

Planarity of *para* Hexaphenyl

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We present experimental and theoretical findings on the geometry of polycrystalline *para* hexaphenyl via Raman scattering. The planarity of the molecule is affected by hydrostatic pressure and temperature. Our studies indicate that the potential energy curve which governs the torsional motion between neighboring phenyl rings is “W” shaped. We determine the activation energy to promote the molecule from a nonplanar to a planar state to be 0.04 eV, in good agreement with our quantum chemical calculations. From the relative intensities of the 1280 cm⁻¹ to the 1220 cm⁻¹ Raman modes we show that high pressure planarizes the molecules, modifying the “W”-shaped potential energy curve to a “U”-shaped one. [S0031-9007(99)09073-0]

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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 concerns the planarity of the molecule associated with the arrangement of phenyl rings with respect to each other. The potential energy of two neighboring phenyl rings versus the torsional angle is “W”-shaped and the depth of the two wells governs the planarity of the molecule. We use temperature and pressure dependent Raman scattering to address the issue of planarization. Our experiments on PHP clearly indicate that at higher pressures the molecule becomes planar, i.e., the torsional angle between neighboring phenyl rings decreases, which changes the “W”-shaped potential to a more “U”-like potential.

The PHP powder was obtained from Tokyo Chemical Industries Ltd. Raman measurements were carried out in a backscattering configuration, using the 514.5 nm line of an Ar⁺ laser. The scattered light was detected with a SPEX triple monochromator equipped with a charge-coupled device (CCD) 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 GAUSSIAN94 *ab initio* program [4] with a Restricted Hartree-Fock 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 Becke’s three parameter density functional hybrid method [5].

In the crystalline state the molecules are arranged in layers with the long axes nearly perpendicular to the layers, so that the thickness of a layer is approximately the length of the molecule. PHP has a monoclinic unit cell, space group P2₁/a with $a = 8.091 \text{ \AA}$, $b = 5.568 \text{ \AA}$, and $c = 26.24 \text{ \AA}$, and the monoclinic angle $\beta = 98.17^\circ$ [7]. Within the classification of polynuclear aromatic hydrocarbons, this structure is of the herringbone type and shows outstanding optical properties [6].

Experimental x-ray data show that increasing the oligomer length of poly *para*-phenylene (PPP) reduces the lattice constants a and b , which are perpendicular to the chain direction [7,8]. This implies that on increasing the oligomer length the crystallographic packing in the ab plane is increased. Molecular simulations predict this trend: interring torsional angles of approximately 45°–50° for biphenyl and terphenyl [9], 30°–40° for hexaphenyl [7], and 27° in single isolated PPP chains [10] are found theoretically. This means that increased packing is a consequence of stronger planarization.

A closer look at x-ray data reveals that PPP and its oligomers adopt conformations such that the phenyl rings within each molecule are *on the average* coplanar, but undergo torsional motion with respect to the single bond connecting them [7]. The torsions cause large Debye-Waller factors for the carbon atoms not situated along the long axis of the molecule. The nature of the torsional motion of the neighboring phenyl rings is determined by at least two opposing influences: the *intramolecular repulsion* between ortho hydrogen and the tendency towards planarization in a π -electron system due to the resonance interaction [11]. The crystalline environment, however, tends to planarize the molecules. A torsional

angle of 27° is predicted in isolated PPP chains and 17° in crystalline environment [10]. Simulations of crystalline packed PHP show a torsional angle of $\pm 20^\circ$ [12].

The Raman spectrum of the oligophenyls has been described by several authors [13–18] and is mainly characterized by four intense modes of A_g symmetry. It has been observed that the Raman intensity ratio of the interring C-C stretch mode at 1280 cm^{-1} to the C-H in-plane bending mode at 1220 cm^{-1} (I_{1280}/I_{1220}) is inversely proportional to the number of π conjugated phenyl rings in the polymer chain [14,15,19]. It is therefore also an indicator of planarity since simulations show that a higher number of conjugated phenyl rings result in a lower torsional angle between them [7,9,10]. For biphenyl $I_{1280}/I_{1220} \approx 25$ and beyond hexaphenyl I_{1280}/I_{1220} is close to unity. Even Raman spectra of the *anions* of the oligophenyls (from *p*-terphenyl to *p*-hexaphenyl) show that I_{1280}/I_{1220} decreases with increasing oligomer length [16].

