



Energetic study of benzothiazole and two methylbenzothiazole derivatives: Calorimetric and computational approaches



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ABSTRACT

This work reports an experimental and computational thermochemical study for benzothiazole and two of its methyl benzothiazole derivatives, 2-methylbenzothiazole and 2,5-dimethylbenzothiazole.

Values of the standard ($p^\circ = 0.1$ MPa) molar energy of combustion of the three compounds were measured by rotating bomb combustion calorimetry. The standard molar enthalpy of the corresponding transitions from condensed to gaseous phases, at $T = 298.15$ K, was obtained from high temperature Calvet microcalorimetry measurements. The experimental results enable the calculation of the standard molar enthalpy of formation in the gaseous state, at $T = 298.15$ K, for the afore-mentioned compounds, the results being discussed in terms of structural and energetic contributions.

The gas-phase enthalpies of formation were computationally estimated from high-level *ab initio* molecular orbital calculations at the G3//B3LYP level of theory. The computed values compare very well with the experimental results obtained in this work and show that, in terms of enthalpy, the methyl substituents lead to an increase on the stability of the compounds, in a similar way to that already described for the corresponded benzoxazole derivatives.

Furthermore, this composite approach was also used to obtain information about the gas-phase basicity, proton and electron affinities and adiabatic ionization enthalpies.

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1. Introduction

Benzothiazoles constitute a class of heterocyclic compounds with a wide spectrum of biological activity, being used for a large variety of therapeutic uses [1–3]. For example, 2-methylbenzothiazole may serve as promising lead scaffolds for further elaboration as anti-tuberculosis drugs and as possible anti-malaria drugs [4]. On the other hand, structures with benzothiazole moiety have large molecular hyper-polarizability, being a good alternative for the non-linear optics (NLO) materials [5]. In addition, such compounds can also have application as polidentate ligands, in laser technology as laser dyes [6].

The knowledge of the thermodynamic properties of these heterocyclic compounds, particularly the correspondent enthalpies of formation, in condensed and gaseous states, enables a better understanding of their chemical behaviour, for future development of their applications. Following our interest in the study of heterocycles with a benzene-fused ring associated to a five-membered

ring containing heteroatoms of oxygen or sulfur [7,8], we report herein the thermochemical experimental and computational results on benzothiazole, 2-methylbenzothiazole and 2,5-dimethylbenzothiazole (figure 1) in order to evaluate the energetic effects associated to the methylation on the homo and heterocyclic rings.

The experimental work available in the literature concerning the thermochemistry of benzothiazoles is scarce. Steele *et al.* [9] carried out a thermochemical study of benzothiazole for which the enthalpies of combustion and vaporization have been determined. From a theoretical study, Gomes *et al.* [10] estimated the gas-phase enthalpy of formation of benzoxazole from G3(MP2)//B3LYP calculations and provided a value about $17 \text{ kJ} \cdot \text{mol}^{-1}$ lower than that from the experiments [9]. The gas-phase enthalpy of formation of the benzothiazole was also calculated at the Gaussian-4 (G4) level of theory using the atomization reaction procedure [11], with a difference $12.1 \text{ kJ} \cdot \text{mol}^{-1}$ between the experimental [9] and the calculated G4 values. The present computational analysis indicates the same deviation, and that justifies why in this work we proceeded to the experimental redetermination of this value.

Additionally, high level *ab initio* calculations have been used to estimate the gas-phase standard molar enthalpy of formation of these compounds, as well as the gas-phase basicity, the proton and electron affinities and adiabatic ionization enthalpies.

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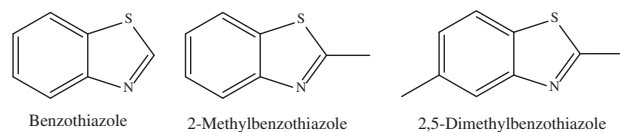


FIGURE 1. Molecular structures of the studied compounds.

2. Experimental

2.1. Materials

The liquid compounds, benzothiazole [95-16-9] and 2-methylbenzothiazole [120-75-2], were purified by repeated fractional distillation under reduced pressure. The solid compound 2,5-dimethylbenzothiazole [95-26-1] was purified by repeated sublimation under reduced pressure. The purity of each compound was checked by gas chromatography and the initial and final purities of the samples are presented in table 1.

The combustion calorimetric system was calibrated with benzoic acid, NIST Standard Reference Material (SRM 39j), while the Calvet microcalorimeter was calibrated with undecane (≥ 0.99 mass fraction purity, Sigma-Aldrich) and with naphthalene (≥ 0.99 mass fraction purity, Sigma-Aldrich), for the liquids and the solid compounds, respectively.

The power scale of the differential scanning calorimeter (DSC) was calibrated with a highly pure indium sample (0.99999 mass fraction purity, Aldrich), whereas three high-purity reference materials [12], benzoic acid (NIST SRM 39j), tin (0.998 mass fraction purity, Aldrich) and indium, were used to calibrate the temperature scale.

The literature values of the specific densities used were $\rho = 1.238 \text{ g} \cdot \text{cm}^{-3}$ for benzothiazole [13], $\rho = 1.173 \text{ g} \cdot \text{cm}^{-3}$ for 2-methylbenzothiazole [14] and $\rho = 1.176 \text{ g} \cdot \text{cm}^{-3}$ for 2,5-dimethylbenzothiazole [15], and the relative atomic masses used for the elements were the ones recommended by the IUPAC commission in 2009 [16].

