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Knowledge of a Molecule: An Experimental and Theoretical Study of the Structure and Enthalpy of Formation of Tetrahydro-2*H*-1,3-oxazine-2-thione

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ABSTRACT: In a continuation of our investigations of the thermochemistry of heterocyclic ring systems and sulfur-containing compounds, the standard molar enthalpy of formation of tetrahydro-2*H*-1,3-oxazine-2-thione (CAS no. 17374-18-4) at $T = 298$ K has been evaluated both experimentally and computationally. Combined enthalpies of combustion and sublimation, measured by rotary bomb combustion calorimetry and the Knudsen effusion technique, yielded a gas-phase enthalpy of formation of $-(104.0 \pm 5.5)$ $\mathrm{kJ \cdot mol^{-1}}$. The G3 value of -104.6 $\mathrm{kJ \cdot mol^{-1}}$ calculated using an isodesmic bond separation reaction is in excellent agreement with the experimental result. The variation in enthalpy of formation with ring size is discussed, and the G3 enthalpy of formation of tetrahydro-2*H*-1,3-thiazine-2-thione (72.4 $\mathrm{kJ \cdot mol^{-1}}$) was also computed for this purpose.

1. INTRODUCTION

Species with the thiocarbamate and dithiocarbamate ester functional groups [>N−C(=S)−O− and >N−C(=S)−S−, respectively] are of active interest and importance to the organic chemistry community. These functional groups represent the core structure present in oxazines, oxazolines, thiazines, thiazolines, and derivatives thereof, which represent a family of common heterocyclic compounds.[1] These heterocyclic moieties are often present as constituents of natural products[2,3] and are employed in synthetic organic chemistry.[4,5] The importance of thioglycosyl heterocycles has recently emerged in the area of carbohydrate chemistry.[6] A variety of leaving groups based on these heterocycles have been investigated,[7,8] and it has been determined that *S*-thiazolinyl[9] and *S*-benzoxazolyl[10,11] derivatives possess superior glycosyl donor properties for stereoselective glycosylations and expeditious oligosaccharide synthesis. Tetrahydro-2*H*-1,3-oxazine-2-thione has been somewhat less studied, although its application in the synthesis of thioenamides[12,13] and as an anomeric leaving group[14] has recently emerged.

After a long hiatus from a comprehensive study of such species early in the last century,[15] the organic thermochemistry community has only in the last 10 years shown renewed interest in such compounds.[16−21] In contrast, the thermochemical study of ionic, metal, and more "inorganic" thiocarbamates and dithiocarbamates has been quite popular over the years.[22−32]

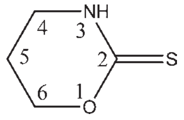

Figure 1. Structural formula of tetrahydro-2*H*-1,3-oxazine-2-thione (**1**).

The current study returns us to the organic thiocarbamate and dithiocarbamate esters and in particular to the enthalpy of formation of the cyclic compound tetrahydro-2*H*-1,3-oxazine-2-thione (Figure 1). The thermochemical investigation of this six-membered-ring species complements that of the related

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five-membered-ring compound 1,3-oxazolidine-2-thione[20] and provides an opportunity to study changes in enthalpies of formation associated with changes in ring size.

Table 1. Physical Properties of Compounds Used in Combustion Experiments at $T = 298.15$ K

compound	ρ / $g\cdot cm^{-3}$	$(\delta V/\delta T)_P\cdot 10^7$ / $dm^3\cdot g^{-1}\cdot K^{-1}$	c_P / $J\cdot K^{-1}\cdot g^{-1}$
polyethene	0.918	7.650	1.99[a]
Vaseline	0.870[b]	8.374[c]	2.22[d]
cotton	1.5	9.69[e]	1.48
tetrahydro-2*H*-1,3-oxazine-2-thione	1.39[f]	(3.354)[g]	1.192[h]

[a] Determined by DSC in our laboratory. [b] Value taken from ref 39. [c] Value taken from ref 41. [d] Value taken from ref 42. [e] Value taken from ref 43. [f] Value determined by flotation in our laboratory. [g] Estimated value. [h] Value taken from ref 18.

