

Experimental and Theoretical Study of the Structures and Enthalpies of Formation of the Synthetic Reagents 1,3-Thiazolidine-2-thione and 1,3-Oxazolidine-2-thione

María Victoria Roux,* Manuel Temprado, Pilar Jiménez, Concepción Foces-Foces, and Rafael Notario

Instituto de Química Física “Rocasolano”, CSIC, Serrano 119, 28006 Madrid, Spain

Archana R. Parameswar, Alexei V. Demchenko, and James S. Chickos

Department of Chemistry and Biochemistry, University of Missouri—St. Louis, One University Boulevard, St. Louis, Missouri 63121-4499

Carol A. Deakyne and Alicia K. Ludden

Department of Chemistry, University of Missouri—Columbia, 601 S. College Avenue, Columbia, Missouri 65211-7600

Joel F. Liebman

Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, 1000 Hilltop Circle, Baltimore, Maryland 21250-1000

Received: April 14, 2009; Revised Manuscript Received: June 16, 2009

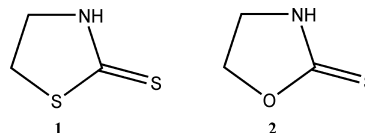
This paper reports an experimental and a theoretical study of the structures and standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of the synthetic reagents 1,3-thiazolidine-2-thione [CAS 96-53-7] and 1,3-oxazolidine-2-thione [CAS 5840-81-3]. The enthalpies of combustion and sublimation were measured by rotary bomb combustion calorimetry, and the Knudsen effusion technique and gas-phase enthalpies of formation values at $T = 298.15$ K of (97.1 ± 4.0) and $-(74.4 \pm 4.6)$ $\text{kJ}\cdot\text{mol}^{-1}$ for 1,3-thiazolidine-2-thione and 1,3-oxazolidine-2-thione, respectively, were determined. G3-calculated enthalpies of formation are in reasonable agreement with the experimental values. In the solid state, 1,3-thiazolidine-2-thione exists in two polymorphic forms (monoclinic and triclinic) and 1,3-oxazolidine-2-thione exists in the triclinic form. The isostructural nature of these compounds and comparison of their molecular and crystal structures have been analyzed. The experimental X-ray powder diffractograms have been compared with the calculated patterns from their structures for identification of the polymorphic samples used in this study. A comparison of our results with literature thermochemical and structural data for related compounds is also reported.

Introduction

Oxazolidine and thiazolidine thiones are important heterocyclic compounds that have been extensively studied along with a variety of their derivatives. Synthetic usefulness of 1,3-thiazolidine-2-thione **1** (also referred to as 2-mercaptothiazoline) is in trans-acylation reactions with 3-acylthiazolidine thiones as intermediates.¹ Recently, these materials have found applications as a versatile anomeric leaving group (*S*-thiazoliny) in chemical glycosylations and expeditious oligosaccharide syntheses.^{2,3} 1,3-Oxazolidine-2-thione (also referred to as 2-mercaptooxazoline and ethylene carbamodithioate), **2**, and particularly its 4- and/or 5-substituted chiral derivatives have found broad application as auxiliaries in the asymmetric synthesis of a broad range of substrates and natural compounds.^{4–6} Recently, we reported the fusion enthalpies and heat capacities of several thio- and dithiocarbamates including 1,3-thiazolidine-2-thione and 1,3-oxazolidine-2-thione.⁷

This paper reports some other properties of these versatile materials including experimental enthalpies of formation of the

condensed and gas phases. From a crystallographic viewpoint, the purpose of the present study is to compare the molecular and crystal structures of both compounds and the analogous derivatives as well as to check the isostructural nature of compounds **1** and **2**. Theoretical methods are also applied to evaluate structures and complement the experimental gas-phase enthalpies of formation.



Of the forty million organic compounds currently known, enthalpies of formation for approximately 0.01% have been evaluated by experimental calorimetric measurements. The vast majority of these measurements have been on specific classes of compounds, very often with unique structural features from which group increments and associated strain corrections have been derived. The classic monograph by Benson⁸ and the numerous studies that inspired this work come immediately to

* To whom correspondence should be addressed. E-mail: victoriaroux@iqfr.csic.es.

mind. However, despite the success of these group additivity studies, there are many chemical species for which such analysis has been thwarted by the absence or paucity of data. In some instances, a group value is derived from a single thermochemical measurement of a compound containing that group. In such cases in the literature, sometimes the group increment has been derived, e.g., (C)₂CNOH from cyclohexanone oxime,⁹ while in others the compound stands in splendid isolation, such as saccharin from which the acylsulfonamide functional group and the associated (C_b)CONHSO₂(C_b) group increment was not derived.¹⁰ In this latter case, the acylsulfonamide group is found in a five-membered ring that plausibly introduces additional ring strain. The contribution of the acylsulfonamide group cannot be deduced without further experimental data. The current study provides the enthalpies of formation of compounds with two novel functionalities –NHC(S)O– and –NHC(S)S– whose group contributions are likewise constrained within a five-membered ring.

