



# Experimental and computational thermochemical study of benzofuran, benzothiophene and indole derivatives



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## ABSTRACT

The standard enthalpies of formation of benzofuran-, indole-, and benzothiophene-2-carboxylic acids, and 2-acetylbenzofuran in the condensed phase were measured at  $T = 298.15$  K from experimental determinations of their energies of combustion by isoperibolic calorimetry. The enthalpies, temperatures of melting, purities and heat capacities of the compounds were determined using differential scanning calorimetry. Using thermogravimetry the enthalpies of sublimation were obtained and subsequently, the standard enthalpies of formation in the gas-phase and at  $T = 298.15$  K for the four compounds were derived. The results of this analysis were compared with the values obtained by the Gaussian-4 procedure using the atomization method. The computational results are in good agreement with the experimental values. The influence of the heteroatom (oxygen, nitrogen and sulfur) and acetyl or carboxyl groups on the standard enthalpy of formation is also discussed.

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## 1. Introduction

Structure and energy are very important concepts and, therefore, are fundamental to modern chemistry. There is a close relationship between these concepts because the energy associated with a particular molecular structure depends on the atoms, bond lengths and angles of the molecule. The enthalpies of formation are useful for understanding the connection between molecular structure and reactivity. Furthermore, this information is necessary in order to calculate the amount of energy released or absorbed in a chemical reaction and to assess the relative stability of molecules.

One of the primary objectives of thermochemistry is to assign the standard enthalpy of formation to each substance. The formation reactions are usually impossible to perform; therefore, an experimental measurement of the energy of formation cannot be directly obtained. However, the enthalpy of formation in the solid phase of a substance can be determined using the energy of combustion. This parameter depends on the inter- and intra-molecular interactions in the crystal lattice. However, with the enthalpy of formation in the gas phase, intermolecular interactions are eliminated and the energetic effects produced by inserting a specific

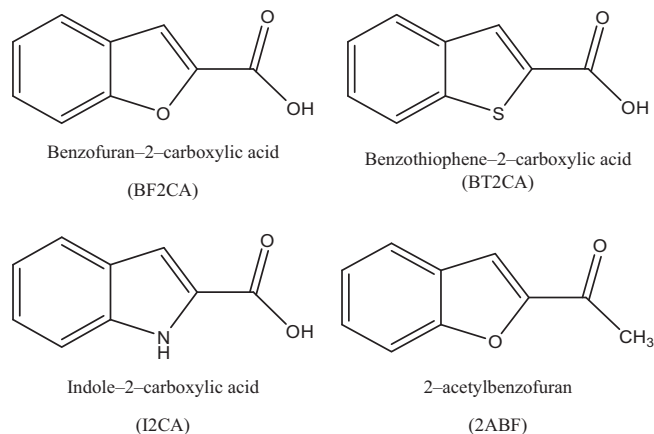
heteroatom or functional group into the molecular structure can be compared.

In our Thermochemistry Laboratory, we are interested in determining thermodynamic properties of aromatic heterocyclic compounds that include oxygen, nitrogen and sulfur; our aim is to understand the effects that these heteroatoms and other substituents have on the thermochemical parameters, particularly the enthalpies of formation. We have previously reported experimental studies that determined energies of combustion and enthalpies of formation in the condensed phase of several series of heterocycles, such as 2-SH-benzazoles [1] and the series 2-acetylpyrrole, 2-acetylfuran and 2-acetylthiophene [2].

Currently, we are interested in studying the thermochemical parameters of carboxylic derivatives of benzofuran, indole and benzothiophene that include: benzofuran-2-carboxylic acid (BF2CA), indole-2-carboxylic acid (I2CA) and benzothiophene-2-carboxylic acid (BT2CA). The difference between these compounds is the presence of oxygen, nitrogen or sulfur as a heteroatom. We also aim to discover the influence of the acetyl and carboxyl groups by studying 2-acetylbenzofuran (2ABF), whose structure is similar to BF2CA, but differs at the acetyl group. The compounds studied here are formed by a benzene ring and a furan, pyrrole or thiophene heterocycle and share two carbon atoms with a bond between them. Figure 1 shows the molecular structures of the compounds studied in this work.

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**FIGURE 1.** Molecular structures of the compounds studied in this work.

The derivatives of benzofuran, indole and benzothiophene are common in nature and are part of numerous drugs and pharmaceuticals. The 2ABF and BF2CA molecules have antibacterial properties [3], and BF2CA is also used to prepare polyolefins [4]. I2CA acts as a corrosion inhibitor for copper against sulfuric acid [5] and has potential applications in the treatment of respiratory tract diseases, such as asthma, chronic bronchitis and pulmonary emphysema [6]. BT2CA is an antihypercalcemic [7–9] and hypolipidemic agent [10] and is used to treat leukemia [11]. Despite the wide industrial and pharmaceutical applications of the compounds studied in this work, and with the exception of a recent thermochemical study including one of the compounds [12], no experimental values of the standard molar energies of combustion and the standard molar enthalpies of formation were found in the literature.

