



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 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 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 π - π 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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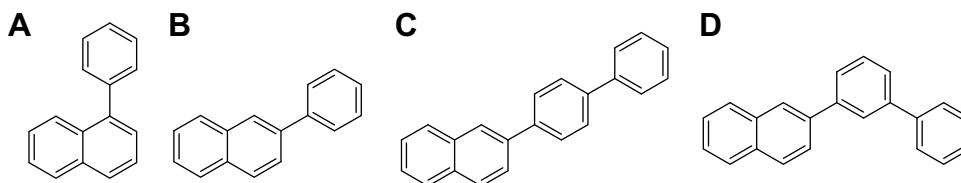


FIGURE 1. Structural formulas of: 1-phenylnaphthalene (A); 2-phenylnaphthalene (B); 2-(biphen-4-yl)naphthalene (C), and 2-(biphen-3-yl)naphthalene (D).

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 cm^3), and DMF (30 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].

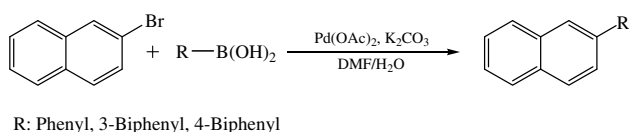


FIGURE 2. Scheme of the reaction procedure used in the syntheses based on the Suzuki–Miyaura cross-coupling methodology.

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} 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:

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

where m is the mass sublimed from the effusion cell, T is the temperature at which the sublimation occurred, t is the experimental time, M is the molar mass of the sample, R is the gas constant ($R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), A_0 is the area of the orifice, and w_0 is the transmission probability factor, calculated by the following equation

$$w_0 = \{1 + (3l/8r)\}^{-1}, \quad (3)$$

where l and r are the thickness and the radius of the effusion orifice, respectively. Data concerning the thickness, radius, and the transmission probability factor calculated for each orifice is presented as supporting information.

2.4. Differential scanning calorimetry

The temperatures and the standard molar enthalpies of fusion for 2-phenylnaphthalene, 2-(biphen-3-yl)naphthalene, and for 2-(biphen-4-yl)naphthalene were measured in a power compensation differential scanning calorimeter, model SETARAM DSC 141,

TABLE 1

Experimental results obtained by microcalorimetry drop method for the enthalpy of vaporization of 1-phenylnaphthalene

$m_{\text{compound}}/\text{mg}$	T/K	E^a/J	$\Delta_{1298.15 \text{ K}}^{\text{g},T} H_{\text{m}}^{\circ}/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{298.15 \text{ K}}^{\text{g}} H_{\text{m}}^{\circ}(\text{g})/(\text{kJ} \cdot \text{mol}^{-1})$
8.92	386.02	4.542	103.75	22.2 ± 0.5
5.95	385.31	2.946	100.88	
7.72	386.02	3.927	103.66	
8.66	385.86	4.369	102.81	
7.18	385.99	3.671	104.18	
7.06	386.02	3.615	104.35	
$\Delta_{1298.15 \text{ K}}^{\text{g}} H_{\text{m}}^{\circ}(T = 298.15 \text{ K}) = (81.0 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$				

The overall uncertainty includes the uncertainty of the calibration experiments, the uncertainty of the enthalpy of vaporization of *n*-undecane and the uncertainty associated with the heat capacity correction.

^a “ E ” – experimental energy measured in the Calvet microcalorimeter.

using a heating rate of $3.33 \cdot 10^{-2} \text{ K} \cdot \text{s}^{-1}$ and hermetically sealed steel crucibles.

The temperature and heat flux scales were calibrated by measuring the temperature and the heat of fusion of naphthalene [CAS Number 91-20-3], benzil [CAS Number 134-81-6], benzoic acid [CAS Number 65-85-0] (NBS Standard Reference Material 39i), and *p*-anisic acid [CAS Number 100-09-4], using the same experimental procedure [10].

Three unsuccessful attempts were done in order to measure the temperature and enthalpy of fusion of 1-phenylnaphthalene. In the experiments, 5 mg of the compound were maintained during 48 h in the differential scanning calorimeter cell at 173 K. In all attempts only a reproducible but small glass transition was observed at 227 K during the heating from 173 K to 298 K at $3.33 \cdot 10^{-2} \text{ K} \cdot \text{s}^{-1}$. The compound was also kept during 48 h at a temperature of 2 K lower than the previously found glass transition without any crystallization.

