalpy of formation of **5** in the crystalline state was determined.

TABLE 2. Vapor Pressures of 1,4-Dithiane Sulfone

T, K	$t,^a$ s	$\Delta m,^b$ mg	$p,^c$ Pa
339.43	31080	4.31	0.139
342.36	30480	5.62	0.186
345.48	30120	7.83	0.263
348.45	24300	8.17	0.342
350.89	18000	7.79	0.442
354.52	23220	13.84	0.611

[a] Time for the experiment. [b] Mass of sublimed substance. [c] Vapor pressure.

TABLE 3. Experimentally Determined Standard Molar Energy of Combustion and the Standard Molar Enthalpy of Combustion, Sublimation, and Formation in the Crystalline and Gaseous State at the Temperature $T = 298.15$ K for 1,4-Dithiane Sulfone

thermodynamic properties	experimental values^a
$\Delta_c U°_m$	−3478.5 ± 2.1
$\Delta_c H°_m$	−3488.4 ± 2.1
$\Delta_f H°_m$(cr)	−432.9 ± 2.2
$\Delta_{sub} H°_m$	99.9 ± 1.2
$\Delta_f H°_m$(g)	−333.0 ± 2.5

[a] All values in kJ mol^{-1}.

The enthalpy of sublimation, $\Delta_{sub} H°_m$, was obtained from vapor pressure measurements by a Knudsen-type mass-loss effusion technique, Table 2.

Values determined for the standard molar energy of combustion, $\Delta_c U°_m$, the standard molar enthalpy of combustion, $\Delta_c H°_m$, the enthalpy of sublimation, $\Delta_{sub} H°_m$, and the enthalpy of formation in the crystalline, $\Delta_f H°_m$(cr), and gaseous state, $\Delta_f H°_m$(g), of 1,4-dithiane sulfone are collected in Table 3.

No experimental results for the energies and enthalpies of combustion, sublimation, and formation have been found in the literature for comparison with our results.

Molecular and Electronic Structures. To our knowledge, the molecular structure of 1,4-dithiane sulfone has not been studied. The optimized geometry, at the MP2(FULL)/6-31G(3df,2p) level of theory, is presented in Table 4.

The most stable form is the chair conformation, belonging to the symmetry point group C_1 (see Figure 3). The chair structure is similar to that of cyclohexane but is more puckered to accommodate the bond angles and bond lengths characteristic for sulfur.

TABLE 4. MP2(FULL)/6-31G(3df,2p)-Calculated Structure of 1,4-Dithiane Sulfone. Bond Lengths in Ångstroms and Bond Angles in Degrees

S_1-O_{ax}	1.441
S_1-O_{eq}	1.436
S_1-C_2	1.763
C_2-C_3	1.517
C_3-S_4	1.791
OS_1O	120.8
$S_1C_2C_3$	111.2
$C_2C_3S_4$	113.0
$C_3S_4C_5$	98.4
$C_6S_1C_2$	102.4
Θ^a	108.2
Φ^b	63.0

[a] The mean bond angle in the ring. [b] The mean torsional angle in the ring.

$\Delta E = +23.6 \text{ kJ mol}^{-1}$
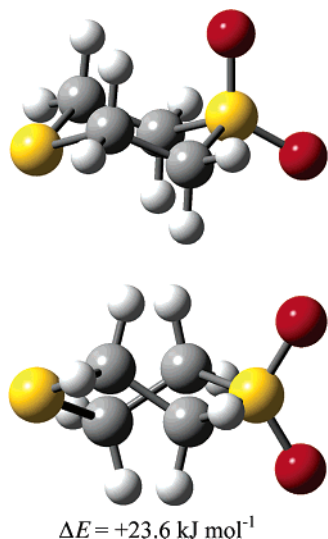
FIGURE 3. Above, the chair conformation of 1,4-dithiane sulfone. Below, the 1,4-twist conformation. ΔE is the relative energy with respect to the chair conformation, evaluated at the HF/6-31G(d) level.

