



Thermodynamic study of 2-aminothiazole and 2-aminobenzothiazole: Experimental and computational approaches



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ABSTRACT

This work reports an experimental and computational thermochemical study of two aminothiazole derivatives, namely 2-aminothiazole and 2-aminobenzothiazole.

The standard ($p^\circ = 0.1$ MPa) molar energies of combustion of these compounds were measured by rotating bomb combustion calorimetry. The standard molar enthalpies of sublimation, at $T = 298.15$ K, were derived from the temperature dependence of the vapor pressures of these compounds, measured by the Knudsen-effusion technique and from high temperature Calvet microcalorimetry. The conjugation of these experimental results enabled the calculation of the standard molar enthalpies of formation in the gaseous state, at $T = 298.15$ K, for the compounds studied. The corresponding standard Gibbs free energies of formation in crystalline and gaseous phases were also derived, allowing the analysis of their stability, in these phases.

We have also estimated the gas-phase enthalpies of formation from high-level molecular orbital calculations at the G3(MP2)//B3LYP level of theory, the estimates revealing very good agreement with the experimental ones.

The importance of some stabilizing electronic interactions occurring in the title molecules has been studied and quantitatively evaluated through Natural Bonding Orbital (NBO) of the corresponding wavefunctions and their Nucleus Independent Chemical Shifts (NICS) parameters have been calculated in order to rationalize the effect of electronic delocalization upon stability.

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1. Introduction

As an extension of our recent studies on the structural properties and energetics of heterocyclic compounds with a benzene ring fused to a five-membered ring containing heteroatoms of oxygen or sulfur [1–3], we have performed the determination of some thermodynamic properties of two aminothiazole derivatives: 2-aminothiazole and 2-aminobenzothiazole (structural formulae in figure 1).

The thiazole ring is a structure present in many drugs with a diversity of biological actions including antimicrobial [4], analgesic [5] and antitumor activities [6]. Recently, thiazoles became the subject of an increased interest since they can also be used as suitable non-linear optical materials [7]. In order to increase the knowledge on the thermophysical and thermochemical data for this class of compounds and, inherently, on their reactivity characteristics, crucial for future practical applications, it is important the

study of thermodynamic properties such as vapor pressure, Gibbs free energies, enthalpies of formation and of phase transitions, among other parameters.

In this work, the standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation, in crystalline phase, $\Delta_f H_m^\circ(\text{cr})$, at $T = 298.15$ K, of both compounds were derived from their standard molar internal energies of combustion, in oxygen, at the temperature of 298.15 K, measured by rotating bomb combustion calorimetry. Their standard molar enthalpies of sublimation, $\Delta_{\text{cr}}^\circ H_m^\circ$, at $T = 298.15$ K, were derived indirectly from the temperature dependence of the vapor pressures measured using the Knudsen-effusion technique, and directly using high temperature Calvet microcalorimetry. From the experimental results, the standard molar enthalpies of formation in the gaseous state, at $T = 298.15$ K, were derived and are discussed in terms of structural contributions, in order to evaluate the enthalpic influences of the amino group both on the pentagonal ring containing the two heteroatoms and on the adjacent benzene ring. The standard Gibbs free energies of formation in crystalline and gaseous phases were also determined, allowing a thermodynamic analysis on the stability of these compounds.

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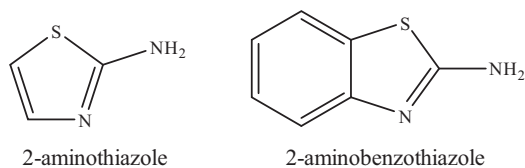


FIGURE 1. Molecular structures of the compounds studied.

Additionally, using high level *ab initio* based calculations, the gas-phase standard molar enthalpies of formation of these compounds, as well as the gas-phase basicities, proton and electron affinities and adiabatic ionization enthalpies, were estimated. In addition, we obtained information about their natural bond orbitals (NBO), HOMO and LUMO energy gaps, as well as the relevant magnetic parameters (NICS) which help characterizing the aromaticity of the title compounds.

2. Experimental

2.1. Materials

2-Aminothiazole (C₃H₄N₂S; CAS No. 96-50-4) and 2-aminobenzothiazole (C₇H₆N₂S; CAS No. 136-95-8) were supplied by Alfa Aesar and were purified by repeated sublimation under reduced pressure. The corresponding purity was checked by gas chromatography equipped with a flame ionization detector (GC-FID, Agilent 4890D) containing a HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 m × 0.530 mm i.d. with 1.5 μm film thickness); nitrogen was used as a carrier gas. Table 1 summarizes the initial and the final purity mass fractions of the samples.