Experimental Procedures

Materials and Purity Control. Dithiocarbamate **1** [1,3-thiazolidine-2-thione] [CAS 96-53-7], commercially available from Acros, was additionally purified by crystallization using dichloromethane as solvent. The synthesis of thiocarbamate, **2** [1,3-oxazolidine-2-thione] [CAS 5840-81-3], was accomplished using the corresponding amino alcohol as starting material. Thus, for the synthesis of **2**, 2-aminoethanol was reacted with CS₂ in the presence of triethylamine in methanol at 0 °C followed by treatment with 30% H₂O₂ in accordance with the published procedures.¹¹ Thioamide **2** was obtained in 73% yield. The synthetic derivative was then purified by crystallization using a mixture of dichloromethane and hexanes as solvent. The characterization and spectral data for the compound 1,3-oxazolidine-2-thione were essentially the same as those reported previously.¹¹ The samples were carefully dried under vacuum at *T* = 50 °C. Determination of purities, assessed by GC and DSC using the fractional fusion technique,¹² indicated that the mole fraction of impurities in the compounds was less than 0.001 and 0.006 for **1**, and **2**, respectively. No solid–solid phase transitions were observed over the temperature interval from *T* = 298.15 K to the corresponding melting points *T*_{fus} = 377.0 K and *T*_{fus} = 370.6 K for 1,3-thiazolidine-2-thione and 1,3-oxazolidine-2-thione, respectively.⁷

Thermochemical Measurements. The enthalpies of formation in the crystalline state were determined by combustion calorimetry using an isoperibol combustion calorimeter equipped with a rotary bomb. Details of the technique and procedure used have been previously described.^{13,14} The energies of combustion of 1,3-thiazolidine-2-thione and 1,3-oxazolidine-2-thione were determined by burning the solid samples in pellet form. The pelleted compounds were enclosed in polyethylene bags. Vaseline was used as auxiliary material to limit the amount of sulfur in the samples to only 8 mmol.¹⁵ The bomb was filled with oxygen to a pressure of *p* = 3.04 MPa. The energy of the combustion experiments was always referenced to the final temperature of 298.15 K. From the combustion energies, the enthalpies of formation in the condensed state were calculated.

The enthalpies of sublimation were evaluated from the temperature dependence of the vapor pressures (Clausius–Clapeyron equation). Vapor pressures of 1,3-thiazolidine-2-thione and 1,3-oxazolidine-2-thione evaluated over a 18 and 28 K temperature interval, respectively, were measured using the Knudsen effusion technique.¹⁶ The apparatus consists, essentially, of a stainless steel sublimation chamber immersed in a thermoregulated water

jacket and connected to a high-vacuum system (*p* = 1 × 10^{−4} Pa). The Knudsen cell was weighed with a Mettler AT-21 microbalance, reproducible to within ±0.000005 g, before and after each effusion time period, *t*, to determine the mass, *m*, of sublimed material. The vapor pressure, *p*, for each temperature, *T*, was calculated from the equation

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

where *a* is the area of the effusion orifice, *W_a* the corresponding Clausing coefficient,¹⁷ and *M* the molar mass of the studied compounds. The atomic weights of the elements are those recommended by IUPAC in 2005.¹⁸

X-ray Crystallography. X-ray powder diffraction patterns of the commercial sample of **1** and the synthetic product **2** were recorded on a Philips PW1830 powder diffractometer with Cu Kα radiation. The single-crystal structures of **1** (two polymorphic forms) and **2** have been previously reported,^{19,20} and their computed powder diffraction patterns were obtained using the program PLATON.²¹

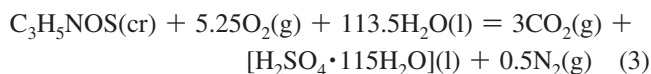
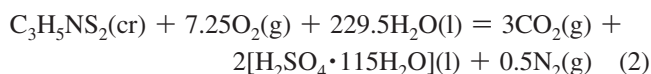
Computational Details. Standard ab initio molecular orbital calculations²² were performed with the Gaussian 03 series of programs.²³ The energy of each of the compounds studied was calculated using Gaussian-*n* theory at the G3 level.²⁴ We also reoptimized the geometries at the MP2(full)/6-31G(3df,2p) level to obtain more reliable molecular structures for the compounds studied.

The charge distribution has been analyzed using a population partition technique, the natural bond orbital (NBO) analysis of Reed and Weinhold.^{25–27} The NBO analysis has been performed using the NBO program²⁸ implemented in the Gaussian 03 package.²³

Results

Experimental Determination of the Enthalpies of Formation in the Gas Phase. The enthalpies of formation in the gas state, Δ_f*H*^o_m(g), were determined by combining the standard enthalpies of formation of the crystalline 1,3-thiazolidine-2-thione and 1,3-oxazolidine-2-thione, Δ_f*H*^o_m(cr), with their standard enthalpies of sublimation, Δ_{cr}^g*H*^o_m, both referenced to *T* = 298.15 K.