2.5. Computational thermochemistry details

The geometry optimizations, as well as the fundamental vibrational frequency calculations, were performed for all compounds using density functional theory (DFT) with the hybrid exchange correlation functional (B3LYP) [11,12] at the 6-311++G(d,p) level of theory. The frequencies were scaled using the scale factor of 0.9688 [13]. The heat capacities and the enthalpic corrections to 298.15 K in the gaseous state were determined for all the compounds using the scaled vibrational frequency calculations.

All theoretical calculations were performed using the Gaussian 03 software package [14].

3. Results

The standard molar enthalpy of vaporization, at $T = 298.15 \text{ K}$, measured in the high temperature Calvet microcalorimeter, for 1-phenylnaphthalene is shown in table 1.

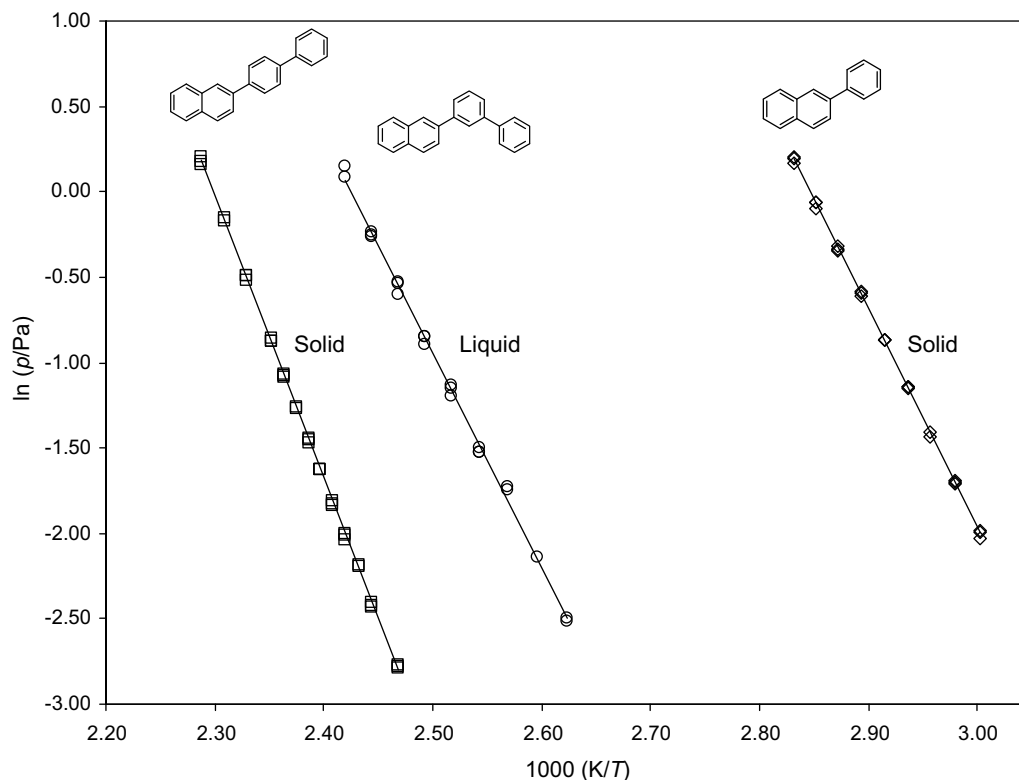


FIGURE 3. Plots of $\ln(p/\text{Pa})$ versus $1/T (\text{K}^{-1})$ for the studied compounds.

