

Conformation of *p*-terphenyl under hydrostatic pressure

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The conformation of *p*-terphenyl ($C_{18}H_{14}$) and deuterated *p*-terphenyl ($C_{18}D_{14}$) has been investigated, using high-pressure infrared spectroscopy at liquid-helium temperatures. First-principles calculations, together with the experimental results, were performed to determine the structure of *p*-terphenyl in the twisted conformation. At low temperatures and pressures, *p*-terphenyl belongs to the C_2 point group of symmetry. In this configuration, the central ring is twisted with respect to the plane of the outer rings. The symmetry of the molecule is nearly C_{2h} , consistent with previous x-ray diffraction measurements. © 2004 American Institute of Physics. [DOI: 10.1063/1.1634560]

I. INTRODUCTION

Conjugated molecules such as biphenyl, *p*-terphenyl, *p*-quaterphenyl, and *p*-hexaphenyl are widely used in light-emitting devices¹ and as laser dyes.² The optical properties of these molecules are affected very significantly by structural phase transitions. Conformational changes in the molecules, which occur at critical temperatures and pressures, are of technological and fundamental interest.

Structural changes in polyphenyl molecules have been the subject of intensive study for the last 25 years. Structural phase transitions have been studied extensively in biphenyl,^{3–9} *p*-terphenyl,^{10–20} *p*-quaterphenyl,^{13,21,22} and *p*-hexaphenyl.²³ In the case of biphenyl and quaterphenyl, there is agreement that the twisted conformation belongs to the D_2 symmetry group. The results of recent studies^{24,25} are consistent with this model. In the case of *p*-terphenyl, however, there is uncertainty about the symmetry of the molecule in the twisted conformation.

In its twisted conformation, the *p*-terphenyl molecule can be characterized by two angles of twist, associated with the two outer phenyl rings (Fig. 1). If both angles are of the same sign and have the same value, then the molecule has C_{2h} symmetry. If the twist angles have different signs, then the symmetry group is D_2 . If the twist angles have slightly different values, then the symmetry group is C_2 . We will denote such low-symmetry configurations C_2' and C_2'' , if molecule resembles that of C_{2h} or D_2 symmetry, respectively. There is also a possibility of having one outer ring twisted whereas other rings remain in the same plane. In this case, the molecule also belongs to the C_2 group. These configurations are illustrated in Fig. 1.

As was demonstrated previously,^{24,25} there are certain IR-active modes in polyphenyl molecules that become inactive upon the phase transition from the twisted to the planar conformation. In this paper we present the results of infrared

(IR) spectroscopy experiments at high pressures, as well as numerical calculations of the molecular structure of *p*-terphenyl. The results of the calculations show that the C_{2h} configuration has a lower energy than the D_2 configuration. The IR absorption peaks which disappear upon the phase transition match those calculated by *ab initio* methods for the C_2' structure. The calculations indicate that the C_2' conformation is very slightly perturbed from C_{2h} symmetry.

II. EXPERIMENT

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 wedged zinc selenide windows. The spectral range was 500–5000 cm^{-1} and the instrumental resolution was 2 cm^{-1} . The type-I-diamond absorption band between 1100 and 1400 cm^{-1} prevented us from taking data in this range. Further details of the experimental setup are given in Ref. 24.

Two samples were investigated. First, prolated *p*-terphenyl ($C_{18}H_{14}$), hereafter referred to simply as *p*-terphenyl, was measured. Second, deuterated *p*-terphenyl ($C_{18}D_{14}$), or terphenyl-*d*₁₄, was measured. In the latter sample, every hydrogen atom was replaced by a deuterium atom, with an isotopic purity of 98%.²⁶ The IR spectra for *p*-terphenyl are shown in Fig. 2 and spectra for deuterated *p*-terphenyl are shown in Fig. 3. The displayed frequency range corresponds to hydrogen bending modes. These bending modes are in- and out-of-plane modes, as observed in biphenyl. When pressure is raised above a critical value, several IR absorption peaks abruptly disappear from the spectrum. No hysteresis was observed in our experiments.

