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# Thermochemical Characterization of Sulfur-Containing Furan Derivatives: Experimental and Theoretical Study

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**Abstract:** The thermochemical properties of three sulfur-containing furan derivatives, 2-furanmethanethiol, furfuryl methyl sulfide, and methyl 2-methyl-3-furyl disulfide, were investigated using experimental and theoretical methods. Standard molar enthalpies of combustion were determined by combustion calorimetry, while enthalpies of vaporization were obtained through Calvet microcalorimetry. These experimental results allowed for the calculation of standard molar enthalpies of formation in the gas phase at 298.15 K. Theoretical calculations using high-level quantum chemical methods (G3) were performed to complement the experimental data. A comparison between experimental and theoretical values revealed good agreement, validating the computational approach. This study enhances the understanding of the energetic properties of sulfur furan derivatives, contributing reliable thermochemical data to existing databases and aiding in the development of predictive models for related molecular systems.

**Keywords:** 2-furanmethanethiol; furfuryl methyl sulfide; methyl 2-methyl-3-furyl disulfide; rotating-bomb combustion calorimetry; enthalpy of vaporization; calvet microcalorimetry; standard molar enthalpy of formation



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## 1. Introduction

Furan derivatives containing sulfur functionalities play a crucial role as intermediates in a wide range of chemical and biological processes. Their distinctive aroma profiles make them highly valuable in the food, flavor, and fragrance industries. For instance, 2-furanmethanethiol is known for its characteristic "roasted coffee" aroma, contributing significantly to the flavor profiles of certain wines, roasted coffee, and soy sauce [1–3]. Similarly, compounds like furfuryl methyl sulfide and methyl 2-methyl-3-furyl disulfide are important aroma compounds, often associated with cooked vegetables and meats [4–6].

These sulfur-containing furans are characterized by exceptionally low odor threshold values, making them especially important in shaping the characteristic aroma of cooked meat. Research into meat cooking has shown that high temperatures promote the formation of various volatile sulfur compounds, which can arise through advanced stages of the Maillard reaction, hydrolysis, or the thermal degradation of amino acids [7].

A comprehensive understanding of the thermochemical behavior and sensory impact of these sulfur-containing furans is essential for optimizing food processing techniques, enhancing flavor quality, and developing novel food products with appealing sensory attributes. Despite their significance, reliable thermochemical data for these compounds

remain limited, especially for 2-furanmethanethiol, furfuryl methyl sulfide, and methyl 2-methyl-3-furyl disulfide.

To address this gap, the present study undertakes a detailed thermochemical investigation of these three compounds, whose structural formulae are depicted in Figure 1. Experimental measurements of their standard molar enthalpies of combustion were obtained by combustion calorimetry, while enthalpies of vaporization were determined using Calvet microcalorimetry. These experimental results enabled the calculation of their standard molar enthalpies of formation in the gas phase. In addition, high-level quantum chemical calculations (G3) were employed to provide theoretical values and a deeper understanding of their molecular energetics.

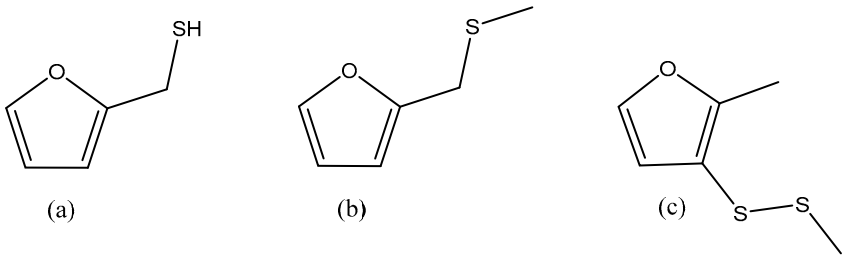


**Figure 1.** Structural formula of (**a**) 2-furanmethanethiol; (**b**) furfuryl methyl sulfide; (**c**) methyl 2-methyl-3-furyl disulfide.

By combining experimental data with theoretical insights, this study offers a robust framework for understanding the thermochemical properties of these furan derivatives. The findings not only contribute valuable data to thermochemical databases but also facilitate the development of predictive models for furan-based systems, thereby expanding their potential applications in both scientific research and industrial processes.