TABLE 2

Knudsen-effusion results for the studied compounds for small, medium and large orifices

Oven	T/K	t/s	p/Pa			10 ² · Δ ln(p/Pa)		
			Small	Medium	Large	Small	Medium	Large
<i>2-Phenylnaphthalene (cr)</i>								
O1	333.11	33011	0.132	0.137	0.137	-2.4	-0.1	0.5
O2	335.63	33011	0.185	0.183	0.180	2.4	0.4	-0.9
O3	338.20	33011		0.244	0.239		0.2	-1.3
O1	340.61	9905	0.316	0.318	0.320	-0.4	-0.2	1.1
O2	343.13	9905	0.420	0.421	0.419	0.1	0.1	0.8
O3	345.69	9905	0.558	0.553	0.544	0.6	-0.2	-0.4
O1	348.12	13608	0.729	0.707	0.716	1.2	-1.6	1.4
O2	350.62	13608	0.939	0.941	0.909	-0.1	0.9	-0.7
O3	353.19	13608	1.212	1.224	1.185	-1.4	0.5	-0.6
<i>2-(Biphen-4-yl)naphthalene (cr)</i>								
O1	405.17	33828	0.062	0.062	0.063	0.2	2.1	3.0
O2	409.14	33828	0.091	0.088	0.089	-0.6	-2.5	-1.1
O1	411.18	14757	0.111	0.112		-0.2	1.7	
O3	413.18	33828	0.135	0.134	0.131	0.1	-0.3	-2.1
O2	415.14	14757	0.164	0.160	0.161	0.8	-1.7	-0.1
O1	417.19	12533	0.197	0.197	0.197	-0.2	-0.3	0.8
O3	419.09	14757	0.237	0.235	0.230	0.2	-0.6	-1.5
O2	421.14	12533	0.283		0.280	-1.0		-1.1
O3	423.09	12533	0.339	0.342	0.336	-1.0	-0.3	-0.8
O3	425.19	14820	0.418	0.424	0.416	0.7	1.8	1.3
O1	429.21	7136	0.609	0.609	0.597	2.2	1.3	1.1
O2	433.15	7136	0.855	0.839		1.3	-1.7	
O3	437.19	7136	1.171	1.222	1.194	-2.3	0.5	0.4
<i>2-(Biphen-3-yl)naphthalene (l)</i>								
O3	381.08	38464	0.081	0.083		1.4	5.5	
O2	385.17	38464			0.117			-1.6
O1	389.15	38464		0.174			0.4	
O1	389.17	12101			0.177			6.4
O3	393.18	14510	0.216	0.218	0.223	-2.0	-5.1	-3.1
O2	397.15	14510		0.323	0.303		2.1	-3.7
O3	397.17	12101	0.315			3.3		
O1	401.14	14510	0.410	0.429	0.427	-1.9	-1.4	-0.4
O2	405.18	5645	0.546	0.585	0.588	-4.6	-3.9	0.9
O3	409.08	5645	0.767	0.773	0.790	-0.3	-3.5	1.3
O1	413.17	7184	1.087	1.156		4.0	6.1	

The standard molar enthalpies of sublimation/vaporization at the mean temperature, $\langle T \rangle$, were derived, for 2-phenylnaphthalene (cr), 2-(biphen-3-yl)naphthalene (l), and 2-(biphen-4-yl)naphthalene (cr), using the integrated form of the Clausius–Clapeyron equation (4):

$$\ln(p/\text{Pa}) = a - b \cdot (K/T), \quad (4)$$

where a is a constant and $b = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/R$ or $b = \Delta_{\text{l}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/R$.

TABLE 3

Experimental results for the studied compounds where a and b are from the Clausius–Clapeyron equation: $\ln(p/\text{Pa}) = a - b \cdot (K/T)$, and $b = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/R$ or $b = \Delta_{\text{l}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/R$; $R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

