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Phase Transition thermodynamics of poliphenylbenzenes

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The energetic and structure of solid phase aromatic compounds are ruled not only by the ever present van der Waals interactions but also by the so-called aromatic interactions [1]. These are orientation dependent electrostatic interactions [2] and thus they have a profound impact in the crystal structure and stability of these compounds. In this work we continue the study on the solid-gas equilibrium thermodynamics of a series of poliphenylbenzenes. The enthalpy, entropy and Gibbs energy of sublimation for 1,2,4,5-tetraphenylbenzene and hexaphenylbenzene (represented schematically in figure 1) were derived from the temperature dependence of vapour pressure obtained in a combined quartz-crystal/Knudsen mass-loss effusion apparatus. These results were compared with previous ones for less substituted analogues showing an interesting pattern in volatility. This pattern can be rationalized taking into account three factors: the existence of aromatic π - π interactions, the rotational freedom of the substituting phenyls and the entropy term related to the positional degeneracy in the crystal lattice.

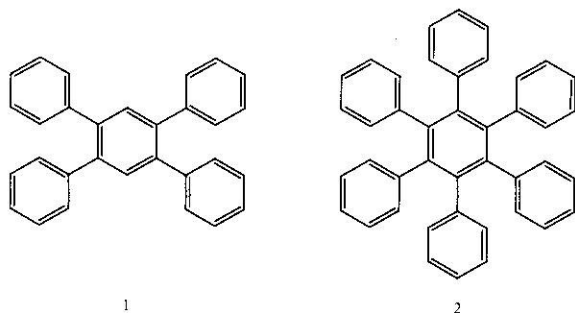


Figure 1 – Schematic structure of 1,2,4,5-tetraphenylbenzene (1) and hexaphenylbenzene (2).

[1] Hunter, C.; Lawson, K.; Perkins, J.; Urch, C. *J. Chem. Soc., Perkin Trans. 2* **2001**, 651-669.

[2] Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2002**, 124, 104-112.

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SUBLIMATION THERMODYNAMICS OF POLIPHENYLBENZENES

Introduction

The energetic and structure of solid phase aromatic compounds are ruled not only by the ever present van der Waals interactions but also by the so called aromatic interactions [1]. These are orientation dependent electrostatic interactions [2] and thus they have a profound impact in the crystal structure and stability of these compounds. In this work we continue the study on the solid-gas equilibrium thermodynamics of a series of polyphenylbenzenes. The enthalpy, entropy and Gibbs energy of sublimation for 1,2,4,5-tetra-phenylbenzene and hexaphenylbenzene were derived from the temperature dependence of vapour pressure obtained in a combined Knudsen-Quartz crystal mass loss effusion apparatus. From Calvet microcalorimetry it was derived the enthalpy of sublimation for 1,2,4-triphenylbenzene. These results were compared with previous ones for less substituted analogues showing an interesting pattern in volatility...

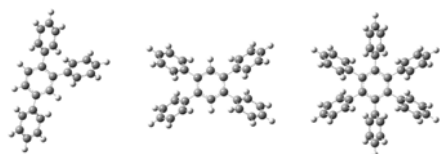


Figure 1 – Optimized geometries for 1,2,4-triphenylbenzene, 1,2,4,5-tetra-phenylbenzene and hexaphenylbenzene at the MP2/cc-pVDZ level of theory.

Experimental

Synthesis, purification and characterization

The compounds 1,2,4-triphenylbenzene and 1,2,4,5-tetra-phenylbenzene were synthesised by the Suzuki-Miyaura cross-coupling methodology as illustrated in figure 2 for the case of the tetra-substituted polyphenylbenzene.

All the three compounds were purified by standard recrystallization techniques and sublimation under reduced pressure. They were characterized by X-ray crystallography, elemental analysis, ¹H-RMN and UV-Vis spectroscopy.

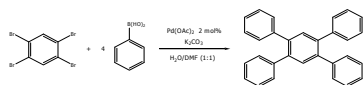


Figure 2 – Suzuki-Miyaura cross-coupling reaction scheme for 1,2,4,5-tetra-phenylbenzene.

Calvet microcalorimetry

The standard ($p^0 = 10^5$ Pa) molar enthalpy of sublimation for 1,2,4-triphenylbenzene at $T = 298.15$ K was determined by the Calvet microcalorimetry drop method [3] in a high temperature Calvet microcalorimeter, model SETARAM HT 1000, using the following equation:

$$\Delta_{\text{vap}}H^0(298.15 \text{ K}) = \Delta H_{\text{exp}} - \{H^0(g, T) - H^0(g, 298.15 \text{ K})\} \quad (1)$$

where the value of $\{H^0(g, T) - H^0(g, 298.15 \text{ K})\}$, calculated by computational thermochemistry, represents the enthalpy correction for the process of heating one mole of the gas from 298.15 K to T . The value of ΔH_{exp} refers to the heat measured by the calorimeter during the processes of heating the sample from 298.15 K to the temperature of the hot zone, T_h , and of its sublimation at that temperature T .

Figure 3 shows the Calvet microcalorimeter assembly in our laboratory and a scheme of the apparatus.

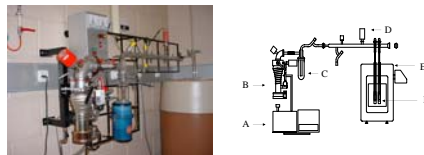


Figure 3 – Picture and schematic view of the Calvet drop method assembly, consisting of the vacuum line and a Calvet microcalorimeter Setaram, model HT1000D: A (rotary vacuum pump); B (diffusion pump); C (liquid nitrogen glass trap); D (Pirani and Penning gauges); E (HT1000D calorimeter block); F (calorimetric cells).