This research is part of a larger initiative focused on systematically studying the energetics of furan derivatives. Previous work in this series has explored 2-furancarbonitrile, 2-acetylfuran, and 3-furaldehyde [8], vinylfurans [9], methylfurans [10], dimethylfuran derivatives [11] and furfurylamines [12], further enhancing our understanding of this diverse class of compounds.

## 2. Materials and Methods

### *2.1. Compounds and Purity Control*

The compounds, 2-furanmethanethiol, (CAS 98-02-2), furfuryl methyl sulfide, (CAS 1438-91-1), and methyl 2-methyl-3-furyl disulfide, (CAS 65505-17-1), were commercially obtained from MERCK (Darmstadt, Germany), with assessed mass fraction purities of 0.98, 0.97, and 0.98, respectively. To further enhance purity, the liquid compounds were subjected to repeated distillation under reduced pressure. The final purity of all compounds was confirmed by gas chromatography analysis using an Agilent 4890D instrument (Agilent, Santa Clara, CA, USA) equipped with an HP-5 column (15 m length, 0.530 mm diameter) composed of 5% diphenyl and 95% dimethylpolysiloxane. Detection was achieved with a flame ionization detector (FID) powered by hydrogen. The carrier gas used during the experiments was a mixture of nitrogen and compressed air. This analysis confirmed that the purity of the compounds exceeded 0.999, meeting the requirements for combustion calorimetry experiments.

### *2.2. Combustion Calorimetry Measurements*

The standard ($p^o$ = 0.1 MPa) molar enthalpies of combustion of the three compounds under study were measured in an isoperibol rotating-bomb calorimeter, firstly constructed at the University of Lund, Sweden according to the design of Sunner [13]. A detailed

description can be found in the literature [14]. The combustion experiments were carried out in a stainless-steel bomb lined with platinum, with internal fittings machined from platinum. The internal volume of the bomb was 0.258 $dm^3$.

To ensure complete combustion and efficient heat transfer, the bomb was equipped with a rotating mechanism capable of axial and end-over-end motion. This rotation caused the deionized water within the bomb to wash all internal surfaces, resulting in a homogeneous final solution.

The bomb's rotation began when the temperature rise reached approximately 63% of its total value and continued until the experiment concluded. This procedure accounted for the frictional work of the rotating bomb in the temperature corrections applied for water stirring and heat exchange with the surrounding isothermal jacket [15].

The calibration of the calorimetric system was performed following the procedure described by Coops et al. [16] by the combustion of benzoic acid NIST Thermochemical Standard 39j, with a certified massic energy of combustion, under bomb conditions of $-(26{,}434 \pm 3)$ $J \cdot g^{-1}$ [17]. The energy equivalent of the calorimeter was determined as $\varepsilon_{cal} = (25{,}164.0 \pm 2.1)$ $J \cdot K^{-1}$, where the uncertainty quoted is the standard deviation of the mean. The calibration results were corrected to give the energy equivalent of the calorimeter, $\varepsilon_{cal}$, corresponding to the average mass of 5222.5 g of water added to the calorimeter.

The liquid samples were burnt enclosed in polyester bags made from Melinex® (DuPont Teijin Films, Hopewell, VA, USA). The energy of combustion of the Melinex®, $\Delta U$ (Melinex), was calculated using the value of the massic energy of combustion of dry Melinex, $\Delta_c u^o = -(22{,}902 \pm 5)$ $J \cdot g^{-1}$ [18], after making a correction for the mass fraction of water, $w = 0.0032$ [18].

The combustion procedure for the organosulfur compounds followed the method described by Waddington et al. [19]. In each experiment, 15.00 $cm^3$ of water was added to the bomb, which was then pressurized to 3.04 MPa with oxygen without prior flushing.

Calorimeter temperatures were measured with a precision of $\pm 1 \times 10^{-4}$ K at 10 s intervals using a quartz crystal thermometer (Hewlett–Packard HP 2804A, Palo Alto, CA, USA) connected to a PC programmed to calculate the adiabatic temperature change. A minimum of 100 readings were recorded for the main period, as well as for the before and after periods. Data acquisition and calorimeter control were managed using the LABTERMO software, Porto, Portugal [20].