Effusion orifices	a	b/K	r^2	$\langle T \rangle/K$	$p(\langle T \rangle)/\text{Pa}$	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}(\langle T \rangle, p(\langle T \rangle))/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
<i>2-Phenylnaphthalene (cr)</i>							
A	36.87 ± 0.29	12950 ± 101	0.9996		0.421	107.7 ± 0.8	313.8 ± 2.4
B	36.47 ± 0.13	12810 ± 45	0.9999		0.421	106.5 ± 0.4	310.4 ± 1.1
C	36.12 ± 0.19	12696 ± 64	0.9998		0.416	105.6 ± 0.5	307.6 ± 1.5
Global results	36.48 ± 0.14	12817 ± 47	0.9997	343.15	0.420	106.6 ± 0.4	310.5 ± 1.1
<i>2-(Biphen-4-yl)naphthalene (cr)</i>							
A	37.74 ± 0.15	16421 ± 63	0.9998		0.287	136.5 ± 0.5	324.2 ± 1.2
B	38.11 ± 0.20	16576 ± 85	0.9997		0.288	137.8 ± 0.7	327.2 ± 1.7
C	37.81 ± 0.23	16456 ± 97	0.9997		0.284	136.8 ± 0.8	324.9 ± 1.9
Global results	37.90 ± 0.12	16488 ± 49	0.9997	421.18	0.286	137.1 ± 0.4	325.5 ± 1.0
<i>2-(Biphen-3-yl)naphthalene (l)</i>							
A	30.60 ± 0.51	12625 ± 203	0.9987		0.304	105.0 ± 1.7	264.3 ± 4.3
B	30.72 ± 0.61	12654 ± 244	0.9978		0.317	105.2 ± 2.0	264.9 ± 5.1
C	30.02 ± 0.70	12381 ± 278	0.9975		0.314	102.9 ± 2.3	259.2 ± 5.8
Global results	30.45 ± 0.36	12557 ± 142	0.9975	397.13	0.312	104.4 ± 1.2	262.9 ± 3.0

Figure 3 presents $\ln(p/\text{Pa}) = f(1/T/K)$ plots for the global results obtained for the studied compounds. The experimental results and the residuals of the Clausius–Clapeyron equation obtained for each effusion cell are presented in table 2.

The parameters of the Clausius–Clapeyron equation, the calculated standard deviations, the standard molar enthalpies and entropies of sublimation/vaporization at the mean temperature, $\langle T \rangle$, are presented in table 3. The experimental Knudsen data concerning 2-(biphen-3-yl)naphthalene is clearly more scattered than the other compounds. The uncertainty increase in the liquid compound reflects some experimental difficulties during the effusion measurements, like the bumping of the liquid inside the cell during the initial evacuation step of the system. The standard molar enthalpies of sublimation/vaporization at the mean temperature are determined by the parameter b of the Clausius–Clapeyron equation and the molar entropies of sublimation/vaporization at $p(\langle T \rangle)$ and at the mean temperature, $\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}(\langle T \rangle, p(\langle T \rangle))$ or $\Delta_{\text{l}}^{\text{g}} S_{\text{m}}(\langle T \rangle, p(\langle T \rangle))$, are calculated by equations (5) and (6):

$$\Delta_{\text{cr}}^{\text{g}} S_{\text{m}}(\langle T \rangle, p(\langle T \rangle)) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/\langle T \rangle, \quad (5)$$

$$\Delta_{\text{l}}^{\text{g}} S_{\text{m}}(\langle T \rangle, p(\langle T \rangle)) = \Delta_{\text{l}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle)/\langle T \rangle. \quad (6)$$

The standard molar enthalpies of sublimation/vaporization at $T = 298.15 \text{ K}$ are determined by equations (7) and (8):

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle) + (298.15 \text{ K} - \langle T \rangle) \cdot \Delta_{\text{cr}}^{\text{g}} C_{p,m}^{\circ}, \quad (7)$$

$$\Delta_{\text{l}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = \Delta_{\text{l}}^{\text{g}} H_{\text{m}}^{\circ}(\langle T \rangle) + (298.15 \text{ K} - \langle T \rangle) \cdot \Delta_{\text{l}}^{\text{g}} C_{p,m}^{\circ}, \quad (8)$$

where $\Delta_{\text{cr}}^{\text{g}} C_{p,m}^{\circ} = C_{p,m}^{\circ}(\text{g}) - C_{p,m}^{\circ}(\text{cr})$ and $\Delta_{\text{l}}^{\text{g}} C_{p,m}^{\circ} = C_{p,m}^{\circ}(\text{g}) - C_{p,m}^{\circ}(\text{l})$. The $\Delta_{\text{cr}}^{\text{g}} C_{p,m}^{\circ}$ values for 2-phenylnaphthalene, 2-(biphen-3-yl)naphthalene, and 2-(biphen-4-yl)naphthalene were calculated using the group additivity method for the estimation of the value of $C_{p,m}^{\circ}(\text{cr})$ and the computational calculations for the calculation of the value of $C_{p,m}^{\circ}(\text{g})$. The value of $C_{p,m}^{\circ}(\text{cr})$ for 2-phenylnaphthalene (2-PhN) was estimated using the following equation:

$$C_{p,m}^{\circ}(\text{2-PhN}, \text{cr}) = C_{p,m}^{\circ}(\text{Naphthalene}, \text{cr}) + C_{p,m}^{\circ}(\text{p-Terphenyl}, \text{cr}) - C_{p,m}^{\circ}(\text{Biphenyl}, \text{cr}). \quad (9)$$