The pressure-dependent shifts of several out-of-plane hydrogen bending modes in *p*-terphenyl are plotted in Fig. 4. The frequencies shift discontinuously for certain peaks; namely, the peaks at 567, 573, and 912 cm^{-1} . This observation, together with the disappearance of other peaks, indi-

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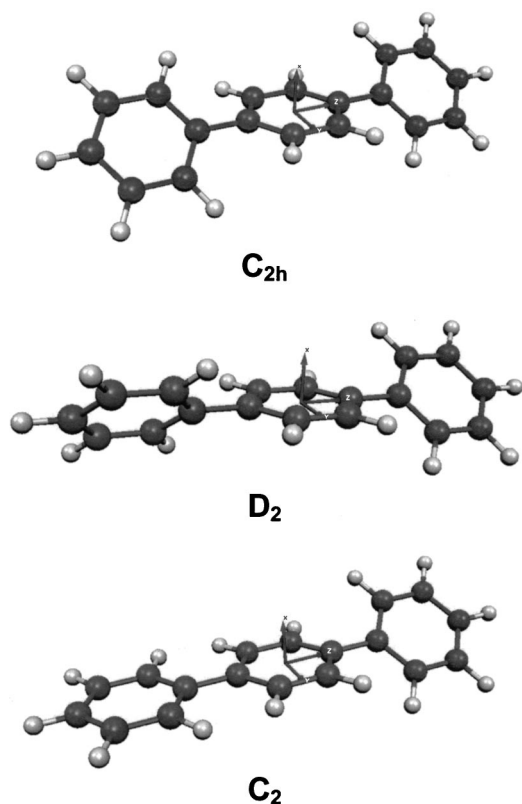


FIG. 1. Three possible nonplanar conformations of *p*-terphenyl. As a guide to the eye, a set of Cartesian axes are shown for each conformation.

icates the existence of a phase transition. The transition pressure lies between 0.2 and 0.6 GPa, consistent with previous studies,²⁷ which determined a phase transition at approximately 0.5 GPa.

III. NUMERICAL ANALYSIS

Previous theoretical studies have investigated the conformation of the *p*-terphenyl molecule.^{28,29} We performed *ab initio* calculations of *p*-terphenyl using the GAUSSIAN 98 software package.³⁰ All calculations were done using the density functional theory (DFT) approach with the Becke three-

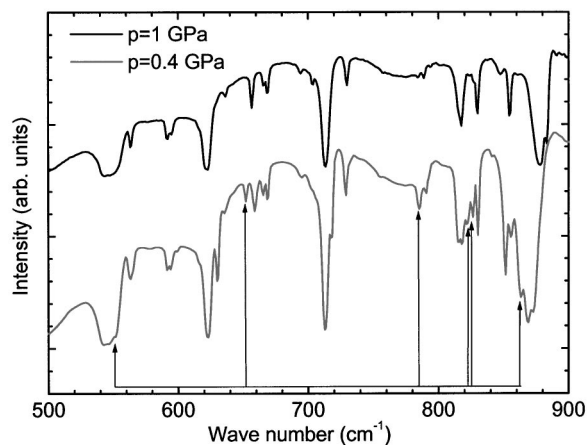


FIG. 3. IR spectrum of deuterated *p*-terphenyl below and above the phase transition pressure. Note that the peak at 625 cm^{-1} is not a disappearing peak, but rather merges with the peak at 622 cm^{-1} .

parameter hybrid functional of Lee, Yang, and Parr.³¹ We used two basis sets, 6-31+G(*d*) and 6-311+G(*d*), to obtain ground state energies and vibrational frequencies for the *p*-terphenyl molecule in different configurations. In addition, higher basis sets were used to check the consistency of the ground-state energy calculations.

