20th International Conference on Chemical Thermodynamics

Warsaw, POLAND
August 3-8, 2008
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.

![Structural formulas](image)

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. Though 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.


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.

EXPERIMENTAL

Synthesis, Purification and Characterization

The three isomers, 2,5-diphenylpyridine, 2,6-diphenylpyridine, and 3,5-diphenylpyridine, were synthesized using the Suzuki–Miyaura cross-coupling reaction (Scheme 1) followed by purification of the crude product by recrystallization with methanol and successive sublimation under vacuum.

Static-Bomb Combustion Calorimetry

The standard (g) mass energy of combustion for the studied compounds were determined, at T = 298.15 K, using a bomb calorimeter.

Static Apparatus: Absolute Capacitance Manometer

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

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.

RESULTS

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH₂⁰ (kJ·mol⁻¹)</th>
<th>ΔS₂⁰ (J·K⁻¹·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-DPPy</td>
<td>285.9 ± 0.3</td>
<td>7.0 ± 0.2</td>
</tr>
<tr>
<td>2,6-DPPy</td>
<td>291.9 ± 0.4</td>
<td>7.2 ± 0.2</td>
</tr>
<tr>
<td>3,5-DPPy</td>
<td>289.6 ± 0.3</td>
<td>6.9 ± 0.2</td>
</tr>
</tbody>
</table>

DISCUSSION

The X-ray data show a weak C-H…π interaction for 2,6-diphenylpyridine, and a strong interaction for 3,5-diphenylpyridine. It was observed that the crystaline packing of the 2,5-DPPy (orthorhombic cell) is significantly different from 2,6-DPPy (monoclinic cell).

From the experimental thermodynamic results it was found that the 2,5-DPPy and 2,6-DPPy isomers are significantly more stable than the 3,5-DPPy isomer. The energetics of the structures is in agreement with the structural (experimental and computational) and UV-vis results.

REFERENCES