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Thermochemistry of 1,3-Dithiacyclohexane 1-Oxide (1,3-Dithiane Sulfoxide): Calorimetric and Computational Study

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The enthalpies of combustion and sublimation of 1,3-dithiacyclohexane 1-oxide (1,3-dithiane sulfoxide, **2**) were measured by a rotating-bomb combustion calorimeter and the Knudsen effusion technique, and the gas-phase enthalpy of formation was determined, $\Delta_f H^\circ_m(g) = -98.0 \pm 1.9$ kJ mol^{-1}. This value is not as large (negative) as could have been expected from comparison with thermochemical data available for the thiane/thiane oxide reference system. High-level ab initio molecular orbital calculations at the MP2(FULL)/6-31G(3df,2p) level were performed, and the optimized molecular and electronic structures of **2** afforded valuable information on (1) the relative conformational energies of **2**-axial and **2**-equatorial—the latter being 7.1 kJ mol^{-1} more stable than **2**-axial, (2) the possible involvement of $n_S \rightarrow \sigma^*_{C-S(O)}$ hyperconjugation in **2**-equatorial, (3) the lack of computational evidence for $\sigma_{S-C} \rightarrow \sigma^*_{S-O}$ stereoelectronic interaction in **2**-equatorial, and (4) the relevance of a repulsive electrostatic interaction between sulfur atoms in 1,3-dithiane sulfoxide, which apparently counterbalances any $n_S \rightarrow \sigma^*_{C-S(O)}$ stabilizing hyperconjugative interaction and accounts for the lower than expected enthalpy of formation for sulfoxide **2**.

Introduction

The combination of experimental calorimetric measurements, particularly of the standard enthalpies of formation, and theoretical examination of model molecules constitutes a powerful tool for the understanding of the conformational and chemical behavior of organic compounds. Over the past few years, we have reported several applications of this approach in the study of six-membered sulfur-containing heterocycles.[1-6]

In this regard, the interest in tricoordinated sulfur compounds in general, and sulfoxides in particular, has increased exponentially in the past two decades as a consequence of the enormous potential of the chiral

sulfinyl group as auxiliary in asymmetric synthesis.[7-11] Nevertheless, the nature of the S−O bond in sulfoxides is still a matter of controversy,[12-14] as is the interpretation of the conformational behavior of thiane oxide and derivatives.[14]

Very recently,[6] the calorimetric and computational examination of 1,3-dithiane sulfone **1** suggested that repulsive electrostatic interaction between sulfur atoms offsets any $n_S \rightarrow \sigma^*_{C-SO_2}$ stabilizing interaction in this heterocycle (eq 1).

$$\tag{1}$$
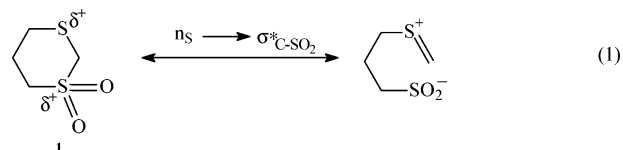
Analogous 1,3-dithiane 1-oxide (sulfoxide **2**) has now been examined, with particular attention given to po-

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§ Centro de Investigación y de Estudios Avanzados del IPN.

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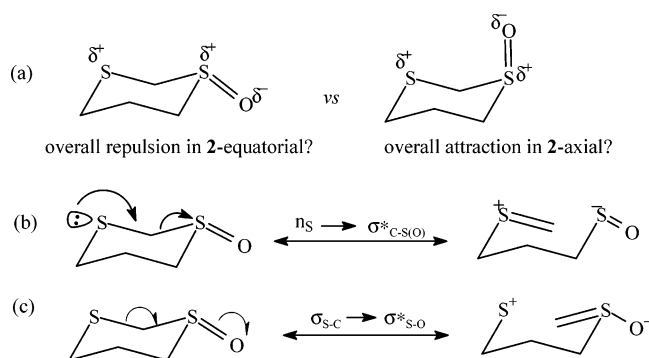(10) Carreño, M. C. *Chem. Rev.* **1995**, *95*, 1717.