A summary of the energy calculations is given in Table I. It is clear that the C_{2h} isomer is consistently more energetically favorable than the D_2 isomer. This result is consistent with previous x-ray diffraction experiments, which indicated that the molecules in a *p*-terphenyl crystal have C_{2h} symmetry at low temperatures.³² The calculated energy difference, however, is only $\sim 1\text{ meV/molecule}$. Our results contradict those obtained in Ref. 28, where it was suggested that the D_2 isomer has a lower energy than the C_{2h} isomer. One possible reason for such a discrepancy is that in Ref. 28, a *semiempirical* method was used (CS-INDO), which is usually less accurate than *ab initio* methods. The C_2 structure was unstable—during the calculations, it relaxed to the C_2' conformation. In addition to the ground-state energies, we also calculated vibrational frequencies for both *p*-terphenyl and deuterated *p*-terphenyl. A comparison between theoretical

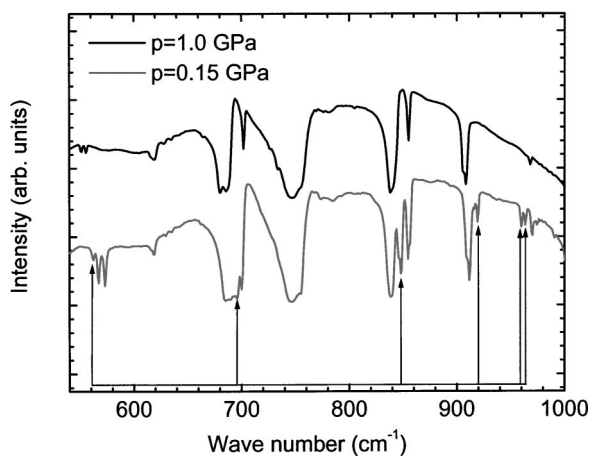


FIG. 2. IR spectrum of *p*-terphenyl below and above the phase transition pressure.

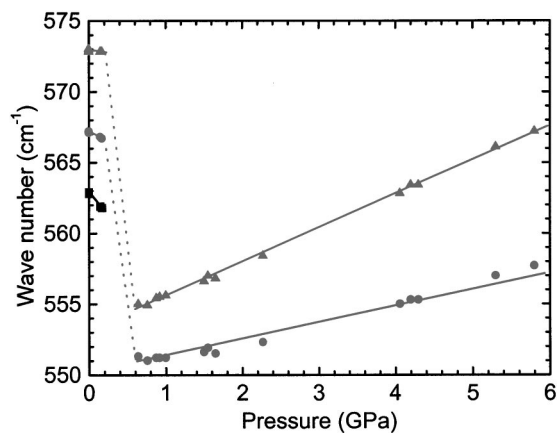


FIG. 4. Frequencies of three hydrogen bending modes in *p*-terphenyl, as a function of pressure.

TABLE I. Ground-state energies of *p*-terphenyl molecules in different conformations relative to the planar conformation.

Symmetry group	Energy (meV)			
	Basis set			
	6-31 +G(<i>d</i>)	6-311 +G(<i>d</i>)	6-311 ++G(2 <i>d</i> , <i>p</i>)	6-311 ++G(2 <i>df</i> ,2 <i>dp</i>)
Planar, D_{2h}	0	0	0	0
Twisted, C_{2h}	-163.39	-175.57	-178.65	-146.61
Twisted, D_2	-162.41	-174.24	-176.21	-145.39

and experimental results, discussed in Sec. V, indicates that the symmetry is the C'_2 conformation, which is a very slight perturbation of the C_{2h} isomer.

IV. GROUP THEORY

To explain the disappearance of IR activity for certain vibrational modes, we applied group theory to analyze the normal modes of the molecule. In this analysis, the *z*-axis is directed along the main axis of the molecule, the *x*-axis is in the molecular plane for the planar conformation, and the *y*-axis is perpendicular to the plane. This analysis was performed for the three possible conformations shown in Fig. 1, as well as the planar conformation.