Results of a typical combustion experiment on each compound are given in Table 1. The values of the standard massic energy of combustion, Δ_c*u*^o, refers to the combustion reactions 2 and 3 for 1,3-thiazolidine-2-thione and 1,3-oxazolidine-2-thione, respectively.



The individual results for the standard massic energy of combustion, Δ_c*u*^o, obtained in all the combustion experiments together with the mean value and its standard deviation, are given in Table 2.

The enthalpies of sublimation, Δ_{cr}^g*H*^o_m, for both compounds were obtained from the temperature dependence of the vapor pressures (Clausius–Clapeyron equation, Table 3) by the Knudsen effusion method. The results of the Knudsen effusion

TABLE 1: Results of Typical Combustion Experiments of 1,3-Thiazolidine-2-thione and 1,3-Oxazolidine-2-thione^a

	1,3-thiazolidine-2-thione	1,3-oxazolidine-2-thione
m' (compound) ^b /g	0.59138	0.75586
m'' (polyethylene) ^b /g	0.07914	0.07909
m''' (vaseline) ^b /g	0.24527	0.25285
m'''' (fuse) ^b /g	0.00219	0.00269
ΔT_c /K	1.0500	1.1208
ε (calor) ^c ($-\Delta T_c$)/kJ	-30.3059	-32.3491
ε (cont.) ^d ($-\Delta T_c$)/kJ	-0.0521	-0.0563
ΔU_{ign}^e /kJ	0.4941	0.4941
ΔU_{dec} (HNO ₃) ^f /kJ	0.0290	0.0746
ΔU_{dil} (H ₂ SO ₄) ^g /kJ	-0.006	-0.0029
ΔU (corr. to std states) ^h /kJ	0.0142	0.0218
$-m''\Delta_c u^\circ$ (vaseline)/kJ	3.6700	3.6675
$-m'''\Delta_c u^\circ$ (polyethylene)/kJ	11.3038	11.6533
$-m''''\Delta_c u^\circ$ (fuse)/kJ	0.0382	0.0469
$\Delta_c u^\circ$ (compound)/kJ·g ⁻¹	-25.8870	-22.4166

^a $T_{\text{th}} = 298.15$ K; $V_{\text{bomb}} = 0.260$ dm³; $p_{\text{gas}}^i = 3.04$ MPa; $m_{\text{water}}^i = 10.00$ g. ^b Masses obtained from apparent mass. ^c ε (calor) = energy equivalent of the whole system but the contents of the bomb. ^d ε (cont.) = energy equivalent of the contents of the bomb $\varepsilon(\text{cont.})(-\Delta T_c) = \varepsilon^i(\text{cont.})(T^i - 298.15 \text{ K}) + \varepsilon^i(\text{cont.})(298.15 \text{ K} - T^i + \Delta T_{\text{corr}})$. ^e Experimental energy of ignition. ^f Experimental energy of formation of nitric acid. ^g Experimental energy of formation of sulfuric acid. ^h ΔU (corr. to std states) is the standard state correction.

TABLE 2: Individual Values of the Standard Massic Energy of Combustion, $\Delta_c u^\circ$ (kJ g⁻¹), at 298.15 K

1,3-thiazolidine-2-thione	1,3-oxazolidine-2-thione
-25.8655	-22.4054
-25.8545	-22.4254
-25.8930	-22.4166
-25.9016	-22.4012
-25.8792	-22.4335
-25.8870	-22.4191
-25.8801 ± 0.0072	-22.4169 ± 0.0049

experiments for oxazolidine-2-thione and thiazolidine-2-thione calculated by means of eq 1 are summarized in Table 3, where p represents the vapor pressure, Δm the mass loss during time t at temperature T , and $\delta p/p$ the fractional deviation of the experimental vapor pressures from those computed using eq 4. The highest error for the vapor pressure, p , is $5 \times 10^{-3} p$, computed as the sum of the estimated errors of all quantities in eq 1.

An equation of the type

$$\ln(p/\text{Pa}) = -B(T/\text{K})^{-1} + A \quad (4)$$

was used to fit to the results reported in Table 3.

