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Calorimetric and Computational Study of 1,3- and 1,4-Oxathiane Sulfones

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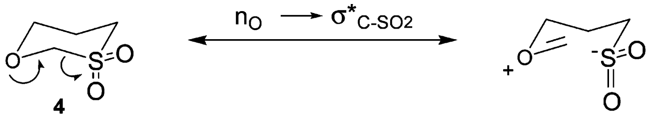

The enthalpies of formation in the condensed and gas states, $\Delta_f H°_m$(cd) and $\Delta_f H°_m$(g), of 1,3- and 1,4-oxathiane sulfones were derived from their respective enthalpies of combustion in oxygen, measured by a rotating bomb calorimeter and the variation of vapor pressures with temperatures determined by the Knudsen effusion technique. Standard ab initio molecular orbital calculations at the G2(MP2) and G3 levels were performed, and a theoretical study on molecular and electronic structure of the compounds has been carried out. Calculated $\Delta_f H°_m$(g) values at the G3 level using atomization reactions agree well with the experimental ones. These experimental and theoretical studies support that the destabilization found in 1,3-oxathiane sulfone, 11.2 kJ mol^{-1} respecting to 1,4-oxathiane sulfone, is due to the electrostatic repulsion between the negative charges of the axial oxygen of the sulfone and the oxygen of the ring and apparently masks any stabilization originating from the hyperconjugative $n_O \rightarrow \sigma^*_{C-SO_2}$ stereoelectronic interaction.

Introduction

Thermodynamic data such as the enthalpy of formation, symbolized as $\Delta_f H°_m$, offer a powerful tool for the understanding of the relative importance of steric, electrostatic, and stereoelectronic interactions that are responsible for the contrasting structural, conformational, and reactivity trends exhibited by oxygen- and sulfur-containing six-membered heterocycles.[1] In this regard, comparison of the enthalpies of formation of isomeric compounds is particularly useful because it exhibits their relative stability, as a consequence of the stabilizing and/or repulsive interactions of interest.

Recently, we reported the enthalpies of formation of thiane sulfone **1**,[2] 1,3-dithiane sulfone **2**,[3] and 1,4-dithiane sulfone **3** in the gas state.[4] Comparison of the enthalpy of formation of 1,3-dithiane sulfone and 1,4-dithiane sulfone shows the 1,3-isomer to be 6.7 kJ mol^{-1} less stable, probably due to diminished electrostatic repulsion between the positively charged sulfur heteroatoms in 1,4-dithiane sulfone **3**[4] (Figure 1).

In this context, the determination of the enthalpy of formation for 1,3-oxathiane sulfone **4** and 1,4-oxathiane sulfone **5** was deemed of interest. In particular, a relevant question is whether a hyperconjugative $n_O \rightarrow \sigma^*_{C-SO_2}$ interaction will be operative in the 1,3-oxathiane sulfone **4**. Indeed, the highly electronegative SO_2 sulfonyl group should lead to a low-energy $\sigma^*_{C-SO_2}$ orbital with good accepting properties (Figure 2).

Results

Experimental Determination of the Enthalpy of Formation in the Gas Phase. The enthalpy of formation in the gas state of 1,3- and 1,4-oxathiane sulfone, $\Delta_f H°_m$(g), was determined from the experimental values of the standard enthalpy of

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(1) Juaristi, E.; Notario, R.; Roux, M. V. *Chem. Soc. Rev.* **2005**, *34*, 347.

(2) Roux, M. V.; Temprado, M.; Jiménez, P.; Dávalos, J. Z.; Notario, R.; Guzmán-Mejía, R.; Juaristi, E. *J. Org. Chem.* **2003**, *68*, 1762.

(3) Roux, M. V.; Temprado, M.; Jiménez, P.; Notario, R.; Guzmán-Mejía, R.; Juaristi, E. *J. Org. Chem.* **2004**, *69*, 1670.

(4) Roux, M. V.; Temprado, M.; Jiménez, P.; Notario, R.; Guzmán-Mejía, R.; Juaristi, E. *J. Org. Chem.* **2006**, *71*, 2581.