In this paper, we report the experimental determination of the energies of combustion using two different calorimeters, a static bomb calorimeter for BF2CA, I2CA and 2ABF and a rotatory bomb calorimeter for BT2CA. We also report the results of fusion enthalpy and temperature and heat capacity measurements at  $T = 298.15$  K, determined using differential scanning calorimetry (DSC). Rate of mass loss data were determined using thermogravimetry measurements, and from their dependence on the temperature, the sublimation enthalpy was obtained.

In addition to the experimental work, computational calculations were performed according to the Gaussian-4 method using the atomization method to calculate the enthalpies of formation of the gaseous phases at  $T = 298.15$  K for each of the studied compounds. The computational and experimental values were compared, and the influence of the heteroatom and the acetyl or carboxyl groups on the stability of each molecule is discussed.

## 2. Experimental

### 2.1. Materials and purity control

Compound samples were supplied by Sigma–Aldrich Co. The purities in mole fraction reported by the manufacturer were as follows: 0.99 for BF2CA; 0.98 for I2CA; 0.98 for BT2CA and 0.99 for 2ABF. These purity values were first checked using DSC to confirm the supplier's data. 2ABF and BF2CA were used without further purification. I2CA was purified by two successive sublimations under reduced pressure at a maximum temperature of 453.15 K. BT2CA was purified by recrystallization from ethanol (HPLC grade). Table 1 summarizes the chemical identifications, sources and purities of the investigated substances and the calorimetric standards utilized in this work.

The purities, melting temperatures, enthalpies of fusion and the molar heat capacities of the compounds were determined using a Perkin Elmer DSC7 calorimeter. Prior to the melting experiments, the equipment was calibrated for temperature and heat flow by analyzing the temperature and enthalpy of fusion of a high-purity indium metal with a certified  $T_{\text{fus}} = 429.75$  K and  $\Delta_{\text{fus}}H = 28.6$  J·g<sup>-1</sup> [13]. All fusion experiments were conducted under a constant flow of nitrogen at 20 cm<sup>3</sup>·min<sup>-1</sup> using hermetically sealed aluminum pans. For each experiment, 1.0 to 5.0 mg of sample was weighed on a Mettler Toledo UMX2 balance (sensitivity,  $\pm 10^{-7}$  g). The purity of the compounds was determined using the fractional melting technique, in which the melting temperature was taken as the onset temperature of the melting curve and the enthalpy of fusion was determined by integrating the melting curve using a straight baseline.

In the first analysis, a sample of each compound was heated from room temperature to 15 K above its melting temperature with a heating rate of  $T = 10$  K·min<sup>-1</sup>. This analysis was conducted in order to detect impurities or other thermal effects in addition to fusion. For the four compounds studied in this work, no signals were detected within the detection limit of the calorimeter. For subsequent experiments, heating was restricted to a maximum of  $T = 10.0$  K before and after the melting temperature with a heating rate of  $T = 1.0$  K·min<sup>-1</sup>.

The heat capacity of the solid phase at  $T = 298.15$  K of each compound was determined using DSC under the same experimental conditions as the melting experiments, except that the temperature range was from (288.15 to 308.15) K scanned at a rate of  $T = 1.0$  K·min<sup>-1</sup>. Prior to the  $C_p$  measurements, the DSC7 device was calibrated utilizing synthetic sapphire as a reference material, which has a known heat capacity of 0.775 J·K<sup>-1</sup> at  $T = 298.15$  K [13,14].

The densities of BF2CA and BT2CA at  $T = 298.15$  K were determined by measuring the mass and volume of a pellet of the compound, while the densities of I2CA and 2ABF were obtained from references [15,16], respectively. The relative atomic masses used for calculations of all molar quantities were obtained from the 2011 IUPAC recommendations [17].

### 2.2. Combustion calorimetry

Combustion experiments for BF2CA, 2ABF and I2CA were conducted in a static-bomb isoperibolic calorimeter using an 1108 dual valve bomb (Parr Instrument Company) constructed of stainless steel with an internal volume of 0.345 dm<sup>3</sup>. The calorimeter was calibrated for combustion experiments using benzoic acid NIST Standard Reference Material 39j, whose certified combustion energy is  $-(26434 \pm 3)$  J·g<sup>-1</sup> [18].

Tablets of approximately 1.0 g of each compounds were burned in a platinum crucible under a pressure of  $p = 3.04$  MPa of high purity oxygen (Air Liquide Corp., mass fraction of 0.99999) and in presence of 1.0 cm<sup>3</sup> of deionized water. For each combustion experiment, the ignition temperature was selected so that the final temperatures were as close as possible to  $T = 298.15$  K after the temperature increase caused by combustion. Before each experiment, the atmospheric nitrogen was removed from inside the combustion vessel by passing oxygen for five minutes. The bomb was placed in a calorimetric cuvette, which contained 2000.0 g of distilled water weighed on a Sartorius BP 12000-S balance (sensitivity  $\pm 0.1$  g).

To reach a well-defined final state, combustion experiments involving the sulfur compound BT2CA were conducted in a rotatory-bomb calorimeter, which was equipped with a 1004 C Parr Instrument combustion vessel [19]. The bomb has an inner volume of 0.348 dm<sup>3</sup> and an internal platinum lining. The calorimetric set was also calibrated using benzoic acid NIST 39j.

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