

COMMUNICATIONS

Flattening of organic molecules under pressure

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The different conformations of molecular compounds play important roles in biochemistry and organic solid-state technology. Hydrostatic pressure has been applied to *para*-quaterphenyl to probe its molecular structure at liquid-helium temperatures. The molecules transform from a twisted to a planar conformation at a critical pressure of 0.9 GPa. This conformational change results in the abrupt disappearance of five infrared-absorption peaks. A group-theoretical analysis shows that the peaks, which correspond to out-of-plane hydrogen bending modes, disappear due to the transition from a low to a high symmetry. © 2001 American Institute of Physics.

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With the recent advances in organic light-emitting diodes¹ and lasers,² organic materials have received renewed attention for optoelectronic applications. Organic molecules such as terphenyl and quaterphenyl have been used in blue laser dyes for over 30 years.³ The conformations of polyphenyls, in solution and in molecular crystals, affect the optical properties significantly. To probe molecular and crystalline structures, hydrostatic pressure can be tuned over a wide range.^{4,5} In general, the vibrational properties of molecular crystals under pressure have been a subject of fundamental interest in solid-state physics and chemistry.⁶ Here we report the observation of a “flattening” of *para*-quaterphenyl molecules at a critical pressure of 0.9 GPa. In contrast to most high-pressure vibrational studies, which use Raman scattering, we have used IR spectroscopy to investigate the molecular structure under pressure. The sensitivity of this technique has revealed significant changes in the vibrational properties due to the conformational change of *para*-quaterphenyl. Our experimental and theoretical approach should prove to be applicable to a wide range of molecular systems.

In polyphenyls, previous experimental studies have used x-ray diffraction⁷ and Raman spectroscopy^{8,9} to investigate phase transitions. Under ambient conditions, the phenyl rings are free to undergo torsional oscillations about the single carbon–carbon bonds. Theoretical studies have modeled the phase transition mechanism with a double-well torsional potential.^{10,11} At low temperatures and ambient pressure, the inner phenyl rings are at an angle of 23° to each other, and the angle between inner and outer rings is 17°.

A graphical representation of the twisted conformation is shown in Fig. 1(a). Since the phenyl rings are frozen at specific angles, the phase is referred to as *ordered*. At high temperatures, however, the rings are free to oscillate. In this

disordered phase, the molecule is, on average, planar [Fig. 1(b)]. The transition from the ordered to the disordered state is a result of a competition between two different types of forces. Intramolecular forces, primarily the repulsion between neighboring *ortho*-hydrogen atoms, tend to twist the rings. Intermolecular forces, which involve the interaction between the π orbitals of neighboring molecules, tend to make the rings lie in a plane.¹² In this study we have used hydrostatic pressure to increase the strength of the intermolecular forces.¹³ Above a critical pressure, the transformation from a low to a high symmetry results in the abrupt disappearance of specific IR-active peaks.

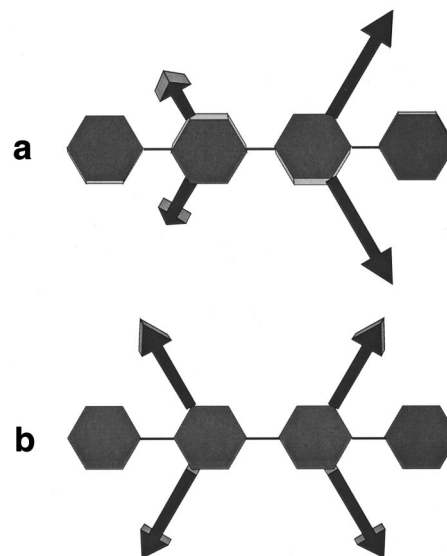


FIG. 1. Schematic diagrams of *para*-quaterphenyl in the (a) twisted and (b) planar conformations. Phenyl rings are represented by the hexagons. The dipole moments of the carbon–hydrogen pairs are represented by the arrows, for a particular out-of-plane bending mode. In this mode, the upper hydrogen atoms are out of phase with the lower hydrogen atoms.

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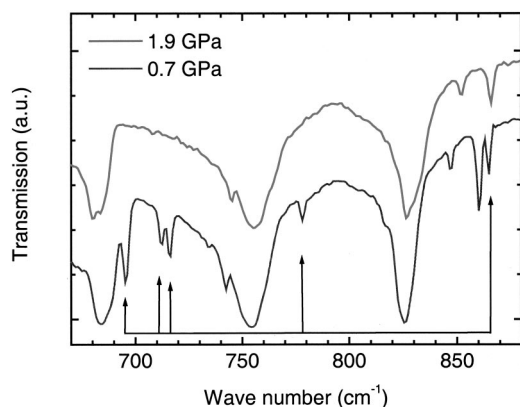


FIG. 2. IR spectra of *para*-quateryphenyl taken at pressures of 0.7 and 1.9 GPa, at a temperature of 8 K. Five IR-absorption peaks disappear at high pressure, as indicated by the arrows. Note that of the three peaks near 860 cm^{-1} , the two lower-frequency peaks shift to higher frequencies while the highest-frequency peak disappears.