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TABLE 1. Results of Combustion Experiments of 1,3-Dithiane Sulfoxide at $T = 298.15$ K

m'(compound) (g)[a]	0.557226	0.544664	0.547180	0.551257	0.550834
m''(polyethene) (g)[a]	0.081776	0.079628	0.086835	0.090012	0.085123
m'''(Vaseline) (g)[a]	0.340431	0.358065	0.341233	0.365167	0.337337
m''''(fuse) (g)[a]	0.002172	0.002410	0.002385	0.002443	0.002194
ΔT_c/K $= (T_f - T_i + \Delta T_{corr})$ (K)	1.2024	1.2159	1.2028	1.2497	1.1968
ϵ(cal) $(-\Delta T_c)$ (kJ)[b]	-34.7157	-35.1034	-34.7253	-36.0801	-34.5533
ϵ(cont) $(-\Delta T_c)$ (kJ)[c]	-0.0607	-0.0614	-0.0607	-0.0634	-0.0604
ΔU_{ign} (kJ)[d]	0.0004	0.0004	0.0004	0.0004	0.0004
ΔU_{dec} (HNO$_3$) (kJ)[e]	0.0524	0.0535	0.0550	0.0509	0.0458
ΔU_{diln} (H$_2$SO$_4$) (kJ)[f]	-0.00397	-0.00370	-0.00376	-0.00382	-0.00384
ΔU(corr. to std states) (kJ)	0.0205	0.0211	0.0207	0.0219	0.0206
$-m\Delta_c u^\circ$(polyethene) (kJ)	3.7921	3.6925	4.0267	4.1740	3.9473
$-m\Delta_c u^\circ$(Vaseline) (kJ)	15.6895	16.5022	15.7264	16.8295	15.5469
$-m\Delta_c u^\circ$(fuse) (kJ)	0.0379	0.0420	0.0416	0.0426	0.0382
$\Delta_c u^\circ$(compound) (kJ g^{-1})	-27.2557	-27.2770	-27.2652	-27.2614	-27.2647
$\langle \Delta_c u^\circ(298.15 \text{ K}) \rangle$ (kJ g^{-1})			-27.2648 ± 0.0035		

[a] Masses obtained from apparent mass. [b] ϵ(cal), energy equivalent of the whole system but the content of the bomb. [c] ϵ(cont), energy equivalent of the contents of the bomb ϵ(cont)$(-\Delta T_c) = \epsilon^i$(cont)$(T^i - 298.15 \text{ K}) + \epsilon^i$(cont)$(298.15 \text{ K} - T^f + \Delta T_{corr.})$. [d] Experimental energy of ignition. [e] Experimental energy of formation of nitric acid. [f] Experimental energy of formation of sulfuric acid.

SCHEME 1

TABLE 2. Vapor Pressures of 1,3-Dithiane Sulfoxide

T (K)	t (s)[a]	Δm (mg)[b]	p (Pa)[c]	10^2 $(\delta p/p)$
319.68	22560	5.54	0.253	-1.80
322.06	21660	7.21	0.344	1.99
325.42	20880	9.94	0.494	0.84
328.44	19020	12.41	0.681	0.02
330.90	11460	9.62	0.879	-0.83
333.64	23760	26.98	1.19	0.54
337.24	10800	17.44	1.71	-0.48

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

tential thermochemical or computational manifestations of electrostatic[6] (e.g., $S^{\delta+}$-----$^{\delta+}S(O)$ repulsion or $S^{\delta+}$-----$^{\delta-}O{=}S$ attraction, Scheme 1a) and stereoelectronic interactions[13-15] (e.g., $n_S \rightarrow \sigma^*_{C-S(O)}$ or $\sigma_{S-C} \rightarrow \sigma^*_{S-O}$ hyperconjugation, Scheme 1b,c).

