



## Phase transition thermodynamics of phenyl and biphenyl naphthalenes

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### ABSTRACT

This work is focussed on the thermodynamics of phase transition for some naphthalene derivatives: 1-phenyl naphthalene, 2-phenyl naphthalene, 2-(biphen-3-yl)naphthalene, and 2-(biphen-4-yl)naphthalene. The Knudsen mass-loss effusion technique was used to measure the vapour pressures of the following compounds: 2-phenyl naphthalene (cr), between  $T = (333.11 \text{ and } 353.19) \text{ K}$ ; 2-(biphen-4-yl)naphthalene (cr), between  $T = (405.17 \text{ and } 437.19) \text{ K}$ ; 2-(biphen-3-yl)naphthalene (l), between  $T = (381.08 \text{ and } 413.17) \text{ K}$ . From the temperature dependence of the vapour pressure, the standard, ( $p^\circ = 10^5 \text{ Pa}$ ), molar enthalpies, entropies, and Gibbs free energies of sublimation for 2-phenyl naphthalene and 2-(biphen-4-yl)naphthalene were derived as well as the standard molar enthalpy, entropy, and Gibbs free energy of vaporization for 2-(biphen-3-yl)naphthalene at  $298.15 \text{ K}$ . The temperatures and the standard molar enthalpies of fusion were measured by differential scanning calorimetry and the standard molar entropies of fusion were derived. For 1-phenyl naphthalene the standard molar enthalpy of vaporization at  $298.15 \text{ K}$  was measured directly using the Calvet microcalorimetry drop method.

The 1-phenyl naphthalene is liquid at room temperature, showing a remarkably low melting point when compared to the 2-phenyl naphthalene isomer and naphthalene. A regular decrease of volatility with the increase of a phenyl group in *para* position at the 2-naphthalene derivatives was observed. In 2-(biphen-3-yl)naphthalene, the *meta* substitution of the phenyl group results in a significantly higher volatility than in the respective *para* isomer.

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### 1. Introduction

Aromatic compounds are of general interest in many fields of science, namely in polymer chemistry [1], nanotechnology, molecular biology, and molecular energetics. The study of their thermodynamic properties in the condensed phase and of their phase transition equilibria becomes of fundamental importance.

The properties of polymers can be evaluated by an extrapolation of the properties of the constituting monomers. Aromatic  $\pi$ - $\pi$  stacking interactions are cohesive forces present in aromatic compounds, and they are one of the most important factors determining their phase transition thermodynamics, packing structure, and conformation of macromolecules [2]. Enhanced electron correlation, arising from the inter- and intra-molecular interactions of various aromatic moieties, strongly influences some other thermophysical properties of the materials like electric and thermal conductivity.

This work is focused on the sublimation and vaporization study of four naphthalene derivatives: 1-phenyl naphthalene (1-PhN), 2-phenyl naphthalene (2-PhN), 2-(biphen-3-yl)naphthalene (2-

B3PhN), and 2-(biphen-4-yl)naphthalene (2-B4PhN), illustrated in figure 1.

The aim of this study is to verify the energetic differentiation in the condensed phase arising either by the change in position of one phenyl group or by the addition of a second phenyl to 2-phenyl naphthalene. Subtle structural changes, like those presented in converting one structural isomer to another, can cause more pronounced deviations in the crystal packing and cohesive energy and entropy of the solid and liquid states.

Therefore, the standard molar enthalpy of vaporization of 1-phenyl naphthalene was measured using the Calvet microcalorimetry drop method. The vapour pressures of 2-phenyl naphthalene, 2-(biphen-3-yl)naphthalene, and 2-(biphen-4-yl)naphthalene, at several temperatures, were determined by the Knudsen mass-loss effusion technique. Through the previous results, the standard molar enthalpies, entropies, and Gibbs free energies of sublimation for 2-phenyl naphthalene and 2-(biphen-4-yl)naphthalene and the standard molar enthalpy, entropy, and Gibbs free energy of vaporization for 2-(biphen-3-yl)naphthalene were derived at  $T = 298.15 \text{ K}$ .

