



Thermodynamic properties of naphthoxazole and naphthothiazole derivatives: Experimental and computational studies [☆]



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ABSTRACT

The energetic study of 2-methylnaphtho[1,2-*d*]oxazole (**MN12O**), 2-methylnaphtho-[2,3-*d*]oxazole (**MN23O**) and 2-methylnaphtho[1,2-*d*]thiazole (**MN12T**) has been performed experimentally and computationally. The enthalpies of combustion and sublimation/vaporization of these compounds were determined, respectively, from static or rotating bomb combustion calorimetry and high temperature Calvet microcalorimetry and/or the Knudsen-effusion studies. These experimental data allow derivation of the corresponding gas-phase standard molar enthalpies of formation of the three compounds. Additionally, we have obtained the gas-phase standard molar enthalpies of formation of these three compounds, as well of the 2-methylnaphtho[2,3-*d*]thiazole (**MN23T**), through high level *ab initio* calculations, at the G3(MP2)//B3LYP and DLPNO-CCSD(T)/cc-pVTZ levels of theory. The computational study of the molecular structures of the compounds has been carried out. Furthermore, a relationship between the energetic and structural characteristics of these molecules was also evaluated.

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1. Introduction

In the context of our interest on thermodynamic properties of heterocyclic compounds presenting a benzene ring fused to a five-membered ring with nitrogen and oxygen/sulphur as heteroatoms, we have been involved in a systematic study to investigate the relationships between structure, energy, and reactivity of several related compounds with different substituents: two chlorobenzoxazoles [1], 2-methylbenzoxazole and 2,5-dimethylbenzoxazole [2], benzothiazole and two methylbenzothiazoles [3], 2-aminothiazole and 2-aminobenzothiazole [4], 2-hydroxybenzothiazole and 2-benzothiazolinone [5], 2-mercaptobenzimidazole [6], 2-phenylbenzoxazole, 2-phenylbenzothiazole, 2-(2-hydroxyphenyl)benzoxazole and 2-(2-hydroxyphenyl)benzothiazole [7], 5-fluoro-2-methylbenzoxazole and 5-fluoro-2-methylbenzothiazole [8]. Complementary studies on some heterocycles with a naphthalene fused to a pentagonal ring containing nitrogen and oxygen/sulphur heteroatoms are reported in the present paper. In fact, knowledge of their energetic parameters is relevant since this information provides support for understanding the formation mechanism of the naphthoazoles, predicting their behaviour and for overcoming difficulties related with their applications. In the literature, the only

available data on 2-methylnaphtho[1,2-*d*]oxazole and 2-methylnaphtho[2,3-*d*]oxazole are the respective enthalpies of combustion and of formation in the condensed phase determined in the 1930s [9].

The present work describes the experimental and computational thermochemical results for two 2-methylnaphthoxazoles, **MN12O** and **MN23O**, and one 2-methyl-naphthothiazole, **MN12T** (Fig. 1). The standard molar enthalpies of formation of the compounds in crystalline phase at $T = 298.15$ K were derived from their standard molar energies of combustion measured by static or rotating bomb combustion calorimetry. The standard molar enthalpies of sublimation/vaporization of these compounds at $T = 298.15$ K were measured directly using high temperature Calvet-drop microcalorimetry or indirectly, from the temperature dependence of the vapour pressures using the Knudsen-effusion technique. Additionally, using high level *ab initio* calculations, the gas-phase standard molar enthalpies of formation of these three compounds were obtained, as well as that of 2-methylnaphtho[2,3-*d*]thiazole (**MN23T**, Fig. 1).

2. Materials and methods

2.1. Materials

The compounds studied experimentally were purchased from Alfa Aesar or TCI Europe; the solids were purified by repeated sub-

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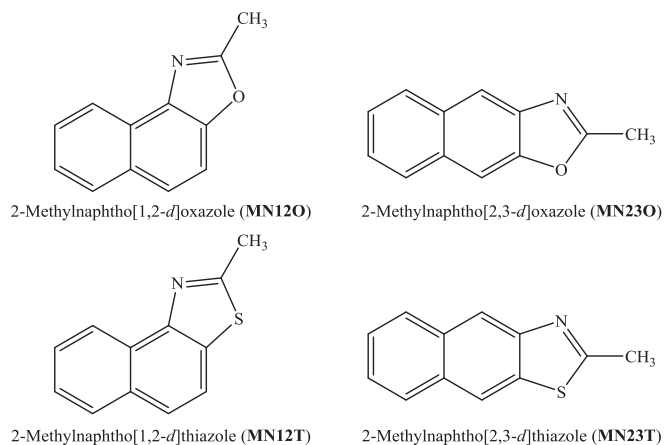


Fig. 1. Structural formula of the studied compounds.

limation under reduced pressure and the liquid was purified by distillation under reduced pressure. Gas chromatography analyses indicated that the sublimed/distilled samples had a mass fraction purity higher than 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 a carrier gas. Table 1 summarizes the initial and the final mass fractions of the samples after purification.