Results

Experimental Determination of the Enthalpy of Formation in the Gas Phase. The enthalpy of formation in the gas state of 1,3-dithiane sulfoxide, $\Delta_f H^\circ_m$(g), was determined from the experimental values of the standard enthalpy of formation in the crystalline state, $\Delta_f H^\circ_m$(cr), and the standard enthalpy of sublimation, $\Delta_{sub} H^\circ_m$, both found at $T = 298.15$ K.

From combustion experimental results corresponding to the reaction

$$C_4H_8OS_2(cr) + 17/2 O_2(g) + 228 H_2O(l) =$$
$$4CO_2(g) + 2[H_2SO_4 \cdot 115 H_2O](l) \quad (2)$$
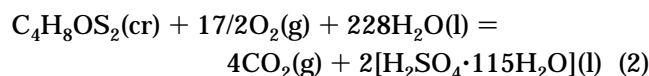
and given in Table 1, the experimental value for the enthalpy of formation in the crystalline state was determined.

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

thermodynamic properties	experimental values[a,b]
$\Delta_c U^\circ_m$	-3714.5 ± 1.6
$\Delta_c H^\circ_m$	-3725.6 ± 1.6
$\Delta_f H^\circ_m$(cr)	-195.7 ± 1.7
$\Delta_{sub} H^\circ_m$	97.7 ± 0.8
$\Delta_f H^\circ_m$(g)	-98.0 ± 1.9

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

The enthalpy of sublimation, $\Delta_{sub} H^\circ_m$, was obtained from vapor pressure measurements by the Knudsen effusion technique, Table 2.
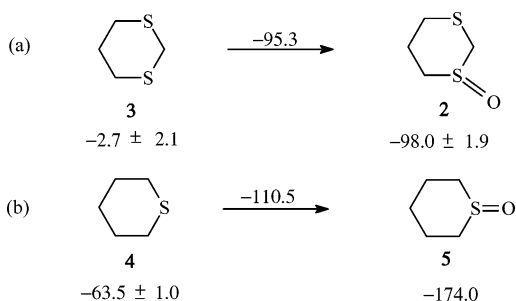
Table 3 collects the determined values for the standard molar energy of combustion, $\Delta_c U^\circ_m$; the standard molar enthalpy of combustion, $\Delta_c H^\circ_m$; sublimation, $\Delta_{sub} H^\circ_m$; and formation in the crystalline, $\Delta_f H^\circ_m$(cr), and gaseous state, $\Delta_f H^\circ_m$(g), of 1,3-dithiane sulfoxide.

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

Comparison of the enthalpy of formation in the gas phase of 1,3-dithiane 1-oxide (**2**, $\Delta_f H^\circ_m$(g) $= -98.0 \pm 1.9$ kJ mol^{-1}, Table 3) with that of 1,3-dithiane (**3**, $\Delta_f H^\circ_m$(g) $= -2.7 \pm 2.1$ kJ mol^{-1}, ref 1) shows that the oxidation process is exothermic by 95.3 kJ mol^{-1} (Scheme 2a). By contrast, oxidation of thiane **4** to thiane oxide **5** is significantly more exothermic ($\Delta\Delta_f H^\circ_m$(g) $= -110.5$ kJ mol^{-1}, Scheme 2b and ref 4).

To explain the lower-than-anticipated enthalpy of formation for 1,3-dithiane sulfoxide **2**, we proceeded to

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SCHEME 2

(a)

3

−2.7 ± 2.1

$\xrightarrow{-95.3}$

2

−98.0 ± 1.9

(b)