In the case of D_2 symmetry, the vibrational modes are classified as follows:

$$\Gamma = 22A \oplus 20B_1 \oplus 24B_2 \oplus 24B_3.$$

Modes belonging to the B_1 , B_2 , or B_3 irreducible representations are IR-active, for a total of 68 IR-active modes. For the C_{2h} group, the vibrational modes are classified as

$$\Gamma = 21A_g \oplus 24B_g \oplus 21A_u \oplus 24B_u.$$

Here, only modes belonging to either A_u or B_u representations are IR-active, yielding a total of 45 IR-active modes. For the molecule belonging to C_2 point group, the modes are given by

$$\Gamma = 42A \oplus 48B.$$

In this case, all modes are IR-active. For the planar configuration, terphenyl belongs to the D_{2h} point group. The vibrational modes are given by

$$\Gamma = 16A_g \oplus 6A_u \oplus 5B_{1g} \oplus 15B_{2g} \oplus 9B_{3g} \oplus 15B_{1u} \oplus 9B_{2u} \oplus 15B_{3u}.$$

Modes belonging to the B_{1u} , B_{2u} , or B_{3u} irreducible representations are IR-active, for a total of 39 IR-active modes.

Upon planarization, certain IR-active peaks become IR-forbidden. We would expect to see 6 modes disappear from the spectrum if *p*-terphenyl belongs to the C_{2h} group, 29 modes if it belongs to the D_2 group, and 51 modes if the molecule has C_2 symmetry. These “disappearing peaks” comprise a special subset of vibrational modes. In the following discussion, we restrict the analysis to those modes that lose IR activity upon planarization.

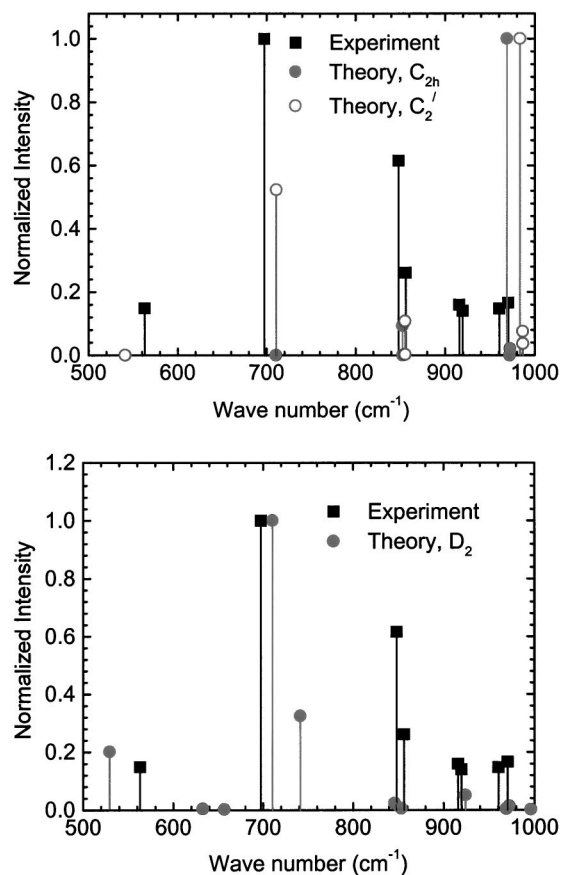


FIG. 5. Vibrational modes that become IR-inactive upon planarization, for *p*-terphenyl. A comparison between theory and experiment is shown for the C_{2h} , C'_2 , and D_2 conformations.

V. COMPARISON BETWEEN THEORY AND EXPERIMENT

In Fig. 5 we present all modes that are IR-inactive in the planar conformation, but become active in the C_{2h} and C'_2 twisted conformations, along with the experimental results. The calculations showed that some modes, which are IR-active according to group theory, have essentially zero intensity. The C'_2 isomer deviates from C_{2h} symmetry only slightly, as the difference in the twist angles of the outer rings is only 0.03° . There is also a distortion of phenyl rings which makes them nonplanar, but this distortion is also very small—the C–C–C–C dihedral angle is 0.04° . Results are also presented for the D_2 isomer. The results for C'_2 (not shown) are nearly identical to those for D_2 .