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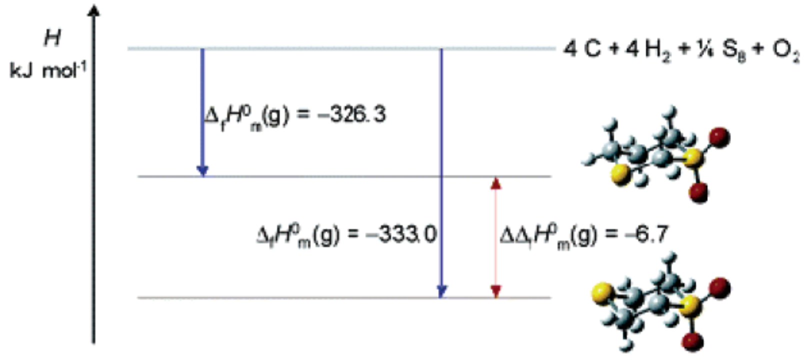

FIGURE 1. Differences in the enthalpy of formation ($\Delta\Delta_f H°_m$, in kJ mol^{-1}) for 1,3-dithiane sulfone **2** and 1,4-dithiane sulfone **3**.[4]

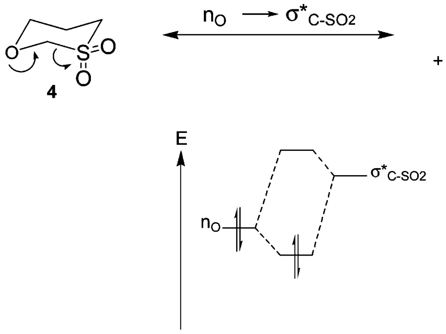

FIGURE 2. 1,3-Oxathiane sulfone **4** might benefit from $n_O \rightarrow \sigma^*_{C-SO_2}$ hyperconjugation (see text).

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.

The experimental value for the enthalpy of formation in the crystalline state was determined from combustion calorimetry experiments. The detailed results for the combustion experiments of each compound obtained according to references 5 and 6 are presented in the Supporting Information (Tables S2 and S3). The enthalpy of sublimation, $\Delta_{sub}H°_m$, was obtained from vapor pressure measurements by the Knudsen effusion technique. The detailed results for all the experiments are presented in the Supporting Information (Table S4).

Table 1 collects the values determined for the standard molar energy of combustion, $\Delta_c U°_m$, and the standard molar enthalpy of combustion, $\Delta_c H°_m$, sublimation, $\Delta_{sub}H°_m$, and formation in the crystalline, $\Delta_f H°_m$(cr), and gaseous states, $\Delta_f H°_m$(g), for both sulfones.

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 structures of oxathiane sulfones have not been studied previously, but the structures of two derivatives of them, 2-methyl-1,3-oxathiane sulfone[7] and 3,5-dimethoxy-1,4-oxathiane sulfone,[8] have been obtained by X-ray diffraction. The optimized geometries of 1,3- and 1,4-oxathiane sulfones at the MP2(full)/6-31G(3*df*,2*p*) level of theory are presented in Figure 3, and the corresponding bond distances and angles are presented in Figure 4. The optimized geometries agree well with those experimentally obtained for both derivatives as it is presented in the Supporting Information (Table S5).

The most stable forms are the chair conformations, belonging to the symmetry point groups C_1 and C_s for 1,3- and 1,4-oxathiane sulfones, respectively. The chair structures are similar to that of cyclohexane but are more puckered to accommodate the bond angles and bond lengths characteristic for sulfur and oxygen.

The twist conformers are also minima of the potential energy surface, but calculations at the HF/6-31G(d) level indicate that they are between 12.5 and 18.5 kJ mol^{-1} and between 29.0 and 32.0 kJ mol^{-1} higher in energy than the respective chair conformers, for 1,3- and 1,4-oxathiane sulfone, respectively. The 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 also has the bond angle OSO and the corresponding O···O nonbonded distance as important structural parameters. Comparison of the structures of oxathiane sulfones with that calculated for thiane sulfone shows that the OSO angles are larger (see Figure 4) and the nonbonded O···O distances are shorter (2.51 and 2.50 Å in 1,3- and 1,4-oxathiane sulfones vs 2.56 Å in thiane sulfone).

