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INTRA-MOLECULAR AROMATIC π-π INTERACTIONS IN ARYLNAPHTHALENES

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Aromatic π-π interactions[1] are non-covalent interactions between aromatic moieties that contribute for the crystal packing of aromatic compounds, for the conformation of bio-macromolecules and are also relevant in molecular recognition processes[2, 3]. The true nature of these interactions remains not yet totally clear. Aromatic π-π interaction is a relatively weak attractive interaction (about 5 to15 kJ·mol^{-1}) that is masked by other overwhelming ones.

In this work, an experimental and theoretical approach concerning the relation between molecular structure and energetic in 1-arylnaphthalene and 1,8-diarylnaphthalene derivatives (illustrated in figure 1) was used to evaluate the intra-molecular π-π interactions between the two aryl groups.
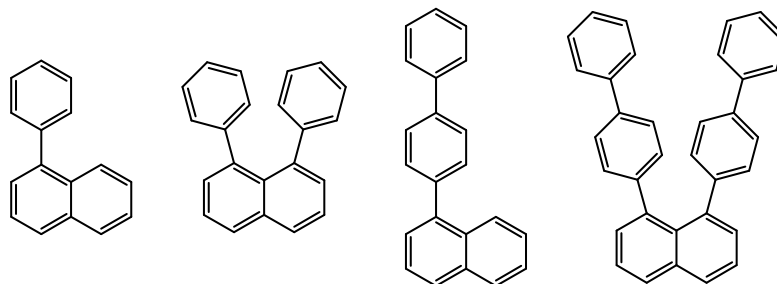

Figure 1. Schematic structural formulas of: 1-phenylnaphthalene, 1,8-diphenylnaphthalene, 1-(biphen-4-yl)naphthalene, 1,8-di(biphen-4-yl)naphthalene.

The compounds were synthesized by the Suzuki-Miyaura cross-coupling reaction[4] and were structurally characterized by X-ray crystallography. A thermodynamic study comprising combustion calorimetry, differential scanning calorimetry (dsc), Calvet microcalorimetry and vapour pressure measurements on a quartz microbalance Knudsen effusion apparatus, was carried out for the mentioned compounds.

The experimental results concerning the aromatic π-π interactions were supported and complemented by a theoretical (DFT and MP2) structural and energetic analysis.

[1] C. Hunter, K. Lawson, J. Perkins, C. Urch, J. Chem. Soc., Perkin Trans. 2001, **2,** 651.
[2] F. Cozzi, J. Siege, Pure Appl. Chem., 1995, **67**, 683.
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AROMATIC π-π INTERACTIONS IN ARYLNAPHTHALENES

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Introduction

Aromatic π-π interactions [1] are non-covalent interactions between aromatic moieties that contribute for the crystal packing of aromatic compounds, for the conformation of bio-macromolecules and are also relevant in molecular recognition processes [2, 3]. The true nature of this relatively weak attractive interaction (about 5 to 15 kJ·mol⁻¹) remains not totally clear.
In this work, an experimental and theoretical approach concerning the relation between molecular structure and energetic in 1-arylnaphthalene and 1,8-diarylnaphthalene derivatives (illustrated in figure 1) is used to evaluate the intra-molecular π-π interactions between the aryl groups.
The compounds were synthesized by the Suzuki-Miyaura cross-coupling reaction [4] and were structurally characterized by X-ray crystallography. A thermodynamic study comprising combustion calorimetry, differential scanning calorimetry (dsc), and vapour pressure measurements on a combined Knudsen-Quartz crystal effusion apparatus is being carried out for the mentioned compounds.
The experimental results concerning the aromatic π-π interactions are supported and complemented by a theoretical (DFT and MP2) structural and energetic analysis.
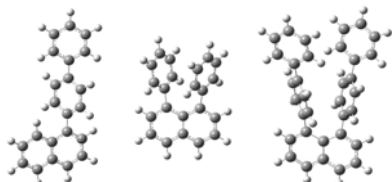

Figure 1 – Optimized geometries for the studied arylnaphthalenes at the MP2/cc-pVDZ level of theory.