TABLE 3: Vapor Pressures, p , of 1,3-Oxazolidine-2-thione and 1,3-Thiazolidine-2-thione

T/K	t/s	$\Delta m/\text{mg}$	p/Pa	$10^2 \cdot (\delta p/p)$	T/K	t/s	$\Delta m/\text{mg}$	p/Pa	$10^2 \cdot (\delta p/p)$
1,3-oxazolidine-2-thione									
325.26	30120	1.43	0.0291	7.33	344.38	21600	7.86	0.230	0.0603
329.32	30120	1.69	0.0394	-10.1	347.08	14520	6.95	0.304	-0.403
333.5	18840	2.20	0.0725	2.60	350.28	18000	11.9	0.421	-0.889
336.99	25020	3.97	0.0991	-4.28	354.18	21960	11.2	0.637	1.06
340.46	25020	5.81	0.160	5.58					
1,3-thiazolidine-2-thione									
333.36	28200	2.17	0.0865	2.44	345.19	10800	2.83	0.296	1.96
336.65	25380	2.60	0.116	-3.46	348.52	16800	5.89	0.403	-0.417
339.79	19560	2.94	0.170	1.82	351.54	16800	7.93	0.545	0.155
342.01	14520	2.81	0.207	-1.43					

The mean experimental temperature [T_m], parameters A and B , and enthalpy and entropy of sublimation at the mean experimental temperature for 1,3-oxazolidine-2-thione and 1,3-thiazolidine-2-thione are given in Table 4.

The uncertainty assigned to the value of the sublimation enthalpies are the standard deviations of the B values including Student's t factor for the 95% confidence level ($t = 2.447$ and 2.306 for 7 and 9 independent measurements for 1,3-oxazolidine-2-thione and 1,3-thiazolidine-2-thione, respectively).²⁹ The standard molar enthalpies of sublimation at $T = 298.15$ K were calculated from eq 5.³⁰

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}[T_{\text{m}}] + 2R(T_{\text{m}} - 298.15) \quad (5)$$

Values for the standard molar sublimation enthalpy at $T = 298.15$ K, 105.0 ± 4.4 and 100.5 ± 3.4 kJ·mol⁻¹ for 1,3-oxazolidine-2-thione and 1,3-thiazolidine-2-thione, respectively, were deduced.

Table 5 collects the values determined for the standard molar energies, $\Delta_c U_{\text{m}}^{\circ}$, and enthalpies of combustion, $\Delta_c H_{\text{m}}^{\circ}$, sublimation, $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}$, and formation in the crystalline, $\Delta_f H_{\text{m}}^{\circ}(\text{cr})$, and gaseous state, $\Delta_f H_{\text{m}}^{\circ}(\text{g})$, of 1,3-thiazolidine-2-thione and 1,3-oxazolidine-2-thione. No experimental results for the energies and enthalpies of combustion, sublimation, and formation have been found in the literature for comparison with our results.

In accordance with normal thermochemical practice, the uncertainties assigned are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of the auxiliary quantities.³¹ To derive $\Delta_f H_{\text{m}}^{\circ}(\text{cr})$ from $\Delta_c H_{\text{m}}^{\circ}(\text{cr})$, the CODATA values of the standard molar enthalpies of formation of H₂O(l) and CO₂(g) at $T = 298.15$ K, $-(285.830 \pm 0.042)$ kJ mol⁻¹ and $-(393.51 \pm 0.13)$ kJ mol⁻¹, respectively, were used.³² The value of the enthalpy of formation of [H₂SO₄·115 H₂O], $-(887.811 \pm 0.042)$ kJ mol⁻¹, was taken from ref 33.

X-ray Crystallography. The crystal structures of 1,3-thiazolidine-2-thione, **1**, and 1,3-oxazolidine-2-thione, **2**, have been previously reported.^{19,20} Compound **1** exists in two polymorphic forms, monoclinic (Cambridge Crystallographic Database,³⁴ CSD refcodes CASHOT, CASHOT01, CASHOT02) and triclinic (CSD refcode CASHOT03), while only a triclinic form is known for compound **2** (the X-ray data has not been deposited with the Cambridge Crystallographic Data Center).

Experimental and simulated X-ray powder diffraction patterns from the reported structures were obtained for identification of the polymorphic form used in this study. The experimental pattern for commercial samples of **1** is in agreement with that calculated for the monoclinic form (see Supporting Information). The experimental diffractogram of compound **2** is consistent

TABLE 4: Parameters A and B and Enthalpy and Entropy of Sublimation

	[T] _m /K	A	B	$\Delta_{\text{cr}}^{\circ}H_{\text{m}}^{\circ}$ [T _m]/kJ·mol ⁻¹	$\Delta_{\text{cr}}^{\circ}S_{\text{m}}^{\circ}$ [T _m]/J·mol ⁻¹ K ⁻¹
1,3-oxazolidine-2-thione	339.72	34.9 ± 0.7	12540 ± 229	104.3 ± 4.4	307.0 ± 10.0
1,3-thiazolidine-2-thione	342.42	33.5 ± 0.5	12001 ± 172	99.8 ± 3.4	291.4 ± 12.8

TABLE 5: Experimentally Determined Standard Molar Energy of Combustion and the Standard Molar Enthalpy of Combustion, Sublimation, and Formation in the Crystalline and Gaseous States at T = 298.15 K for 1,3-Thiazolidine-2-thione and 1,3-Oxazolidine-2-thione

thermodynamic properties	experimental values ^a	
	1,3-thiazolidine-2-thione	1,3-oxazolidine-2-thione
$\Delta_{\text{c}}U_{\text{m}}^{\circ}$	-3085.1 ± 2.1	-2312.1 ± 1.3
$\Delta_{\text{c}}H_{\text{m}}^{\circ}$	-3095.7 ± 2.1	-2317.7 ± 1.3
$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr})$	-3.4 ± 2.1	-179.4 ± 1.4
$\Delta_{\text{cr}}^{\circ}H_{\text{m}}^{\circ}$	100.5 ± 3.4	105.0 ± 4.4
$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})$	97.1 ± 4.0	-74.4 ± 4.6

^a All values in kJ mol⁻¹.

with its calculated pattern, although it was crystallized from a mixture of dichloromethane/hexane solvents instead of an aqueous solution²⁰ looking for new polymorphic forms.