The electrical energy for ignition was determined from the change in potential difference across a 1400 μF condenser discharged through a platinum wire (Ø = 0.05 mm, Goodfellow, Huntingdon, UK).

Corrections for carbon soot formation were made based on the standard massic energy of combustion of carbon, $\Delta_c u^o = 33$ $kJ \cdot g^{-1}$ [16]. The cotton thread fuse had an empirical formula of $CH_{1.686}O_{0.843}$, $\Delta_c u^o = -16240$ $J \cdot g^{-1}$ [16]. The nitric acid formed was analyzed by Devarda's alloy method [21], and corrections were based on $\Delta_f U^o_m$ ($HNO_3$, aq, 0.1 $mol \cdot dm^{-3}$) = $-59.7$ $kJ \cdot mol^{-1}$ [16], from 1/2 $N_2$(g), 5/4 $O_2$(g), and 1/2 $H_2O$(l).

The specific densities used to calculate the mass from the apparent mass in air were $\rho = 1.132$ $g \cdot cm^{-3}$ for 2-furanmethanethiol, $\rho = 1.07$ $g \cdot cm^{-3}$ for furfuryl methyl sulfide, and $\rho = 1.163$ $g \cdot cm^{-3}$ for methyl 2-methyl-3-furyl disulfide [22].

The relative atomic masses used were those recommended by the IUPAC Commission in 2021 [23].

### *2.3. Calvet Microcalorimetry Measurements*

The standard molar enthalpies of vaporization for the studied furans were determined using the vacuum sublimation technique [24], which has been previously validated in our laboratory for liquid vaporization measurements [25]. The measurement procedure,

along with a detailed description of the apparatus, has been previously reported [26], including experimental results obtained during its validation using reference compounds such as benzoic acid, phenanthrene, anthracene, and ferrocene. For the experiments, samples of about 3–8 mg of the compound contained in a small glass capillary tube sealed at one end and a blank capillary with a similar mass were simultaneously dropped at room temperature into the preheated calorimetric cells of a high-temperature Calvet microcalorimeter (Setaram HT1000D, Lyon, France) at a specified temperature, $T$. After the samples reached thermal equilibrium, they were removed from the hot zone through vacuum vaporization [26].

The microcalorimeter was calibrated for each temperature using *n*-undecane. The value used for the standard molar enthalpy of vaporization, at $T$ = 298.15 K, for *n*-undecane was (56.6 ± 0.6) kJ·mol$^{-1}$ [27].

### 2.4. Computational Details

Energetic calculations were conducted using the G3 composite method [28]. This method employs MP2(FU)/6-31G(d) geometries and combines energies from MP2, MP4, and QCISD(T) single-point calculations. Scaled zero-point energies from Hartree-Fock/6-31G(d) were included, along with spin-orbit and higher-level corrections, to approximate the QCISD(T, FU)/G3 large results. Absolute enthalpies at 298.15 K were determined by adding thermal contributions (vibrational, translational, rotational, and $pV$) to the 0 K energies. All calculations were performed using the Gaussian 09 software package (Gaussian, Inc., Wallingford, CT, USA) [29].

## 3. Results

### 3.1. Combustion Calorimetry—Standard Molar Enthalpies of Formation in the Condensed Phase

Detailed results for each combustion experiment performed for 2-furanmethanethiol, furfuryl methyl sulfide, and methyl 2-methyl-3-furyl disulfide are presented in Tables S1–S3 in the Supplementary Materials. Table 1 shows the results of a typical combustion experiment for each compound studied. The individual values of $\Delta_c u^o$, together with their means and the standard deviation, refer to the combustion reaction described by Equations (1)–(3), yielding $H_2SO_4 \cdot 115H_2O$ (l):

$$C_5H_6OS\ (l) + 7.5O_2\ (g) + 113H_2O\ (l) \rightarrow 5CO_2\ (g) + H_2SO_4 \cdot 115H_2O\ (l) \quad (1)$$

$$C_6H_8OS\ (l) + 9O_2\ (g) + 112H_2O\ (l) \rightarrow 6CO_2\ (g) + H_2SO_4 \cdot 115H_2O\ (l) \quad (2)$$

$$C_6H_8OS_2\ (l) + 10.5O_2\ (g) + 228H_2O\ (l) \rightarrow 6CO_2\ (g) + 2H_2SO_4 \cdot 115H_2O\ (l) \quad (3)$$