4

−63.5 ± 1.0

$\xrightarrow{-110.5}$

5

−174.0

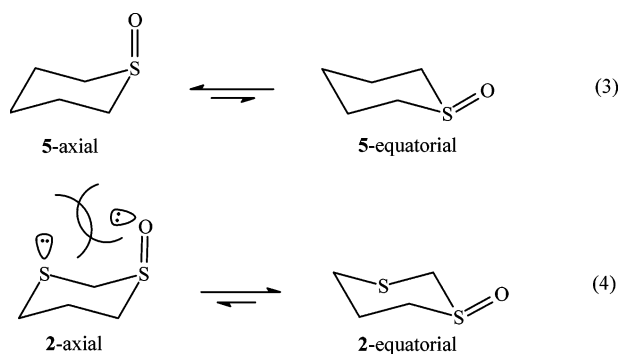**FIGURE 1.** Chair conformation of 1,3-dithiane sulfoxide **2**, with the oxygen atom in the equatorial position.

compare its molecular and electronic structure with those of 1,3-dithiane **3**, sulfone analogue **1**, and thiane sulfoxide **5**.

Molecular and Electronic Structures. To our knowledge, there is not any experimental determination of the molecular structure of 1,3-dithiane sulfoxide. The optimized geometry, at the MP2(FULL)/6-31G(3df,2p) level of theory, is presented in Figure S1 of the Supporting Information.

In contrast with thiane oxide **5** that is more stable in the axial conformation (eq 3),[4,14,16−22] 1,3-dithiane 1-oxide **2** adopts preferentially the equatorial conformation (eq 4). This result is also in line with previous theoretical and experimental studies of sulfoxide **2**.[14,19,22−29]

5-axial   **5-equatorial**   (3)

2-axial   **2-equatorial**   (4)

The most stable form of **2** is the chair conformation, belonging to the symmetry point group C_s (see Figure 1). The chair structure is similar to that of cyclohexane but is more puckered to accommodate the bond angles and bond lengths characteristic of sulfur. All the possible
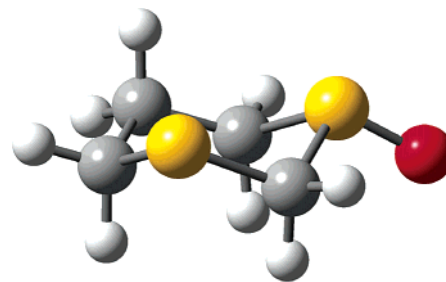
twisted and boat conformers, six in each case, are higher in energy than the chair conformers.

According to our high level [MP2(FULL)/6-31G(3df,2p)] calculations, the conformer with the oxygen atom in the axial position (**2**-axial in eq 4) is 7.1 kJ mol^{-1} higher in energy. This gas-phase estimate is in fair agreement with the experimentally obtained value $\Delta G^{\circ}_{298K} = 2.7$ kJ mol^{-1} in methanol.[25,26,28] The higher energy of **2**-axial relative to **2**-equatorial has been ascribed to a repulsive interaction between the lone electron pairs at sulfur and oxygen in the axial sulfinyl group—the so-called repulsive gauche effect (eq 4).[14,30]

Since the calorimetric measurements are carried out with solid samples of sulfoxide **2**, we deemed it important to establish whether the axial or equatorial conformation of this six-membered heterocycle is present in the solid state. Thus, solid-state NMR spectroscopy was applied to determine the conformation adopted by **2** in the material employed for the calorimetric studies. Figure S2 of the Supporting Information illustrates the ^{13}C CP-MAS NMR spectrum of interest.

The similarity of the ^{13}C NMR chemical shifts observed in solution,[28] where the predominance of **2**-equatorial was established, and in the solid sample (Figure S2 of the Supporting Information) suggest that the equatorial orientation of the sulfinyl S=O group is also preferred in the solid state.

The structural data summarized in Figure S1 are in line with expectation from $n_S \rightarrow \sigma^*_{C-S(O)}$ hyperconjugation in **2** (Scheme 1b) since comparison with the structural data for 1,3-dithiane **3** shows a shortening of the S(3)−C(2) bond length (from 1.789 Å in **3** to 1.780 Å in **2**) and a lengthening of the C(2)−S(1) bond (from 1.789 Å in **3** to 1.799 Å in **2**).[31,32]

On the other hand, the structural data in Figure S1 helps discard the possibility of $\sigma_{S-C} \rightarrow \sigma^*_{S-O}$ hyperconjugation in **2**-equatorial since one would expect the S−O bond length in **2** to be significantly longer relative to **5**. In fact, the calculated S−O bond length in sulfoxide **2** (1.482 Å) is slightly shorter than that calculated for reference sulfoxide **5** (1.487 Å).