To generate pressures up to 5 GPa, we used a piston-cylinder diamond-anvil cell.¹⁴ Type-I diamonds with culet diameters of 700 μm were used. After a 250- μm -thick stainless steel gasket was indented to a thickness of 100 μm , a 340 μm hole was drilled in the center of the indentation. Nitrogen was used as a pressure medium and was loaded into the gasket hole, along with the sample by liquid immersion.¹⁵ To determine the pressure at liquid helium temperatures, we measured the IR absorption peak of the ν_3 vibrational mode of carbon dioxide impurities in the solid nitrogen matrix.¹⁶

Mid-IR absorption spectra were obtained with a Bomem DA8 vacuum Fourier transform IR spectrometer with a KBr beamsplitter. The samples were kept at a temperature of 8 K in a Janis continuous-flow liquid-helium cryostat with zinc selenide windows. The spectral range was 500–5000 cm^{-1} and the instrumental resolution was 1 cm^{-1} . An off-axis parabolic mirror and light-concentrating cone focused the light through the first diamond and onto the sample. The light then passed through the second diamond and onto a Ge:Cu photoconductor detector.

IR spectra obtained at pressures of 0.7 and 1.9 GPa are shown in Fig. 2. Five peaks disappear at high pressure, as indicated by the arrows. The pressure at which the phase transition occurs is evidently between these two pressures. The pressure was increased and decreased several times, and no hysteresis near the critical point was observed in our experiments. The disappearance of the IR absorption peaks stands in contrast to Raman measurements of *para*-hexaphenyl, in which the area of the carbon–carbon stretch mode decreases by a factor of 2–3 upon planarization.⁹ In our measurements, the reduction in peak areas is at least a factor of 25. The reason for this difference is that, in the planar conformation, the symmetry is such that the Raman mode is still allowed but certain IR modes are not allowed.

The pressure dependence of three peaks in the range 840–870 cm^{-1} is plotted in Fig. 3(a). The discontinuity in the slope of the frequency versus pressure plots suggests the presence of a phase transition. More convincing evidence is provided by measuring the peak areas as a function of pres-

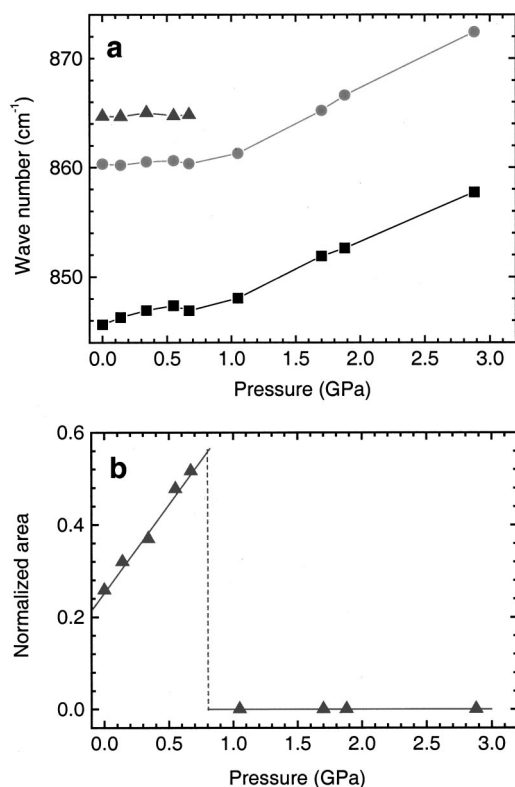


FIG. 3. (a) Peak frequencies of three IR-active modes as a function of pressure. The mode at 864 cm^{-1} (triangles) disappears in the pressure range of 0.7–1.0 GPa. (b) Area of the 864 cm^{-1} mode divided by that of the 860 cm^{-1} mode as a function of pressure. Solid and dashed lines are guides to the eye.

sure. The area of the peak at 864 cm^{-1} divided by the area of the peak at 860 cm^{-1} is plotted in Fig. 3(b). The gradual increase in the normalized area before the phase transition is due to a decrease in the area of the peak at 860 cm^{-1} . After the phase transition, the normalized area is zero to within experimental uncertainty. It can be seen from Fig. 3(b) that the phase transition occurs between 0.7 and 1.0 GPa. At pressures slightly below the phase transition, there appears to be a softening of the modes at 847 and 860 cm^{-1} , perhaps as a result of nonlinear coupling between the hydrogen modes and the torsional modes of the phenyl rings.

