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Calorimetric and Computational Study of 1,3-Dithiacyclohexane 1,1-Dioxide (1,3-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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The enthalpies of combustion and sublimation of 1,3-dithiacyclohexane 1,1-dioxide (1,3-dithiane sulfone) were measured by a rotating-bomb combustion calorimeter and the Knudsen effusion technique, and the gas-phase enthalpy of formation was determined, $\Delta_f H_m^\circ(g) = -326.3 \pm 2.0$ kJ mol^{-1}. Standard ab initio molecular orbital calculations at the G2(MP2) level were performed, and a theoretical study on molecular and electronic structure of the compound has been carried out. Calculated $\Delta_f H_m^\circ(g)$ values agree very well with the experimental one. These experimental and theoretical studies support the relevance of the repulsive electrostatic interaction between sulfur atoms in 1,3-dithiane sulfone, that apparently counterbalances any $n_S \rightarrow \sigma^*_{C-SO_2}$ stabilizing hyperconjugative interaction.

Introduction

Over the past few years, we have been involved in the systematic thermochemical study of selected oxygen and sulfur six-membered heterocycles.[1–5] Of fundamental interest in this work is the understanding of structural effects on thermodynamic stabilities that are reflected on the enthalpies of formation for the compounds of interest.

Consider, for example, the known[6] enthalpies of formation (gas phase) in the series cyclohexane **1**, oxacyclohexane (oxane) **2**, and thiacyclohexane (thiane) **3** collected in Figure 1. Relative to cyclohexane, the enthalpy of formation of oxane is much more negative, −123.4 and −223.4 kJ mol^{-1}, respectively. By contrast, the enthalpy of formation of thiane, −63.5 kJ mol^{-1}, is less negative than that for cyclohexane. These data can be explained to a large part by consideration of the lower electronegativity of sulfur relative to oxygen, which results in diminished Coulombic attraction between the carbon and sulfur atoms and thus weaker C−S bonds relative to C−O bonds.[7]
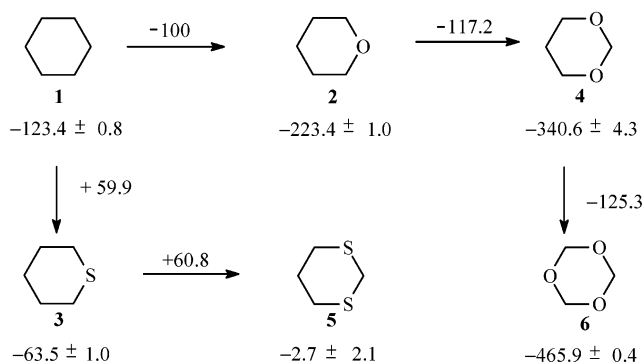

FIGURE 1. Enthalpies of formation ($\Delta_f H_m^\circ$ in kJ mol^{-1}) of the gaseous compounds cyclohexane **1**, oxane **2**, thiane **3**, 1,3-dioxane **4**, 1,3-dithiane **5**, and 1,3,5-trioxane **6**. Differences in enthalpy of formation ($\Delta\Delta_f H_m^\circ$ in kJ mol^{-1}) are shown on the arrows.

Interestingly, introduction of a second heteroatom has very different consequences in the oxygen and sulfur heterocycles. Indeed, conversion of oxane **2** into 1,3-dioxacyclohexane (1,3-dioxane) **4** is a highly exothermic process, $\Delta\Delta_f H_m^\circ = -117.2$ kJ mol^{-1},[8] whereas conversion of thiane **3** into 1,3-dithiacyclohexane (1,3-dithiane) **5** is strongly endothermic, $\Delta\Delta_f H_m^\circ = +60.8$ kJ mol^{-1}.[2] It can be appreciated that introduction of the second oxygen in the **2** to **4** conversion is 17.2 kJ mol^{-1} more exothermic than the original substitution of oxygen for a CH$_2$ methylene group in the **1** to **2** conversion (Figure 1). The additional stabilization of 17.2 kJ mol^{-1} in the conversion of oxane **2** to 1,3-dioxane **4** can be explained in terms of