The bond configuration of all sulfoxides is characterized by a pyramidal arrangement. In terms of the valence

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shell electron pair repulsion (VSEPR) theory,[33] it is an AX$_3$E structure with three ligands and one lone pair of electrons around of the central sulfur atom. It is general evidence[34] that in sulfoxides the X−S−X angle is smaller than the X−S−O angle. This behavior is observed in 1,3-dithiane sulfoxide (see Figure S1). This result is fully consistent with VSEPR predictions, according to which an angle involving multiple bonds will be greater than an angle involving single bonds only.

The C−S(O) −C angle is very similar in sulfoxides **2** and **5** (94.7 and 94.9°, respectively), and it is smaller than in sulfone **1** (101.2°) and also smaller than in sulfide **3** (97.4°). This behavior has been observed in other compounds. The bond angle X−S−X always decreases in going from a sulfone to the analogous sulfoxide, whereas from sulfoxide to sulfide there is an increase in the value.[34] This fact is in apparent disagreement with VSEPR considerations; it would have been expected that the X−S−X angle should further decrease in the analogous sulfides. An explanation[35] for this apparent anomaly may be that, for a general applicability of VSEPR considerations,[36,37] not only the bond angle variation but also the angles of the lone pair must be considered. The situation is especially complicated in the case of sulfides, where three kinds of interactions are present: bond/bond, bond/lone pair, and lone pair/lone pair.

Comparing the bond distances, the C−S bond lengths are very similar in sulfoxides **2** and **5** (and in sulfide **3**) but significantly longer than in sulfone **1**, whereas the C−C bond lengths are very similar in the four compounds.

It has been observed[37,38] 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.[39] The average torsional angle, Φ, which is determined by a delicate balance between valence, torsional, and nonbonded forces, is an easily calculated[1] and convenient index of the puckering in six-membered rings.

The Φ torsional angle of 1,3-dithiane sulfoxide, 64.5°, has a value higher than those calculated for 1,3-dithiane (Φ = 62.5°), 1,3-dithiane sulfone (62.3°), and thiane sulfoxide (61.6°), indicating that the ring of 1,3-dithiane sulfoxide is the most puckered.

The puckering of the ring in 1,3-dithiane sulfoxide can be also studied comparing the angles between planes with those calculated for thiane sulfoxide. The angles in the former are smaller, confirming that the structure is more puckered.

It is evident that the stabilization gained from the apparent $n_S \rightarrow \sigma^*_{C-S(O)}$ hyperconjugative interaction in **2**
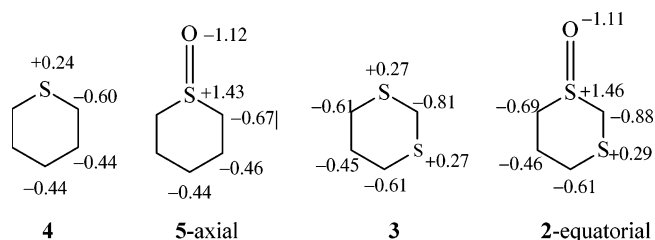
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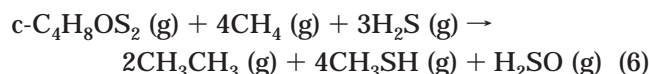
FIGURE 2. Natural charges obtained from a NBO analysis at the MP2(FULL)/6-31G(3df,2p) level, located at the heavy atoms in thiane **4**, thiane oxide **5**-axial, 1,3-dithiane **3**, and 1,3-dithiane sulfoxide **2**-equatorial.