We can also compare the calculated structures of oxathiane sulfones with that calculated for oxathianes (see Figure 4). The CSC angle increases in all the cases when the 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.[9]

It has been observed[10,11] 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.[12] The average torsional angle, Φ, which is determined by a delicate balance among valency, torsional, and nonbonded forces, is an

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[5] Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1967; Chapter 5.

[6] Westrum, E. F., Jr. *Combustion Calorimetry*; Sunner, S.; Månsson, M., Eds.; Pergamon Press: Oxford, 1979; Chapter 7

[7] Pihlaja, K.; Sillanpää, R.; Dahlqvist, M.; Stájer, G.; Ahlgren, M. *Struct. Chem.* **1993**, *4*, 203.

[8] Estrada, M. D.; López-Castro, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 1030.

[9] Hargittai, I. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: New York, 1988; pp 33−53.

[10] Hargittai, I. *The Structure of Volatile Sulphur Compounds*; Akadémiae Kiadó: Budapest and Reidel, Dordrecht, 1985.

[11] Adams, W. D.; Bartell, L. S. *J. Mol. Struct.* **1977**, *37*, 261.

[12] Geise, H. J.; Altona, C.; Romers, C. *Tetrahedron* **1967**, *23*, 439.

TABLE 1. Experimentally Determined Thermodynamic Magnitudes at the Temperature T = 298.15 K for 1,3- and 1,4-Oxathiane Sulfone[a]

	$\Delta_cU°_m$	$\Delta_cH°_m$	$\Delta_fH°_m$(cr)	$\Delta_{sub}H°_m$	$\Delta_fH°_m$(g)
1,3-oxathiane sulfone	−2752.9 ± 1.7	−2757.8 ± 1.7	−561.5 ± 1.8	92.1 ± 0.7	−469.4 ± 1.9
1,4-oxathiane sulfone	−2741.8 ± 1.4	−2746.8 ± 1.4	−572.6 ± 1.5	92.0 ± 1.0	−480.6 ± 1.8

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

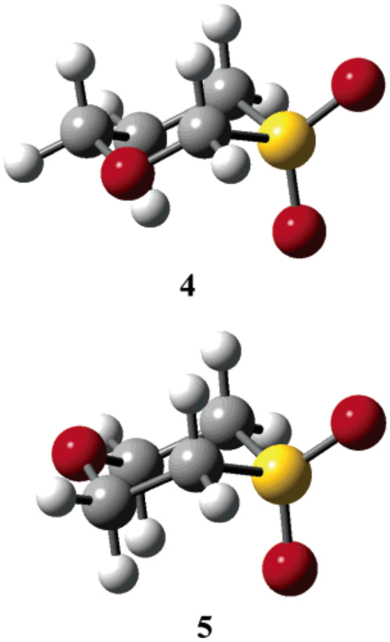

FIGURE 3. Optimized geometries at the MP2(full)/6-31G(3*df*,2*p*) level for 1,3-oxathiane sulfone **4** and 1,4-oxathiane sulfone **5**.

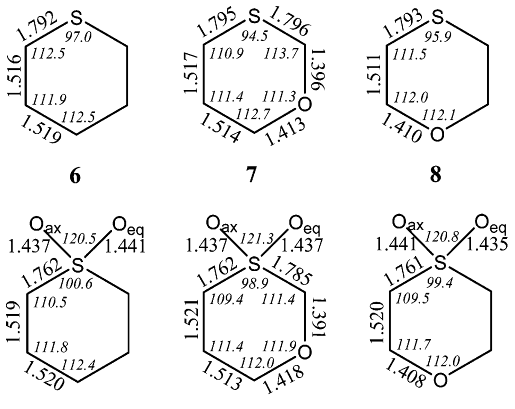

FIGURE 4. Optimized structures for thiane **6**, 1,3-oxathiane **7**, 1,4-oxathiane **8**, and their corresponding sulfones **1**, **4**, and **5** calculated at the MP2(full)/6-31G(3*df*,2*p*) level of theory. Bond distances are in Ångstroms, and angles (italic) are in degrees.

easily calculated[2] and convenient index of the puckering in six-membered rings.