Figure 1 shows I_{1280}/I_{1220} for PHP as a function of temperature. The ratio increases from 0.8 to 1.2 between 300 and 100 K, below which it stays a constant. Since a higher I_{1280}/I_{1220} corresponds to a lower planarity, lowering the temperature causes a decrease in planarity. This behavior is indicative of a structural change where the *averaged* planar conformation observed at room temperature changes to nonplanar at lower temperatures, similar to trends observed in lower polyphenyls [20]. The Raman spectrum of PHP under pressure shows a further decrease in I_{1280}/I_{1220}

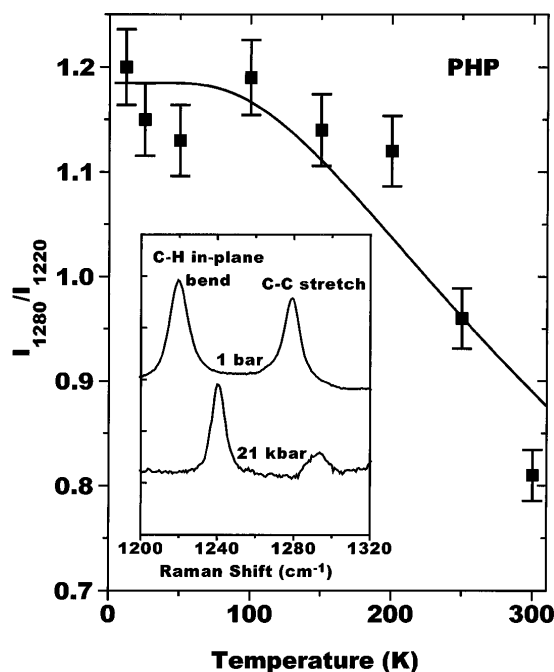


FIG. 1. The ratio of the intensity of the 1280 cm^{-1} to the 1220 cm^{-1} mode in PHP as a function of temperature. The line is a fit to the function in Eq. (1) and the squares are the experimental results. The inset shows the Raman spectrum of PHP at 1 bar and 21 kbar at $T = 300\text{ K}$.

(Fig. 2 and inset of Fig. 1), accompanied by an increase in the frequency of the modes.

Both the temperature- and pressure-dependent Raman studies indicate that the functional dependence of the potential energy of two neighboring phenyl rings versus torsional angle is “W”-shaped as sketched in Fig. 3 [21]. The expectation value $\langle \psi | \hat{\phi} | \psi \rangle$ for the torsional angle operator $\hat{\phi}$ of higher levels is 0 instead of $\pm \delta$ at the minima of the potential in Fig. 3. The ratio I_{1280}/I_{1220} versus temperature (Fig. 1) shows a behavior typical of a thermally activated process described by Boltzmann statistics. The probability for the system to be in a *nonplanar* configuration is proportional to I_{1280}/I_{1220} . Therefore we subtract the Boltzmann term, which is proportional to the probability of finding the PHP molecule in a *planar* configuration, from 1 and we fit the data to

$$I_{1280}/I_{1220} = A[1 - \exp(-\Delta E_{np \rightarrow p}/k_B T)]. \quad (1)$$

Here k_B is Boltzmann’s constant, $\Delta E_{np \rightarrow p}$ is the difference in energy between the nonplanar ground and the planar thermally excited states; $A = I_{1280}/I_{1220}$ at $T = 0\text{ K}$. By fitting the data in Fig. 1 to Eq. (1) we obtain an activation energy $\Delta E_{np \rightarrow p} = 0.04\text{ eV}$.

We also calculated $\Delta E_{np \rightarrow p}$ from the difference in internal energy between the planar and nonplanar configurations of a biphenyl molecule [22]. The Hartree-Fock method yields $\Delta E_{np \rightarrow p} = 0.145\text{ eV}$ compared to the density functional method which yields $\Delta E_{np \rightarrow p} = 0.089\text{ eV}$.