In Fig. 5 it is apparent that there is an intense calculated peak is at 710 cm^{-1} , consistent with experiment. For the D_2 calculations there is also an intense peak at 741 cm^{-1} . In the experimental spectrum, however, there is no disappearing peak near 741 cm^{-1} . This observation, along with the ground state energy calculations, allows us to conclude that the *p*-terphenyl structure is C'_2 . Since the C'_2 conformation deviates from the C_{2h} conformation only slightly, it is surprising that this small perturbation causes large increases in the intensities of certain IR peaks. In Fig. 5, for example, the IR mode at 710 cm^{-1} has zero intensity for the C_{2h} conformation, but it is very intense for the C'_2 conformation. This

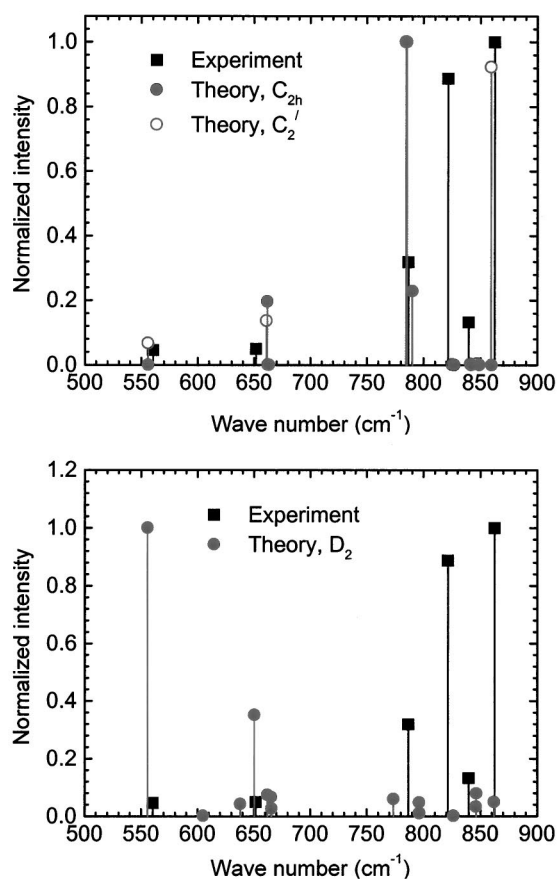


FIG. 6. Vibrational modes that become IR-inactive upon planarization, for deuterated *p*-terphenyl. A comparison between theory and experiment is shown for the C_{2h} , C_2' , and D_2 conformations.

observation is consistent with group theory, since the mode goes from B_{2g} to B as the symmetry is reduced from C_{2h} to C_2' . In general, these results suggest that our combined experimental and theoretical approach provides a very sensitive probe of molecular structure.

We have also performed calculations for deuterated *p*-terphenyl. The results for calculated and experimental IR modes are shown in Fig. 6. It is seen that the C_2' conformation yields a reasonable match between theory and experiment. For the D_2 conformation, however, there is an intense peak, calculated at a frequency of 550 cm^{-1} . Since experiments gave no evidence of such a strong peak in the spectrum, this calculation provides additional evidence that the D_2 configuration is incorrect.

Although the single-molecule calculations reproduced the general features of the IR-spectra, it should be noted that the experimental peaks show fine structure that is not reproduced by the calculations. In $900\text{--}1000\text{ cm}^{-1}$ region (Fig. 5), for example, more peaks were observed in *p*-terphenyl than the calculations predicted. It is possible that this is due to Davydov splitting, which occurs when there is more than one molecule per unit cell. In *p*-terphenyl, there are two molecules per unit cell in the high-pressure phase and four molecules per unit cell in the low-pressure phase, where C_i is the site symmetry in both phases.¹⁸ This causes the number of active modes to double. Of course, some modes may be very closely spaced and not resolved in our experiments.

VI. CONCLUSIONS

In conclusion, our experiments on the vibrational properties of *p*-terphenyl used the fact that these molecules flatten under pressure, resulting in the disappearance of specific IR peaks. Using numerical calculations, we were able to evaluate the frequencies of the molecular vibrations and determine the structure of the molecule in its twisted conformation. The close correspondence between the calculated and experimental spectra indicates that in the twisted conformation, the central ring is rotated around the C–C bond relative to the plane of two other rings. This molecule has C_2 symmetry, as a result of a slight deviation from C_{2h} symmetry. Additional experiments and calculations on deuterated terphenyl support these conclusions.

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