The 1,4-twist conformer is also a minimum in the potential energy surface of 1,4-dithiane sulfone, but calculations at the HF/6-31G(d) level indicate that it is 23.6 kJ mol^{-1} higher in energy than the chair conformer. The 2,5-twist conformer collapsed to the 1,4-twist when the optimization was carried out.

For sulfones, the length of the S=O bonds is the most important structural parameter. The sulfonyl group also has the bond angle OSO and the corresponding O⋯O nonbonded distance as important structural parameters. Comparing the structure of 1,4-dithiane sulfone with that calculated[6] for thiane sulfone, the S−O distances are slightly different, with the S−O$_{ax}$ longer than the S−O$_{eq}$ bond (1.441 and 1.436 Å for the axial and equatorial oxygen, respectively, versus 1.437 and 1.441 Å), the OSO angle is larger (120.8° versus 120.5°), and the nonbonded O⋯O distance is shorter (2.50 versus 2.56 Å). Comparing the structure of 1,4-dithiane sulfone with that

calculated[2] for 1,3-dithiane sulfone, we can see that the nonbonded O⋯O distance is the same, 2.50 Å, and the OSO angle is very similar, 120.8° in 1,4-dithiane sulfone and 120.9° in the 1,3-isomer. The S−O distances are slightly different (1.441 and 1.436 Å for the axial and equatorial oxygen, respectively, versus 1.436 and 1.438 Å).

We can also compare the calculated structure of 1,4-dithiane sulfone with that calculated for 1,4-dithiane.[7] The CSC angle increases from 98.9° to 102.4° when SO$_2$ group is present in the molecule. This behavior has been observed in other compounds. The bond angle XSX always increases when going from sulfide to sulfone.[8] This CSC angle is larger in 1,4-dithiane sulfone compared with those of 1,3-dithiane sulfone and thiane sulfone, 102.4° versus 101.2° and 100.6°, respectively.

It has been observed[9,10] that the introduction of a sulfur heteroatom into a six-membered carbon ring increases the ring puckering in comparison with the conformation of cyclohexane. To measure this ring puckering, we can calculate the average valency and torsional angles, Θ and Φ, respectively.[11] The average torsional angle, Φ, which is determined by a delicate balance between valency, torsional, and nonbonded forces, is an easily calculated[1] and convenient index of the puckering in six-membered rings.

The Φ torsional angle of 1,4-dithiane sulfone, 63.0°, has a value similar to those calculated for 1,3-dithiane sulfone and 1,4-dithiane ($\Phi = 62.3°$ and 62.6°, respectively), indicating that the rings are similarly puckered. The presence of two S atoms in the ring logically increases the puckering comparing to that of thiane or thiane sulfone ($\Phi = 59.4°$ and 59.7°, respectively).

The puckering of the ring in 1,4-dithiane sulfone can be also studied comparing their angles between planes with those calculated for 1,4-dithiane. The angles in the sulfone are smaller confirming that the structure is more puckered.

Theoretical Enthalpies of Formation. G2(MP2)[12] calculated energy, at 0 K, for 1,4-dithiane sulfone is given in Table 5.

To calculate the enthalpy value at 298.15 K, the difference between the enthalpy at temperature T and 0 K is evaluated according to standard thermodynamics.[13] The thermal correction in Gaussian-n theories is made using scaled (0.8929) HF/6-31G(d) frequencies for the vibrations in the harmonic approximation for vibrational energy,[14] 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). G2(MP2) enthalpy at 298.15 K for the compound studied is also collected in Table 5.

In standard Gaussian-n theories, theoretical enthalpies of formation are calculated through atomization reactions. We have

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(13) McQuarrie, D. A.; Simon, J. D. *Molecular Thermodynamics*; University Science Books: Sausalito, CA, 1999.

(14) Each normal mode contributes $Nh/(e^{h\nu/kT} - 1)$ to thermal correction, where N is Avogadro's constant, h is Planck's constant, ν is the frequency, k is Boltzmann's constant, and T is the temperature.