The Φ torsional angles of 1,3- and 1,4-oxathiane sulfones, 60.7° and 61.2°, respectively, have values similar to those calculated for 1,3-oxathiane (Φ = 60.9°) and 1,4-oxathiane (Φ = 60.7°), indicating that all the rings are similarly puckered. The presence of the O atom in the ring logically increases the puckering compared to that of thiane sulfone (Φ = 59.7°) but decreases the puckering compared to that of 1,3- and 1,4-dithiane sulfones, 62.3° and 63.0°, respectively.

Theoretical Enthalpies of Formation. G2(MP2) and G3 calculated energies at 0 K and enthalpies at 298.15 K, for 1,3- and 1,4-oxathiane sulfones, are given in Table 2.

In standard Gaussian-*n* theories, theoretical enthalpies of formation are calculated through atomization reactions. We have detailed this method in previous studies.[13,14] Raghavachari et al.[15] have proposed to use a standard set of isodesmic reactions, the “bond separation reaction”,[16] 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 compounds studied because the bond separation isodesmic reaction for 1,3- and 1,4-oxathiane sulfones, $C_4H_8O_3S$, is

$$C_4H_8O_3S(g) + 4CH_4(g) + H_2O(g) + 2H_2S(g) \rightarrow 2CH_3CH_3(g) + 2CH_3OH(g) + 2CH_3SH(g) + H_2SO_2(g) \quad (1)$$

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

We have used in this work an isodesmic reaction using as a reference $(CH_3)_2SO_2$:

$$C_4H_8O_3S(g) + 4CH_4(g) + H_2O(g) \rightarrow 2CH_3CH_3(g) + 2CH_3OH(g) + (CH_3)_2SO_2(g) \quad (2)$$

The calculated values for the enthalpies of formation of 1,3- and 1,4-oxathiane sulfones, at the G2(MP2) and G3 levels of theory, using atomization and isodesmic reactions,[17] are shown in Table 3. The $\Delta_fH°_m$ value obtained from atomization reaction at the G2(MP2) level has been modified adding spin−orbit and bond additivity (BAC) corrections.[18] The method has been detailed in a previous study.[19]

As can be seen in Table 3, the best theoretical values are those obtained at the G3 level of theory using atomization reactions, in very good agreement with the experimental ones. The calculated difference between the enthalpies of formation

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(13) Notario, R.; Castaño, O.; Abboud, J.-L. M.; Gomperts, R.; Frutos, L. M.; Palmeiro, R. *J. Org. Chem.* **1999**, *64*, 9011.

(14) Notario, R.; Castaño, O.; Gomperts, R.; Frutos, L. M.; Palmeiro, R. *J. Org. Chem.* **2000**, *65*, 4298.

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

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

(17) Experimental $\Delta_fH°_m$ values for the reference compounds used in isodesmic reactions, methane and ethane, −74.6 and −84.0 kJ mol^{-1}, respectively, have been taken from: (a) Manion, J. A. *J. Phys. Chem. Ref. Data* **2002**, *31*, 123. $\Delta_fH°_m$ values for methanol and dimethyl sulfone, −201.5 and −373.1 kJ mol^{-1}, respectively, have been taken from: (b) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; TRC Data Series, TRC: Texas, 1994; Vol. 1. And the $\Delta_fH°_m$ value for water, -241.8 kJ mol^{-1}, has been taken from: (c) NIST-JANAF Thermochemical Tables, 4th ed.; Chase, M. W., Jr. *J. Phys. Chem. Ref. Data* **1998**, *Monograph 9*, 1.

(18) Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Montgomery, J. A., Jr.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 10570.