**Table 1.** Individual values of the massic energy of combustion, $\Delta_c u^o$, of the studied compounds at $T$ = 298.15 K. All values are in J·g$^{-1}$.

| 2-Furanmethanethiol | Furfuryl Methyl Sulfide | Methyl 2-methyl-3-furyl Disulfide |
|---|---|---|
| −29,284.68 | −31,152.30 | −28,662.57 |
| −29,287.28 | −31,152.78 | −28,661.47 |
| −29,275.86 | −31,151.91 | −28,642.81 |
| −29,266.72 | −31,152.02 | −28,656.62 |
| −29,270.64 | −31,149.41 | −28,651.97 |
| −29,268.02 | −31,149.29 | −28,649.01 |
| | | −28,648.10 |
| | $\langle \Delta_c u^o \rangle$ [a] | |
| −29,275.5 ± 3.6 | −31,151.3 ± 0.6 | −28,653.2 ± 2.8 |

[a] Mean and standard deviation.

Table 2 lists the derived standard molar energies and enthalpies of combustion and the standard molar enthalpies of formation of the compounds in the condensed phase at $T$ = 298.15 K. To derive $\Delta_f H^o_m(l)$ from $\Delta_c H^o_m(l)$, the following standard molar enthalpies of formation at $T$ = 298.15 K were used: $\Delta_f H^o_m$ ($H_2O$, l) = −(285.830 ± 0.040) kJ·mol$^{-1}$ [30], $\Delta_f H^o_m$ ($CO_2$, g) = −(393.51 ± 0.13) kJ·mol$^{-1}$ [30], and $\Delta_f H^o_m$ ($H_2SO_4$ in 115 $H_2O$, l) = −(887.81 ± 0.01) kJ·mol$^{-1}$ [31].

**Table 2.** Standard ($p^o$ = 0.1 MPa) molar energies of combustion, $\Delta_c U^o_m$, enthalpies of combustion, $\Delta_c H^o_m$, and enthalpies of formation, $\Delta_f H^o_m$, for the three compounds studied at $T$ = 298.15 K. [a] Values in kJ·mol$^{-1}$.

| Compound | $-\Delta_c U^o_m$ (l) | $-\Delta_c H^o_m$ (l) | $\Delta_f H^o_m$ (l) |
|---|---|---|---|
| 2-Furanmethanethiol | 3342.3 ± 1.3 | 3348.5 ± 1.3 | −78.5 ± 1.4 |
| Furfuryl methyl sulfide | 3393.4 ± 1.2 | 4000.8 ± 1.2 | −105.6 ± 1.4 |
| Methyl 2-methyl-3-furyl disulfide | 4591.9 ± 1.6 | 4603.1 ± 1.6 | −105.2 ± 1.8 |

[a] The uncertainties are twice the overall standard deviation of the mean and include the contributions from the calibration with benzoic acid and from the energy of combustion of auxiliary materials.

### *3.2. Vacuum Drop–Microcalorimetric Technique—Enthalpy of Vaporization*

The values for the standard molar enthalpies of vaporization, along with their respective uncertainties, are presented in Table 3. Following standard thermochemical conventions [32,33], the uncertainties associated with the standard molar energies and enthalpies of combustion, formation, and phase transitions are twice the overall standard deviation of the mean. These uncertainties encompass both the errors in the auxiliary quantities used and any calibration uncertainties. The temperature measurement uncertainty was estimated to be below ±0.1 K.