2. EXPERIMENTAL PROCEDURES

2.1. Materials and Purity Control. The synthesis of tetrahydro-2*H*-1,3-oxazine-2-thione (CAS no. 17374-18-4) was accomplished in 62% yield using 3-aminopropanol and CS_2 as starting materials. The product was then purified by crystallization using a mixture of dichloromethane and toluene as the solvent. The characterization and spectral data were essentially the same as reported previously.[33] The sample was carefully dried under vacuum at 50 °C. Determination of purities, which were assessed by gas chromatography (GC) (Trace GC Ultra from Thermo Electron Co.) and differential scanning calorimetry (DSC) (Pyris 1 from PerkinElmer) by the fractional fusion technique,[34] indicated that the mole fraction of

Table 4. Mean Experimental Temperature, Parameters *A* and *B*, and Enthalpy of Sublimation of Tetrahydro-2*H*-1,3-oxazine-2-thione

T_m/K	*A*	*B*	$\Delta_{cr}^{g}H_m^\circ[T_m]/kJ\cdot mol^{-1}$
362.46	33.3 ± 0.9	12930 ± 310	107.5 ± 5.2

Table 2. Results of Combustion Experiments on Tetrahydro-2*H*-1,3-oxazine-2-thione at $T = 298.15$ K[a]

m'(compound)/g[b]	0.65886	0.65802	0.65472	0.64722	0.63997	0.64656
m''(polyethylene)/g[b]	0.07868	0.08534	0.08102	0.08952	0.08075	0.08903
m'''(vaseline)/g[b]	0.20876	0.26392	0.28454	0.32418	0.26269	0.28813
m''''(fuse)/g[b]	0.0024	0.00285	0.00262	0.00242	0.00267	0.00278
ΔT_c/K	−1.0372	−1.1352	−1.1574	−1.2277	−1.1099	−1.1694
ε(calor)$(-\Delta T_c)$/kJ[c]	−29.9651	−32.7979	−33.4389	−35.4689	−32.0669	−33.7848
ε(cont.)$(-\Delta T_c)$/kJ[d]	−0.0517	−0.0570	−0.0583	−0.0622	−0.0557	−0.0590
ΔU_{ign}/kJ[e]	0.4941	0.4941	0.4941	0.4941	0.4941	0.4941
$\Delta U_{dec}(HNO_3)$/kJ[f]	0.0503	0.0518	0.0453	0.0464	0.0429	0.0504
$\Delta U_{diln}(H_2SO_4)$/kJ[g]	−0.0007	−0.0006	−0.0005	−0.0004	−0.0004	−0.0005
ΔU_{corr}/kJ[h]	0.0217	0.0243	0.0250	0.0269	0.0239	0.0253
$-m''\Delta_c u^\circ$(vaseline)/kJ	3.6487	3.9574	3.7569	4.1512	3.7447	4.1286
$-m'''\Delta_c u^\circ$(polyethylene)/kJ	9.6210	12.1635	13.1136	14.9403	12.1067	13.2790
$-m''''\Delta_c u^\circ$(fuse)/kJ	0.0419	0.0497	0.0456	0.0421	0.0466	0.0484
$\Delta_c u^\circ$(compound)/$kJ\cdot g^{-1}$	−25.2454	−25.2399	−25.2181	−25.2218	−25.2476	−25.2289
$\langle\Delta_c u^\circ(298.15\ K)\rangle/kJ\cdot g^{-1}$			−(25.2336 ± 0.0051)			

[a] For definitions of the symbols, see refs 44 and 57. $T_{th} = 298.15$ K; $V_{bomb} = 0.260\ dm^3$; $p^i_{gas} = 3.04$ MPa; $m^i_{water} = 10.00$ g. [b] Mass was obtained from the apparent mass. [c] ε(calor) is the energy equivalent of the whole system except the contents of the bomb. [d] ε(cont.) is the energy equivalent of the contents of the bomb. [e] Experimental energy of ignition. [f] Experimental energy of formation of nitric acid. [g] Experimental energy of formation of sulfuric acid. [h] Energy of correction to standard states.

