# Experimental and computational thermochemical study of two fluorobenzazoles: 5-fluoro-2-methylbenzoxazole and 5-fluoro-2-methylbenzothiazole

Ana L.R. Silva, Jorge M. Gonçalves, Maria D.M.C. Ribeiro da Silva *

Centro de Investigação em Química, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

A R T I C L E  I N F O

A B S T R A C T

An energetic study of 5-fluoro-2-methylbenzoxazole (FMBO) and of 5-fluoro-2-methylbenzothiazole (FMBT), in condensed and gaseous states, has been performed using calorimetric techniques and computational calculations. The standard ($p° = 0.1$ MPa) molar enthalpies of formation of FMBO and FMBT, in the liquid phase, at $T = 298.15$ K, were derived from the corresponding standard molar energies of combustion, measured by rotating-bomb combustion calorimetry. At $T = 298.15$ K, the standard ($p° = 0.1$ MPa) molar enthalpy of vaporization, for each compound, was determined, by a direct method, using the vacuum drop microcalorimetric technique. For each compound, from this last value and from the enthalpy of formation of the liquid compounds, the corresponding standard ($p° = 0.1$ MPa) enthalpy of formation in the gaseous phase has been calculated. Additionally, the gas-phase standard molar enthalpies of formation of these two compounds were estimated computationally at the G3(MP2)//B3LYP level of theory, as well as their gas-phase basicities and proton affinities.

© 2018 Elsevier Ltd.

## 1. Introduction

The present work is part of an extensive study on the thermochemical properties of 1,3-benzazole compounds, containing the pentagonal heterocyclic ring fused to a benzenic ring, in order to evaluate the energetic effect of different substituents on the rings, namely the methyl, the amine, the mercaptan, the chlorine and the fluorine groups [1–6]. Further, we intend to analyse the energetic effect associated to different heteroatoms (nitrogen, oxygen and sulphur) in position one of the pentagonal ring for this class of molecules. Hence, we report new experimental results for the energies of combustion and the enthalpies of vaporization of two benzazole fluorinated derivatives, the 5-fluoro-2-methyl-benzoxazole, FMBO, and the 5-fluoro-2-methylbenzothiazole, FMBT, (Fig. 1), measured by rotating bomb combustion calorimetry, at $T = 298.15$ K, and high temperature Calvet microcalorimetry, respectively. From these results, the standard ($p° = 0.1$ MPa) molar enthalpies of formation of both benzazole derivatives, in condensed and gaseous states, were derived. It is important to highlight that

the combustion of FMBT, a compound containing fluorine and sulphur atoms, origins a final bomb solution containing a mixture of sulphuric and hydrofluoric acids whose thermodynamic parameters (e.g. enthalpies of dissolution of the gases on the solution) needed for the calculations are unknown. To overcome this difficulty, we designed comparison experiments using standard samples of benzoic acid and thianthrene, jointly with an aqueous solution of hydrofluoric acid, in adequate proportions to guarantee identical qualitative and quantitative compositions of the final states of these comparison experiments and those of the combustion reactions of FMBT [7]. Considering this procedure, corrections to the standard state are required only to the initial states, except a minor correction to the final states since the amounts of gas in the final states were slightly different.

Additionally, the gas-phase standard molar enthalpies of formation of these compounds were estimated computationally at the G3(MP2)//B3LYP level of theory, as well as their gas-phase basicities and proton affinities.

The results obtained allow correlation of the energetic parameters with the structural characteristics of the molecules, which is important to contribute for the knowledge on the reactivity of the species.

* Corresponding author.

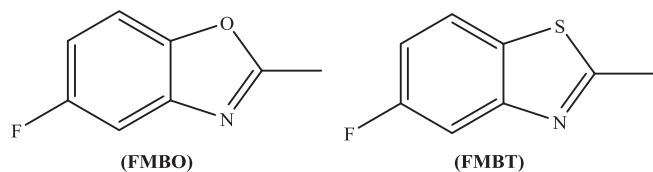E-mail address: mdsilva@fc.up.pt (M.D.M.C. Ribeiro da Silva).

**Figure 1.** Structures of 5-fluoro-2-methylbenzoxazole (**FMBO**) and of 5-fluoro-2-methylbenzothiazole (**FMBT**) studied experimentally and computationally.

## 2. Experimental

### 2.1. Materials and purity analysis

5-fluoro-2-methylbenzoxazole (FMBO, CAS No. 701-16-6) and 5-fluoro-2-methylbenzothiazole (FMBT, CAS No. 399-75-7) were supplied by TCI Europe (+98%), being then purified by repeated fraction distillation under reduced pressure ($T = 376$ K and $p = 4.1$ kPa and $T = 428$ K and $p = 10.0$ kPa, respectively). Gas chromatography analysis indicated that the distilled samples of both compounds had a mass fraction purity >0.999. The analyses were carried out on an Agilent 4890D gas chromatography–flame ionization detector (GC-FID) apparatus, equipped with 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 the carrier gas. Table 1 summarizes the provenance, method of purification and the final purity of the studied samples.