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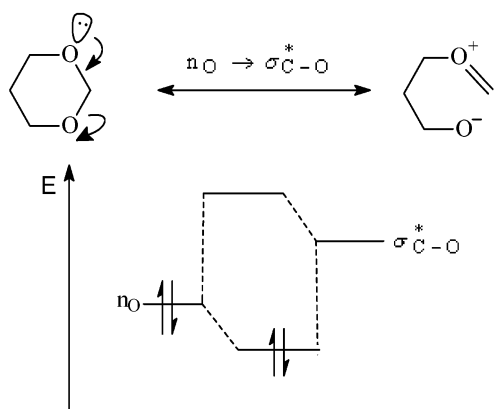
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FIGURE 2. 1,3-Dioxane **4** benefits from $n_O \rightarrow \sigma^*_{C-O}$ hyperconjugation, and this is reflected in the extraordinary negative enthalpy of formation (see text).

an "anomeric" $n_O \rightarrow \sigma^*_{C-O}$ stereoelectronic interaction; i.e., the diheterocycle **4** benefits from "double bond−no bond" hyperconjugation,[9] as depicted in Figure 2. In line with this interpretation, the experimental enthalpy of formation for 1,3,5-trioxane, **6**, is 125.3 kJ mol^{-1} more negative than the enthalpy of formation for 1,3-dioxane **4**. That is, the substitution of a third methylene group for an oxygen (in **4** → **6**) is 25.3 kJ mol^{-1} more stabilizing than the first substitution in **1** → **2**. This additional stabilization can be rationalized in terms of stereoelectronic stabilization in the three O−C−O segments.

Interestingly, analysis of the series cyclopentane (enthalpy of formation -76.4 ± 0.8 kJ mol^{-1}), tetrahydrofuran (enthalpy of formation -184.2 ± 0.8 kJ mol^{-1}), and 1,3-dioxolane (enthalpy of formation -298.0 ± 1.4 kJ mol^{-1}) shows that the additional stabilization is worth only 6.0 kJ mol^{-1}; i.e., significantly smaller than the 17.2 kJ mol^{-1} stabilization observed in 1,3-dioxane **4** relative to oxane **2** (vide supra).[1] This finding suggests that, as anticipated,[9] structural factors influence the magnitude of the stereoelectronic interaction. In the present systems, $n_O \rightarrow \sigma^*_{C-O}$ hyperconjugation is seen to be more effective in the six-membered ring relative to the five-membered analogue. We are grateful to one of the reviewers for suggesting this comparative analysis.

By contrast, analysis of the experimental enthalpies of formation for the sulfur-containing heterocycles exhibits, within the margin of error in the measurements, a lack of extra stabilization upon substitution of a second sulfur for a methylene group in the conversion of thiane **3** to 1,3-dithiane **5** (Figure 1). That is, there is no evidence for $n_S \rightarrow \sigma^*_{C-S}$ hyperconjugation in the S−CH$_2$−S segment. Indeed, $\Delta_f H^o_m$ for thiane **3** is 59.9 ± 1.0 kJ mol^{-1} less negative than $\Delta_f H^o_m$ for cyclohexane **1**, and $\Delta_f H^o_m$ for 1,3-dithiane **5** is 60.8 ± 2.1 kJ mol^{-1} less negative than $\Delta_f H^o_m$ for **3**. The lack of "double bond−no bond" stabilization in 1,3-dithiane **5** can be explained in terms of the lower electronegativity of sulfur relative to oxygen and by a correspondingly by high σ^*_{C-S} orbital energy that makes it a poor σ acceptor.[10]

An interesting question is whether hyperconjugative $n_S \rightarrow \sigma^*_{C-SO_2}$ interaction will be operative in the 1,3-dithiacyclohexane 1,1-dioxide (1,3-dithiane sulfone) derivative **7**. Indeed, the highly electronegative SO$_2$ sulfonyl group[11] should lead to a lower-energy $\sigma^*_{C-SO_2}$ orbital with better accepting properties. Thus, double bond−no bond stereoelectronic stabilization in 1,3-dithiane sulfone **7** (eq 1) should be manifested in a more negative enthalpy of formation.[12] The present paper reports experimental and theoretical determination of the enthalpy of formation of 1,3-dithiane sulfone **7**.