(19) Roux, M. V.; Jiménez, P.; Dávalos, J. Z.; Notario, R.; Juaristi, E. *J. Org. Chem.* **2001**, *66*, 5343.

TABLE 2. G2(MP2) and G3 Calculated Energies at 0 K and Enthalpies at 298.15 K, for the Oxathiane Sulfones Studied[a]

	G2(MP2)		G3	
compound	E_0	H_{298}	E_0	H_{298}
1,3-oxathiane sulfone, **4**	−780.015773	−780.007379	−780.667113	−780.658719
1,4-oxathiane sulfone, **5**	−780.022073	−780.013743	−780.673254	−780.664924

[a] All Values in Hartrees.

TABLE 3. G2(MP2) and G3 Calculated Enthalpies of Formation for the Oxathiane Sulfones Studied from Atomization and the Isodesmic Reaction (eq 2)[a]

	G2(MP2)		G3		
compound	atomization	isodesmic	atomization	isodesmic	experimental
1,3-oxathiane sulfone, **4**	−475.0	−477.5	−468.5	−479.9	−469.4 ± 1.9
1,4-oxathiane sulfone, **5**	−491.7	−494.2	−484.8	−496.2	−480.6 ± 1.8

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

of the two oxathiane sulfones studied is 16.6 and 16.3 kJ mol^{-1}, at the G2(MP2) and G3 levels, respectively, in good agreement with the experimental difference, 11.2 kJ mol^{-1}.

Discussion

The precise structural parameters calculated at the MP2(full)/6-31G(3*df*,2*p*) level for thiane **6**, 1,3-oxathiane **7**, 1,4-oxathiane **8**, and their corresponding sulfones **1**, **4**, and **5** (Figure 4) are in line with expectations based on $n_O \rightarrow \sigma^*_{C-SO_2}$ hyperconjugation in 1,3-oxathiane sulfone **4**. In particular, it can be appreciated that the C−SO$_2$ bond distance decreases ca. 0.03 Å in going from thiane **6** to its sulfone derivative **1**, and this finding may be ascribed to bond shortening as consequence of the increased electronegativity of the sulfonyl group relative to sulfur in the thioether. It is observed that, as expected, the C−SO$_2$ bond length also decreases ca. 0.03 Å in going from 1,4-oxathiane **8** to the corresponding sulfone **5**. By contrast, the C−SO$_2$ bond length changes little (only ca. −0.01 Å) in going from 1,3-oxathiane **7** to its corresponding sulfone **4** (Figure 4). The observed reduced shortening in 1,3-oxathiane sulfone **4** may be explained in terms of the participation of a double bond−no bond canonical structure, as indicated in Figure 2.[20]

This interpretation seems to be supported by NBO charge calculations (Figure 5). The calculated charge at sulfur is consistent at +2.46 to +2.47 for sulfones **1**, **2**, **3**, and **5**, but a smaller charge of +2.43 is seen in 1,3-oxathiane sulfone **4**, again in line with participation of the double bond−no bond canonical structure (Figure 2) that places some negative charge at the sulfonyl group. Although admittedly small, this charge difference of 0.03 appears reliable when one considers that all other sulfones studied in this project (thiane sulfone **1**, 1,3-dithiane sulfone **2**, 1,4-dithiane sulfone **3**, and 1,4-oxathiane sulfone **5**), where the $n_X \rightarrow SO_2$ stereoelectronic interaction is not anticipated, consistently afford a calculated charge of +2.46 to +2.47. Furthermore, a 0.03 charge difference may be significant upon consideration that the double bond−no bond canonical form corresponding to electron transfer is expected to contribute to only a small degree (no more than 5%).

Above (see the Introduction), it was supposed that the 1,4-dithiane sulfone **3** is more stable than the 1,3-isomer **2** due to the diminished electrostatic repulsion of the two sulfur atoms.