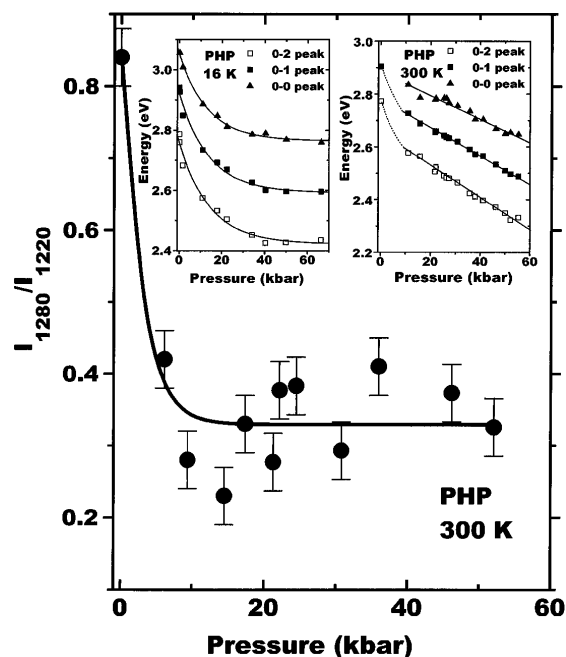


FIG. 2. Ratio of the intensity of the 1280 cm^{-1} mode to the 1220 cm^{-1} mode as a function of pressure at $T = 300\text{ K}$. The solid line is a guide to the eye. The insets show the energy positions of 0-0, 0-1, and 0-2 vibronic peaks observed in the PL spectra of PHP at 16 and 300 K under pressure.

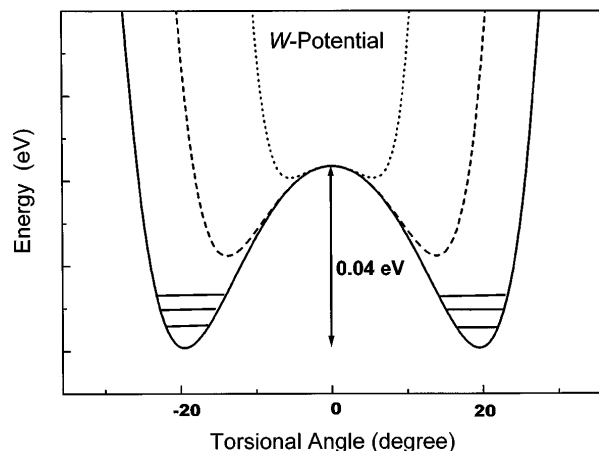


FIG. 3. Schematic of the potential energy curve between two neighboring phenyl rings versus torsional angle in PHP. The thick line represents the potential at ambient pressure whereas the dotted and the dashed lines represent the changing of the “W” potential energy curve to a “U” shape at higher pressures. The angle corresponding to the minimum in potential energy is chosen in accordance with Ref. [12], and the well depth is derived from our experiment.

From the energy calculations of a PPP chain in Ref. [10] it is observed that $\Delta E_{np \rightarrow p} = 0.065$ eV. The calculated values for the activation energy are higher for two reasons: biphenyl is shorter than hexaphenyl and calculations for both biphenyl and PPP chain are done for *isolated molecules*, where we expect the planarizing forces to be weaker than for our sample which is an ensemble of *long molecules* in a *crystalline* environment.

Therefore the molecule undergoes a structural change with increasing temperature, which promotes it to a higher energy state, namely, the more planar configuration. This description does not require a change in 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. 3. This in turn means that the energetic difference ($\Delta E_{np \rightarrow p}$) between the nonplanar 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 a constant (Fig. 2). Using the known average bulk modulus of terphenyl (67 kbar) in the range of up to 10 kbar and the unit cell parameters for PHP, we calculate the average energy stored per PHP molecule at a pressure of 10 kbar to be of the order of 0.1 eV, which is much higher than the activation energy required for planarization ($\Delta E_{np \rightarrow p}$). Therefore we conclude that at 10 kbar all the molecules are completely planarized. Confirming this, we found that varying the temperature at 20 kbar does not result in any change of I_{1280}/I_{1220} indicating that maximum planarity has been reached. The former observa-

tion shows that the “U”-shaped potential has already been reached by 15 kbar, and that increasing the temperature cannot cause further planarization.

We note that there is no broadening of the Raman lines as a function of pressure (Fig. 1, inset). Broadening of all Raman lines is typical for samples consisting of different conjugation lengths [23]. Therefore the observed Raman modes are from a similar distribution of conjugation lengths *both under pressure and at 1 bar*. This excludes that pressure only affects certain isolated rings since that would lead to a broader distribution of conjugation lengths and broadening of the Raman modes.