(1)
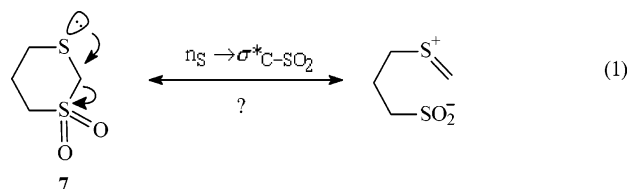
Results and Discussion

Experimental Determination of the Enthalpy of Formation in the Gas Phase. From combustion calorimetry results given in Table 1 and vapor pressure determinations by the Knudsen effusion technique, Table 2, the experimental values of the standard enthalpies of combustion, sublimation, and formation in the crystalline and gaseous state of 1,3-dithiane sulfone, at a temperature of 298.15 K, have been derived and are reported 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, there is not any experimental determination of the molecular structure of 1,3-dithiane sulfone. 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_s (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 of sulfur.

The three twist conformers are also minima of the potential energy surface of the molecule studied, but calculations at the HF/6-31G(d) level indicate that they are 14.4, 16.3, and 23.2 kJ mol^{-1} higher in energy than the chair conformer. The three boat conformers are saddle points of first order, corresponding to transition states in the potential energy surfaces.

For sulfones, the length of the S=O bonds is the most important structural parameter. The sulfonyl group has also the bond angle OSO, and the corresponding O⋯O nonbonded distance as important structural parameters. Comparing the structure of 1,3-dithiane sulfone with that calculated[4] for thiane sulfone, the S−O distances are slightly shorter in the first compound (1.436 and 1.438 Å for the axial and equatorial oxygen, respectively, versus 1.437 and 1.441 Å), the OSO angle is larger (120.9°

(9) See, for example: Juaristi, E.; Cuevas, G. *The Anomeric Effect*; CRC Press: Boca Raton, FL, 1995.

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(11) (a) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. (b) Simpkins, N. *Sulphones in Organic Synthesis*; Pergamon Press: London, 1993.

(12) Evidence for $n_O \rightarrow \sigma^*_{C-S(O)}$ hyperconjugation has been advanced: Crich, D.; Mataka, J.; Zakharov, L. N.; Rheingold, A. L.; Wink, D. J. *J. Am. Chem. Soc.* **2002**, *124*, 6028.

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

m'(compound)/g[a]	0.601743	0.618917	0.612163	0.615286	0.615221
m''(polyethene)/g[a]	0.086588	0.084844	0.084862	0.083001	0.081853
m'''(Vaseline)/g[a]	0.322090	0.312548	0.319916	0.402379	0.340677
m''''(fuse)/g[a]	0.002274	0.002519	0.002288	0.002509	0.002497
$\Delta T_c/K = (T_f - T_i + \Delta T_{corr})/K$	−1.1313	−1.1275	−1.1338	−1.2649	−1.1646
ϵ(calor) $(-\Delta T_c)$/kJ[b]	−32.6625	−32.5520	−32.7339	−36.5184	−33.6228
ϵ(cont) $(-\Delta T_c)$/kJ[c]	−0.0568	−0.0565	−0.0569	−0.0643	−0.0586
ΔU_{ign}/kJ[d]	0.0004	0.0004	0.0004	0.0004	0.0004
$\Delta U_{dec}(HNO_3)$/kJ[e]	0.0461	0.0489	0.0503	0.0603	0.0545
$\Delta U_{diln}(H_2SO_4)$/kJ[f]	−0.00365	−0.00393	−0.00378	−0.00378	−0.00388
ΔU(corr to std states)/kJ[g]	0.0207	0.0203	0.0205	0.0237	0.0212
$-m'' \Delta_c u°$ (polyethene)/kJ	4.0152	3.9344	3.9352	3.8489	3.7957
$-m''' \Delta_c u°$ (Vaseline)/kJ	14.8442	14.4044	14.7440	18.5445	15.7008
$-m'''' \Delta_c u°$ (fuse)/kJ	0.0396	0.0439	0.0399	0.0437	0.0435
$\Delta_c u°$ (compound)/kJ g^{-1}	−22.8615	−22.8789	−22.8767	−22.8593	−22.8685
$\langle \Delta_c u°$ (298.15 K)$\rangle$/kJ g^{-1}			−22.8690 ± 0.0040		