2.2. Differential scanning calorimetry

The temperature and the enthalpy of fusion of the 2,5-dimethylbenzothiazole were determined using a differential scanning calorimetry (DSC, Setaram DSC 141). The samples were sealed in aluminium crucibles and five runs were done, under nitrogen atmosphere, using a heating rate of $(3.3 \times 10^{-2}) \text{ K} \cdot \text{s}^{-1}$. The temperature and power scales of the calorimeter were calibrated under the same conditions as the experimental determinations.

2.3. Rotating-bomb combustion calorimetry

The standard ($p^\circ = 0.1 \text{ MPa}$) massic energy of combustion of the three compounds were measured in an isoperibol rotating-bomb calorimeter, originally developed at the Lund University [17] and installed in our Department, where several improvements have been performed as it has been described previously [18]. The apparatus and the technique have been already described [18], so only the more relevant aspects are presented here. The calorimetric system is equipped with a stainless steel twin valve bomb (internal volume: 0.258 dm^3), lined with platinum. Calorimeter temperatures were measured to $\pm(1 \times 10^{-4}) \text{ K}$, at time intervals of 10 s,

using a Hewlett-Packard (HP-2804A) quartz thermometer, interfaced to a PC. The final temperature was close to $T = 298.15 \text{ K}$ and the bomb rotation is started when the temperature rise in the main-period reached about 0.63 of its total value, continuing until the end of each experiment [19].

The energy equivalent of the calorimeter was determined using benzoic acid with a certified massic energy of combustion, under standard bomb conditions, of $-(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$. Calibration experiments were made in oxygen at $p = 3.04 \text{ MPa}$, with 1.00 cm^3 of water added to the bomb, without making the rotation. For six calibration experiments, the energy equivalent of the calorimeter obtained was $\varepsilon_{\text{cal}} = (25146.4 \pm 1.3) \text{ J} \cdot \text{K}^{-1}$, for an average mass of water added to the calorimeter of 5222.5 g . The uncertainty mentioned is the standard deviation of the mean.

The samples of the liquid compounds benzothiazole and 2-methylbenzothiazole were burnt enclosed into Melinex[®] bags, under oxygen at $p = 3.04 \text{ MPa}$, in the presence of 10.00 cm^3 of deionized water, to ensure the formation of $\text{H}_2\text{SO}_4 \cdot 115\text{H}_2\text{O}$ (l). The Melinex bags were made according to the technique described by Skinner *et al.* [20], in which the massic energy of combustion of dry Melinex was $-(22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$. The crystalline compound 2,5-dimethylbenzothiazole was burnt in pellet form in the same conditions (oxygen at $p = 3.04 \text{ MPa}$; bomb with 10.00 cm^3 of deionized water). For the cotton thread fuse (empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$), the standard massic energy of combustion is $\Delta_c u^\circ = -16240 \text{ J} \cdot \text{g}^{-1}$ [21]. These values of massic energy for cotton and Melinex were previously confirmed in our laboratory.

At the end of the calorimetric measurements, the nitric acid formed was determined using the Devarda allow method [22] and the correction energy for the formation of $0.1 \text{ mol} \cdot \text{dm}^{-3}$ HNO_3 (aq) solution from N_2 (g), O_2 (g) and H_2O (l) was based on $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ [23].

The electric energy for ignition was determined from the change in potential difference on discharge of a $1400 \mu\text{F}$ condenser across a platinum wire. The value for the pressure coefficient of specific energy $(\partial u / \partial p)_T = -0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$ at $T = 298.15 \text{ K}$, a typical value for organic compounds, was assumed [24]. The standard massic energy of combustion, $\Delta_c u^\circ$, was calculated by a similar procedure to that developed by Hubbard *et al.* [25] for compounds with general formula $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$, and implemented by Good *et al.* [26] for sulfur compounds.

2.4. Calvet microcalorimetry

The enthalpies of phase transition of the compounds were measured with a high-temperature Calvet microcalorimeter (Setaram HT 1000), using the “vacuum sublimation” drop microcalorimetric method described by Skinner [27], adapted to the study of liquid samples by Ribeiro da Silva *et al.* [28]. The details of the apparatus and the technique were previously described [29].

Samples of about 5 mg of compound were dropped simultaneously with the corresponding blank tube, at $T = 298.15 \text{ K}$, into the reaction vessel in the microcalorimeter, held at the hot-zone temperature. The three compounds, benzothiazole, 2-methylbenzothiazole and 2,5-dimethylbenzothiazole, were studied at three different temperatures, $T = 391 \text{ K}$, $T = 432 \text{ K}$ and $T = 321 \text{ K}$, respectively. After the tubes reached thermo stability, the sample was removed from the hot-zone by vaporization/sublimation into the vacuum.

TABLE 1
Purification and analysis details of the samples studied.

Chemical name	Source	Lot certificate purity	Purification method	Final molar purity	Analysis method
Benzothiazole (l)	Sigma-Aldrich	0.973	Distillation	0.9986	GC ^a
2-Methylbenzothiazole (l)	Alfa Aesar	0.995	Distillation	0.9995	GC ^a
2,5-Dimethylbenzothiazole (cr)	Alfa-Aesar	0.998	Sublimation	0.9996	GC ^a

^a GC: Gas-liquid chromatography.

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