The values of $C_{p,m}^{\circ}(\text{cr})$ for 2-(biphen-3-yl)naphthalene (2-B3PhN) and 2-(biphen-4-yl)naphthalene (2-B4PhN) were estimated using the following equation:

$$C_{p,m}^{\circ}(\text{2-B3PhN}, \text{2-B4PhN}, \text{cr}) = C_{p,m}^{\circ}(\text{Naphthalene}, \text{cr}) + 2 \cdot C_{p,m}^{\circ}(\text{p-Terphenyl}, \text{cr}) - 2 \cdot C_{p,m}^{\circ}(\text{Biphenyl}, \text{cr}). \quad (10)$$

The value of $C_{p,m}^{\circ}(l)$ for 2-phenylnaphthalene (2-PhN) was calculated by the following equation:

$$C_{p,m}^{\circ}((2\text{-PhN}), l) = C_{p,m}^{\circ}(\text{Naphthalene}, l) + C_{p,m}^{\circ}(\text{Biphenyl}, l) - C_{p,m}^{\circ}(\text{Benzene}, l). \quad (11)$$

The value of $C_{p,m}^{\circ}(l)$ for 2-(biphen-3-yl)naphthalene (2-B3PhN) was calculated by the following equation:

$$C_{p,m}^{\circ}((2\text{-B3PhN}), l) = C_{p,m}^{\circ}(\text{Naphthalene}, l) + 2 \cdot C_{p,m}^{\circ}(\text{Biphenyl}, l) - 2 \cdot C_{p,m}^{\circ}(\text{Benzene}, l). \quad (12)$$

Considering the methodology above, the following $\Delta_{cr}^{\circ}C_{p,m}^{\circ}$ and $\Delta_{f}^{\circ}C_{p,m}^{\circ}$ were derived: $\Delta_{cr}^{\circ}C_{p,m}^{\circ}(\text{2-phenylnaphthalene}) = -(28 \pm 10) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $\Delta_{cr}^{\circ}C_{p,m}^{\circ}(\text{2-(biphen-3-yl)naphthalene}) = -(25 \pm 10) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $\Delta_{cr}^{\circ}C_{p,m}^{\circ}(\text{2-(biphen-4-yl)naphthalene}) = -(25 \pm 10) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $\Delta_{f}^{\circ}C_{p,m}^{\circ}(\text{2-phenylnaphthalene}) = -(102 \pm 10) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $\Delta_{f}^{\circ}C_{p,m}^{\circ}(\text{2-(biphen-3-yl)naphthalene}) = -(143 \pm 10) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

The following literature values of heat capacities at 298.15 K were considered: $C_{p,m}^{\circ}(\text{naphthalene}, cr) = 165.69 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [15]; $C_{p,m}^{\circ}(p\text{-terphenyl}, cr) = 278.66 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [16]; $C_{p,m}^{\circ}(\text{biphenyl}, cr) = 198.39 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [17]; $C_{p,m}^{\circ}(\text{naphthalene}, l) = 196.06 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [17]; $C_{p,m}^{\circ}(\text{biphenyl}, l) = 259.54 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [18]; $C_{p,m}^{\circ}(\text{benzene}, l) = 135.69 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [19]. The values of $C_{p,m}^{\circ}(g)$ at 298.15 K were estimated computationally: $C_{p,m}^{\circ}(\text{1-phenylnaphthalene}, g) = 217.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $C_{p,m}^{\circ}(\text{2-phenylnaphthalene}, g) = 217.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $C_{p,m}^{\circ}(\text{2-(biphen-3-yl)naphthalene}, g) = 301.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $C_{p,m}^{\circ}(\text{2-(biphen-4-yl)naphthalene}, g) = 301.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

