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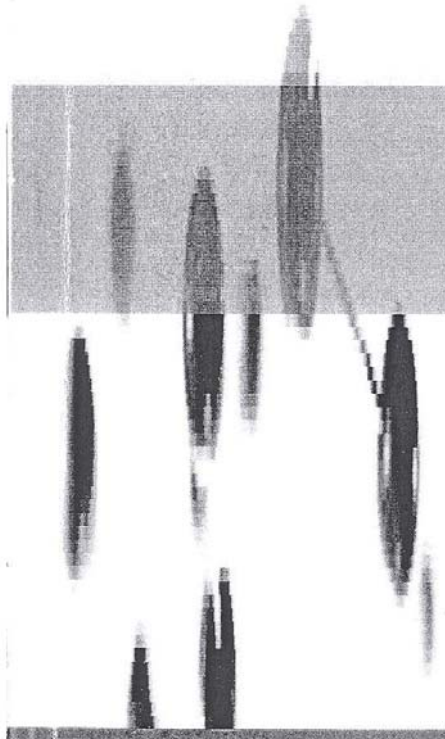

Abstracts Book

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Thermodynamic Study of Phenyl and Biphenyl Naphthalenes

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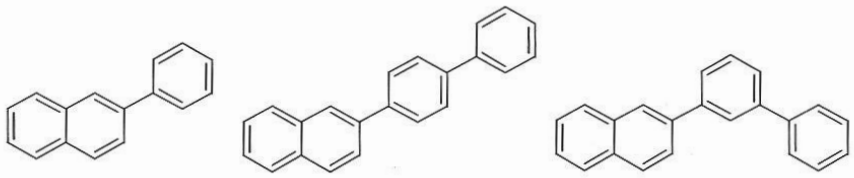
In this work, a contribuition to the thermodynamic study of phenyl and polyphenyl naphthalenes will be presented. The thermodynamic results obtained in the study of phase transition (fusion and sublimation) as well the vapor pressures at different temperatures, will be used to evaluate the energetics of solid-liquid and solid-gas equilibrium. This work is part of a more wide project dealing with the thermodynamic study of oligomers of conducting polymers [1].



I II III

Figure 1 -
I: 2-phenylnaphthalene,
II: 2-(1,1'-biphenyl)-4-ylnaphthalene,
III: 2-(1,1'-biphenyl)-3-ylnaphthalene

For each of these compounds, the vapor pressures at different temperatures were measured by the Knudsen effusion method using the nine cells knudsen effusion apparatus recently described [2]. Based on the previous results the standard molar enthalpies, entropies and Gibbs functions of sulblimation were derived at 298.15 K.
The temperature, molar enthalpies and entropies of fusion were measured by differential scanning calorimetry (DSC).
The thermodynamic results obtained in the study will be used to evaluate the energetics of solid-liquid and solid-gas equilibrium in terms of the contribuition of the increment and relative position of the phenyl group.

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Aim

- The aim of this work is the study of phase change thermodynamics of phenyl and polyphenyl naphthalenes. The obtained thermodynamic results will be used to evaluate the energetic of solid-liquid and solid-gas equilibrium in terms of the contribution of the increment and relative position of the phenyl group.

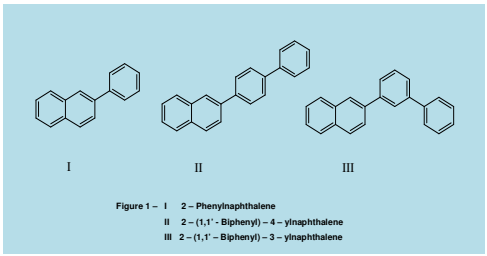


Figure 1 – I 2 – Phenylnaphthalene
II 2 – (1,1' - Biphenyl) – 4 – ylnaphthalene
III 2 – (1,1' – Biphenyl) – 3 – ylnaphthalene

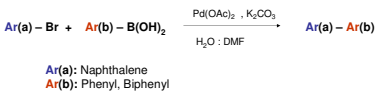
- By the Knudsen effusion method, the vapour pressures (from 0.1 to 1.0 Pa) at different temperatures were measured. Based on these results, the standard molar enthalpies, entropies and Gibbs energies of sublimation were derived for 2-phenylnaphthalene (333,11–353,19 K) and 2-(1,1'-biphenyl)-4-ylnaphthalene (405,17–437,19 K) and of vaporization for 2-(1,1'-biphenyl)-3-ylnaphthalene (381,08–413,17 K), at 298,15 K.

