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THERMODYNAMIC STUDY OF DIPHENYLPYRIDINES

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Polyphenylpyridines are promising compounds for the use in electronic material (OLED's; photovoltaic cells; sensors; OTET's) due to their high electronic correlation. The energetic and structural study of compounds with potential application as conducting or electronics organic materials is actually an important research target in our laboratory[1-3].

This work focuses the thermodynamic study of some diphenylpyridine isomers, shown in figure 1, in order to understand the relationship between structure, energetics and electronic correlation.
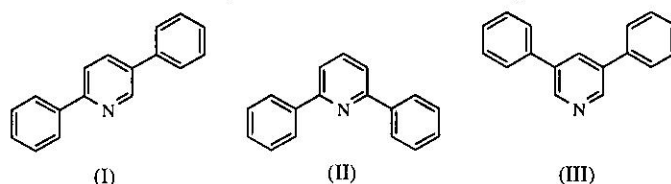

Figure 1. Schematic structural formulas of: (I) 2,5-diphenylpyridine; (II) 2,6-diphenylpyridine; (III) 3,5-diphenylpyridine.

The compounds were synthesized using the Suzuki-Miyaura methodology[4]. For the three isomers, the standard molar enthalpies of formation on crystalline state were derived, at T=298.15 K, by static bomb combustion calorimetry. The vapour pressures of the considered compounds were determined by a static apparatus based on a MKS capacitance diaphragm manometer recently described in the literature[5]. Based on the previous results the standard molar enthalpies, entropies and Gibbs functions of sublimation were derived at T=298.15 K. Trough the standard molar enthalpies of formation in the condensed phase and the standard molar enthalpies of sublimation, the standard molar enthalpies of formation in the gaseous phase were derived for the three isomers. The relationship between structure, energetics and electronic correlation will be discussed based on the experimental energetics results and *ab-initio* calculation.

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THERMODYNAMIC STUDY OF DIPHENYLPYRIDINES

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AIM

Polyphenylpyridines are interesting organic compounds due to the conjugated aromatic π system and thus they are promising compounds for the use in electronic materials. This work presents, the thermodynamic study of diphenylpyridines isomers (Figure 1) and is focused on the relationship between energetic and structural properties.

❏ The compounds were synthesized using the Suzuki-Miyaura cross-coupling reaction and characterized structuraly by X-ray.
❏ The vapour pressures of 2,5-diphenylpyridine, 2,6-diphenylpyridine and 3,5-diphenylpyridine were measured on a Static apparatus based on a MKS capacitance diaphragm manometer.
❏ The standard molar enthalpies of sublimation were measured by Calvet microcalorimetry and the temperature, standard molar enthalpies and entropies of fusion by differential scanning calorimetry.
❏ The standard molar enthalpies of formation in gas phase were derived based on the standard molar enthalpies of formation in crystalline phase, determined by static-bomb combustion calorimetry, and the standard molar enthalpies of sublimation for the three isomers.
❏ The three isomers were studied by ab-initio computational chemistry: geometry optimization, energetic analysis and aromaticity analysis (NICS).
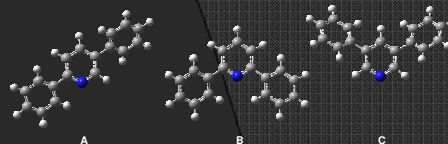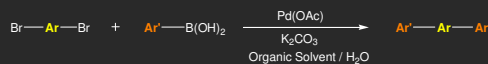

Figure 1 - 2,5–diphenylpyridine (A); 2,6-diphenylpyridine (B); 3,5-diphenylpyridine (C)

EXPERIMENTAL

Synthesis, Purification and Characterization

The three isomers, 2,5-diphenylpyridine, 2,6-diphenylpyridine, and 3,5-diphenylpyridine, were synthesized using the Suzuki – Miyaura[1] cross – coupling method based on a procedure optimized for an water – organic solvent.

$$Br \!-\! Ar \!-\! Br \;+\; Ar' \!-\! B(OH)_2 \xrightarrow[\text{Organic Solvent / H}_2\text{O}]{\text{Pd(OAc)}\;\;\text{K}_2\text{CO}_3} Ar' \!-\! Ar \!-\! Ar'$$

Ar: Pyridine
Ar': Phenyl

❏ The compounds were purified by recrystallization with methanol and successive sublimation under vacuum.
❏ The purity and the characterization of the compounds were performed by G.C. (gas chromatography), elemental analysis, NMR spectroscopy and X-ray (Figure 3). [2]