[a] Masses obtained from apparent mass. [b] ϵ (calor), energy equivalent of the whole system less the content of the bomb. [c] ϵ (cont), energy equivalent of the contents of the bomb ϵ (cont)$(-\Delta T_c) = \epsilon^i$(cont)$(T^i - 298.15$ K$) + \epsilon^i$(cont)$(298.15$ 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. [g] ΔU (corr to std states).

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

T (K)	t^a (s)	Δm^b mg	p^c (Pa)	$10^2 (\delta p/p)$
342.02	29880	4.60	0.155	−3.93
346.24	29700	6.99	0.238	1.24
349.30	22740	7.42	0.332	3.52
352.10	22800	9.85	0.441	−0.257
355.38	22500	13.05	0.596	−0.596
358.31	22740	17.48	0.793	−1.58

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

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

thermodynamic properties	experimental values[a,b]
$\Delta_c U_m^° $ [c]	−3481.5 ± 1.7
$\Delta_c H_m^°$ [d]	−3491.4 ± 1.7
$\Delta_f H_m^°$(cr)[e]	−429.9 ± 1.8
$\Delta_{sub} H_m^°$ [f]	103.6 ± 0.9
$\Delta_f H_m^°$(g)[g]	−326.3 ± 2.0

[a] All values in kJ mol^{-1}. [b] This work. [c] Standard molar energy of combustion. [d] Standard molar enthalpy of combustion. [e] Standard molar enthalpy of formation in the crystalline state. [f] Standard molar enthalpy of sublimation. [g] Standard molar enthalpy of formation in the gaseous state.

TABLE 4. MP2(FULL)/6-31G(3df,2p)-Calculated Structure of 1,3-Dithiane Sulfone[a]

S_1-O_{ax}	1.436	OS_1O	120.9
S_1-O_{eq}	1.438	$S_1C_2S_3$	113.3
S_1-C_2	1.775	$C_2S_3C_4$	98.0
C_2-S_3	1.781	$S_3C_4C_5$	113.6
S_3-C_4	1.793	$C_4C_5C_6$	112.3
C_4-C_5	1.517	$C_5C_6S_1$	112.5
C_5-C_6	1.519	$C_6S_1C_2$	101.2
C_6-S_1	1.763	Θ[b]	108.5
		Φ[c]	62.3

[a] Bond lengths in angstroms and bond angles in degrees. [b] The mean valency angle in the ring. [c] The mean torsional angle in the ring.

versus 120.5°), and the nonbonded O···O distance is shorter (2.50 Å versus 2.56 Å).

We can also compare the calculated structure of 1,3-dithiane sulfone with that calculated for 1,3-dithiane. The CSC angle increases from 97.4° to 101.2° when SO$_2$ group
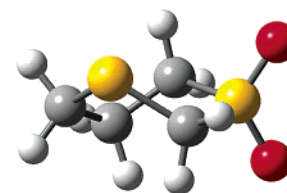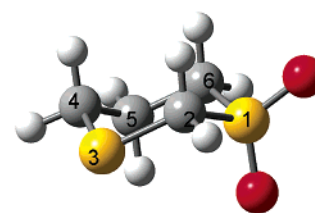
$\Delta E = +14.4$ kJ mol^{-1}

FIGURE 3. (Top) chair conformation of 1,3-dithiane sulfone. (Bottom) most stable twist conformation. ΔE is the relative energy with respect to the chair conformation, evaluated at the HF/6-31G(d) level.