TABLE 5. G2(MP2)-Calculated Energies, at 0 K, and Enthalpies, at 298.15 K, for 1,4-Dithiane Sulfone (All Values in Hartrees)

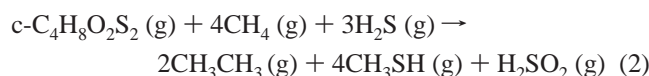|	G2(MP2)		G2(MP2)+ ^{a}	
compd	E_0	H_{298}	E_0	H_{298}
1,4-dithiane sulfone	−1102.64007	−1102.63115	−1102.64014	−1102.63123

^{a} Values obtained using the G2(MP2) scheme, from geometries optimized at the MP2(FULL)/6-31G(3df,2p) level. See text.

TABLE 6. Enthalpy of Formation at $T = 298.15$ K of 1,4-Dithiane Sulfone, Experimental and Calculated from Atomization and Isodesmic Reactions (All Values in kJ mol^{-1})

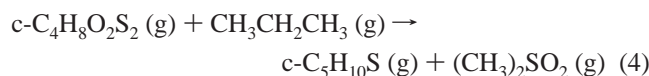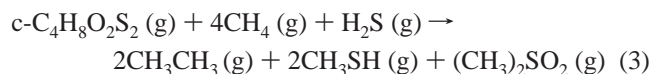|	G2(MP2)			G2(MP2)+			
compd	atomization	isodesmic (2)	isodesmic (3)	atomization	isodesmic (2)	isodesmic (3)	exptl
1,4-dithiane sulfone	−333.8^a	−338.5	−336.1	−333.9^a	−337.7	−335.8	−333.0 ± 2.5

^{a} Value obtained from atomization reaction including spin−orbit and bond additivity corrections. See text.

detailed this method in previous studies.[15,16] Raghavachari et al.[17] have proposed to use a standard set of isodesmic reactions, the "bond separation reactions",[18] where all formal bonds between nonhydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages, to derive the theoretical enthalpies of formation. However, this method is not applicable in the case of the compound studied, because the bond separation isodesmic reaction for 1,4-dithiane sulfone, c-$C_4H_8O_2S_2$, is

$$c\text{-}C_4H_8O_2S_2 \text{ (g)} + 4CH_4 \text{ (g)} + 3H_2S \text{ (g)} \rightarrow$$
$$2CH_3CH_3 \text{ (g)} + 4CH_3SH \text{ (g)} + H_2SO_2 \text{ (g)} \quad (2)$$

and the experimental enthalpy of formation of one of the reference compounds, H_2SO_2, is not available.

We have used in this work two isodesmic reactions using as reference $(CH_3)_2SO_2$:

$$c\text{-}C_4H_8O_2S_2 \text{ (g)} + 4CH_4 \text{ (g)} + H_2S \text{ (g)} \rightarrow$$
$$2CH_3CH_3 \text{ (g)} + 2CH_3SH \text{ (g)} + (CH_3)_2SO_2 \text{ (g)} \quad (3)$$

$$c\text{-}C_4H_8O_2S_2 \text{ (g)} + CH_3CH_2CH_3 \text{ (g)} \rightarrow$$
$$c\text{-}C_5H_{10}S \text{ (g)} + (CH_3)_2SO_2 \text{ (g)} \quad (4)$$

The calculated values for the enthalpy of formation of 1,4-dithiane sulfone, at the G2(MP2) level of theory, using atomization and isodesmic reactions,[19] are shown in Table 6. The $\Delta_fH°_m$ value obtained from atomization reaction has been modified adding spin−orbit and bond additivity (BAC) corrections.[20] The method has been detailed in a previous study.[21]

A further step in the obtaining of theoretical values of $\Delta_fH°_m$ is the consideration of a more sophisticated basis set in the

optimization of the geometries. The availability of 3d orbitals in sulfur is the main factor responsible for its reactivity behavior, and so, the adequate description of the geometry and electronic properties of sulfur containing compounds would require the inclusion of supplementary d functions in the basis set. We have reoptimized the geometry of the compound studied at the MP2(FULL)/6-31G(3df,2p) level and have also carried out the single-point calculations using a similar scheme as in G2(MP2) formalism.[12] This approach will be designed as G2(MP2)+. Calculated energy, at 0 K, and enthalpy at 298.15 K are given in Table 5. The $\Delta_fH°_m$ values for the compound studied, calculated at this computational level, are collected in Table 6.