Static-Bomb Combustion Calorimetry

❏ The standard massic energy of combustion for crystalline for the studied compounds were determined, at T = 298.15 K, using a isoperibol static-bomb combustion calorimeter.
❏ Temperature were measured with a resolution of $\pm 2 \times 10^{-5}$ K at intervals of 10 seconds, with a calibrated ultra-stable thermistor (Thermometrics model S10) using a 7½ digits nano-ohm meter (HP model 34420A) interfaced to a computer programmed to compute the adiabatic temperature change based on software LABTERMO V3.0. [3]

Static Apparatus: Absolute Capacitance Manometer

❏ The vapour pressures were measured using the Static apparatus recently described in the literature. [4]
❏ The Static apparatus, is based on a absolute (MKS Baratron 631A) type capacitance diaphragm manometer, enables the measurement of vapour pressures in the pressure range (0.4 – 133) Pa and (0.4 – 1333) Pa and temperature range (243 to 473) K.

Calvet Microcalorimetry

❏ The standard (p^o = 10^5 Pa) molar enthalpies of sublimation for the three compounds were measured by Calvet microcalorimetry, model SETARAM HT 1000, using a similar technique of the drop-method. [5] The measuring procedure and the description of the apparatus is described in the literature. [6]

Differential Scanning Calorimetry

❏ The temperature and the standard molar enthalpies of fusion for the studied compounds were measured using a power compensation differential scanning calorimeter, model SETARAM DSC 141, at a heating rate of 2 K·min⁻¹.
❏ The temperature scale and heat flow scale were calibrated based on measurements performed with naphthalene, *p*-anisic acid, benzoic acid, indium and tin using the same procedure of the previously experiments.

COMPUTATIONAL CHEMISTRY

❏ The structure and energetics of pyridine (Py), 2,5-diphenylpyridine (2,5-DPPy), 2,6-diphenylpyridine (2,6-DPPy) and 3,5-diphenylpyridine (3,5-DPPy) were studied by computational chemistry using density functional theory (DFT) [7], second-order Møller-Plesset perturbation theory (MP2) [8] and spin-component-scaled second-order Møller-Plesset perturbation theory (SCS-MP2).[9]
- The geometry optimizations were performed by DFT with the B3LYP/6-311++G(d,p) level of theory and MP2 with the cc-pvdz basis set.
- Fundamental frequencies calculations were performed by DFT with the B3LYP/6-311++G(d,p) level of theory.
- At the level of theory B3LYP/6-311++G(d,p), the NICS (Nucleus Independent Chemical Shifts) were calculated for a set of ghost atoms scanning (-2 to +2 Å) from the center of the pyridine ring.

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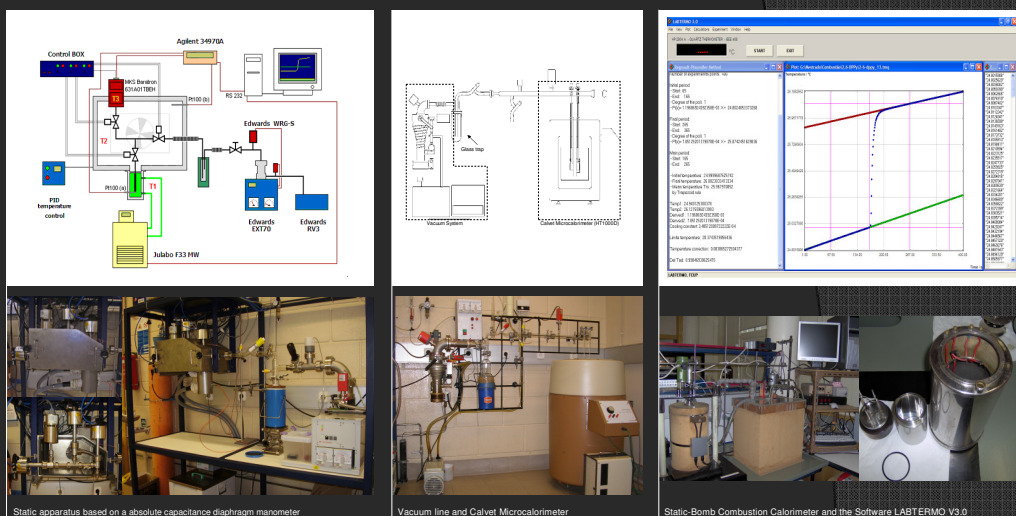[9] - S. Grimme, *J. Chem. Phys.*, 2003, 118, 909

Static apparatus based on a absolute capacitance diaphragm manometer

Vacuum line and Calvet Microcalorimeter

Static-Bomb Combustion Calorimeter and the Software LABTERMO V3.0

Figure 2 – Images and schematic representations of the experimental measuring apparatus.