In the solid state and at the molecular level, compounds **1** and **2** exist in the keto (thione) tautomeric form wherein some degree of delocalization is observed in the S=C–N fragment. The S1–C1, C1–N1, and O/S–C1 lengths (Table 6 and numbering scheme in Figure 1) are in concordance with the corresponding average values obtained from the Cambridge Crystallographic Database (CSD)³⁴ for the 1,3-oxazolidine/1,3-thiazolidine-2-thione derivatives (9 and 13 compounds, respectively) and also for the X–CS–NH fragments with X = O, S (S=C1 = 1.678(18) Å, C1–N1 = 1.339(20) Å for 221 entries of which 79 correspond to X = O with C1–O2 = 1.339(20) Å and 142 to X = S with C1–S2 = 1.743(15) Å (standard deviation of the sample in parentheses). It is interesting to note that just in a few examples (16 structures) the enol (enethiol) form has been observed, and both tautomeric forms are present in each molecule of 2,5-dimercaptothiadiazole³⁵ (CSD refcode DMCTDZ) with C=S and C–SH values of 1.669(2) and 1.743(2) Å, respectively).

The molecular structure of **1** (in both polymorphs) and **2** are very similar in terms of bond distances and angles apart from the differences due to the substitution of the S atom by an O atom in the five-membered ring, but differ in the puckering of this ring (Table 6). Within the crystal, the molecules are linked by N–H···S=C hydrogen bonds forming centrosymmetric dimers, although in the monoclinic form of **1** there are two molecules in the asymmetric unit (Figure 1). The triclinic polymorph of **1** and **2** are strictly isostructural even in terms of the weak C–H···O/S intermolecular contacts and, furthermore, effectively isomorphous (same space group and similar cell dimensions and atomic coordinates) after performing the transformation indicated as follows: the reported unit cell and coordinates for **2** must be transformed as follows: $A = -a$, $B = -b$, $C = -a + c$ (vectorial notation) to 5.738(3), 5.928(4), and 7.685(6) Å and 87.98(7), 68.63(5) and 77.85(5)°, and the (3/2, 1, -1/2) translation should be applied to the new atomic coordinates in order to be coincident with those reported for compound **1** (triclinic form). The significant differences in the geometrical parameters of the contacts (D/H···A distances and D–H···A angle) can be attributed not only to the nature of the

acceptors (S vs O) but to the different conformation of the five-membered ring (planar in this form of **1** vs distorted half-chair in **2**).

Theoretical Molecular and Electronic Structures. Molecular structures of 1,3-thiazolidine-2-thione, 1,3-oxazolidine-2-thione, and all molecules relevant to the thermochemical analyses were optimized at the MP2(Full)/6-31G(3df,2p) level of theory. The equilibrium structures of 1,3-thiazolidine-2-thione and 1,3-oxazolidine-2-thione are shown in Figure 2, and calculated bond distances and angles are collected in Table 6.

As it can be seen, the optimized structures agree well with the experimental crystal structures. The X-ray results indicate a larger delocalization with more contribution of C–S single bonding, the calculated S1–C1 bonds being shorter and the C1–N1 bonds being longer than the experimental ones. In both compounds, the thioketo tautomers are significantly more stable than the thiol tautomers. At the G3 level of theory, the thione forms are 33.5 and 34.7 kJ mol⁻¹ more stable than the thiol forms for thiazolidine-2-thione and oxazolidine-2-thione, respectively.

A population analysis using natural bond orbital (NBO) analysis has also been carried out^{25–27} to obtain the natural atomic charges (the nuclear minus summed populations of the natural atomic orbitals on the atoms) that characterize the ground electronic state of the compounds studied. The calculated charges with the hydrogen atoms summed into the heavy atoms for both compounds are reported in Figure 3.

As expected, differences in size, electronegativity, and bond polarities associated with oxygen and sulfur result in large differences in the electronic structures of the two compounds.