The disappearance of IR activity is illustrated in Fig. 1 for a normal mode in which the hydrogen atoms bend out of the phenyl-ring planes. The arrows represent the dipole moments of the four oscillating hydrogen atoms. It can be seen from Fig. 1(a) that out-of-plane displacements of hydrogen atoms on one ring *shorten* the projection of the dipole moment onto the main axis of the twisted molecule, whereas displacements on the other ring *lengthen* the projection. This results in a net dipole moment along the main axis, so that the mode is IR active. For the planar conformation [Fig. 1(b)], however, the dipole moment vectors exactly cancel each other, so that the mode is IR inactive. For purposes of illustration, it was assumed that an oscillating hydrogen atom is repelled by the neighboring phenyl ring. This repulsive interaction causes the equilibrium position of the hydrogen atom to bend out of its own phenyl-ring plane. An attractive potential would yield the same qualitative result.

To obtain a rigorous basis for these observations, we applied group theory to analyze the normal vibrational modes of the molecules. The twisted conformation of *para*-quaterphenyl belongs to the D_2 point group. The vibrational modes can be classified as follows:

$$\Gamma = 29A \oplus 27B_1 \oplus 32B_2 \oplus 32B_3.$$

Modes belonging to the B_1 , B_2 , or B_3 irreducible representations are IR active, for a total of 91 IR-active modes. For the planar configuration, *para*-quaterphenyl belongs to the D_{2h} point group. The vibrational modes are given by

$$\Gamma = 21A_g \oplus 8A_u \oplus 7B_{1g} \oplus 20B_{1u} \oplus 12B_{2g} \oplus 20B_{2u} \oplus 20B_{3g} \oplus 12B_{3u}.$$

In our convention, the z axis is along the length of the molecule, the y axis is out of the plane, and the x axis is in the plane. Modes belonging to the B_{1u} , B_{2u} , or B_{3u} irreducible representations are IR active, for a total of 52 IR-active modes. Therefore, certain IR absorption peaks should disappear upon planarization, in qualitative agreement with our observations.

Fundamental frequencies in the range 600–900 cm^{-1} correspond to out-of-plane hydrogen bending modes. Since there are eighteen hydrogen atoms, there are eighteen out-of-plane bending modes. Using a group theory technique, we obtained symmetry-adapted linear combinations of atomic displacements corresponding to the normal modes of the molecule. Each of these eighteen modes may, in principle, have a different frequency. If we consider interactions only between nearest-neighbor and next-nearest-neighbor hydrogen atoms, then several of these modes are degenerate. In our analysis, intermolecular interactions were ignored.

With those assumptions, the distinct modes that become IR-inactive upon planarization are given by

$$\begin{aligned} S_6 &= \frac{1}{2}(\theta_2 + \theta_9 - \theta_{11} - \theta_{18}), \\ S_{10} &= \frac{1}{2}(\theta_3 + \theta_8 - \theta_{12} - \theta_{17}), \\ S_{14} &= \frac{1}{2}(\theta_4 + \theta_7 - \theta_{13} - \theta_{16}), \\ S_{17} &= \frac{1}{2}(\theta_5 + \theta_6 - \theta_{14} - \theta_{15}), \\ S_{18} &= \frac{1}{2}(\theta_5 - \theta_6 - \theta_{14} + \theta_{15}) \end{aligned} \quad \begin{array}{l} (B_1 \text{ symmetry}) \\ \\ \\ (B_3 \text{ symmetry}), \end{array}$$

where θ_i denotes the out-of-plane coordinate for the i th hydrogen atom, starting from the leftmost atom ($i = 1$) and proceeding in a clockwise direction. Positive displacements are defined to be in the $+y$ direction. The symmetries are those in the twisted conformation (B_2 modes are IR active in both conformations). The mode S_{14} is illustrated in Fig. 1. Note that the inner four hydrogen atoms give rise to two frequencies, S_{17} and S_{18} , whereas the other quartets give rise to only one frequency each. This difference results from the assumption that pairs of hydrogen atoms that are third-nearest neighbors

and beyond do not interact. For those distant neighbors, the B_3 mode that becomes IR inactive is degenerate with a B_2 mode that remains IR active. The net result is that five distinct frequencies should become IR inactive, in agreement with our observations.

Our assumption that third-nearest-neighbor hydrogen atoms do not interact may be overly simplistic. In that case, five distinct B_3 modes would become IR inactive upon planarization. These modes would probably be stronger than the B_1 modes, so that the five disappearing peaks that we observe may in fact be B_3 modes. Investigations of biphenyl and terphenyl under pressure, under way in our laboratory, should enable us to determine the identities of the five disappearing peaks with more specificity.

In conclusion, we have observed a phase transition in *para*-quaterphenyl, at liquid helium temperatures, at a critical pressure of $P = 0.9 \pm 0.2$ GPa. The planarization of the molecules causes the disappearance of five IR-active peaks. Given the sensitivity of this experimental approach, future studies may be conducted to probe conformations in more complex organic molecules that are important in biochemistry.

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