RESULTS
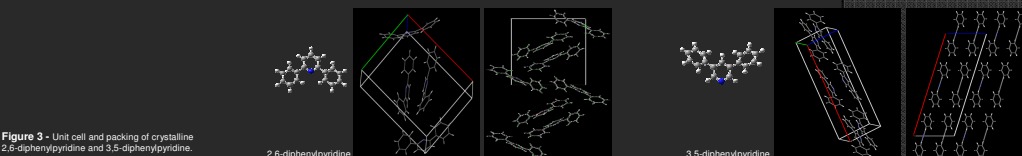
Figure 3 - Unit cell and packing of crystalline 2,6-diphenylpyridine and 3,5-diphenylpyridine.
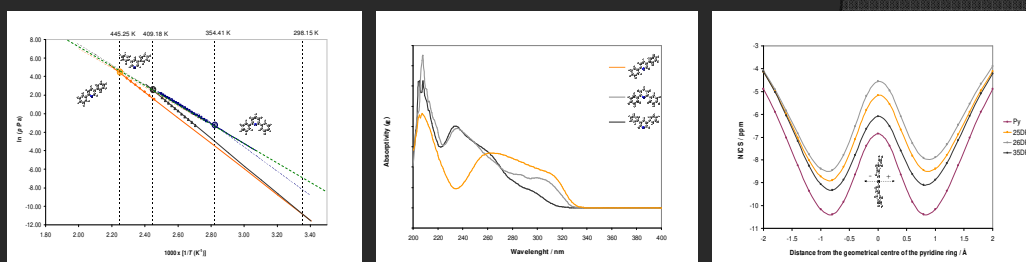
2,6-diphenylpyridine

3,5-diphenylpyridine

Figure 4 – Plots of ln (p/Pa) = f(1/T) for the results obtained for each compound. Triple points (circles); 2,6-DPPy - blue lines; 2,5-DPPy - orange lines; 3,5-DPPy - grey lines

Figure 5 – UV-vis spectra of the studied compounds in ethanol (c = 1x10⁻⁴ M) obtained using a diode array spectrophotometer (Agilent UV-vis model 8453) at 298.15 K.

Figure 6 – NICS-scan diagram obtained at the B3LYP/6-311++G(d,p) level of theory for NICS values (ppm) versus the distance from the centre of the pyridine ring plane (Å).

Table 1 – Temperature, standard molar enthalpies and entropies of fusion.

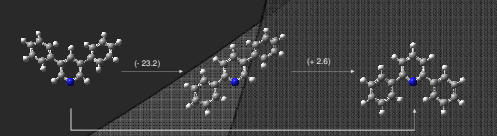| Compound	T_{fus} / K	$\Delta_l^{cr} H_m^o$ / kJ·mol⁻¹	$\Delta_l^{cr} S_m^o$ / J·K⁻¹·mol⁻¹
2,5 - Diphenylpyridine	445.25 ± 0.88	28.7 ± 0.4	64.5 ± 0.8
2,6 - Diphenylpyridine	354.41 ± 0.22	18.7 ± 0.7	52.7 ± 1.9
3,5 - Diphenylpyridine	409.18 ± 0.30	31.8 ± 0.8	77.8 ± 2.0

Figure 7 – Experimental molar enthalpies of isomerization (kJ·mol⁻¹) between the diphenylpyridines isomers.

DISCUSSION

❏ The X-ray data show a weak C-H...π interaction for 2,6-diphenylpyridine and a π...π interaction for 3,5-diphenylpyridine. It was observed that the crystalline packing of the 2,6-DPPy (orthorhombic cell) is significantly different from 3,5-DPPy (monoclinic cell).
❏ Crystalline 2,5-DPPy isomer is significantly less volatile than the other isomers. Identical volatilities of the liquid phase was observed for the three isomers.
❏ The UV-vis spectra of the 2,5-DPPy isomer presents a shift in the absorption band (π → π*) to a higher wavelength compared to the other isomers.
❏ A significant asymmetry is observed in the NICS values profile. A decrease of the NICS values is observed in the isomers with a 2- and 6- position substitution, indicating an increase of conjugation of the phenyl with the pyridine ring, in agreement with a smaller dihedral angle between the ring as observed in X-ray data and in the Ab-initio optimized geometries.
❏ From the experimental thermochemistry results it was found that the 2,5-DPPy and 2,6-DPPy isomers are significantly energetically more stable than the 3,5-DPPy isomer. The energetics of the isomers is in agreement with the structural (experimental and computational) and UV-vis results.