Experimental

Synthesis, purification and characterization

All the compounds were synthesised by the Suzuki-Myaura cross-coupling methodology as illustrated in figure 2 for the case of 1,8-diphenylnaphthalene.
All the three compounds were purified by standard recristalization techniques and sublimation under reduced pressure. They were characterized by X-ray crystallography, elemental analysis and ¹H-RMN.
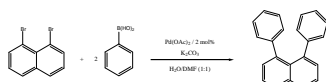

Figure 2 – Suzuki-Myaura cross-coupling reaction scheme for 1,8-diphenylnaphthalene.

X-Ray Crystallography

Solid state crystalline characterization of the compounds shows the conformations assumed by the molecules. The supramolecular structure can be related with sublimation thermodynamics.
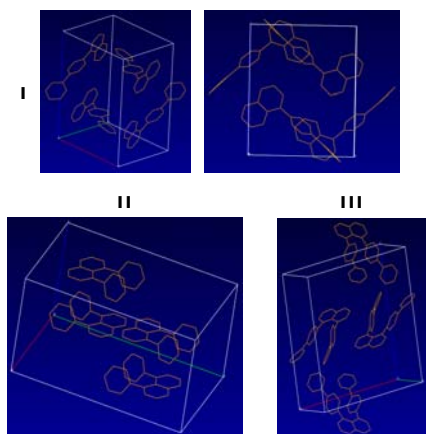

Figure 3 – Unit cells for (I) 1-(byphen-4-yl)naphthalene (II) 1,8-diphenylnaphthalene and (III) 1,8-di(byphen-4-yl)naphthalene. I and II crystallizes in P21/c and III crystallizes in P21/n space groups. Hydrogen's are omitted for clarity.

Knudsen-Quartz crystal effusion technique

The phase transition thermodynamics for this series of compounds were studied on a Knudsen-Quartz crystal effusion apparatus (KNQ) recently developed in our laboratory. This technique is based on the simultaneous gravimetric and quartz crystal microbalance mass loss detection that enables the decrease of the sample size and effusion time and can be used at temperatures up to 650 K.
A fraction of the vapour effused from the cell's orifice condenses on the surface of the quartz crystal causing a decrease in the resonance frequency, f.
The rate of change of the crystal frequency with time, (df/dt), is proportional to the mass, Δm, of vapour effused from the cell during the time interval Δt allowing the calculation of vapour pressure at equilibrium from the Knudsen equation:

$$p = (\Delta m/\Delta t \cdot A_o \cdot w_o) \cdot (2\pi RT/M_M)^{0.5} \qquad (2)$$

Measuring the change of slope, (df/dt), with temperature (figure 5), and using the Clausius-Clapeyron equation one obtains the molar enthalpy, entropy and Gibbs energy of sublimation at the mean temperature $<T>$. A heat capacity correction is then applied for the determination of these thermodynamic parameters at T = 298.15 K.
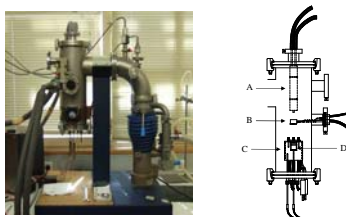

Figure 4 – Picture and schematic view of the Knudsen-Quartz apparatus: A (cold-finger); B (quartz crystal resonator); C (oven); D (Knudsen cell).
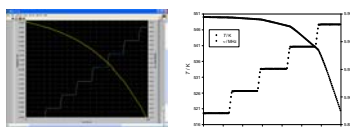

Figure 5 – Data aquisition on a typical KNQ experiment showing the change of the slope (df/dt) with temperature.
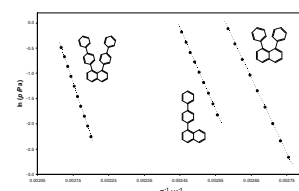

Figure 6 – Plots of $\ln(p/Pa) = f(1/T)$ for the three compounds studied by the KNQ technique. R^2 for the straight lines are: 1,8-di(byphen-4-yl)naphthalene, 0.99996; 1-(byphen-4-yl)naphthalene, 0.99992; 1,8-diphenylnaphthalene, 0.99999.

Computational Study

• Geometry optimization at the MP2/cc-pVDZ level of theory.

• ZPE and thermal correction to the enthalpy (H_{corr}) for 298.15 K were determined based on the frequencies calculation at the B3LYP/6-311++G(d,p) level.

• Use of an homodesmic reaction scheme (figure 7) for the evaluation of the intra-molecular π-π interaction.