- By differential scanning calorimetry (dsc), the following parameters were measured:
  - Melting temperatures
  - Standard molar enthalpies of melting
  - Standard molar entropies of melting

Experimental

Synthesis

- The compounds were synthesized by Suzuki cross-coupling reaction based in a procedure optimized for an water - DMF solution. [1]



Ar(a): Naphthalene
Ar(b): Phenyl, Biphenyl

- The compounds were purified by recrystallization with ethanol and sublimation under vacuum.

- The purity and the characterization of the compounds were performed by G.C. (gas chromatography), elemental analysis and NMR spectroscopy .

DSC (Differential Scanning Calorimetry)

- DSC (Setaram, model DSC 141)
  Hermetic closed stainless steel crucibles were used in this work using 5 to 20 mg of sample in each experiment.

- The temperature and heat flow calibration was based on measurements performed with benzil, naphthalene, p-anisic acid and benzoic acid, as recommended in the literature[2], with 2 K·min^{-1} as the scanning rate.

- The temperature scanning of the samples were done in all the cases at 2 K·min^{-1}, from 298 K to a final temperature, 30K above the melting temperature.

Knudsen effusion method

- The vapour pressures at different temperatures were measured using the Knudsen effusion apparatus as recently described in the literature.[3]

- The used Knudsen effusion apparatus enables the simultaneous operation of nine cells, which may be controlled at three different temperatures, during one effusion experiment.

- By keeping the same temperature for each group of three effusioon cells with different orifice areas, deviation of results from the equilibrium pressures at three different temperatures may be checked simultaneously.

- In one experimental run the equilibrium pressures at three different temperatures are determined.

Figure 2 – Picture of the Knudsen effusion apparatus

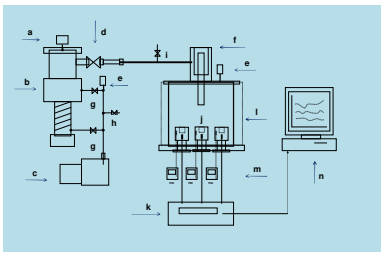


Figure 3 – Schematic representation of the new effusion apparatus. a, inverted magnetron gauge Edwards AIM-S; b, oil diffusion pump Edwards cryo-cooled diffstak CR160; c, Rotary pump Edwards RV12; d, isolation valve Edwards IPV40 MKS; e, Pirani gauges Edwards APG-M; f, glass cold finger for liquid nitrogen; g, Speedivalves Edwards SP25K; h, air admittance valve AV10K; i, teflon greaseless gas admittance valve J. Young ALS1; j, aluminium blocks (ovens); k, data logger Agilent 34970A; l, glass bell jar; m, PID temperature controllers Omron E5CN; n, computer.

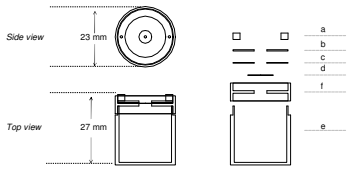


Figure 4 – Schematic side and top views of the effusion cell. a, brass ring; b, brass disk; c, teflon disk; d, platinum foil; e and f, aluminium cell with aluminium lid. At the bottom: picture of the nine cells with a detail of the platinum orifice.

Results

Table 1 – Temperature, standard molar enthalpies and entropies of melting

Compound	T_{fus} / K	$\Delta_{cr}^{l} H_m$ / kJ·mol^{-1}	$\Delta_{cr}^{l} S_m^o$ / J·K^{-1}·mol^{-1}
2 - Phenylnaphthalene	373.3 ± 0.2	21.1 ± 0.1	56.4 ± 1.0
2 - (1,1'-Biphenyl)-4-ylnaphthalene	489.1 ± 0.5	26.6 ± 0.1	54.5 ± 0.7
2 - (1,1'-Biphenyl)-3-ylnaphthalene	346.17 ± 0.06	22.1 ± 0.3	63.9 ± 1.7

Table 2 – Fitting parameters of the equation $\ln(p/p^o) = a + b/(T/K)$, where p^o = 1 Pa, and the thermodynamic parameters of sublimation at the mean temperature