Table 3. Vapor Pressures, *p*, of Tetrahydro-2*H*-1,3-oxazine-2-thione

T/K	*t*/s[a]	Δm/mg[b]	*p*/Pa[c]	$10^2\cdot(\delta p/p)$[d]	*T*/K	*t*/s[a]	Δm/mg[b]	*p*/Pa[c]	$10^2\cdot(\delta p/p)$[d]
344.98	27660	0.809	0.0174 ± 0.0017	10.6	363.53	19500	4.03	0.126 ± 0.013	16.2
345.02	34380	1.05	0.0181 ± 0.0018	13.7	366.27	22020	4.64	0.129 ± 0.013	−6.84
348.05	31560	0.957	0.0181 ± 0.0018	−19.7	366.58	25200	5.99	0.145 ± 0.015	2.07
350.91	25860	1.17	0.0270 ± 0.0027	−8.63	369.68	28860	10.53	0.224 ± 0.022	14.8
354.08	26880	1.91	0.0428 ± 0.0043	4.65	369.83	30120	8.91	0.182 ± 0.018	−6.42
354.55	21780	1.69	0.0468 ± 0.0047	8.47	370.94	29880	9.23	0.190 ± 0.019	−13.2
357.09	27120	2.38	0.0527 ± 0.0053	−5.39	373.20	22260	10.39	0.288 ± 0.029	7.74
357.64	26106	2.46	0.0569 ± 0.0057	−3.22	376.57	23340	15.03	0.399 ± 0.040	9.16
358.64	27960	2.67	0.0578 ± 0.0058	−12.4	379.90	19800	13.75	0.433 ± 0.043	−13.1
361.90	17640	2.23	0.0769 ± 0.0077	−17.0	379.95	21600	18.34	0.529 ± 0.053	6.97
362.01	23580	3.71	0.0956 ± 0.0096	4.90					

[a] Time for the experiment. [b] Mass of sublimed substance. [c] Vapor pressure with the error chosen as $10^{-1}\cdot p$ (see the text). [d] δp denotes the deviation of the experimental vapor pressure from the value computed using eq 3.

Table 5. Adjustment of the Enthalpy of Sublimation of Tetrahydro-2*H*-1,3-oxazine-2-thione to T = 298.15 K

$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}[T_{\mathrm{m}}]/\mathrm{kJ\cdot mol^{-1}}$	$T_{\mathrm{m}}/\mathrm{K}$	$C_{p,c}(298\ \mathrm{K})/\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$C_{p,c}(298\ \mathrm{K})\Delta T^{a}/\mathrm{kJ\cdot mol^{-1}}$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}\ [298.15]/\mathrm{kJ\cdot mol^{-1}}$
107.5 ± 5.2^{b}	362.46	138.0^{c}	1.4 ± 0.4	108.9 ± 5.2
		154.0^{d}	1.5 ± 0.5	109.0 ± 5.2

[a] $C_{p,c}\Delta T/\mathrm{kJ\cdot mol^{-1}} = [0.75 + 0.15\cdot(C_{p,c}/\mathrm{J\cdot mol^{-1}\cdot K^{-1}})][(T_{\mathrm{m}}/\mathrm{K}) - 298.15]/1000$ (see ref 60). [b] The uncertainty in this value represents two standard deviations of the B value. [c] Estimated using values for the thione (**1**). [d] Estimated using values for the enethiol (**2**).

impurities in the compound was less than 0.001. No solid−solid phase transitions were observed over the temperature interval from T = 268.15 K to the corresponding melting point, T_{fus} = 400.2 K.[18]

2.2. Procedures for the Thermochemical Measurements. *2.2.1. Combustion Calorimetry.* 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 described previously.[35,36] The energy equivalent of the calorimeter, ε(calor), was determined from the combustion of benzoic acid (NIST standard reference sample 39j), having a specific energy of combustion of $\Delta_{\mathrm{c}}u = -(26434 \pm 3)\ \mathrm{J\cdot g^{-1}}$ under certificate conditions. From 10 calibration experiments, ε(calor) was found to be $(28891.0 \pm 2.0)\ \mathrm{J\cdot K^{-1}}$, where the uncertainty quoted is the standard deviation of the mean. Frequent calibration experiments were made throughout the series of combustion experiments. Thianthrene was used as a secondary reference material[37] to confirm the chemistry of the combustion process and the accuracy of the energy corrections involved in the analysis of the results. The standard molar energy obtained, $\Delta_{\mathrm{c}}u^{\circ} = -(33465.3 \pm 5.9)\ \mathrm{J\cdot g^{-1}}$, was in good agreement with the recommended value,[37] $\Delta_{\mathrm{c}}u^{\circ} = -(33468 \pm 4)\ \mathrm{J\cdot g^{-1}}$.