As can be seen in Table 5, all of the $\Delta_fH°_m$ values for 1,4-dithiane sulfone, calculated from G2(MP2) and G2(MP2)+ energies, are in very good agreement with the experimental value. The average values obtained at the G2(MP2) and G2(MP2)+ levels, from the atomization and isodesmic reactions are −336.1 and −335.8 kJ mol^{-1}, close to the experimental value, −333.0 ± 2.5 kJ mol^{-1}.

Discussion

Relative to cyclohexane **6**, the enthalpy of formation of thiane **1** is much less negative, −123.3 and −63.5 kJ mol^{-1}, respectively (Figure 4).[22] These thermodynamic data ($\Delta\Delta_fH°_m = +59.8$ kJ mol^{-1}) give evidence of the relative strength of the C−C and C−S bonds; the longer C−S bonds result in diminished Coulombic attraction between the heteroatom and bonded carbon atoms, and thus weaker C−S bonds.[1]

Introduction of a second sulfur heteroatom in the thiane **1** to 1,4-dithiane **7** conversion shows additivity of the endothermic $CH_2 \rightarrow S$ process since $\Delta\Delta_fH°_m = +56.6$ kJ mol^{-1}.[7] Therefore, the observation in the present work that substitution of a methylene group by a sulfur heteroatom in thiane sulfone **3** (ref 6) to afford 1,4-dithiane sulfone **5** is endothermic by +61.8 kJ mol^{-1} [$\Delta_fH°_m(\mathbf{3}) = -394.8$ kJ mol^{-1} and $\Delta_fH°_m(\mathbf{5}) = -333.0$ kJ mol^{-1}] is in agreement with anticipation (Figure 1).

A comparison of the conversion of sulfone **3** to dithiane sulfones **4** and **5** clearly shows that 1,3-dithiane sulfone **4** to be 6.7 kJ mol^{-1} less stable than **5**.

As mentioned in the Introduction, it was shown recently that the enthalpy of formation of 1,3-dithiane sulfone **4** is less negative by 7.7 kJ mol^{-1} than expected. This finding was

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(19) Experimental $\Delta_fH°_m$ values for the reference compounds used in isodesmic reactions 2 and 3, methane, ethane, propane, hydrogen sulfide, methanethiol, thiane and dimethyl sulfone, −74.9, −83.8, −104.7, −20.6, −22.8, −63.5, and −373.0 kJ mol^{-1}, respectively, have been taken from NIST compilation: Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. *Neutral Thermochemical Data* in *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

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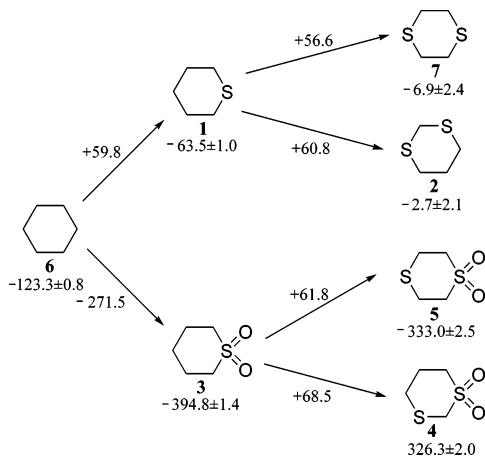
FIGURE 4. Comparison of the experimental gas-phase enthalpies of formation of cyclohexane and sulfur-containing heterocycles. All values in kJ mol^{-1}.
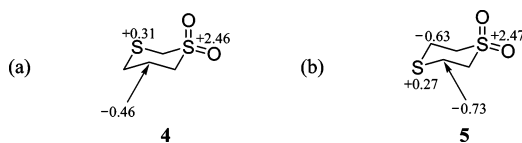

FIGURE 5. NBO charges [MP2(FULL)/6-31G(d)] at selected heavy atoms in sulfones **4** and **5**.

interpreted in terms of a repulsive electrostatic interaction between sulfur atoms in 1,3-dithiane sulfone **4** (Figure 5a). According to this argument, a similar electrostatic repulsion in 1,3-dithiane sulfone **4** must be less important in 1,4-dithiane sulfone **5**, where the positively charged sulfurs are separated by three bonds (Figure 5b).

