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RESUMOS / ABSTRACTS

Thermodynamic and Theoretical Study of Diphenylpyridines

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The energetic and structural study of phenylpyridines has been a theme of research in our laboratory^[1,2] due to their interesting electronic correlation capabilities. This work focuses the thermodynamic study of some diphenylpyridine isomers (Figure 1), in order to understand the relationship between structure and energetics.

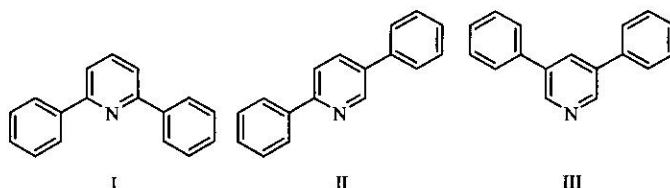


Figure 1. Schematic structural formulas of: (I) 2,6-diphenylpyridine; (II) 2,5-diphenylpyridine; (III) 3,5-diphenylpyridine.

Therefore, the compounds shown in figure 1, were synthesized using the Suzuki-Miyaura methodology.^[3] The standard molar enthalpies of formation for the three isomers on crystalline state will be derived, at $T=298.15$ K by static bomb combustion calorimetry. The vapour pressures of the three isomers will be determined by a static apparatus based on a MKS capacitance diaphragm manometer recently described in the literature.^[4] Through 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 will be derived for the three isomers.

Computational chemistry (Density Functional Theory DFT) will be used in order to perform the geometry optimizations, energetic analysis and to derive the vibrational frequencies for the selected isomers.

References:

- [1] Ribeiro da Silva, M.A.V., Matos, M.A.R., Rio, C.A., Morais, V.M.F., Wang, J., Nichols, G. and Chickos, J.S. (2000), *A Thermochemical and Theoretical Study of the Phenylpyridine Isomers*, Journal Physical Chemistry, 104, 1774–1778.
- [2] Rocha, M. A., Low, J. N., Gomes, L. R., Quesada, A. and Santos, L. M. N. B. F. (2007), *2,6-Diphenylpyridine*, Acta Crystallographica, E63, o4833.
- [3] Miyaura, N. and Suzuki, A. (1995), *Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds*, Chemical Reviews, 95, 2457-2483.
- [4] Monte, M. J. S., Santos, L. M. N. B. F., Fulem, M., Fonseca, J. M. S. and Sousa, C. A. D. (2006), *New Static Apparatus and Vapor Pressure of Reference Materials: Naphthalene, Benzoic Acid, Benzophenone, and Ferrocene*, Journal Chemical and Engineering Data, 51, 757-766.

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Presentation: POSTER



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Aim

- Phenyl and polyphenylpyridines are promising compounds for the use in electronic material [organic light-emitting diodes (OLEDs), photovoltaic cells, sensors, thin film transistors (OTFTs)] because of the possibility of a high electronic correlation.

The aim of this work is the energetic and structural study of diphenylpyridine isomers (Figure 1), in order to understand the relationship between structure, energetics and electronic correlation.

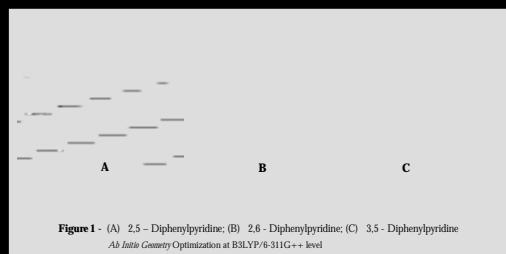


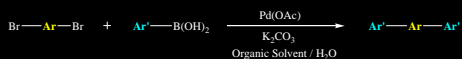
Figure 1 - (A) 2,5 - Diphenylpyridine; (B) 2,6 - Diphenylpyridine; (C) 3,5 - Diphenylpyridine
Ab Initio Geometry Optimization at B3LYP/6-311G++ level

- The compounds were synthesized (Suzuki-Miyaura cross-coupling reaction^[1]) purified and characterized in our laboratory.
- The vapour pressures of 2,5-diphenylpyridine was measured on a static apparatus based on a MKS capacitance diaphragm manometer recently described in the literature.^[2]
- The three isomers and 2,4-diphenylpyridine were studied by ab-initio computational chemistry: geometry optimization, energetic analysis and aromaticity analysis (NICS).

Experimental

Synthesis

- The compounds were synthesized by Suzuki cross-coupling reaction based on a procedure optimized for an water – organic solvent.^[1]



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 2).^[2]

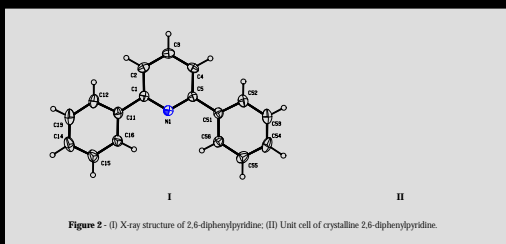


Figure 2 - (I) X-ray structure of 2,6-diphenylpyridine; (II) Unit cell of crystalline 2,6-diphenylpyridine.

Static Apparatus: Absolute Capacitance Manometer

- The vapour pressures for 2,5-diphenylpyridine were measured using the static apparatus described in the literature.^[2]
- The Static apparatus, based on a MKS capacitance diaphragm manometer, enables the measurement of vapour pressures in the pressure range (0.4 – 133) and (0.4 – 1333) Pa and temperature range (243 to 473) K.