The energy of combustion was determined by burning the solid sample in pellet form. The pelleted compound was enclosed in polyethylene bags. Vaseline was used as auxiliary material to limit the amount of sulfur in the samples to only 8 mmol, following the recommendation of Sunner and Lundin,[38] in order to obtain complete oxidation of the atoms of sulfur to hexavalent sulfur and also by the necessity of avoiding sulfuric acid in high concentrations in the final state. The empirical formula and massic energy of combustion of our polyethylene, $C_{0.960}H_{2.000}$ and $-(46371 \pm 4)\ \mathrm{J\cdot g^{-1}}$, respectively, and those of our cotton-thread fuse, $C_{1.000}H_{1.740}O_{0.871}$ and $(17410 \pm 37)\ \mathrm{J\cdot g^{-1}}$, respectively, were determined in our laboratory. The specific energy of combustion of Vaseline used was $-(46086 \pm 5)\ \mathrm{J\cdot g^{-1}}$.[39]

The bomb was filled with oxygen to a pressure of p = 3.04 MPa. After disassembly of the calorimeter, the bomb gases were slowly released, and the absence of CO and SO_2 was checked with Dräger tubes (mass-fraction sensitivity levels were approximately $1\cdot10^{-6}$ and $1\cdot10^{-7}$, respectively). Analysis of the liquid phase in the bomb was made as described in ref 35. The absence of SO_3^{2-} and NO_2^{-} was checked by calibrated ionic chromatography (PerkinElmer Optima 4300 DV). The quantity of nitric acid was taken as the difference between the total acid and the theoretical quantity of sulfuric acid calculated from the mass of sample. The corrections for nitric acid formation[40] were based on the value of $-59.7\ \mathrm{kJ\cdot mol^{-1}}$ for the standard molar energy of formation of 0.1 $\mathrm{mol\cdot dm^{-3}}$ HNO_3(aq) from N_2(g), O_2(g), and H_2O(l). All samples were weighed with a Mettler AT-21 microbalance having a sensitivity of $\pm\ 1\cdot10^{-6}$ g. For the correction of apparent mass to mass, conversion of the energy of the actual bomb process to that of the isothermal process, and the correction to standard states, we used the values given in Table 1. Corrections to the standard states were made according to Hubbard et al.[44] The atomic weights of the elements were those recommended by IUPAC in 2005.[45] The energy of solution of carbon dioxide in water at T = 298.15 K, $\Delta_{\mathrm{sol}}U(\mathrm{CO_2})$, was taken as $-17.09\ \mathrm{kJ\cdot mol^{-1}}$, and the solubility constant, $K(\mathrm{CO_2})$, as 0.03440 $\mathrm{mol\cdot dm^{-3}\cdot atm^{-1}}$ at T = 298.15 K.[46] The energy of the combustion experiments was always referenced to the final temperature T_{th} = 298.15 K. From the combustion energies, the enthalpies of formation in the condensed state were calculated.

2.2.2. Vapor Pressure Measurements. The enthalpy of sublimation was evaluated from the temperature dependence of the vapor pressure (Clausius−Clapeyron equation). Vapor pressures evaluated over a 35 K temperature interval were measured by a mass-loss Knudsen effusion method[47] using the technique described in ref 48. The apparatus consists essentially of a stainless steel sublimation chamber immersed in a thermoregulated water jacket and connected to a high-vacuum system (p = $1\cdot10^{-4}$ 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 using eq 1:

$$p = \left(\frac{\Delta m}{W_a a t}\right)\left(\frac{2\pi R T}{M}\right)^{1/2} \qquad (1)$$

where R is the gas constant ($8.314\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$), a is the area of the effusion orifice [$(6.69 \pm 0.01)\cdot10^{-3}\ \mathrm{cm^2}$], W_a is the corresponding Clausing coefficient[49] (0.986 ± 0.003), and M is the molar mass of the species studied (C_4H_7ONS, 117.170).