The specific densities of 2-aminothiazole and 2-aminobenzothiazole are, respectively, $\rho = 1.2410 \text{ g} \cdot \text{cm}^{-3}$ and $\rho = 1.2590 \text{ g} \cdot \text{cm}^{-3}$ [8].

2.2. Vapour pressures measurements

The vapor pressures of the compounds studied were determined using the Knudsen effusion method. The experimental equipment has been designed and constructed in our research group and the detailed description of the procedure and technique used were published previously [9]. The apparatus is prepared for the simultaneous use of nine effusion cells grouped in three series (“Small” – series A; “Medium” – series B; “Large” – series C). The areas and transmission probability factors of the effusion orifices are presented in table S1 of the Supplementary information. During an effusion experiment, each aluminum block is kept at a constant temperature, different from the other two blocks. The temperature of each block is measured by a platinum resistance thermometer Pt-100 class 1/10.

For the temperature T , the vapor pressure p of the crystalline compound is related to the mass m of the sample sublimed from each effusion cell, during the time period t by equation (1), where M is the molar mass of the effusing vapor, R is the gas constant, A_0

is the area of the effusion orifice and w_0 is the respective transmission probability factor.

$$p = (m/A_0 w_0 t) \cdot (2\pi RT/M)^{1/2}. \quad (1)$$

2.3. High-temperature microcalorimetry

The enthalpies of sublimation of the two compounds were also measured with a high-temperature Calvet microcalorimeter (Setaram HT 1000), using the “vacuum sublimation” drop microcalorimetric method described by Skinner [10]. The details of the apparatus and the technique used were previously described in detail [11].

Samples, about (4 to 6) mg, of the compounds contained in thin glass capillary tubes were simultaneously dropped, together with empty ones, at a known room temperature into each of the calorimetric cells (reference and reaction) held at $T = 350 \text{ K}$ for 2-aminothiazole and $T = 417 \text{ K}$ for 2-aminobenzothiazole, and then removed from the hot zone by vacuum sublimation. The Calvet microcalorimeter was calibrated with naphthalene and anthracene, for $T = 350 \text{ K}$ and $T = 417 \text{ K}$, respectively. The corresponding constants of the calorimeter, k , were obtained as the average of six independent experiments. The derived results and the respective expanded uncertainties are $k = (1.0088 \pm 0.0034)$ and $k = (1.0442 \pm 0.0072)$, respectively.

2.4. Rotating-bomb combustion calorimetry

The standard ($p^\circ = 0.1 \text{ MPa}$) massic energy of combustion of the title compounds were measured in an isoperibol rotating bomb calorimeter, originally developed at the Lund University [12] and installed in our Department, where several improvements have been introduced as previously described [13], so only the more relevant aspects are presented herein. The calorimetric system is equipped with a stainless steel twin valve bomb (internal volume: 0.258 dm³), lined with platinum. Calorimeter temperatures were measured using a Hewlett-Packard (HP-2804A) quartz thermometer. The final temperature was close to $T = 298.15 \text{ K}$ and the bomb rotation starts when the temperature rise in the main-period reached about 0.63 of its total value, continuing until the end of each experiment [14].

The energy equivalent of the calorimeter was determined using benzoic acid, NIST Standard Reference Material (SRM 39j), 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 cm³ of water added to the bomb, without making the rotation. Two sets of six calibration experiments were performed, due to changes in the calorimeter. From these calibration experiments, the values of the energy equivalent of the calorimeter obtained were: $\varepsilon_{\text{cal}} = (25157.4 \pm 1.1) \text{ J} \cdot \text{K}^{-1}$ and $\varepsilon_{\text{cal}} = (25161.3 \pm 1.5) \text{ J} \cdot \text{K}^{-1}$, for 2-aminothiazole and 2-aminobenzothiazole, respectively. The uncertainty mentioned is the standard deviation of the mean.

The samples of 2-aminothiazole were burnt in pellet form, enclosed into Melinex[®] bags, under oxygen at $p = 3.04 \text{ MPa}$, in the presence of 20.00 cm³ of deionized water, whereas the samples

TABLE 1
Provenance and mass fraction purity of the samples studied.

Chemical name	Source	Lot certificate purity ^a	Purification method	Final mass fraction purity	Method of analysis ^b
2-Aminothiazole (cr)	Alfa Aesar	0.998	Sublimation	0.9999	GC
2-Aminobenzothiazole (cr)	Alfa Aesar	0.984	Sublimation	0.9999	GC

^a Values referred to the fraction of the GC area, as stated in the certificates of analysis of the manufacturer.

^b GC, Gas-liquid chromatography.

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