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.[13]

It has been observed[14,15] 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.[16] The average torsional angle, Φ, which is determined by a delicate balance between valency, torsional, and nonbonded forces, is an easily calculated[4] and convenient index of the puckering in six-membered rings.

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(15) Adams, W. D.; Bartell, L. S. *J. Mol. Struct.* **1977**, *37*, 261.
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TABLE 5.   G2(MP2)-Calculated Energies, at 0 K, and Enthalpies, at 298.15 K, for 1,3-Dithiane Sulfone[a,b]

compound	G2(MP2)		G2(MP2)+[c]	
	E_0	H_{298}	E_0	H_{298}
1,3-dithiane sulfone, **7**	−1102.63595	−1102.62698	−1102.63602	−1102.62704

[a] All values in hartrees. [b] 1 hartree = 2625.5 kJ mol^{-1}. [c] 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 1,3-Dithiane Sulfone, Experimental and Calculated from Atomization and Isodesmic Reactions

compound	G2(MP2)			G2(MP2)+			
	atomization	isodesmic (3)	isodesmic (4)	atomization	isodesmic (3)	isodesmic (4)	experimental
1,3-dithiane sulfone, **7**	−322.8[b]	−327.3	−325.1	−323.0[b]	−326.7	−324.8	−326.3 ± 2.0

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

The Φ torsional angle of 1,3-dithiane sulfone, 62.3°, has a value similar to that calculated for 1,3-dithiane (Φ = 62.5°), indicating that both rings are similarly puckered. The presence of two S atoms in the ring logically increases the puckering comparing to that of thiane sulfone (Φ = 59.7°).
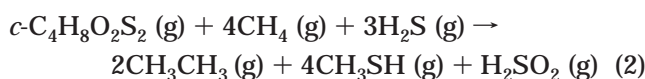
The puckering of the ring in 1,3-dithiane sulfone can be also studied comparing their angles between planes with those calculated for 1,3-dithiane. The angles in the sulfone are smaller confirming that the structure is more puckered.

Theoretical Enthalpies of Formation. G2(MP2)[17]-calculated energy, at 0 K, for 1,3-dithiane sulfone is given in Table 5.

The enthalpy value at 298.15 K has been evaluated according to standard thermodynamics.[18] 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,[19] 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 3.
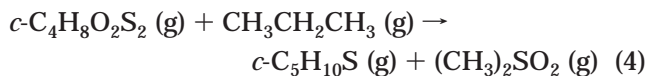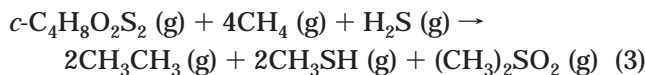
In standard Gaussian-n theories, theoretical enthalpies of formation are calculated through atomization reactions. We have detailed this method in previous studies.[20] Raghavachari et al.[21] have proposed to use a standard set of isodesmic reactions, the "bond separation reactions",[22] where all formal 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 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 1,3-dithiane sulfone, at the G2(MP2) level of theory, using atomization and isodesmic reactions,[23] are shown in Table 6. The $\Delta_fH_m^\circ$ value obtained from atomization reaction has been modified adding spin−orbit and bond additivity (BAC) corrections.[24] The method has been detailed in a previous study.[3]

A further step in obtaining theoretical values of $\Delta_fH_m^\circ$ 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.[17] This approach will be designed as G2-(MP2)+. Calculated energy, at 0 K, and enthalpy at

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(19) Each normal mode contributes $Nh\nu/(e^{h\nu/kT} - 1)$ 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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(23) Experimental $\Delta_fH_m^\circ$ values for the reference compounds used in isodesmic reactions 3 and 4, 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.; March 2003, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