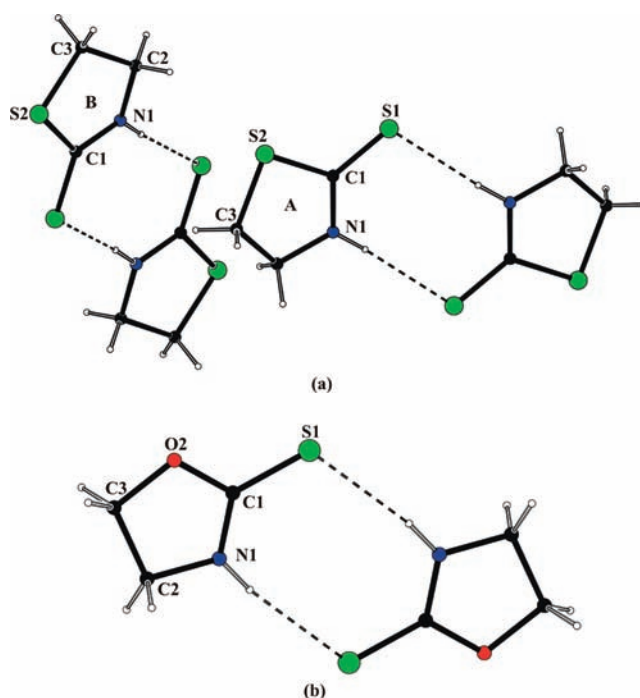


Figure 1. (a) Dimeric aggregation in the monoclinic form of **1** showing the relative disposition of the independent molecules. (b) Due to the isomorphism between the triclinic form of **1** and **2**, only the dimeric association of the latter is represented.

TABLE 6: Geometric Parameters (Angstroms, degrees)^a

compound	X-ray results			ab initio results ^b		
	monoclinic		triclinic	1	2	
	1, Mols. A/B		1			
S1–C1	1.675(2)/1.674(2)		1.671(2)	1.672(3)	1.625	1.618
S/O–C1	1.741(2)/1.740(2)		1.745(2)	1.348(4)	1.746	1.348
S/O–C3	1.823(2)/1.822(2)		1.812(2)	1.468(5)	1.802	1.432
C1–N1	1.319(2)/1.320(2)		1.319(3)	1.315(4)	1.354	1.360
N1–C2	1.466(2)/1.467(2)		1.456(2)	1.462(5)	1.445	1.445
C2–C3	1.519(2)/ 1.522(2)		1.528(3)	1.515(6)	1.516	1.517
C1–S/O–C3	92.8(1)/93.0(1)		93.8(1)	109.1(3)	92.3	108.8
S/O–C1–N1	111.4(1)/111.4(1)		111.4(1)	110.4(3)	109.3	108.4
C1–N1–C2	118.0(1)/118.2(1)		119.5(1)	112.8(3)	116.1	110.7
N1–C2–C3	106.5(1)/106.6(1)		108.1(2)	100.9(4)	104.0	98.4
C2–C3–S/O	105.8(1)/105.8(1)		107.3(1)	104.2(3)	104.1	104.1
S/O–C1–S1	121.9(1)/121.8(1)		121.3(1)	121.5(3)	124.1	123.8
N1–C1–S1	126.7(1)/126.9(1)		127.3(1)	128.2(3)	126.6	127.8
S/O–C1–N1–C2	8.5(2)/7.4(2)		−0.7(2)	−4.4(4)	−16.1	−15.7
C1–N1–C2–C3	−21.9(2)/−20.6(2)		0.2(2)	12.8(4)	36.0	28.0
N1–C2–C3–S/O	23.6(2)/22.8(2)		0.4(2)	−15.4(4)	−37.4	−29.4
C2–C3–S/O–C1	−17.6(1)/−17.4(1)		−0.7(2)	14.3(4)	26.5	22.8
C3–S/O–C1–N1	6.2(1)/6.7(1)		0.8(2)	−6.7(4)	−7.5	−5.4
N1⋯S	3.367(2)/3.384(2)		3.359(2)	3.462(4)		
H⋯S	2.48/2.49		2.53	2.57		
>N–H⋯S	171/176		171	171		

^a The numbering system used in this study, common to both compounds **1** and **2**, is shown in Figure 1. ^b Values calculated at the MP2(Full)/6-31G(3df,2p) level of theory and therefore necessarily refer to gas-phase species.

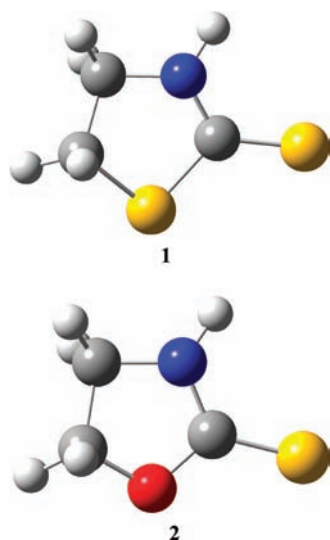


Figure 2. MP2(Full)/6-31G(3df,2p)-optimized structures of 1,3-thiazolidine-2-thione, **1**, and 1,3-oxazolidine-2-thione, **2**.