Knudsen-Quartz crystal effusion technique

The phase transition thermodynamics of 1,2,4,5-tetra-phenylbenzene and hexaphenylbenzene 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 amount and effusion time and can be used at temperatures up to 650 K.

The vapour pressure of the sample at temperature T is translated into an electrical signal of the quartz crystal resonator as the vapour effused from the cell's orifice condenses on its surface, causing the resonance frequency, f_r , to decrease as it happens. Therefore 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:

$$p = (\Delta m / \Delta t A_o \cdot W_o) \cdot (2\pi R T / M_{\text{ref}})^{0.5} \quad (2)$$

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 $\langle T \rangle$. A heat capacity correction is then applied for the determination of these thermodynamic parameters at $T = 298.15$ K.

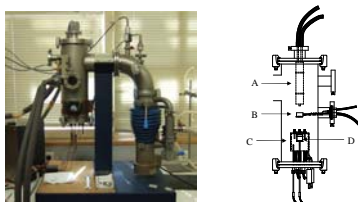


Figure 4 – Picture and schematic view of the Knudsen-Quartz apparatus: A (cold-finger); B (quartz crystal resonator); C (oven); D (Knudsen cell).

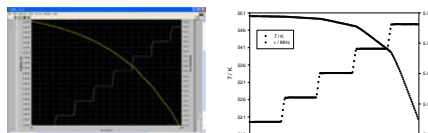


Figure 5 – Data acquisition on a typical KNQ experiment showing the change of the slope (df/dt) with temperature.

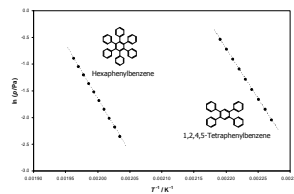
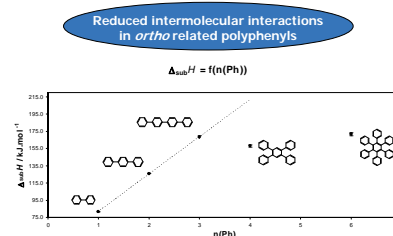


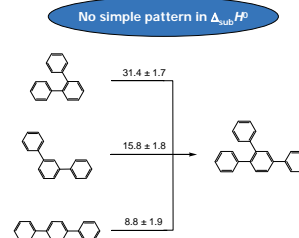
Figure 6 – Plots of $\ln(p/\text{Pa}) = f(1/T)$ for the two compounds studied by the KNQ technique.

Results

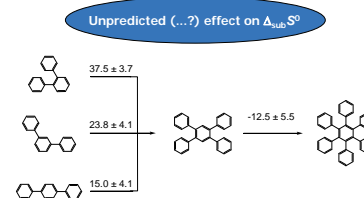
The results obtained in this work can be summarized and correlated with previous determined values for terphenyls [4] in three elucidative schemes. All the values are molar quantities and refer to $T = 298.15$ K.



Scheme 1 – Plot of $\Delta_{\text{sub}}H^0$ versus the number of phenyl groups relative to benzene for the represented compounds. There is a substantial negative deviation from the trend of linear polyphenyls.



Scheme 2 – Increment scheme of $\Delta_{\text{sub}}H^0$, in $\text{kJ}\cdot\text{mol}^{-1}$, showing the enthalpic effect of introducing a phenyl group in a given terphenyl. The significant differences indicate a strong dependence of volatility with the relative positions of the phenyl rings.



Scheme 3 – Increment scheme of $\Delta_{\text{sub}}S^0$, in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Adding two more phenyl groups to 1,2,4,5-tetra-phenylbenzene results in an unexpected decrease of $\Delta_{\text{sub}}S^0$ in hexaphenylbenzene...

Discussion

✓ Simple GCM's (Group Contribution Methods) are inapplicable to this class of compounds.

✓ Reduced possibilities for π - π intermolecular interactions on going from the linear to the *ortho* related polyphenyls result in lower than expected $\Delta_{\text{sub}}H^0$.

✓ Hexaphenylbenzene is an interesting case:

- Lower $\Delta_{\text{sub}}H^0$ because of the lack of π - π intermolecular interactions due to steric constraints;
- Lower $\Delta_{\text{sub}}S^0$ due to increased structural symmetry of the molecule which leads to a degeneracy of 12 equivalent positions in the crystal lattice and hence raises the entropy of the solid.

⊗ The pattern in volatility for polyphenylbenzenes can be rationalized taking into account three factors: the existence of intermolecular aromatic π - π interactions, the rotational freedom of the substituting phenyls and the entropy term related to the positional degeneracy in the crystal lattice.

References

- [1] C. Hunter, K. Lawson, J. Perkins, C. Urch, *J. Chem. Soc. Perkin Trans. 2* (2001) 651-669.
- [2] S. Tsuzuki, K. Honda, T. Uchinari, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.* 124 (2002) 104-112.
- [3] L.M.N.B.F. Santos, B. Schneider, O.O.P. Fernandes, M.A.V. Ribeiro da Silva, *Thermochim. Acta* 415 (2004) 15-20.
- [4] M.A.V. Ribeiro da Silva, L.M.N.B.F. Santos, L.M.S.S. Lima, *J. Chem. Thermodyn.* 40 (2008) 375-385.