2.3. Computational Details. Standard ab initio molecular orbital calculations[50] were performed using the Gaussian 03 series of programs.[51] The energy of each of the compounds studied was calculated using Gaussian-n theory at the G3 level.[52] 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 was analyzed using a population partition technique, the natural bond orbital (NBO) analysis of Reed and Weinhold,[53−55] using the NBO program[56] implemented in the Gaussian 03 package.[51]

3. RESULTS

3.1. Experimental Determination of the Enthalpies of Formation in the Gas Phase. The enthalpy of formation in the gas state, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{g})$, was determined by combining the standard enthalpy of formation in the crystalline state, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{cr})$, with the standard enthalpy of sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$, both referenced to T = 298.15 K.

The experimental value of the enthalpy of formation in the crystalline state was determined from the results of combustion experiments (Table 2) corresponding to the reaction shown in eq 2:

$$\begin{aligned} &C_4H_7ONS(cr) + 6.75O_2(g) \\ &\quad + 112.5H_2O(l) \rightarrow 4CO_2(g) \\ &\quad + [H_2SO_4 \cdot 115H_2O](l) + 0.5N_2(g) \end{aligned} \qquad (2)$$

In accordance with normal thermochemical practice, the uncertainties assigned in each case are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of the auxiliary quantities.[58] To derive $\Delta_f H_m^\circ$(cr) from $\Delta_c H_m^\circ$(cr), the CODATA[59] values of the standard molar enthalpies of formation of H_2O(l) and CO_2(g) at T = 298.15 K, −(285.830 ± 0.042) kJ·mol^{-1} and −(393.51 ± 0.13) kJ·mol^{-1}, respectively, were used. The value of the enthalpy of formation of $H_2SO_4 \cdot 115H_2O$, −(887.811 ± 0.042) kJ·mol^{-1}, was taken from ref 41

The enthalpy of sublimation, $\Delta_{cr}^{g} H_m^\circ$, was obtained from the temperature dependence of the vapor pressure according to the Clausius−Clapeyron equation:

$$\ln(p/\text{Pa}) = -B(\text{T/K})^{-1} + A \qquad (3)$$

where A is a constant and $B = \Delta_{cr}^{g} H_m^\circ[T_m]/R$. The standard molar enthalpy of sublimation at the mean temperature, T_m, of the experimental range was derived from the slope of the line.

The results of the Knudsen effusion experiments calculated by means of eq 1 are summarized in Table 3. The error for the vapor pressure, p, was taken as $10^{-1} \cdot p$, which was initially chosen visually but, more formally, allowed for the values (within their assigned error bars) of the vapor pressure measured at nominally identical temperatures to be numerically indistinguishable [e.g., the value at T/K = 344.98 (p/Pa = 0.0174 ± 0.0017) equals that at T/K = 345.02 (p/Pa = 0.0181 ± 0.0018); the value at T/K = 361.90 (p/Pa = 0.0769 ± 0.0077) equals that at T/K = 362.01 (p/Pa = 0.0956 ± 0.0096); the value at T/K = 379.90 (p/Pa = 0.433 ± 0.043) equals that at T/K = 379.95 (p/Pa = 0.529 ± 0.053)].

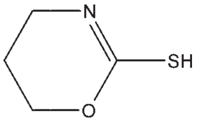

Figure 2. Structural formula of 5,6-dihydro-4*H*-1,3-oxazine-2-thiol (**2**).

Table 6. Experimentally Determined Standard Molar Enthalpies of Combustion, Sublimation, and Formation in the Crystalline and Gaseous States at T = 298.15 K for Tetrahydro-2*H*-1,3-oxazine-2-thione[a]

$\Delta_c H_m^\circ$	−(2963.4 ± 1.6)
$\Delta_{cr}^{g} H_m^\circ$	109.0 ± 5.2
$\Delta_f H_m^\circ$(cr)	−(213.0 ± 1.7)
$\Delta_f H_m^\circ$(g)	−(104.0 ± 5.5)

[a] All values in kJ·mol^{-1}.