is more than counterbalanced by a repulsive interaction that is reflected in the small experimental enthalpy of formation for 1,3-dithiane sulfoxide **2** ($\Delta_f H^\circ_m(g) = -98.0$ kJ mol^{-1}, Table 3). To get information that could help understand the nature of the destabilizing effect in 1,3-dithiane sulfoxide **2** that apparently counterbalances the $n_S \rightarrow \sigma^*_{C-S(O)}$ stabilizing interaction, the charge distribution in the compounds of interest was analyzed by means of the natural bond orbital (NBO) method of Weinhold et al.[40,41] In Figure 2, we have collected the natural atomic charges (the nuclear charges minus summed natural populations of the natural atomic orbitals on the atoms) at the heavy atoms for the compounds of interest.

Most significant is the very large positive charge generated at the sulfur atom upon oxidation, from values between +0.24 and +0.27 in thioethers **4** and **3** to +1.43 and +1.46 in sulfoxides **5** and **2**. Indeed, the large experimentally observed **4** to **5** process ($\Delta\Delta_f H^\circ_m = -110.5$ kJ mol^{-1}, Scheme 2b) reflects the substantial electrostatic attraction between positive sulfur ($q = +1.43$, eq 5) and the negative C(3,5) carbons in sulfoxide **5** ($q = -0.46$, eq 5). In contrast, in equatorial 1,3-dithiane sulfoxide **2**, the attractive electrostatic stabilization is offset by a repulsive electrostatic interaction between sulfurs ($q = +1.46$ and +0.29, eq 5). Eq 5 also includes the NBO charges of interest in axial 1,3-dithiane sulfoxide **2**; it is appreciated that the charge on sulfur (**3**) is independent of the conformation.

(5)
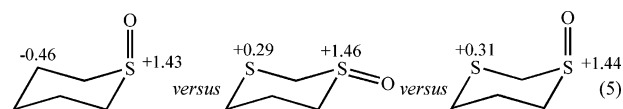
Theoretical Enthalpies of Formation. G2(MP2)[42] calculated energies, at 0 K, for 1,3-dithiane sulfoxide **2** in both equatorial and axial conformations are given in Table 4. As can be seen in this table, the equatorial conformer is the most stable one.

To calculate enthalpy values at 298.15 K, the difference between the enthalpy at temperature T and 0 K is evaluated according to standard thermodynamics.[43] The thermal correction in Gaussian-n theories is made using scaled (0.8929) HF/6-31G(d) frequencies for the vibrations

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TABLE 4. G2(MP2) Calculated Energies (at 0 K) and Enthalpies (at 298.15 K) for 1,3-Dithiane Sulfoxide 2, in Both Equatorial and Axial Forms[a]

	G2(MP2)		G2(MP2)+[b]	
	E_0	H_{298}	E_0	H_{298}
equatorial	−1027.48624	−1027.47787	−1027.48527	−1027.47690
axial	−1027.48352	−1027.47518	−1027.48256	−1027.47422

[a] All values in Hartrees. [b] Values obtained using the G2(MP2) scheme, from geometries optimized at the MP2(FULL)/6-31G(3df,2p) level. See text.
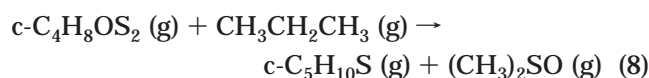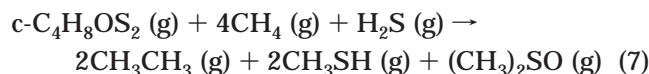
in the harmonic approximation for vibrational energy,[44] the classical approximation for translation ($3/2RT$) and rotation ($3/2RT$ for nonlinear molecules and RT for linear molecules), and an additional RT for converting energy to enthalpy (the pV term). G2(MP2) enthalpies at 298.15 K for the compound studied are also collected in Table 4.