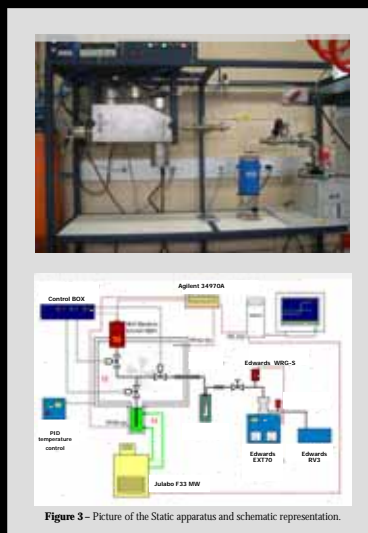
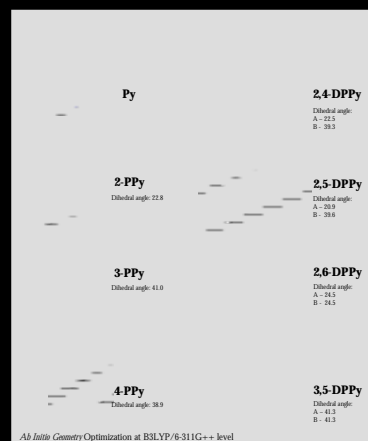


Figure 3 - Picture of the Static apparatus and schematic representation.

Computational Chemistry

- Pyridine (Py), 2-phenylpyridine (2-PPy), 3-phenylpyridine (3-PPy), 4-phenylpyridine (4-PPy), 2,4-diphenylpyridine (2,4-DPPy), 2,5-diphenylpyridine (2,5-DPPy), 2,6-diphenylpyridine (2,6-DPPy) and 3,5-diphenylpyridine (3,5-DPPy) were studied by computational chemistry.
- The geometry optimizations and fundamental frequencies calculations were performed by density functional theory (DFT)^[3] with the hybrid exchange correlation functional B3LYP at the level of theory 6-311++G(d,p).
- Considering the same level of theory [B3LYP/6-311++G(d,p)], the NICS (Nucleus Independent Chemical Shifts) were calculated for a set of ghost atoms.



Ab Initio Geometry Optimization at B3LYP/6-311G++ level

Results

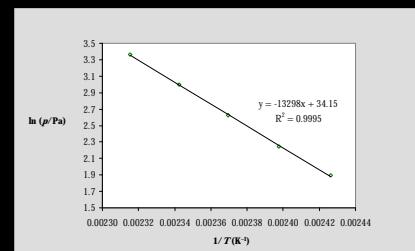


Figure 4 - Plot of $\ln(p/Pa) = f(1/T)$ for the results obtained for 2,5-diphenylpyridine

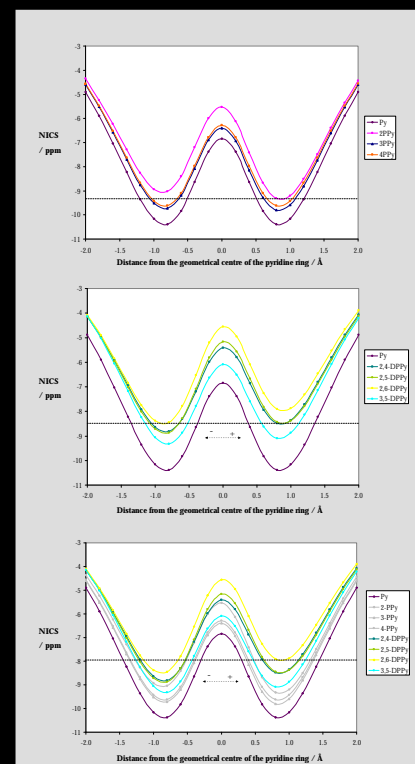


Figure 5 - NICS-scan diagram at the B3LYP/6-311++G(d,p) level of theory for NICS values (ppm) versus the distance from the centre of the pyridine ring plane (Å).

Discussion

- From the X-Ray structure of 2,6-diphenylpyridine a weak C-H... π interaction was found. The dihedral angles between the mean planes of the pyridine rings and the phenyl rings are 29.88 (18)^o (ring attached to C2), and 26.58 (17)^o (ring attached to C6).
- The standard molar enthalpy of sublimation for 2,5-diphenylpyridine, at $T=288.15$ K is (114.3 ± 1.2) kJ \cdot mol⁻¹, considering the value for the heat capacity of sublimation of -30 J \cdot K⁻¹ \cdot mol⁻¹.
- It is observed an asymmetry in the NICS values profile versus the distance from the geometrical centre of the pyridine ring.
- There is evidence of a correlation between the NICS (aromaticity) values and conjugation (dihedral angles of phenyl ring).

References

- [1] Miyaura, N. and Suzuki, A. (1995), *Palladium-Catalyzed Cross-Coupling Reactions of Organoboronic Compounds*, Chemical Reviews, 95, 2457-2483. [2] Rocha, M. A., Lima, J. N., Gomes, L. R., Queiroz, A. and Santos, L. M. N. B. F. (2007), 2,6-Diphenylpyridine. Acta Crystallographica, B63, 04833. [3] Monte, M. J. S., Santos, L. M. N. B. F., Falcão, M., Fonseca, J. M. S. and Sousa, C. A. D. (2000), *New State Apparatus and Vapour Pressure of Reference Materials: Naphthalene, Benzene, Acid Benzoic, and Fennone*, Journal Chemical and Engineering Data, 51, 797-806. [4] Becke, A.D. J. (1993), *A New Mixing of Hartree-Fock and Local Density Functional Theories*, Journal of Chemical Physics, 98, 3698-3692.