Orifice	a	b	r^2	$\langle T \rangle$ / K	$p(\langle T \rangle)$ / Pa	$\Delta_{cr}^{g} H_m(\langle T \rangle)$ / kJ·mol^{-1}	$\Delta_{cr}^{g} S_m(\langle T \rangle, p(\langle T \rangle))$ / J·K^{-1}·mol^{-1}
2-Phenylnaphthalene (cr)							
Small	36.38 ± 0.23	-12780 ± 78	0.9998		0.424	106.3 ± 0.6	309.6 ± 1.9
Medium	36.53 ± 0.13	-12831 ± 44	0.9999	343.15	0.421	106.7 ± 0.4	310.9 ± 1.1
Large	36.13 ± 0.19	-12699 ± 65	0.9998		0.416	105.6 ± 0.5	307.7 ± 1.6
Global Results	**36.37 ± 0.13**	**-12779 ± 44**	**0.9997**	**343.15**	**0.420**	**106.2 ± 0.4**	**309.6 ± 1.1**
2-(1,1'-Biphenyl)-4-ylnaphthalene (cr)							
Small	37.74 ± 0.15	-16421 ± 63	0.9998		0.287	136.5 ± 0.5	324.2 ± 1.2
Medium	38.11 ± 0.20	-16576 ± 85	0.9997	421.18	0.288	137.8 ± 0.7	327.2 ± 1.7
Large	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**
2-(1,1'-Biphenyl)-3-ylnaphthalene (l)							
Small	30.60 ± 0.51	-12625 ± 203	0.9987		0.304	105.0 ± 1.7	264.3 ± 3.3
Medium	30.72 ± 0.61	-12654 ± 244	0.9978	397.13	0.317	105.2 ± 2.0	264.9 ± 3.6
Large	30.02 ± 0.70	-12381 ± 278	0.9975		0.314	102.9 ± 2.3	259.2 ± 3.8
Global Results	**30.45 ± 0.36**	**-12557 ± 142**	**0.9975**	**397.13**	**0.312**	**104.4 ± 1.2**	**262.9 ± 2.7**

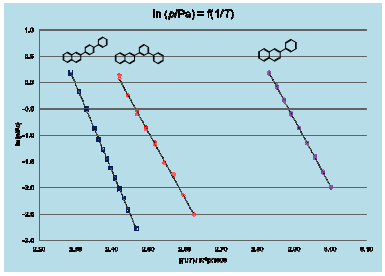


Figure 5 – Plots of ln (p/Pa) = f(1/T) for the global results obtained for each compound

Table 3 – Standard (p^o = 10^5 Pa) molar enthalpies, entropies and Gibbs energies of sublimation and vaporization at T = 298.15 K for the studied compounds

Compound	$\Delta_{cr}^{g} H_m$ / kJ·mol^{-1}	$\Delta_{cr}^{g} S_m^o$ / J·K^{-1}·mol^{-1}	$\Delta_{cr}^{g} G_m$ / kJ·mol^{-1}
2 - Phenylnaphthalene (cr)	107.8 ± 0.5	211.7 ± 1.6	44.7 ± 0.7
2 - (1,1'-Biphenyl)-4-ylnaphthalene (cr)	142.0 ± 1.1	233.0 ± 3.0	72.5 ± 1.4
2 - (1,1'-Biphenyl)-3-ylnaphthalene (l)	120.5 ± 1.6	204.2 ± 4.3	59.7 ± 1.7

Discussion

- The 2-(1,1'-biphenyl)-3-ylnaphthalene (phenyl in ***meta*** position) show a melting temperature 143 K lower than the 2-(1,1'-biphenyl)-4-ylnaphthalene (phenyl in ***para*** position).
- An increase of 5.5 kJ·mol^{-1} in the standard molar enthalpies of melting was observed from 2-phenylnaphthalene to 2-(1,1'-biphenyl)-4-ylnaphthalene (***para***). the standard molar enthalpies of melting of the 2-(1,1'-biphenyl)-3-ylnaphthalene (***meta***) is identical to the 2-phenylnaphthalene.
- At the same reference temperature the 2-Phenylnaphthalene has a higher vapour pressure than 2-(1,1'-biphenyl)-4-ylnaphthalene (***para***) as expected.
- Using the obtained results, the vapour pressure, of the two biphenyl isomers can be estimated: 66 and 119 Pa at the temperature of melting (T=489.1 K) of the 2-(1,1'-biphenyl)-4-ylnaphthalene (***para***). This results show that the volatility of the ***meta*** isomer is higher that the ***para*** isomer. The difference in volatility between the two isomers (***meta*** and ***para***) is anyway much smaller than could be expected from the big difference of the melting temperatures.

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