The standard molar entropies of sublimation/vaporization, at $T = 298.15 \text{ K}$, were calculated by the following equations:

$$\Delta_{cr}^{\circ}S_m^{\circ}(T = 298.15 \text{ K}) = \Delta_{cr}^{\circ}S_m^{\circ}(T, p(T)) + \Delta_{cr}^{\circ}C_{p,m}^{\circ} \cdot \ln(298.15 \text{ K}/T) - R \cdot \ln\{p^{\circ}/p(T)\} \quad (13)$$

$$\Delta_{f}^{\circ}S_m^{\circ}(T = 298.15 \text{ K}) = \Delta_{f}^{\circ}S_m^{\circ}(T, p(T)) + \Delta_{f}^{\circ}C_{p,m}^{\circ} \cdot \ln(298.15 \text{ K}/T) - R \cdot \ln\{p^{\circ}/p(T)\} \quad (14)$$

where $p^{\circ} = 10^5 \text{ Pa}$. The standard molar Gibbs free energies of sublimation/vaporization were calculated through equations (15) and (16), where the parameters are referred to $T = 298.15 \text{ K}$:

$$\Delta_{cr}^{\circ}G_m^{\circ} = \Delta_{cr}^{\circ}H_m^{\circ} - 298.15 \cdot \Delta_{cr}^{\circ}S_m^{\circ} \quad (15)$$

$$\Delta_{f}^{\circ}G_m^{\circ} = \Delta_{f}^{\circ}H_m^{\circ} - 298.15 \cdot \Delta_{f}^{\circ}S_m^{\circ} \quad (16)$$

The standard molar enthalpy, entropy and Gibbs free energy of sublimation for 2-(biphen-3-yl)naphthalene were estimated based on the experimental values of fusion and vaporization. For the temperature correction calculation the values of heat capacity determined previously were used.

Table 4 lists the derived standard ($p^{\circ} = 10^5 \text{ Pa}$) molar enthalpies, entropies, and Gibbs free energies of sublimation/vaporization and the vapour pressures, at $T = 298.15 \text{ K}$, for naphthalene, 1-phenylnaphthalene, 2-phenylnaphthalene, 2-(biphen-3-yl)naphthalene, and 2-(biphen-4-yl)naphthalene.

TABLE 4

Standard molar enthalpies, entropies and Gibbs free energies of sublimation/vaporization and vapour pressures, at $T = 298.15 \text{ K}$, for naphthalene, 2-phenylnaphthalene, 2-(biphen-4-yl)naphthalene, and 2-(biphen-3-yl)naphthalene

Compound	$\Delta_{cr}^{\circ}H_m^{\circ}/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{cr}^{\circ}S_m^{\circ}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	$\Delta_{cr}^{\circ}G_m^{\circ}/(\text{kJ} \cdot \text{mol}^{-1})$	p/Pa
Naphthalene (cr)	72.698 ± 0.038 [20]	168.08 ± 0.13 [20]	22.583 ± 0.002 [20]	11.06
2-Phenylnaphthalene (cr)	107.8 ± 0.6	211.5 ± 1.8	44.8 ± 0.8	$(14.4 \pm 4.7) \cdot 10^{-4}$
2-(Biphen-4-yl)naphthalene (cr)	140.2 ± 1.3	228.0 ± 3.6	72.2 ± 1.7	$(2.3 \pm 1.5) \cdot 10^{-9}$
2-(Biphen-3-yl)naphthalene (cr)	131.4 ± 1.4	234.2 ± 3.6	61.5 ± 1.8	$(1.7 \pm 1.2) \cdot 10^{-6}$
	$\Delta_{f}^{\circ}H_m^{\circ}/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{f}^{\circ}S_m^{\circ}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	$\Delta_{f}^{\circ}G_m^{\circ}/(\text{kJ} \cdot \text{mol}^{-1})$	
2-(Biphen-3-yl)naphthalene (l)	118.6 ± 1.5	198.5 ± 4.1	59.4 ± 2.0	$(4.0 \pm 3.1) \cdot 10^{-6}$

TABLE 5

Fusion temperatures (T_{onset}), standard molar enthalpies of fusion, $\Delta_{cr}^{\circ}H_m^{\circ}$, and standard molar entropies of fusion, $\Delta_{cr}^{\circ}S_m^{\circ}$, for 2-phenylnaphthalene, 2-(biphen-3-yl)naphthalene, and 2-(biphen-4-yl)naphthalene