In standard Gaussian-*n* theories, theoretical enthalpies of formation are calculated through atomization reactions. We have detailed this method in previous studies.[45,46] Raghavachari et al.[47] have proposed the use of a standard set of isodesmic reactions, the bond separation reactions,[48] 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 1,3-dithiane sulfoxide, c-$C_4H_8OS_2$, is

$$c\text{-}C_4H_8OS_2 \text{ (g)} + 4CH_4 \text{ (g)} + 3H_2S \text{ (g)} \rightarrow$$
$$2CH_3CH_3 \text{ (g)} + 4CH_3SH \text{ (g)} + H_2SO \text{ (g)} \quad (6)$$

and the experimental enthalpy of formation of one of the reference compounds, H_2SO, is not available.

We have used in this paper two isodesmic reactions using as reference $(CH_3)_2SO$

$$c\text{-}C_4H_8OS_2 \text{ (g)} + 4CH_4 \text{ (g)} + H_2S \text{ (g)} \rightarrow$$
$$2CH_3CH_3 \text{ (g)} + 2CH_3SH \text{ (g)} + (CH_3)_2SO \text{ (g)} \quad (7)$$

$$c\text{-}C_4H_8OS_2 \text{ (g)} + CH_3CH_2CH_3 \text{ (g)} \rightarrow$$
$$c\text{-}C_5H_{10}S \text{ (g)} + (CH_3)_2SO \text{ (g)} \quad (8)$$

The calculated values for the enthalpy of formation of 1,3-dithiane sulfoxide, in equatorial and axial forms, at the G2(MP2) level of theory using atomization and isodesmic reactions[49] are shown in Table 5. The $\Delta_f H°_m$ value obtained from the atomization reaction has been modified adding spin−orbit and bond additivity (BAC) corrections.[50] The method has been detailed in a previous study.[3]

(44) 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.

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SCHEME 3[a]
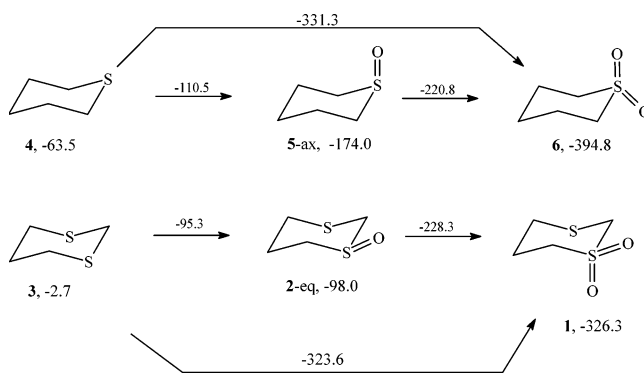
[a] Enthalpies of formation (kJ mol⁻¹).

A further step in the obtaining of theoretical values of $\Delta_f H°_m$ 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.[42] This approach will be designed as G2(MP2)+. Calculated energies, at 0 K, and enthalpies at 298.15 K are given in Table 4. The $\Delta_f H°_m$ values for the compound studied, calculated at this computational level, are collected in Table 5. As it can be seen in that table, all of the $\Delta_f H°_m$ values for 1,3-dithiane sulfoxide in the equatorial form show that it is the most stable one, calculated from G2(MP2) and G2(MP2)+ energies, and these values are more negative than the experimental value.

Discussion

Scheme 3 summarizes the thermochemical data for the oxidation of thiane **4** and 1,3-dithiane **3**. As discussed in the present paper, the oxidation of 1,3-dithiane **3** to sulfoxide **2** is much less exothermic than the oxidation of thiane **4** to sulfoxide **5**, and this observation is explained in terms of electrostatic repulsion between sulfurs. In contrast, the oxidation of 1,3-dithiane sulfoxide **2** to sulfone **1** is more exothermic than the corresponding oxidation of thiane sulfoxide **5** to thiane sulfone **6**, probably as the result of the $n_S \rightarrow \sigma^*_{C−SO2}$ stabilizing interaction that is possible in **1** but not in **6**. This interpretation implies that most of the energetic cost of the electrostatic repulsion between sulfurs is paid in the initial sulfide to sulfoxide oxidation step. Nevertheless,