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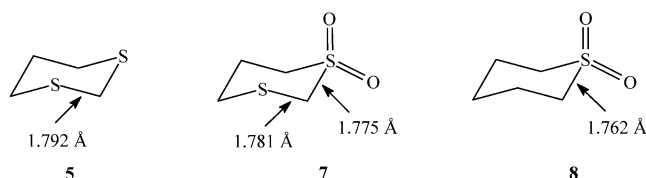
FIGURE 4. Salient bond lengths calculated at the MP2-(FULL)/6-31G(3df,2p) level for 1,3-dithiane (**5**, this work), 1,3-dithiane sulfone (**7**, this work), and thiane sulfone (**8**, ref 4).
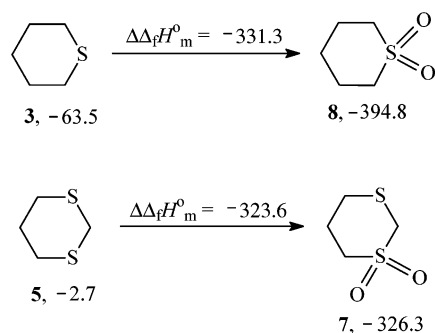

FIGURE 5. Differences in the enthalpy of formation ($\Delta\Delta_f H^o_m$, in kJ mol^{-1}) for the conversion of thiane **3** into thiane sulfone **8**, and for the conversion of 1,3-dithiane **5** into 1,3-dithiane sulfone **7**.

298.15 K are given in Table 5. The $\Delta_f H^o_m$ values for the compound studied, calculated at this computational level, are collected in Table 6.

As it can be seen in Table 6, all of the $\Delta_f H^o_m$ values for 1,3-dithiane sulfone, calculated from G2(MP2) and G2-(MP2)+ energies, are in very good agreement with the experimental value.

Is There $n_S \rightarrow \sigma^*_{C-SO_2}$ Hyperconjugation? Comparison of the molecular structures calculated for 1,3-dithiane **5** and 1,3-dithiane sulfone **7** provides evidence for $n_S \rightarrow \sigma^*_{C-SO_2}$ hyperconjugation in the latter sulfone **7** (eq 1). Figure 4 collects the most relevant bond length parameters in the optimized structures for 1,3-dithiane **5**, 1,3-dithiane sulfone **7** and, for comparison purposes, thiane sulfone **8**.

Salient observations from analysis of the structural data summarized in Figure 4 are the significant shortening in S(3)−C(2) bond length from 1.792 Å in 1,3-dithiane **5** to 1.781 Å in 1,3-dithiane sulfone **7** and the substantial increase in the C(2)−SO$_2$ bond length from 1.762 Å in thiane sulfone **8** to 1.775 Å in 1,3-dithiane sulfone **7**. These structural differences are in line with the double bond−no bond canonical contribution depicted in eq 1.

Nevertheless, no thermochemical evidence can be advanced to support $n_S \rightarrow \sigma^*_{C-SO_2}$ hyperconjugation in 1,3-dithiane sulfone **7** since the anticipated stabilization should be reflected in the experimental (and theoretical) enthalpy of formation. In particular, comparison of the $\Delta_f H^o_m$ values for thiane **3**, ($\Delta_f H^o_m = -63.5$ kJ mol^{-1}, ref 6) and thiane sulfone **8**, ($\Delta_f H^o_m = -394.8$ kJ mol^{-1}, ref 4) suggests that the enthalpy of formation for 1,3-dithiane sulfone **7** should be greater (more negative) than $\Delta_f H^o_m = -334.0$ kJ mol^{-1}. However, as shown in Figure 5, the experimentally observed $\Delta_f H^o_m = -326.3$ kJ mol^{-1} (Table 3) actually indicates a destabilization worth 7.7 kJ mol^{-1} (Figure 5).
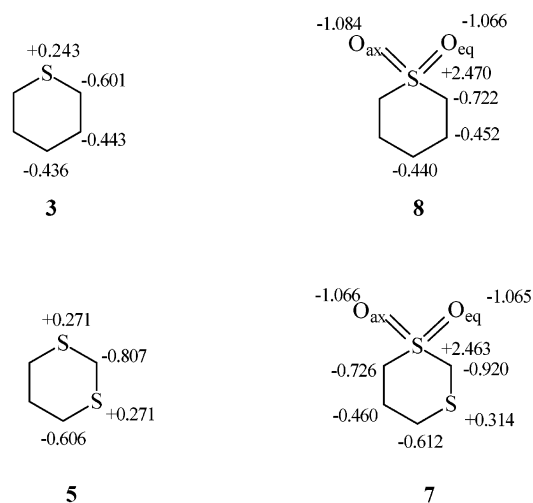
FIGURE 6. Natural charges obtained from a NBO analysis at the MP2(FULL)/6-31G(3df,2p) level, located at the heavy atoms in thiane **3**, 1,3-dithiane **5**, 1,3-dithiane sulfone **7**, and thiane sulfone **8**.