Compound	$T_{\text{onset}}/\text{K}$	$\Delta_{cr}^{\circ}H_m^{\circ}(T_{\text{onset}})/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_{cr}^{\circ}S_m^{\circ}(T_{\text{onset}})/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
2-Phenylnaphthalene	373.5 ± 0.2	17.90 ± 0.12	47.9 ± 0.3
2-(Biphen-4-yl)naphthalene	489.5 ± 0.5	25.10 ± 0.10	51.3 ± 0.2
2-(Biphen-3-yl)naphthalene	346.3 ± 0.1	18.50 ± 0.18	53.4 ± 0.5

The experimental temperatures, standard molar enthalpies and entropies of fusion for 2-phenylnaphthalene, 2-(biphen-3-yl)naphthalene, and 2-(biphen-4-yl)naphthalene are presented in table 5.

4. Discussion

In the literature no data concerning the thermodynamics of phase transition of the studied compounds were found.

The compound 1-phenylnaphthalene is liquid at room temperature, showing a remarkably low temperature of melting when compared with the 2-phenylnaphthalene isomer ($m.p = 373.5 \text{ K}$) and naphthalene ($m.p. = 353.35 \pm 0.04 \text{ K}$) [8]. It is also worth mentioning that the enthalpy of melting of 2-phenylnaphthalene, $\Delta_{cr}^{\circ}H_m^{\circ}(373.5 \text{ K}) = (17.90 \pm 0.12) \text{ kJ} \cdot \text{mol}^{-1}$, is lower than the enthalpy of melting of naphthalene $\Delta_{cr}^{\circ}H_m^{\circ}(353.35 \text{ K}) = (19.06 \pm 0.08) \text{ kJ} \cdot \text{mol}^{-1}$ [8]. A significant increment of $7.2 \text{ kJ} \cdot \text{mol}^{-1}$ on the enthalpy of fusion was found for the addition of a phenyl group in the *para* position from 2-phenylnaphthalene to 2-(biphen-4-yl)naphthalene.

The standard molar enthalpy of vaporization of 1-phenylnaphthalene, $\Delta_{f}^{\circ}H_m^{\circ}(298.15 \text{ K}) = (81.0 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$, is about $15 \text{ kJ} \cdot \text{mol}^{-1}$ lower than the standard molar enthalpy of vaporization of 2-phenylnaphthalene, $\Delta_{f}^{\circ}H_m^{\circ}(298.15 \text{ K}) = (95.5 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$ (estimated using the values of the thermodynamic parameters relative to the fusion, sublimation and heat capacity correction to 298.15 K).

Using the following literature data for naphthalene together with the results obtained in this work for 2-phenylnaphthalene and 2-(biphen-4-yl)naphthalene, a gradual increment on $\Delta_{cr}^{\circ}C_m^{\circ}(298.15 \text{ K})$ and $\Delta_{cr}^{\circ}H_m^{\circ}(298.15 \text{ K})$, with the increment of a phenyl group was found. The trend in $\Delta_{cr}^{\circ}S_m^{\circ}(298.15 \text{ K})$ is less regular than in $\Delta_{cr}^{\circ}H_m^{\circ}(298.15 \text{ K})$ and this is therefore reflected in the trend of the $\Delta_{cr}^{\circ}G_m^{\circ}(298.15 \text{ K})$ of the series. The volatility of naphthalene is lower than what could be expected from the extrapolation of the 2-phenylnaphthalene and 2-(biphen-4-yl)naphthalene results. This result is in agreement with the greater structural symmetry of naphthalene relative to the phenyl-naphthalene derivatives and should reflect an additional contribution to the entropy of crystalline naphthalene.

The 2-(biphen-3-yl)naphthalene, *meta* substitution of the phenyl group, is significantly more volatile than the *para* isomer, 2-(biphen-4-yl)naphthalene. This increase in volatility is ruled by the

smaller packing energy observed in the *meta* isomer. This is in good agreement with the results and conclusions derived recently in our group [21] concerning the volatility and enthalpies of sublimation of *m*-terphenyl and *p*-terphenyl isomers.

The experimental results and the conclusions that could be derived from them are a contribution to the understanding and modelling of the phase equilibrium thermodynamics of phenyl and polyphenyl derivatives of naphthalene.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2008.04.010.

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