The values of the mean experimental temperature, T_m, the parameters A and B, and the enthalpy of sublimation at the mean experimental temperature are given in Table 4.

The uncertainty assigned to the value of $\Delta_{cr}^{g} H_m^\circ[T_m]$ is based on two standard deviations associated with the B value. The standard molar enthalpy of sublimation at T = 298.15 K was adjusted to T = 298.15 K using the equation listed in footnote *a* of Table 5. Although a tentative group value for a cyclic thiocarbamate is currently available (64.6 J·mol^{-1}),[18] as shown previously,[60,61] it is also possible to obtain a reasonable estimate of the heat capacity at T = 298.15 K by estimating the heat capacity of its tautomer, 5,6-dihydro-4*H*-1,3-oxazine-2-thiol (**2**) (see Figure 2), for which there are also group values. These include the contributions of a cyclic secondary methylene group (−CH_2−; 24.6 J·mol^{-1}), a cyclic quaternary sp^2 carbon (=C<; 4.7 J·mol^{-1}), a cyclic ether (−O−; 9.7 J·mol^{-1}), a cyclic tertiary sp^2 nitrogen (=N−; 13.9 J·mol^{-1}), and a thiol (−SH; 51.9 J·mol^{-1}).[60,61] As shown in Table 5, using the values for the two tautomers results in a considerably smaller difference in the temperature adjustment [(1.5 vs 1.4) kJ·mol^{-1}] than is associated with the overall uncertainty in the adjustment (± 0.5 kJ·mol^{-1}). Averaging the two sublimation enthalpies results in a standard molar value of (109.0 ± 5.2) kJ·mol^{-1} at T = 298.15 K.

Table 6 collects the values determined for the standard molar enthalpies of combustion ($\Delta_c H_m^\circ$), sublimation ($\Delta_{cr}^{g} H_m^\circ$), and formation in the crystalline and gaseous states [$\Delta_f H_m^\circ$(cr) and $\Delta_f H_m^\circ$(g), respectively].

3.2. Theoretical Molecular and Electronic Structures. To our knowledge, no experimental crystal or gas-phase structures for this compound are available in the literature with which to compare our quantum-chemically calculated results. The molecular structure of tetrahydro-2*H*-1,3-oxazine-2-thione was optimized at the MP2(full)/6-31G(3df,2p) level of theory. The thione tautomer **1** is significantly more stable than the thiol tautomer **2**. At the G3 level of theory, the thione form is 29.8 kJ·mol^{-1} more stable than the thiol form. The equilibrium structure is shown in Figure 3, and calculated bond distances and angles are collected in Table 7.

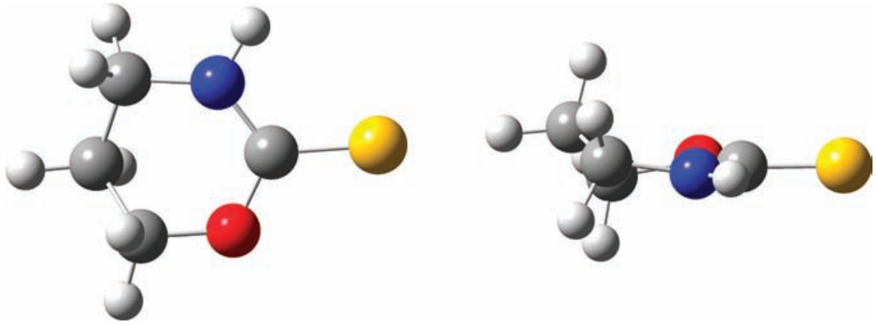

Figure 3. Two views of the MP2(full)/6-31G(3df,2p)-optimized structure of tetrahydro-2*H*-1,3-oxazine-2-thione.

A population analysis using the NBO method[53−55] was also carried out to obtain the natural atomic charges (the nuclear

Table 7. MP2(full)/6-31G(3df,2p)-Optimized Structure of Tetrahydro-2*H*-1,3-oxazine-2-thione[a]

Bond Distances/Å	
C−S	1.633
C2−O	1.340
C6−O	1.427
C2−N	1.350
C4−N	1.449
C4−C5	1.509
C5−C6	1.504
Angles/deg	
N−C−S	123.0
O−C−S	120.0
N−C−O	117.0
C−O−C	117.9
C−N−C	127.6
O−C−C	109.9
N−C−C	108.7
C−C−C	107.1
S−C−N−C	168.9
S−C−O−C	169.7
C−N−C−C	−7.9
C−O−C−C	48.4
N−C−C−C	43.5
O−C−C−C	−64.6

[a] The numbering system used in this study is shown in Figure 1.