The standard atomic masses recommended by the IUPAC Commission in 2013 were used in the calculation of all molar thermodynamic quantities [10].

2.2. Differential scanning calorimetry (DSC)

The temperature and the enthalpy of fusion of **MN23O** and **MN12T** were determined using a Setaram DSC 141 differential scanning calorimeter. The experiments were performed in the range $T = (293–390)$ K under a flow of nitrogen of $50 \text{ cm}^3 \text{ min}^{-1}$. The samples with masses in the range (4–10) mg were sealed in aluminium crucibles, under air, and weighed with a precision of $\pm 0.1 \text{ μg}$ on a microbalance (Mettler-Toledo, UMT2). The heating rate used was $2 \text{ K} \cdot \text{min}^{-1}$. The temperature and power scales of the apparatus were calibrated under the same conditions as the experimental determinations by using the onset and the area, respectively, of the fusion peaks of recommended standard materials [11]. The temperature scale was calibrated with benzoic acid (NIST SRM 39j), tin (Aldrich, mass fraction 0.998), and indium

(Aldrich, mass fraction 0.99999). The power scale was calibrated with indium (Aldrich, mass fraction 0.99999).

2.3. Static-bomb combustion calorimetry

The standard ($p^\circ = 0.1 \text{ MPa}$) massic energies of combustion of compounds studied were determined using two different bomb combustion calorimeters:

- (i) The combustion experiments of **MN12O** and **MN23O** were performed with a static-bomb calorimeter, using a twin valve bomb with an internal volume of 0.290 dm^3 . The apparatus and technique have been described previously [12]. The calibration of the calorimeter was performed by combustion of benzoic acid thermochemical standard (SRM 39j) with massic energy of combustion, under bomb conditions, of $\Delta_c u = -(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$, and corrected to give the energy equivalent, ϵ_{cal} , corresponding to the average mass of water added to the calorimeter (2900.0 g). The energy equivalent of the calorimeter was determined, $\epsilon_{\text{cal}} = (15551.7 \pm 1.2) \text{ J} \cdot \text{K}^{-1}$, where the uncertainty quoted is the standard deviation of the mean.
- (ii) The combustion experiments of **MN12T** were performed with a rotating-bomb calorimeter, in which the twin valve bomb is of stainless-steel, lined with platinum (internal volume: 0.258 dm^3). The apparatus and technique have been previously described in the literature [13]. This system was calibrated with benzoic acid (SRM 39j); the value of the energy equivalent of the calorimeter was $\epsilon_{\text{cal}} = (25146.4 \pm 1.3) \text{ J} \cdot \text{K}^{-1}$, where the cited uncertainty is the standard deviation of the mean of six independent experiments. The ϵ_{cal} value refers to an average mass of 5222.5 g of water added to the calorimeter.

The standard massic energy of combustion, $\Delta_c u^\circ$, was calculated by a similar procedure to that developed by Hubbard et al. [14,15]. Further details about the experimental procedure are provided in the Supporting Information.

2.4. High-temperature microcalorimetry

The enthalpies of sublimation of crystalline **MN23O** and **MN12T** and the enthalpy of vaporization of liquid **MN12O** were measured with a high-temperature Calvet microcalorimeter (Setaram HT 1000), using the “vacuum sublimation” drop microcalorimetric method described by Skinner [16], adapted to the study of liquid samples by Ribeiro da Silva et al. [17]. The apparatus and the technique used were previously described in detail [18].

Table 1

Provenance and mass fraction purity of the studied compounds and materials used.

Compound	CAS No.	Supplier	Purification method	Final mass fraction purity
MN12O	85-15-4	TCI Europe, +99%	Fraction distillation ^a	0.9994 ^b
MN23O	20686-66-2	TCI Europe, +98%	Sublimation ^a	0.9999 ^b
MN12T	2682-45-3	Alfa Aesar, +99%	Sublimation ^a	0.9994 ^b
Benzoic acid	65-85-0	NBS SRM 39j	–	0.999996 ^c
Tin	7440-31-5	Sigma-Aldrich	–	0.998 ^d
Indium	7440-74-6	Sigma-Aldrich	–	0.99999 ^d
Oxygen	–	Air Liquide	–	>0.99995 ^d
Naphthalene	91-20-3	Sigma-Aldrich	–	0.9999 ^b
Undecane anhydrous	544-76-3	Sigma-Aldrich	–	0.999 ^d

^a Under reduced pressure.

^b Method of analysis: GC, Gas-liquid chromatography.

^c Mass spectrometric and coulometric measurements.

^d Provided by the manufacturer.

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