Experimental Section

Experimental Procedures. Material and Purity Control. 1,4-Dithiane sulfone was synthesized following the procedure of Clennan et al.[23] using 1,4-dithiane sulfoxide as precursor. The sulfoxide was previously obtained according to the procedure described by Khan and co-workers.[24] In a round-bottom 1000-mL flask was placed 5.0 g (36.7 mmol) of 1,4-dithiane sulfoxide and 370 mL of water. The resulting solution was treated with 12.25 g of MgSO$_4$ dissolved in 360 mL of water, and then with 3.9 g (24.6 mmol) of KMnO$_4$ in 240 mL of water. The reaction mixture was stirred for 1.5 h, treated with 15 g (78.9 mmol) of sodium metabisulfite to destroy the excess of oxidizing reagent. The resulting colorless mixture was filtered, extracted with CH$_2$Cl$_2$, and evaporated at reduced pressure. The crude product was purified by flash column chromatography (CH$_2$Cl$_2$–EtOAc, 4:1) to afford the expected sulfone (4.9 g, 88% yield).

The sample was carefully dried under vacuum at 50 °C. Determination of purity, assessed by GC and DSC by the fractional fusion technique,[25,26] indicated that the mole fraction of impurities was less than 0.001.

Thermochemical Measurements. The enthalpy of formation in the gas state, $\Delta_f H°_m$(g) of 1,4-dithiane sulfone, was determined by combining the standard enthalpy of formation of the crystalline

compound, $\Delta_f H°_m$(cr), with its standard enthalpy of sublimation, $\Delta_{sub} H°_m$. The enthalpy of formation in the crystalline state was determined from combustion calorimetry using an isoperibol combustion calorimeter equipped with a rotary bomb. Details of the technique and procedure used have been previously described.[27] The energy of combustion was determined by burning the solid samples in pellet form. The pelleted compound was enclosed in polyethene bags. Vaseline was used as auxiliary material to have less than 8 mmol of sulfur in the samples.[28] The energy of the combustion experiments was always referred to the final temperature of 298.15 K. From the combustion energy, the enthalpy of formation in the condensed state was calculated. The enthalpy of sublimation was determined by measurements of the vapor pressures over a 15 K temperature interval using the Knudsen-effusion technique,[29] and the enthalpy of sublimation was deduced from the temperature dependence of the vapor pressures (Clausius–Clapeyron). Heat capacity measurements were previously determined in this laboratory by means of differential scanning calorimetry.[30] From the experimental results the standard enthalpies of combustion, sublimation and formation in the crystalline and gaseous state at the temperature of 298.15 K have been derived and are reported in Table 3.

Computational Details. Standard ab initio molecular orbital calculations[17] were performed with the Gaussian 03 series of programs.[31] The energies of the compound studied were calculated using Gaussian-2 theory, at the G2(MP2) level.[12]

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. We have also reoptimized the geometry at the MP2(full)/6-31G(3df,2p) level and carried out the single-point calculations using a similar scheme as in G2(MP2) formalism.

The charge distribution in the compounds has been analyzed using a population partition technique, the natural bond orbital (NBO) analysis of Reed and Weinhold.[3,32,33] The NBO analysis has been performed using the NBO program[34] implemented in the Gaussian 03 package.[31]

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Supporting Information Available: Experimental details, tables of results for the determination of $\Delta_f H°_m$, optimized structures in Cartesian coordinates and energies, and IR, Raman, ^{1}H NMR, and ^{13}C NMR spectra and DSC curve of purity control for 1,4-dithiacyclohexane 1,1-dioxide (1,4-dithiane sulfone). This material is available free of charge via the Internet at http://pubs.acs.org.

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