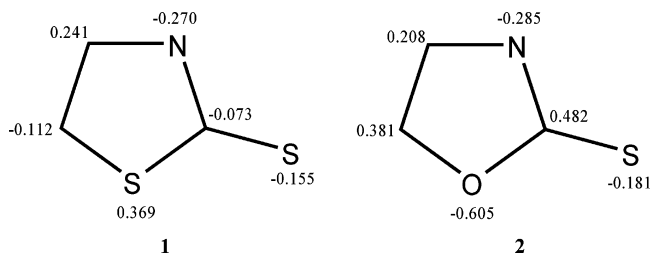


Figure 3. MP2(Full)/6-31G(3df,2p)-calculated NBO atomic charges with hydrogens summed into heavy atoms in 1,3-thiazolidine-2-thione, **1**, and 1,3-oxazolidine-2-thione, **2**.

In the case of 1,3-thiazolidine-2-thione, the sulfur atom of the ring and the CH₂ group nearer to the N atom have positive charges associated with them in relation to the other heavy atoms which are associated with negative charges. In 1,3-oxazolidine-

2-thione, the oxygen atom of the ring has a negative charge whereas the positive charge is located at the thiocarbonyl C atom of the ring and the two CH₂ groups.

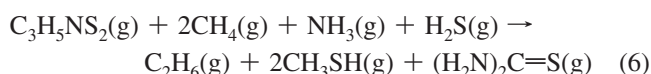
The NBO analysis also describes the bonding in terms of the natural hybrid orbitals. In 1,3-thiazolidine-2-thione, the hybridization of the ring sulfur atom is sp², with more than 80% p character to form C–S bonds, whereas the hybridization of the ring oxygen atom in 1,3-oxazolidine-2-thione is sp² (ca. 70% p character) to form C–O bonds. Moreover, sulfur and oxygen atoms have sp and p lone pairs that may delocalize into the vicinal antibonding orbitals.

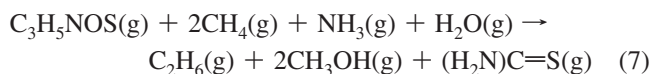
Theoretical Enthalpies of Formation. G3-calculated energies at *T* = 0 K and enthalpies at *T* = 298 K for the two compounds studied are given in the Supporting Information.

The standard procedure in obtaining enthalpies of formation in Gaussian-n theories is through atomization reactions.^{36,37} Raghavachari et al.³⁸ proposed using a standard set of isodesmic reactions, the “bond separation reactions”,²² where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages to derive the theoretical enthalpies of formation.

In this work it is not convenient to use the isodesmic bond separation reactions because the experimental enthalpy of formation of one of the reference compounds, thioformaldehyde H₂C=S, has not been well determined. There are two values reported in the literature,^{39,40} very different from one another and with very large uncertainties.

Consequently, two similar isodesmic reactions 6 and 7, using thiourea ((H₂N)₂C=S) as a reference in both, have been used

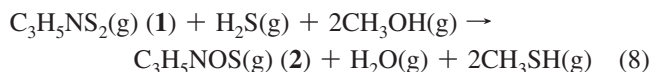




The enthalpies of formation of 1,3-thiazolidine-2-thione and 1,3-oxazolidine-2-thione have been calculated using the G3-calculated enthalpies of reaction and the experimental enthalpies of formation of the species involved^{41–43} in these reactions. The results are shown in Table 7. There is a reasonable agreement between experimental and theoretical results with the theoretical values predicting the compounds to be slightly more stable than when measured experimentally.

Discussion

It is perhaps surprising that the atomization and isodesmic reactions result in very nearly the same enthalpy of formation and that the discrepancies between the calculated and experimental enthalpies of formation for species **1** and **2** are also nearly the same, ca. 7 kJ mol⁻¹, while we would have expected better agreement with the use of isodesmic reactions as found in other G3 studies. Wishing better agreement between calculations and experiment, we now ask whether the enthalpies of formation of some key species are incorrect. A possibly errant value is that for (H₂N)₂C=S (g), especially noting the earlier complications in the calorimetry of sulfur-containing species. Accordingly, consider the following reaction:



The G3-calculated enthalpy of reaction is -37.8 kJ mol⁻¹. From this one finds the difference in the enthalpies of formation of species **1** and **2** is -173.7 kJ mol⁻¹, in complete agreement with the experimental difference of -171.5 ± 3.5 kJ mol⁻¹. This gives us increased confidence in our experimental and computational results.