**Table 3.** Microcalorimetric standard ($p^o$ = 0.1 MPa) molar enthalpies of vaporization at $T$ = 298.15 K.

| Compound | $\frac{T}{K}$ [a] | $\Delta^{g,T}_{l,298K} H^o_m$ [b] | $\Delta^{T}_{298.15K} H^o_m$ | $\Delta^{g}_{l} H^o_m$(298.15K) [c] |
|---|---|---|---|---|
| 2-Furanmethanethiol | 329.0 | 52.2 ± 0.1 | 3.6 | 48.6 ± 1.0 |
| Furfuryl methyl sulfide | 334.3 | 58.3 ± 0.3 | 5.1 | 53.2 ± 1.2 |
| Methyl 2-methyl-3-furyl disulfide | 334.3 | 62.6 ± 0.5 | 6.1 | 56.5 ± 1.5 |

[a] $u(T)$ = 0.1 K. [b] Mean value and standard deviation of the mean of six experiences. [c] The uncertainties are twice the overall standard deviation of the mean and include the contributions from the calibration.

The observed enthalpy of vaporization at the experimental temperature $T$, $\Delta^{g,T}_{l,298K} H^o_m$, was adjusted to $T$ = 298.15 K using Equation (S2) in the Supplementary Materials. In this adjustment, the molar heat capacities of the compounds in the gas phase are provided by Equations (S3)–(S5). These expressions were derived from statistical thermodynamics using the molecular vibrational frequencies, which were calculated at the B3LYP/6-31G(d) level of theory and scaled by a factor of 0.961 [34] (see Table S4 provided in the Supplementary Materials).

### *3.3. Computational Results*

To estimate the gas-phase enthalpies of formation for the studied compounds, several hypothetical gas-phase reactions were employed (see Tables S5–S7 in the Supplementary Materials). These reactions assumed that the bonding environments of the reactants and products were similar, which helped to eliminate any systematic errors. Additionally, the auxiliary molecular species involved in these reactions were chosen based on the availability of experimental values for their formation enthalpies in the literature. The calculated reaction enthalpies were combined with the experimental standard molar enthalpies of formation of all the intervening molecules to obtain their gas-phase standard molar en-

thalpies of formation at $T$ = 298.15 K. The calculated G3 absolute enthalpies at $T$ = 298.15 K for 2-furanmethanethiol, furfuryl methyl sulfide, and methyl 2-methyl-3-furyl disulfide and for all the auxiliary molecules used in this study are presented in the Supplementary Materials, Table S8. In the same table, we also present the corresponding experimental standard molar enthalpies of formation in the gas phase at $T$ = 298.15 K, as reported in the literature [10,35–38].

Table 4 summarizes the mean values of the computational estimates for the gas-phase enthalpies of formation together with the experimentally determined $\Delta_f H^o_m(l)$, $\Delta^g_l H^o_m$, and $\Delta_f H^o_m(g)$. As shown in Table 4, the G3 calculations demonstrate excellent agreement with the experimental results for 2-furanmethanethiol and furfuryl methyl sulfide, with discrepancies of less than 2 kJ·mol$^{-1}$. However, for methyl 2-methyl-3-furyl disulfide, the difference was almost 10 kJ·mol$^{-1}$, which is still considered a reasonable estimate.

**Table 4.** Standard ($p^o$ = 0.1 MPa) molar enthalpies of formation, in both liquid and gaseous phases, and standard molar enthalpy of vaporization at $T$ = 298.15 K.

| Compound | $\frac{\Delta_f H^o_m(l)}{kJ \cdot mol^{-1}}$ | $\frac{\Delta^g_l H^o_m}{kJ \cdot mol^{-1}}$ | $\frac{\Delta_f H^o_m(g)}{kJ \cdot mol^{-1}}$ | |
|---|---|---|---|---|
| | | | **Exp** [a] | **G3** [b] |
| 2-Furanmethanethiol | −78.5 ± 1.4 | 48.6 ± 1.0 | −29.9 ± 1.7 | −30.3 ± 4.5 |
| Furfuryl methyl sulfide | −105.6 ± 1.4 | 53.2 ± 1.2 | −52.4 ± 1.8 | −50.8 ± 4.1 |
| Methyl 2-methyl-3-furyl disulfide | −105.2 ± 1.8 | 56.5 ± 1.5 | −48.7 ± 2.3 | −57.5 ± 2.4 |

[a] Uncertainties calculated through the RSS (root–sum–square) method; [b] mean and standard deviation of the mean.