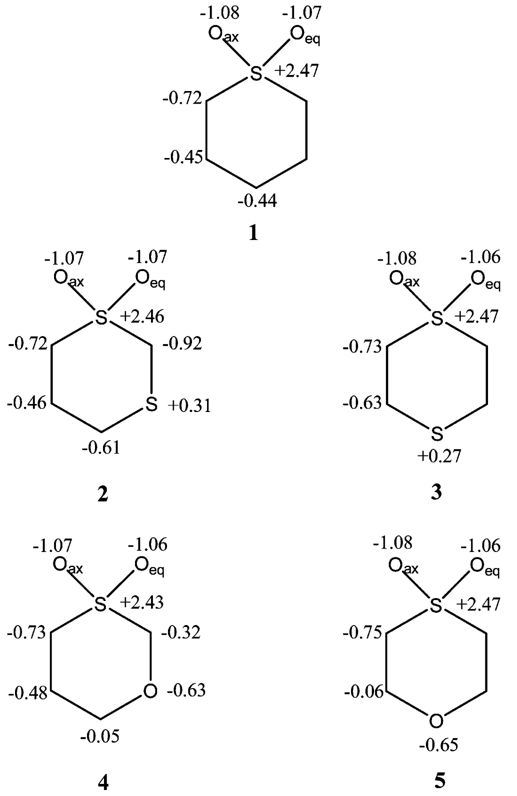

FIGURE 5. NBO positive charges at sulfur calculated from the optimized structures of thiane sulfone **1**, 1,3-dithiane sulfone **2**, 1,4-dithiane sulfone **3**, 1,3-oxathiane sulfone **4**, and 1,4-oxathiane sulfone **5** at the MP2(full)/6-31G(3*df*,2*p*) level of theory.

The negative charges present at the endocyclic oxygens in the oxathiane series (Figure 5) might suggest that the $S^{\delta+}$---$O^{\delta-}$ interaction must be more favorable in the 1,3- than in the 1,4-isomer, with the smaller separation between sulfur and oxygen in the former structure. The enthalpies of formation, both the experimental and theoretical values, indicate, however, the greater stability of the 1,4-isomer. This problem may be interpreted in light of the theoretical results summarized in Figure 5. (1) Apparently, electrostatic repulsion $O^{\delta-}$---$^{\delta-}O_{ax}$ = S in 1,3-oxathiane sulfone **4** counterbalances, at least in part, the attractive term. (2) Interestingly, NBO charges may suggest a stronger $C^{\delta-}$−$^{\delta+}SO_2$ bond in 1,4-oxathiane sulfone **5** relative to the 1,3-isomer. Furthermore, less electrostatic repulsion $O^{\delta-}$−$C^{\delta-}$ is anticipated for the 1,4-oxathiane sulfone, in view of the

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(20) Juaristi, E.; Cuevas, G. *The Anomeric Effect*; CRC Press: Boca Raton, FL, 1995; pp 30−35.

essentially neutral carbon atoms adjacent to the endocyclic oxygen in sulfone **5**, in contrast with the negative charge calculated for the carbon at C(2) in 1,3-oxathiane sulfone **4** (Figure 5).

Experimental Procedures

Material and Purity Control. The procedure described in the literature[21] was slightly modified to synthesize 1,3- and 1,4-oxathiane sulfone. In a round-bottom 100-mL flask was placed 0.9 mL (9.6 mmol) of 1,4-oxathiane or 1.0 g (9.6 mmol) of 1,3-oxathiane and 15 mL of acetic acid. The resulting solution was treated with 15 mL (0.49 mol) of hydrogen peroxide, and the reaction mixture was stirred at ambient temperature for 2 days. The solvent was removed at reduced pressure, and the solid residue was crystallized from CH_2Cl_2−hexane (2:8). In the case of 1,3-oxathiane sulfone, final purification was achieved by sublimation (110 °C/4 mmHg) to give the expected sulfone (1.0 g, 77% yield), mp 129−131 °C (lit. mp 128−130 °C). For 1,4-oxathiane sulfone: (0.9 g, 69% yield) mp 77−79 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.32−2.38 (m, 2H), 3.17−3.21 (m, 2H), 3.84−3.88 (t, 2H), 4.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.5, 50.9, 68.5, 84.4. Anal. Calcd for $C_4H_8O_3S$: C, 35.28; H, 5.92. Found: C, 34.92; H, 6.32.