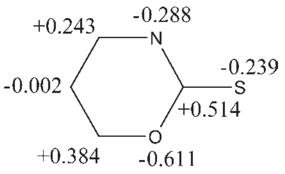

Figure 4. MP2(full)/6-31G(3df,2p)-calculated NBO atomic charges with hydrogens summed into heavy atoms in tetrahydro-2*H*-1,3-oxazine-2-thione.

Table 8. G3-Calculated Energies at $T = 0$ K and Enthalpies at $T = 298$ K for Tetrahydro-2*H*-1,3-oxazine-2-thione in Its Thione (1) and Thiol (2) Tautomeric Forms and for Tetrahydro-2*H*-1,3-thiazine-2-thione (3)[a]

species	E_0	H_{298}
1	−684.443082	−684.435546
2	−684.432122	−684.424197
3	−1007.315922	−1007.307851

[a] All values in hartrees.

charge minus the sum of the populations of the natural atomic orbitals on the atom) that characterize the ground electronic state of the compound studied. The charges calculated with the hydrogen atoms summed into the adjoining heavy atoms are reported in Figure 4.

3.3. Theoretical Enthalpies of Formation. G3-calculated energies at $T = 0$ K and enthalpies at $T = 298$ K of the compound studied for both the thione and thiol tautomeric forms are given in Table 8.

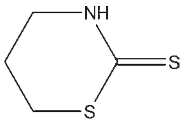

Figure 5. Structural formula of tetrahydro-2*H*-1,3-thiazine-2-thione (**3**).

Table 9. G3-Calculated Enthalpies of Formation for the Studied Compounds Using Atomization and Isodesmic Reactions[a]

compound	atomization	isodesmic (4) or (5)	experimental
tetrahydro-2*H*-1,3-oxazine-2-thione	−109.2	−104.6	−(104.0 ± 5.5)
tetrahydro-2*H*-1,3-thiazine-2-thione	70.4	72.4	−

[a] All values in kJ·mol^{-1}.

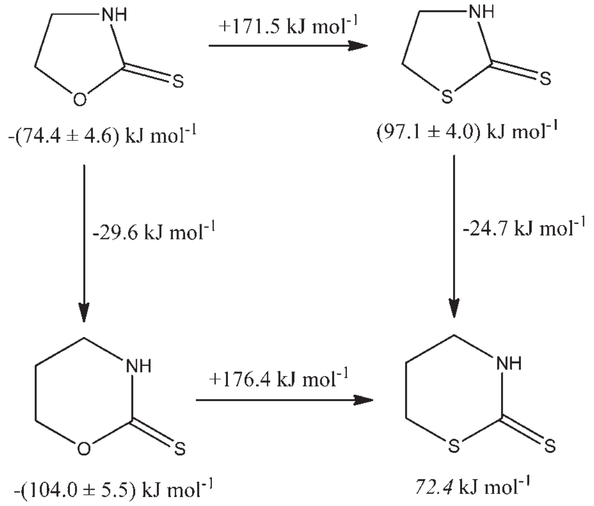

Figure 6. Comparison of the enthalpies of formation (in kJ·mol^{-1}) of a series of related compounds. All values are from experimental measurements except the one for tetrahydro-2*H*-1,3-thiazine-2-thione (shown in italics), which was obtained from G3 quantum-chemical calculations.

The standard procedure for obtaining enthalpies of formation in Gaussian-*n* theories is through atomization reactions.[62,63] Raghavachari et al.[64] have proposed the use of a standard set of isodesmic reactions, the "bond separation reactions",[50] where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing the same kinds of linkages, to derive the theoretical enthalpies of formation.