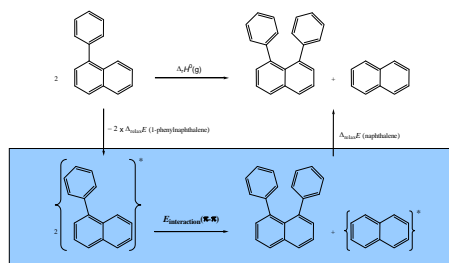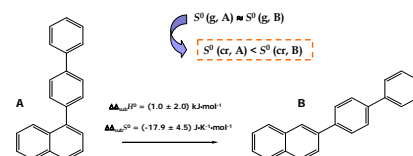• Correlation with experimental results of $\Delta_f H^0$ (g, 298.15 K).

Figure 7 – Homodesmic reaction scheme used for the evaluation of the intra-molecular π-π interaction. The molecules in parenthesis refer to an hypothetical "distorted" species adopting the geometry of that molecular framework in 1,8-diphenylnaphthalene.

Results & Discussion

The sublimation and computational results obtained so far are summarized below...

S^0 (g, A) ≈ S^0 (g, B)

S^0 (cr, A) < S^0 (cr, B)

$\Delta\Delta_{sub}H^0$ = (1.0 ± 2.0) kJ·mol⁻¹
$\Delta\Delta_{sub}S^0$ = (-17.9 ± 4.5) J·K⁻¹·mol⁻¹

Results 1 – The difference in volatility between the two isomers arises mainly from the entropic term. The sublimation parameters for 2-(byphen-4-yl)naphthalene were taken from ref. 5.
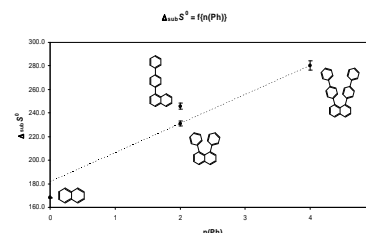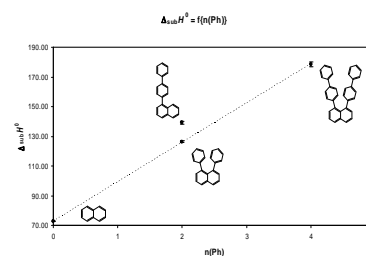
Results 2 – A linearity in $\Delta_{sub}H^0$ (kJ·mol⁻¹) is observed for the series of 1,8-diarylnaphthalenes. This trend is not followed by $\Delta_{sub}S^0$ (J·K⁻¹·mol⁻¹). This is a consequence of the higher structural symmetry of naphthalene which raises it's crystalline entropy relative to the series of phenylnaphthalenes.
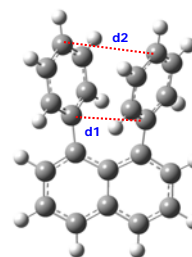
	DFT	MP2	X-Ray
d1 / Å	3.07	2.96	2.98
d2 / Å	4.73	3.87	3.99

Results 3 - Comparison between DFT and MP2 optimized geometries shows a significant shortening of aryl-aryl distance at the MP2 method. This is probably due to the better description of dispersive interactions by MP2 relative to DFT. X-Ray distances are shown for comparison. This fact supports the existence of a significant interaction of dispersive nature between the stacked aryl rings.

Future work…

• Combustion calorimetry is being employed for the determination of $\Delta_f H^0$ (cr, 298.15 K) and subsequent derivation of $\Delta_f H^0$ (g, 298.15 K).
• A series of para-substituted 1,8-diphenylnaphthalenes is being study for the evaluation of the substituent effect on the intra-molecular interaction between the two phenyl rings.
• Other molecular systems are under investigation with the objective of fully explore and characterize the π-π interaction in terms of energetic and structural aspects.

References
[1] C. Hunter, K. Lawson, J. Perkins, C. Urch, *J. Chem. Soc., Perkin Trans. 2*, **2001**, 651-669.
[2] F. Cozzi, J. Siege, *Pure & Appl. Chem.*, **1995**, 67, 683-689.
[3] P. Hobza et. al., *J. Phys. Chem. A*, **2007**, 111, 3446-3457.
[4] N. Miyaura, A. Suzuki, *Chem. Rev.*, **1995**, 95, 2457.
[5] M.A.A. Rocha et. al., *J. Chem. Thermodyn.*, **2008**, doi:10.1016/j.jct.2008.04.010.