## 4. Discussion

One of the most widely used approaches for predicting the enthalpy of formation is the group additivity method [39–45]. This method assumes that the energetic properties of a molecule can be approximated by summing the contributions of small, well-defined molecular groups (such as functional groups or specific bonding patterns). Each group has a known and quantifiable contribution to the overall enthalpy of formation, which is derived from experimental data or theoretical calculations. By breaking down complex molecules into these simpler components, the group additivity method offers a practical way to estimate the energetics of a molecule without the need for detailed measurements of each individual compound. While generally accurate for many types of molecules, the method relies on the assumption that these small groups behave consistently across different molecular contexts. Therefore, its reliability may be limited for compounds with unusual structures or bonding arrangements.

In this context and based on the molecules studied here, we can calculate the enthalpic increments, $\Delta\Delta H^o_m$, associated with introducing a thiol (SH) or a methanethiol (SCH3) group into the furan ring and compare these effects with those of similar molecules reported in the literature.

The scheme of Figure 2 demonstrates that the $CH_3 \rightarrow CH_2SH$ substitution in both furan and benzene results in a nearly identical enthalpic increment of approximately 45 kJ·mol$^{-1}$. This suggests that, in terms of energetic effects, the SH group has a similar effect when introduced into these two molecular environments. However, when we examine the substitution $SH \rightarrow SCH_3$, (−22.5 kJ·mol$^{-1}$ for furan and −13.3 kJ·mol$^{-1}$ for benzene derivative), we find that the introduction of this group seems to have a more stabilizing effect in the case of furan compared to benzene.

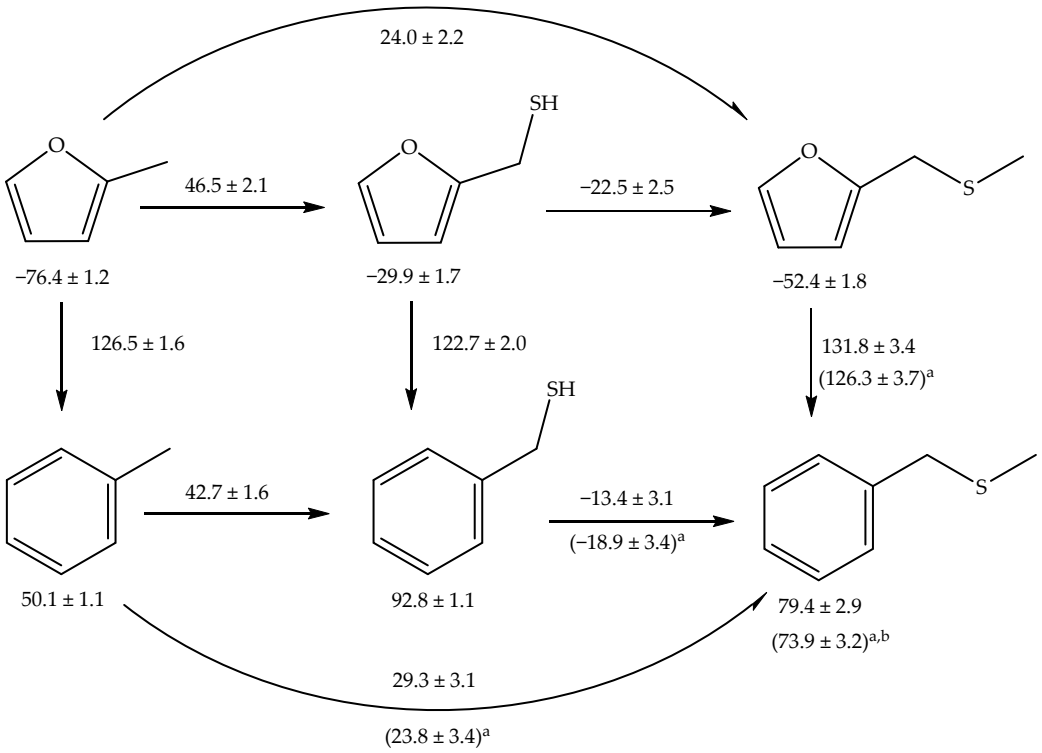


**Figure 2.** Scheme for comparison of enthalpic increments in furans and benzenes. [a] Determined based on the computationally estimated value for methyl benzyl sulfide; [b] estimated value (see Table S9). Values in kJ·mol$^{-1}$.