In this work, it was not convenient to use the isodesmic bond separation reactions because the experimental enthalpy of formation of one of the reference compounds, thioformaldehyde ($H_2C{=}S$), has not been accurately determined. Two values have been reported in the literature,[65,66] but they are very different one from another and have very large uncertainties. Consequently, a similar isodesmic reaction using thiourea [$(H_2N)_2C{=}S$] as a reference (eq 4) was employed for tetrahydro-2*H*-1,3-oxazine-2-thione (C_4H_7NOS):

$$C_4H_7NOS + 3CH_4 + NH_3 + H_2O \rightarrow 2C_2H_6 + 2CH_3OH + (H_2N)_2C{=}S \tag{4}$$

For comparison purposes, we also carried out calculations on a related compound, tetrahydro-2*H*-1,3-thiazine-2-thione (**3**, $C_4H_7NS_2$; see Figure 5), using for the calculation of its enthalpy of formation the isodesmic reaction represented by eq 5:

$$C_4H_7NS_2 + 3CH_4 + NH_3 + H_2O \rightarrow 2C_2H_6 + 2CH_3SH + (H_2N)_2C{=}S \tag{5}$$

The enthalpies of formation of tetrahydro-2*H*-1,3-oxazine-2-thione and tetrahydro-2*H*-1,3-thiazine-2-thione were obtained using the G3-calculated enthalpies of reaction and the experimental enthalpies of formation of the species involved in these reactions.[67] The results are shown in Table 9. There is a very good agreement between the experimental value of the enthalpy of formation for tetrahydro-2*H*-1,3-oxazine-2-thione and the theoretical value calculated using the isodesmic reaction shown in eq 4.

4. CONCLUSION

Very recently, we carried out an experimental and theoretical study of the thermochemistry of two compounds related to those studied in this work, 1,3-oxazolidine-2-thione and 1,3-thiazolidine-2-thione,[20] and we can compare the values of the enthalpies of formation of these compounds with those studied in this work (see Figure 6).

It is interesting to note that the process of changing an oxygen to a sulfur atom in the five-membered rings in Figure 6 but leaving everything else unchanged is some 4.8 $kJ \cdot mol^{-1}$ less endothermic than the corresponding process in a six-membered ring. This is comparable to the 9.3 $kJ \cdot mol^{-1}$ found for the parent unsubstituted rings, i.e., in the transformations of tetrahydrofuran to tetrahydrothiophene and tetrahydropyran to thiane (tetrahydrothiopyran). However, the individual endothermicities are (150.6 ± 1.5) and (159.0 ± 1.4) $kJ \cdot mol^{-1}$, respectively, in these cases, which are very different from those for the above thio- and dithiocarbamates. The enthalpies of formation of the five-membered-ring compounds studied earlier, 1,3-oxazolidine-2-thione and 1,3-thiazolidine-2-thione, decrease on changing to the corresponding six-membered rings of current interest, tetrahydro-2*H*-1,3-oxazine-2-thione and tetrahydro-2*H*-1,3-thiazine-2-thione, by (29.5 ± 7.2) $kJ \cdot mol^{-1}$ and 24.7 $kJ \cdot mol^{-1}$ respectively. The corresponding difference for tetrahydrofuran to tetrahydropyran and tetrahydrothiophene to thiane are (39.3 ± 1.3) $kJ \cdot mol^{-1}$ and (30.0 ± 1.6) $kJ \cdot mol^{-1}$, respectively. It would thus appear that the difference in enthalpies of formation of a five-membered-ring species and the corresponding six-membered-ring species with an additional CH_2 group is thus "about" 30 $kJ \cdot mol^{-1}$. However, it should also be noted that the change in going from tetrahydrofuran-2,5-dione to tetrahydropyran-2,5-dione (more commonly known as succinic anhydride and glutaric anhydride, respectively) is but (4.5 ± 2.5) $kJ \cdot mol^{-1}$, while the change in going from pyrrolidine to piperidine is much larger, (43.8 ± 1.0) $kJ \cdot mol^{-1}$. The word "about" in the previous sentence is sadly accurate: measurements and reliable calculations are available, but understanding the systematics of the enthalpies of five- and six-membered rings such as 1,3-oxazolidine-2-thione and tetrahydro-2*H*-1,3-oxazine-2-thione still eludes us. Such must remain the content of a later study.

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