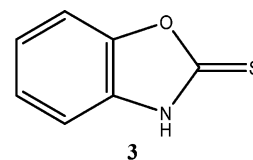
Let us succinctly put our results into context. We recognize species **1** as a cyclic dithiocarbamate. The literature on the enthalpy of formation of acyclic dithiocarbamates consists of *N,N*-dimethyl methyl dithiocarbamate and some derivatives, all in the condensed phase, from a paper over a century old.⁴⁵ Given the complexities inherent in the calorimetry of sulfur-containing species^{13,14,46–51} we are hesitant to analyze these earlier data to derive the (C)N(H)-C(S)-O(C) group increment. Contemporary calorimetric data for cyclic dithiocarbamates is limited to 2-mercaptobenzothiazole,⁵² assuming for our study that this species is, in fact, its dithiocarbamate tautomer. Conceptual interrelation of this species with an acyclic dithiocarbamate, and hence to our alicyclic species, may be made analogous to the aromaticity-driven analysis reported in a recent review.⁵³ However, to make this interrelation requires data for both the cyclic species and the acyclic *N*-methyl methyl dithiocarbamate in the gas phase and the necessary sublimation enthalpy data remain absent. We are also hesitant to apply the thermochemical data and insights from the oxygen analog 2-benzoxazolinone⁵⁴ in that little is seemingly known about carbamates.

TABLE 7: G3-Calculated Enthalpies of Formation for the Compounds Studied Using Atomization and Isodesmic Reactions (all values in kJ mol⁻¹)

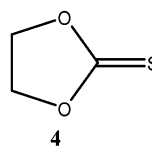
compound	atomization	isodesmic	experimental
1,3-thiazolidine-2-thione, 1	88.4	90.5	97.1 ± 4.0
1,3-oxazolidine-2-thione, 2	-87.9	-83.1	-74.4 ± 4.6

Consider species **2**. The calorimetric data for cyclic thiocarbamates with the >N-C(S)-O- substructure is limited to putatively aromatic 2-mercaptobenzoxazole, solely as solid,⁵² and assumed in the current study to be in its *O*-thiocarbamate tautomer, benzoxazolinone-thione, **3**. The enthalpies of formation of acyclic *O*-thiocarbamates is limited to some alkyl esters of “acyclic” *N*-arenecarbonyl derivatives^{55,56} with the C_{ar}-(CO)-N(H)-C(S)-O-(C) group and the derived enthalpic increment. The *N*-acylation of the thiocarbamate in the literature species and the plausible strain due to the five-membered ring in species **2** thwarts deriving the enthalpic increment of a strainless (C)N(H)-C(S)-O-(C) group.

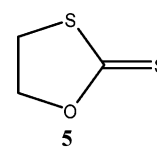
Rearrangement enthalpies of >N-C(=S)-O- species to the isomeric >N-C(O)-S- have not been measured, although this process has been shown to proceed in this direction with measured enthalpies of activation.⁵⁷ Our quantum chemical calculations show that species **2** is less stable than its thiocarbamate isomer by 64.7 kJ mol⁻¹, while the acyclic dimethyl thiocarbamate isomers have a corresponding enthalpy difference of but 50.1 kJ mol⁻¹.



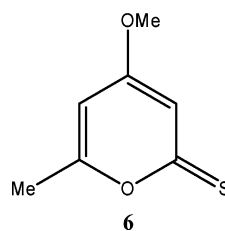
3



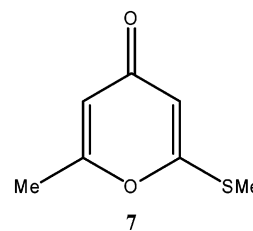
4



5



6



7

Regarding species with the simpler -C(=S)-O- or thionocarboxylate substructure, the greater stability of thiocarboxylates over their thionocarboxylate isomers is documented by the synthetically useful⁵⁸ thermal rearrangement of thionoesters to thioesters and the iodide-catalyzed rearrangement of ethylene thionocarbonate, **4**, and 1,3-oxathiolane-2-thione, **5**, to the isomeric thiolcarbonate and dithiolcarbonate.⁵⁹ Our quantum chemical calculations show methyl thioacetate to be 54.2 kJ mol⁻¹ more stable than its thionoacetate isomer, while γ -thiobutyrolactone is 62.5 kJ mol⁻¹ more stable than its thione isomer. The sole quantitative example of the isomeric thiocarboxylate stabilities involves the measurement of the rearrangement enthalpy of the questionably aromatic 4-methoxy-6-methyl-2-thioxopyrone, **6**, to form 6-methyl-2-methylthio-4-pyrone, **7**.⁶⁰ We end our qualitative discussion here acknowledging little is known about the thermochemistry of pyrones to further guide us or the reader.

Acknowledgment. The authors thank D. Rafael González (Museo Nacional de Ciencias Naturales, CSIC, Madrid) for recording the X-ray powder diffractograms. M.T. would like to thank MEC/SEUI, FPU AP2002-0603, Spain, for financial

support. A.V.D. thanks the National Science Foundation (CHE-0547566) and the American Heart Association (0855743G) for financial support of this research. The support of the Spanish Ministerio de Educación y Ciencia under Projects CTQ2007-60895/BQU and CTQ2006-10178/BQU is gratefully acknowledged.

Supporting Information Available: Procedure for thermochemical measurements; Cartesian coordinates, frequencies, and moments of inertia of the compounds studied; enthalpies of formation and CAS numbers of reference compounds; and the experimental and simulated X-ray powder diffraction patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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