Both samples were carefully dried under a vacuum at 50 °C. Determination of purities, assessed by GC and DSC by the fractional fusion technique,[22,23] indicated that the mole fraction of impurities in all the compounds was less than 0.002. The results obtained in the characterization and purity control are given in the Supporting Information.

Fusion enthalpies and heat capacity measurements and the study of polymorphism of 1,4-oxathiane sulfone were previously carried out in this laboratory by means of differential scanning calorimetry.[24]

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 compounds, $\Delta_f H^\circ_m(cr)$, 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.[25] The energy of combustion was determined by burning the solid samples in pellet form enclosed in polyethene bags and using Vaseline as the auxiliary material. The bomb was filled with oxygen to a pressure of $p = 3.04$ Mpa. 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 in the temperature intervals 307−325 and 307−322 K for 1,3- and 1,4-oxathiane sulfone, respectively, using the Knudsen effusion technique,[26,27] and the enthalpy of sublimation was deduced from the temperature dependence of the vapor pressures (Clausius−Clapeyron). From the experimental results, the standard enthalpies of combustion, sublimation, and formation in the crystalline and gaseous states at the temperature of 298.15 K have been derived and are reported in Table 1.

Computational Details. Standard ab initio molecular orbital calculations[14] were performed with the Gaussian 03 series of programs.[28] The energies of the compound studied were calculated using Gaussian-2 theory, at the G2(MP2) level,[29] and Gaussian-3 theory, at the G3 level.[30]

G2(MP2) and G3 correspond effectively to calculations at the QCISD(T)/6-311+G(3*df*,2*p*) and QCISD(T)/G3large levels, respectively. G3large is a modification of the 6-311+G(3*df*,2*p*) basis set used in G2(MP2) theory and includes more polarization functions for the second row (3*d*2*f*), less on the first row (2*df*), and other changes to improve uniformity. In addition, some core polarization functions are added.[30]

In both methods, single-point energy calculations are carried out 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. G3 also incorporates a spin−orbit correction for atomic species only.[30] We have also reoptimized the geometries at the MP2(full)/6-31G(3*df*,2*p*) level to obtain more reliable molecular structures for the studied compounds.

The charge distribution in the compounds has been analyzed using a population partition technique, the natural bond orbital (NBO) analysis of Reed and Weinhold.[31,32] The NBO analysis has been performed using the NBO program[33] implemented in the Gaussian 03 package.[28]

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Supporting Information Available: Experimental details, comparison of the optimized structures of oxathiane sulfones with the experimental molecular structures of two derivatives measured by X-ray diffraction, optimized structures in Cartesian coordinates, and Raman, IR, GC, mass, ^{1}H NMR, and ^{13}C NMR spectra and DSC curves used for purity control of 1,3- and 1,4-oxathiane sulfone. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Gokel, G. W.; Gerdes, H. M.; Dishong, D. M. *J. Org. Chem.* **1980**, *45*, 3634.

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

(23) Palermo, E. F.; Chiu, J. *Thermochim. Acta* **1976**, *14*, 1.

(24) Temprado, M.; Roux, M. V.; Jiménez, P.; Guzmán-Mejía, R.; Juaristi, E. *Thermochim. Acta* **2006**, *441*, 20.

(25) Roux, M. V.; Dávalos, J. Z.; Jiménez, P.; Flores, H.; Saiz, J. L.; Abboud, J. L. M.; Juaristi, E. *J. Chem. Thermodyn.* **1999**, *31*, 635.

(26) Knudsen, M. *Ann. Phys.* **1909**, *28*, 75.

(27) Jiménez, P.; Roux, M. V.; Dávalos, J.; Martín-Luengo, M. A.; Abboud, J. L. M. *J. Chem. Thermodyn.* **1997**, *29*, 1281.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(29) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(30) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(31) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066.

(32) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(33) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, version 3.1, Madison, WI, 1988.