Thianthrene (Sigma-Aldrich, +97%) used in the comparison experiments, was previously purified by zone melting and by successive sublimations under reduced pressure. The final degree of purity (>0.999, mass fraction) was confirmed by gas chromatography. In these experiments, benzoic acid (NBS SRM 39j) was used as a combustion auxiliary to ensure the correct stoichiometry of the combustion reaction of FMBT. The hydrofluoric acid solution used in these experiments was made by dilution of HF (aq) (mass fraction, 0.40) from Merck and the concentration was checked by titration.

### 2.2. Rotating-bomb calorimetry

The standard ($p° = 0.1$ MPa) massic energies of combustion of compounds studied were determined using a rotating-bomb calorimeter with a stainless-steel twin valve bomb, lined with platinum, whose internal volume is 0.258 dm$^3$, previously described in the literature [8].

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 bomb conditions, of $-(26,434 ± 3)$ J·g$^{-1}$. Calibration experiments were made in oxygen at $p = 3.04$ MPa, with 1.00 cm$^3$ of water added to the bomb, without bomb rotation. Two sets of six calibration experiments were performed, due to changes in the calorimeter. From these calibration experiments, performed before and after some repairs in the

equipment, the values of the energy equivalent of the calorimeter obtained were: $\varepsilon_{cal} = (25146.4 ± 1.3)$ J·K$^{-1}$ (study of FMBO and FMBT) and $\varepsilon_{cal} = (25161.3 ± 1.5)$ J·K$^{-1}$ (used in the comparison experiments). The uncertainties mentioned are the standard deviation of the mean. The $\varepsilon_{cal}$ values refer to an average mass of 5222.5 g of water added to the calorimeter.

The liquid samples of FMBO, enclosed in polyethylene bags (for polyethylene: $\Delta_c u° = -(46282.4 ± 4.8)$ J·g$^{-1}$, a value determined in our laboratory), were burnt under oxygen at $p = 3.04$ MPa, with 10.00 cm$^3$ of deionized water placed in the bomb, to yield a hydrofluoric acid of uniform and well-defined concentration.

For FMBT, the control of the amounts of compounds in normal experiments and in the comparison ones was, as strict as possible, to reproduce with accuracy, the composition of the final states. Thus, the liquid samples ($\approx 0.78$ g) were enclosed in polyethylene bags and burnt under oxygen at $p = 3.04$ MPa, with 10.00 cm$^3$ of deionised water placed in the bomb; for the comparison experiments, pellets of thianthrene ($\approx 0.51$ g) with benzoic acid auxiliary ($\approx 0.16$ g), were ignited in oxygen at $p = 3.04$ MPa, with 10.00 cm$^3$ of 0.399 mol·dm$^{-3}$ HF (aq) added to the bomb. These quantities were carefully adjusted so that the chemical compositions of the final bomb contents for the measurements and comparison experiments were similar. However, there was a slightly discrepancy in the amount of hydrofluoric acid used in both set of experiments ($6.8 × 10^{-4}$ mol), whose effect has been evaluated, being less than 0.014% for the massic energy of combustion in one comparison experiment. Thus, the influence of that discrepancy of the content of HF (aq) solutions on the final results is within their uncertainty interval.

Most of the nitrogen oxide present in both compounds is converted to molecular nitrogen (ca. 90%), and the remaining to aqueous nitric acid. This latter amount was determined using Devarda's alloy method [9]; the energy correction for the formation of 0.1 mol·dm$^{-3}$ HNO$_3$(aq) [10] from N$_2$(g), O$_2$(g) and H$_2$O(l) was based on $-59.7$ kJ·mol$^{-1}$.

The combustion of organic fluorine compounds may be accompanied by the formation of two fluorine-containing products, namely hydrofluoric acid and tetrafluoromethane. However, the compounds studied are not highly fluorinated and the ratio of fluorine to hydrogen not exceed the unity, so it was assumed that no tetrafluoromethane is formed, and all the fluorine present in the compound under study appears as hydrofluoric acid in the reaction products [11]. Moreover, polyethylene bags were used not only for enclosing the samples but also as a source of hydrogen. On the other hand, as the two compounds studied (FMBO and FMBT) contain sulphur, when a sample of each one of them is burned in a pure oxygen atmosphere, sulphur dioxide and trioxide are formed in the respective reactions. If the air in the bomb is not flushed, before charging with oxygen, the nitrogen present in the atmosphere originates nitrogen oxides that catalyse the quantitative conversion of sulphur to sulphur trioxide. The sulphur trioxide produced by the combustion reaction dissolves in the bomb liquid to form sulfuric acid.

**Table 1**
Provenance and mass fraction purity of the studied compounds.

| Compound | CAS No. | Supplier | Purification method | Final mass fraction purity[a] |
|---|---|---|---|---|
| FMBT | 399-75-7 | TCI Europe, +98% | Fraction Distillation | 0.9995 |
| FMBO | 701-16-6 | | (under reduced pressure) | 0.9992 |
| Thianthrene | 92-85-3 | Sigma-Aldrich, +97%) | Zone melting and successive sublimations (under reduced pressure) | > 0.999 |
| Oxygen | – | Air Liquide | – | >0.99995 |
| Benzoic acid | 65-85-0 | NBS SRM 39j | – | – |
| HF solution | – | Merck (mass fraction, 0.40) | – | – |

[a] Method of analysis: GC, Gas-liquid chromatography.