Additionally, we can investigate the enthalpic effect of replacing a furan ring with a benzene ring (as shown by the vertical arrows in Figure 2) and assess whether this substitution leads to an identical energetic effect. Notably, we observe that the enthalpic value for this substitution is slightly higher for the derivatives containing the $SCH_3$ substituent.

Another useful comparison involves the homologous transfer of the substituents from furan to benzene, as can be seen in Figure 3.

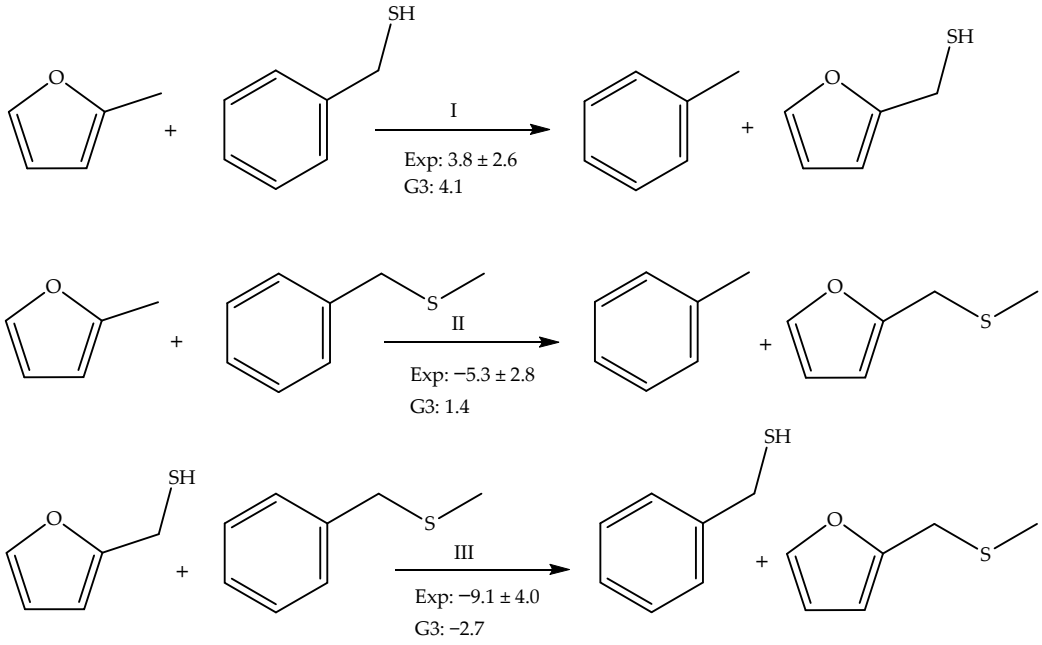


**Figure 3.** Reactions and respective experimental and computational (G3) enthalpies of reaction used for the interpretation of the enthalpy of formation of the compounds. Values in kJ·mol$^{-1}$.

For reactions II and III, it is evident that the G3 computational results do not align quantitatively with the experimental enthalpy of reaction, even when accounting for the associated uncertainty. These considerations led us to question the formation enthalpy value for benzyl methyl sulfide.

Employing the G3 method to estimate the formation enthalpy of benzyl methyl sulfide through five independent reactions (detailed in Table S9 of the Supplementary Materials) yielded a value of $\Delta_f H^o_m(g) = 73.9 \pm 3.4$ kJ·mol$^{-1}$. This computed value suggests a lower formation enthalpy compared to the experimentally reported value $79.4 \pm 2.9$ kJ·mol$^{-1}$. When this estimated formation enthalpy was combined into the scheme depicted in Figure 2 (values in parentheses), the resulting enthalpic increment values for molecules containing the $SCH_3$ substituent exhibited greater consistency, which we consider to be more plausible. Furthermore, using this revised formation enthalpy in the scheme of Figure 3 led to adjusted experimental reaction values of $0.2 \pm 4.2$ kJ·mol$^{-1}$ for reaction II and $-3.6 \pm 4.3$ kJ·mol$^{-1}$ for reaction III. These revised values demonstrate significantly better agreement with the G3 computational results.