The temperatures and the standard molar enthalpies of fusion for 2-phenyl naphthalene, 2-(biphen-3-yl)naphthalene, and 2-(biphen-4-yl)naphthalene were measured by differential scanning calorimetry. From the experimental results the standard molar entropies of fusion were determined.

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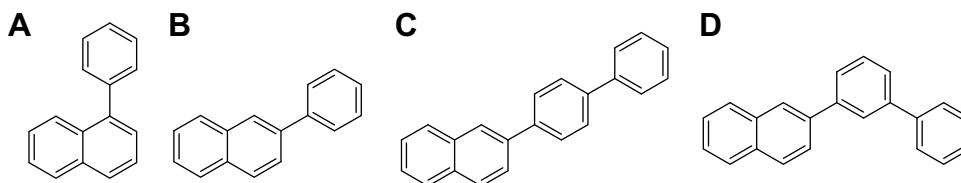


FIGURE 1. Structural formulas of: 1-phenylnaphthalene (A); 2-phenylnaphthalene (B); 2-(biphen-4-yl)naphthalene (C), and 2-(biphen-3-yl)naphthalene (D).

## 2. Experimental section

### 2.1. Synthesis, purification, and characterization

The compounds 2-phenylnaphthalene [CAS Number 612-94-2], 2-(biphen-3-yl)naphthalene, and 2-(biphen-4-yl)naphthalene were synthesized using the Suzuki–Miyaura aryl cross-coupling method by adapting the procedure described in the literature [3,4]. As represented schematically in figure 2 a mixture of  $K_2CO_3$  (15 mmol),  $Pd(OAc)_2$  (0.1 mmol), 2-bromonaphthalene (10 mmol), boronic acid (15 mmol), distilled water ( $35\text{ cm}^3$ ), and DMF ( $30\text{ cm}^3$ ) was stirred for approximately 8 h at 360 K. Afterwards the reaction mixture was extracted four times with ethyl acetate. The product was purified by recrystallization from ethanol. The three compounds were synthesized by this same procedure.

The compound 1-phenylnaphthalene [CAS Number 605-02-7] was obtained commercially from Sigma–Aldrich Chemical Co. with the assessed minimum purity of 0.96 (mass fraction). This compound is liquid and it has been purified by successive fractional distillation under reduced pressure ( $1 \cdot 10^2\text{ Pa}$ ).

The solid compounds were purified by sublimation under reduced pressure ( $<10\text{ Pa}$ ), 2-phenylnaphthalene at  $T = 353\text{ K}$ , 2-(biphen-3-yl)naphthalene at  $T = 405\text{ K}$ , and 2-(biphen-4-yl)naphthalene at  $T = 390\text{ K}$ .

The final purity of the samples was verified by gas chromatography analysis, using an HP 4890 apparatus equipped with an HP-5 column, cross-linked (5% diphenyl and 95% dimethylpolysiloxane) and a flame ionization detector. The mass fraction of the pure compounds were found as: 1-phenylnaphthalene 0.995, 2-phenylnaphthalene 0.998, 2-(biphen-3-yl)naphthalene 0.996, and 2-(biphen-4-yl)naphthalene 0.994.

The samples were characterized by elemental analysis and  $^1H$  NMR ( $CDCl_3$ , TMS). The mass fraction,  $w$ , of C and H were the following: for 1-phenylnaphthalene,  $C_{16}H_{12}$ , found  $w(C) = 94.2$ ,  $w(H) = 5.8$ , calculated  $w(C) = 94.08$ ,  $w(H) = 5.92$ ; for 2-phenylnaphthalene,  $C_{16}H_{12}$ , found  $w(C) = 94.5$ ,  $w(H) = 5.5$ , calculated  $w(C) = 94.08$ ,  $w(H) = 5.92$ ; for 2-(biphen-3-yl)naphthalene,  $C_{22}H_{16}$ , found  $w(C) = 94.4$ ,  $w(H) = 5.6$ , calculated  $w(C) = 94.25$ ,  $w(H) = 5.75$  and for 2-(biphen-4-yl)naphthalene,  $C_{22}H_{16}$ , found  $w(C) = 94.1$ ,  $w(H) = 5.9$ , calculated  $w(C) = 94.25$ ,  $w(H) = 5.75$ . The  $^1H$  NMR spectra were taken in a Bruker AMX-300 instrument (300 MHz), and for the studied compounds agree well with the predicted structures. The  $^1H$  NMR spectrum for each compound is presented as supporting information.