To get information that could help understand the nature of the destabilizing effect in 1,3-dithiane sulfone **7** that apparently counterbalances the $n_S \rightarrow \sigma^*_{C-SO_2}$ 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.[25] In Figure 6 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 created at sulfur upon oxidation, from values ranging +0.24−0.27 in the thioethers **3** and **5** to +2.46−2.47 in the sulfones **7** and **8**. The dramatically large exothermic **3** to **8** process ($\Delta\Delta_f H^o_m = -331.3$ kJ mol^{-1}) reflects the overriding electrostatic attraction with the negative C(3,5) carbons. By contrast, in 1,3-dithiane sulfone **7**, some of the attractive electrostatic stabilization is offset by a repulsive electrostatic interaction between sulfurs.

(5)
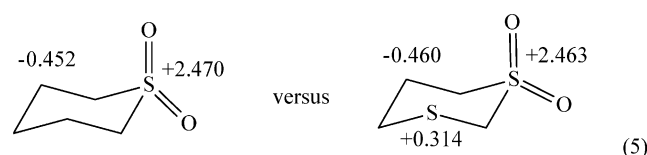
Experimental Section

Material and Purity Control. 1,3-Dithiane sulfone was synthesized following the method of Khan et al.[26] Final purification was accomplished by column chromatography on silica gel (gradient, hexane−ethyl acetate, 9:1 to ethyl acetate) to obtain the pure sulfone. The characterization of 1,3-dithiane sulfone was made by mass spectrometry, ^{1}H NMR, ^{13}C NMR, IR, and Raman spectroscopies. The sample was carefully dried under vacuum at 50 °C. Determination of purity, assessed by DSC by the fractional fusion technique,[27] indicated that the mole fraction of impurities in the compound was less than

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0.001. 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 $T = 268$ K and its fusion melting point $T = 414.0$ K, and no transitions in the solid state were observed.

Thermochemical Measurements. $\Delta_f H_m^o(g)$ was determined in this work by combining the standard enthalpy of formation of the crystalline 1,3-dithiane sulfone, $\Delta_f H_m^o(cr)$, with its standard enthalpy of sublimation, $\Delta_{sub} H_m^o$. This was carried out by combustion calorimetry and by the measurements of their vapor pressures over a 15 K temperature interval. The energies of combustion have been determined using a rotary bomb calorimeter. Details of the technique and procedure used have been previously described.[1] From the combustion energy, the enthalpy of formation in the condensed state was determined. The vapor pressures of the compound were measured using the Knudsen-effusion technique[28] and the enthalpy of sublimation was deduced from the temperature dependence of the vapor pressures (Clausius–Clapeyron).[28] Heat capacities measurements were carried out by means of differential scanning calorimetry.[5] Full experimental details are given as Supporting Information. 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[22] were performed with the Gaussian 98 series of programs.[29] The energies of the compound studied were calculated using Gaussian-2 theory, at the G2(MP2) level.[17]

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.[25] The NBO analysis has been performed using the NBO program[30] implemented in the Gaussian 98 package.[29]

Supporting Information Available: Experimental details, tables of results for the determination of $\Delta_f H_m^o$, optimized structures in Cartesian coordinates, and mass, IR, Raman, ^{1}H NMR, and ^{13}C NMR spectra and DSC curve of purity control for 1,3-dithiacyclohexane 1,1-dioxide (1,3-dithiane sulfone). This material is available free of charge via the Internet at http://pubs.acs.org.

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