Considering both these observations, we propose that the experimental formation enthalpy of benzyl methyl sulfide may be slightly overestimated and that the computationally derived value provides a more reliable estimate.

There is a lack of available data in the literature for methyl 2-methyl-3-furyl disulfide, which makes direct comparison with the results from this study challenging.

However, the computationally estimated value suggests that the experimental value could be more negative than initially indicated. Further studies are required to assess this result more comprehensively.

## 5. Conclusions

This study provides a comprehensive investigation of the thermochemical properties of three sulfur-containing furan derivatives using both experimental and theoretical methods to determine their enthalpies of formation. The combination of combustion calorimetry and Calvet microcalorimetry data with high-level quantum chemical calculations (G3) resulted in reliable thermochemical data that contribute to the understanding of the energetic properties of these compounds.

The enthalpic effects for the introduction of thiol (SH) and methanethiol ($SCH_3$) groups into furan and benzene rings were evaluated. While SH substitutions exhibited nearly identical energetic effects in both ring systems, the $SCH_3$ group initially appeared to have a more stabilizing effect in furan compared to benzene.

To further investigate this difference, we examined reactions II and III, in Figure 3, using both computational and experimental data. A comparison of the experimental and computational results suggested that the experimental formation enthalpy of benzyl methyl sulfide might be slightly overestimated, as indicated by the more consistent enthalpic increments obtained from the computational approach.

By revising the formation enthalpy of benzyl methyl sulfide, we confirmed that the $SCH_3$ substitution exhibits comparable energetic effects in both furan and benzene, establishing a consistent trend across these different molecular environments.

The agreement between the experimental and theoretical results highlights the importance of structure–property relationships in identifying potential outliers. This consistency also guides the decision on whether the experimental value should be re-evaluated or whether a particular structural feature should be investigated in more detail.

In conclusion, despite the significant structural and electronic differences between furan and benzene—namely, the presence of the oxygen heteroatom in furan and the more aromatic nature of benzene—our results demonstrate that the $CH_3 \rightarrow CH_2SH$ and

SH → $SCH_3$ substitutions result in remarkably similar enthalpic effects in both molecules. The near thermoneutrality of reactions I and III further supports this, indicating that the substitutions have an equivalent impact on the enthalpy of formation of furan and benzene.

**Supplementary Materials:** The following Supplementary Materials can be downloaded at: https://www.mdpi.com/article/10.3390/thermo5010011/s1, Table S1. Standard ($p^o$ = 0.1 MPa) massic energy of combustion of 2-furanmethanethiol at $T$ = 298.15 K; Table S2. Standard ($p^o$ = 0.1 MPa) massic energy of combustion of furfuryl methyl sulfide at $T$ = 298.15 K; Table S3. Standard ($p^o$ = 0.1 MPa) massic energy of combustion of methyl-2-methyl-3-furyldisulfide at $T$ = 298.15 K; Table S4. Standard molar heat capacities, in the gaseous phase, derived from statistical thermodynamics using the vibrational frequencies calculated at the basis B3LYP/6-31G(d) level of theory (scaled by a factor of 0.961); Table S5. Computed enthalpies of reaction, $\Delta_r H^o_m$, and formation, $\Delta_f H^o_m$, in the gaseous state of 2-furanmethanethiol using G3 at $T$ = 298.15 K; Table S6. Computed enthalpies of reaction, $\Delta_r H^o_m$, and formation, $\Delta_f H^o_m$, in the gaseous state of furfuryl methyl sulfide using G3 at $T$ = 298.15 K; Table S7. Computed enthalpies of reaction, $\Delta_r H^o_m$, and formation, $\Delta_f H^o_m$, in the gaseous state of methyl-2-methyl-3-furyldisulfide using G3 at $T$ = 298.15 K; Table S8. G3-computed enthalpies and standard molar enthalpies of formation at $T$ = 298.15 K; Table S9. Computed enthalpies of reaction, $\Delta_r H^o_m$, and formation, $\Delta_f H^o_m$, in the gaseous state of benzyl methyl sulfide using G3 at $T$ = 298.15 K.

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