High Pressure Studies on the Planarity of *para*-Hexaphenyl

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Abstract

We present experimental and theoretical findings on the geometry of *para*-hexaphenyl (PHP) molecules in polycrystalline powder. A new method to assess the planarity of PHP via Raman spectroscopy is presented. Based on this method we describe a *W-shaped* potential energy curve which governs the torsional motion between neighboring phenyl rings. We determine the activation energy to promote PHP from a non-planar to a planar state to be 0.04 eV, in good agreement with our quantum chemical calculations. Finally we are able to experimentally planarize the molecules by the application of hydrostatic pressure, which modifies the *W-shaped* potential energy curve to a *U-shaped* one.

Keywords: Organic semiconductors based on conjugated molecules, density functional calculations, Raman spectroscopy

1. Introduction

The *para* substituted oligophenyls were found to be efficient blue laser dyes [1] and the blue photoluminescence with a quantum yield of 30% in the solid state has been the motivation of using *para* hexaphenyl (PHP) as an emitting layer in organic light emitting diodes (LEDs) [2]. While there have been numerous studies trying to understand the electronic properties of these highly luminescent materials [3] there are many unresolved structural questions, one of which is the planarity of the molecule. We use temperature and pressure dependent Raman scattering to address the issue of planarization.

2. Experimental

The PHP powder was obtained from Tokio Chemical Industries Ltd. Raman measurements were carried out in a back-scattering configuration, using the 514.5 nm line of an Ar⁻ laser. The scattered light was detected with a SPEX triple monochromator equipped with a CCD array detector and a holographic supernotch filter. Pressure studies were conducted in a Merrill Bassett type diamond anvil cell (DAC) with cryogenically loaded argon as the pressure medium and ruby luminescence as the pressure calibrant. A Lorentzian curve fitting routine was used to determine the frequencies and intensities of the Raman modes. For our calculations we employed the Gaussian 94 *ab initio* program [4] with Restricted Hartree-Fock (RHF) scheme to perform geometry optimizations, force constant calculations, and dipole moment/polarizability derivatives with a polarized basis set 6-31G* for a biphenyl molecule. Geometry optimization and total energy calculations of the system were also done using a Density Functional Hybrid Method (B3LYP) [5].

3. Results and Discussion

In the crystalline state the molecules are arranged in layers. The long axes of the molecules are nearly perpendicular to the layers and therefore the thickness of a layer is approximately the length of the molecule. At room temperature all the phenyl rings of the oligomers *within one molecule* are arranged on the average in the same plane while the planes of two neighboring molecules are tilted relative to each other. Within the classification of polynuclear aromatic hydrocarbons, this structure is of the herringbone type and shows outstanding optical properties[6].
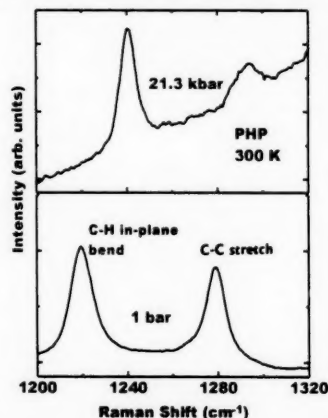

Figure 1: Raman spectra of PHP at 21.3 kbar (top panel) and at 1 bar (bottom panel) at T = 300 K.

The Raman spectrum of the oligophenyls has been described by several authors[7] and is mainly characterized by four intense modes of A_g symmetry. It has been observed that the Raman intensity ratio of the inter-ring C-C stretch mode at 1280 cm⁻¹ to the C-H in-plane bending mode at 1220 cm⁻¹ (I_{1280}/I_{1220}, Fig. 1) is a good indicator of the number of π conjugated phenyl rings in the polymer chain [8]. It is therefore also an indicator for planarity since simulations show that a higher number of conjugated phenyl rings result in a lower torsional angle between