(49) Experimental $\Delta_f H°_m$ values for the reference compounds used in isodesmic reactions 7 and 8, methane, ethane, propane, hydrogen sulfide, methanethiol, ethane, and dimethyl sulfoxide: −74.9, −83.8, −104.7, −20.6, −22.8, −63.5, and −150.5 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.; March 2003, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

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TABLE 5. Enthalpy of Formation at $T = 298.15$ K of 1,3-Dithiane Sulfoxide, Experimental and Calculated from Atomization and Isodesmic Reactions[a]

1,3-dithiane sulfoxide, **2**	G2(MP2)			G2(MP2)+			experimental
	atomization[b]	isodesmic 7	isodesmic 8	atomization[b]	isodesmic 7	isodesmic 8	
2-equatorial	−114.3	−114.6	−112.4	−111.8	−114.1	−110.3	−97.9 ± 1.9
2-axial	−107.2	−107.5	−105.3	−104.6	−107.0	−103.4	

[a] All values in kJ mol^{-1}. [b] Value obtained from atomization reaction including spin−orbit and bond additivity corrections. See text.

the overall conversion of thiane **4** to sulfone **6** is more favorable than the overall conversion of 1,3-dithiane **3** to sulfone **1** (−331.3 and −323.6 kJ mol^{-1}, respectively). Thus electrostatic repulsion between positive sulfurs in sulfone **1** seems to dominate over the stabilizing stereoelectronic effect.[6]

Experimental Procedures

Material and Purity Control. 1,3-Dithiane sulfoxide **2** was synthesized following the method described in the literature by Carlson and Helquist,[51] from 2.0 g of 1,3-dithiane, obtaining 2.13 g of 1,3-dithiane sulfoxide (yield 94%), mp 361.9 K, which is in excellent agreement with the published value given in the literature, 360−361 K. Final purification was accomplished by flash chromatography[52] (eluent: hexanes−ethyl acetate, 9:1). Mass, IR, and Raman spectra confirmed the desired structure. The sample was carefully dried under vacuum at 50°C. Determination of purity, assessed by DSC by the fractional fusion technique,[53] indicated that the mole fraction of impurities in the compound was less than 0.002. The results obtained in the characterization and purity control are given in the Supporting Information. The sample was studied by DSC over the temperature range between $T = 253$ K and its fusion melting point $T = 361.5$ K, and no transitions in the solid state were observed.

Thermochemical Measurements. The enthalpy of formation in the gas state, $\Delta_f H^\circ_m(g)$, was determined by combining the standard enthalpy of formation of the crystalline 1,3-dithiane sulfoxide, $\Delta_f H^\circ_m(cr)$, with its standard enthalpy of sublimation, $\Delta_{sub} H^\circ_m$. 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.[1] The energy of combustion of 1,3-dithiane sulfoxide 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 only around 8 mmol of sulfur in the samples.[54] The bomb was filled with oxygen to a pressure of $p = 3.04$ Mpa. 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 of 1,3-dithiane sulfoxide over an 18 K temperature interval using the Knudsen effusion technique,[55−57] 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.[5] 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.

NMR Study. The ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectra corresponding to a powdered sample were acquired at ambient temperature with 4 ms CP contact time, 5 s recycle delay, high-power proton decoupling, and a spinning rate of 5 kHz. The free induction decay was subjected to standard Fourier transformation and phasing. The chemical shifts were externally referenced to TMS.

Computational Details. Standard ab initio molecular orbital calculations[48] were performed with the Gaussian 98 series of programs.[58] The energies of the compound studied were calculated using Gaussian-2 theory, at the G2(MP2) level.[42]

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.

Supporting Information Available: Experimental details; Figures S1 and S2; Cartesian coordinates and energies; and HPCG, mass, IR, Raman, and DSC curve of purity control for 1,3-dithiacyclohexane 1-oxide (1,3-dithiane sulfoxide). This material is available free of charge via the Internet at http://pubs.acs.org.

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