The relative atomic masses used were those recommended by the IUPAC Commission in 2006 [5].

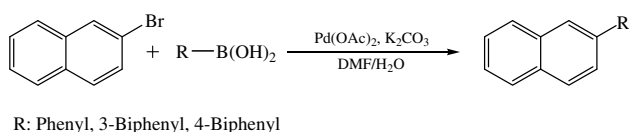


FIGURE 2. Scheme of the reaction procedure used in the syntheses based on the Suzuki–Miyaura cross-coupling methodology.

### 2.2. Calvet microcalorimetry

The standard molar enthalpy of vaporization of 1-phenylnaphthalene was measured in a high temperature Calvet microcalorimeter, model SETARAM HT 1000, using a similar technique of the drop method described by Skinner *et al.* [6]. The measuring procedure and the description of the apparatus have been described recently in detail [7].

Samples of about 5–9 mg of each compound were placed into thin capillary tubes, sealed at one end, and were dropped simultaneously with the corresponded blank tube at room temperature into the hot reaction zone of the calorimeter. The heating of the sample from room temperature to the calorimeter temperature is observed by an endothermic peak. When the calorimetric cells reach thermostability, the sample is removed from the hot-zone by vaporization into the vacuum.

The capillary tubes were weighted on a Mettler Toledo XS-105 Dual Range analytical balance with a sensitivity of  $10^{-5}\text{ g}$ . The blank heat capacity corrections were performed due to differences in the mass of both capillary tubes and the different sensibilities of the two calorimetric cells.

The standard molar enthalpy of vaporization at  $T = 298.15\text{ K}$  was calculated from the experimental value of  $\Delta_{1,298.15\text{ K}}^{g,T}H_m^\circ$ , at the temperature  $T$  of the hot zone using the following equation:

$$\Delta_1^g H_m^\circ(T = 298.15\text{ K}) = \Delta_{1,298.15\text{ K}}^{g,T} H_m^\circ - \{H_m^\circ(g,T) - H_m^\circ(g,298.15\text{ K})\}, \quad (1)$$

where the value of  $\{H_m^\circ(g,T) - H_m^\circ(g,298.15\text{ K})\}$  represents the molar enthalpic correction for the respective heat capacity of the gaseous phase, which was calculated by computational thermochemistry.

The microcalorimeter was calibrated with *n*-undecane (Aldrich Chemical Co., 99%) at the same temperature of the experiments of 1-phenylnaphthalene, using the standard molar enthalpy of vaporization of *n*-undecane,  $\Delta_1^g H_m^\circ(T = 298.15\text{ K}) = (56.580 \pm 0.566)\text{ kJ} \cdot \text{mol}^{-1}$  [8]. The calibration constant of the calorimeter was found to be  $k(T = 386.1\text{ K}) = (0.998 \pm 0.016)$ . The calibration constant was obtained from the average of six independent experiments with the uncertainty being the standard deviation of the mean.

### 2.3. Knudsen effusion

The vapour pressures of 2-phenylnaphthalene, 2-(biphen-3-yl)naphthalene, and 2-(biphen-4-yl)naphthalene were measured by the Knudsen mass-loss effusion technique at several temperatures, in a nine cell Knudsen effusion apparatus described recently in detail [9].

During one effusion experiment, the Knudsen effusion apparatus allows the simultaneous operation of nine cells at three different temperatures.

The measurements for each compound were extended through a chosen temperature interval corresponding to measured vapour pressures around the typical pressure range of 0.1 Pa to 1 Pa.

The vapour pressure of the sample is calculated by the following equation:

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

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