Photoluminescence (PL) of PHP under pressure also reflects the effect of planarization. The PL energy positions show a more rapid pressure dependence below 15 kbar for measurements both at 16 and 300 K, shown in the inset of Fig. 2. The PL emission of PHP is characterized by a well-defined vibronic progression. The highest emissive transition is the 0-0 transition, which takes place between the zeroth vibronic level in the excited state to the zeroth vibronic level in the ground state. The 0-1 transition involves the creation of one phonon. The 0-0 PL transition is not observed at 1 bar due to self-absorption effects. The general trend of a sharp change in the PL energies at lower pressures is clear from the inset in Fig. 2. This agrees very well with the first principles calculation in a PPP chain which predict a decrease in the band gap by almost 1 eV, when the torsional angle between the phenyl rings changes between 50° to 0° [10].

Our data show that the difference in the PL vibronic replicas ($\Delta \nu_{PL}$) is not identical to the frequency of the observed Raman modes. Also the pressure dependence of the Raman modes and $\Delta \nu_{PL}$ is different. The same behavior is observed in the work of Webster and Batchelder [24]. This is due to the PL spectra showing contributions from overtones and combinations of different phonon modes.

In order to describe the effect of planarization on the Raman spectrum of oligophenyls theoretically, we have calculated the Raman spectrum of a simpler molecule, namely the biphenyl and compared the I_{1280}/I_{1220} ratio for the planar and nonplanar geometries. While smaller, the biphenyl molecule is suitable since changes in the torsional angle between neighboring phenyl rings is involved. The planar and the nonplanar biphenyl molecules were optimized with appropriate symmetry restrictions, i.e., D_{2h} and D_2 symmetries, respectively. Since I_{1280}/I_{1220} is much larger for nonplanar biphenyl than for nonplanar PHP, we have to compare the ratio of I_{1280}/I_{1220} for the nonplanar geometry to the planar geometry (Table I). The experimentally obtained ratio of the intensities (I_{1280}/I_{1220}) of the nonplanar geometry to the planar geometry of 4 ($= 1.2/0.3$) for PHP is close to the calculated value of 4.5 ($= 14.5/3.2$) for the biphenyl. Note that we consider the low temperature value of I_{1280}/I_{1220} for the experimental nonplanar geometry since the molecule is most nonplanar at low temperatures and atmospheric pressure. These calculations

TABLE I. Calculated and observed Raman intensities for oligophenyls. The second and the third column give the ratio of the Raman intensity of the 1280 cm^{-1} mode to the 1220 cm^{-1} mode for the nonplanar and planar geometry, respectively. The last column gives I_{1280}/I_{1220} for the nonplanar geometry to that of the planar geometry. For PHP, the nonplanar geometry corresponds to the 1 bar case (10 K) and the planar geometry corresponds to higher pressures.

Structure	I_{1280}/I_{1220} nonplanar	I_{1280}/I_{1220} planar	Nonplanar/planar
Biphenyl (calc.)	14.5	3.2	4.5
PHP (expt.)	1.2	0.3	4.0

support our conclusion that higher pressures planarize the PHP molecule.

Our experimental results are also consistent with scaled quantum mechanical oligomer force field (SQMOFF) vibrational spectra calculations by Cuff and Kertesz [14]. They have calculated the Raman spectrum of PPP for planar and helical geometries. For the planar geometry, I_{1280}/I_{1220} is ~ 0.2 , close to our experimental value of 0.3 for the sample (PHP) under high pressure. The helical geometry, on the other hand, yields a much higher value of $I_{1280}/I_{1220} \approx 6$ compared to the planar geometry.

In conclusion, we have shown evidence that oligophenyls are characterized by a “W”-shaped potential for the energy of two phenyl rings versus their torsional angle. Planarization under pressure is observed as a change in I_{1280}/I_{1220} ratio of the Raman modes. Experimentally we observe this ratio to decrease by a factor of 4 when the molecule changes from a nonplanar to a planar configuration, while the calculations for a biphenyl molecule yield 4.5. Our 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 (activation energy ≈ 0.04 eV) and (b) changing the shape of the potential from a “W” shape to a “U” shape by increasing pressure. The latter effect saturates at around 15 kbar.

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