them [9]. For a biphenyl molecule $I_{1280}/I_{1220} = 25$ and beyond six phenyl rings I_{1280}/I_{1220} is close to unity.
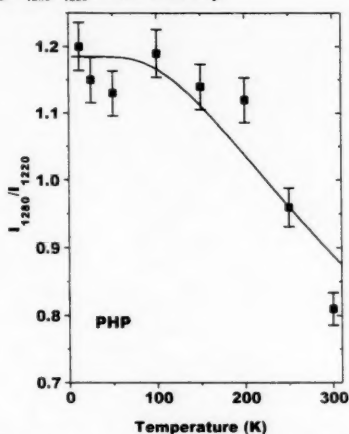

Figure 2: I_{1280}/I_{1220}, as a function of temperature. The bold line is a fit to an Arrhenius-type model [10].
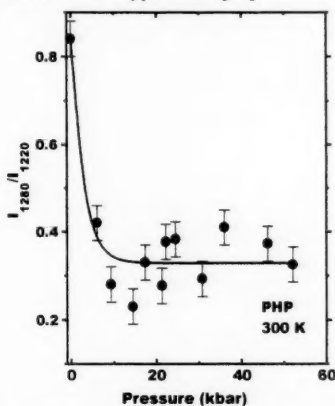

Figure 3: Ratio of the intensity of the 1280 cm^{-1} mode to the 1220 cm^{-1} mode as a function of pressure at T = 300 K.

Both the temperature- and pressure-dependent Raman studies (Figs. 1-3) indicate that the functional dependence of the potential energy of two neighboring phenyl rings versus torsional angle is a W-shaped as sketched in Fig. 4. A higher I_{1280}/I_{1220} corresponds to a lower planarity. In Fig. 2 lowering the temperature leads to an increase of I_{1280}/I_{1220}, which is interpreted as a decrease in planarity. Since the thermal energy available to change from the non-planar to the planar conformation increases with temperature, we describe the data by a simple Arrhenius-type model [10]. In order to obtain a planar conformation higher lying librational level is populated. Modelling the data in Fig. 2 we obtain an activation energy $\Delta E_{np-p} = 0.036$ eV.

We also calculated ΔE_{np6p} from the difference in internal energy between the planar and non-planar configurations of a biphenyl molecule. The Hartree-Fock method yields $\Delta E_{np-p} = 0.145$ eV, the density functional method yields $\Delta E_{np-p} = 0.089$ eV. The calculated values for the activation energy are higher since biphenyl is shorter than PHP and calculations for biphenyl were done for *isolated molecules*, where we expect the

planarizing forces to be weaker than for our sample which is an ensemble of molecules in a *crystalline environment*. The molecule undergoes a structural change with increasing temperature - this description does not require a change of the shape of the potential energy curve. However, upon increasing pressure the potential energy curve does change: it becomes narrower and starts losing the W-shape changing towards a U as shown schematically by the dashed and the dotted line in Fig. 4. This in turn means that the energetic difference between the non-planar and the planar conformation of the molecule decreases with increasing pressure. Our experiment confirms this model. The ratio of I_{1280}/I_{1220} decreases from 0.8 to 0.3 between 0 and 15 kbar, beyond which the ratio remains almost constant (Fig. 3).
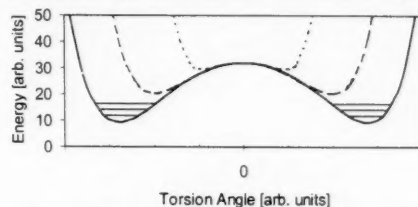

Figure 4: Schematic of the potential energy curve between two neighboring phenyl rings versus torsional angle in PHP.

In conclusion, we have shown that in PHP planarization under pressure is observed as a change in I_{1280}/I_{1220} ratio of the Raman modes. Our Raman experiments show that there are two ways of reaching a more planar configuration: a) promotion of the molecule into a higher energy state by increasing the temperature and b) changing the shape of the potential from a W-shape to a U-shape by increasing pressure.

4. References

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