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First-principles calculation of the conformation and electronic structure of polyparaphenylene

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In this article, an all-electron first-principles total energy calculation with Gaussian-type functions for the wave functions, for the exchange correlation potential, and for the charge density has been applied for single chains of polyparaphenylene (PPP). A local-density approximation within a helical band structure approach has been used. The calculated torsional potential shows a minimum at the torsion angle of 34.8° . The internal coordinates were optimized in the equilibrium conformation and are in good agreement with experimental and other theoretical results. The calculated direct band gap is 2.54 eV compared with the experimental result from UPS spectra of 3.4 eV for the gas phase. The band structure strongly depends on the conformation which suggests that the electronic properties can be modified in a wide range through doping or addition of side groups. © 1998 American Institute of Physics. [S0021-9606(98)30743-6]

I. INTRODUCTION

Polyparaphenylene (PPP) is one of the most attractive conducting polymers both for physicists and chemists because of its optical applications, e.g., light emitting diodes (LEDs),¹ field-effect transistors,² and nonlinear optical devices.³ In particular, the discovery of blue light emission from PPP has caused a new interest in this material.⁴ Compared to many other conducting polymers which normally have low chemical and thermal stability, poor mechanical strength, or limited possibilities in tuning the wavelength, the wide-gap polymeric PPP is stable in air up to 400°C ,⁵ and its electronic structure and optical properties can be modified by several chemical methods.^{6–12}

Experimentally, the conformation of crystalline PPP as well as the crystalline oligomers of the phenyl ring have been studied extensively. The nuclear configuration is known only for finite oligomers. X-ray crystallographic measurements showed that the configuration was not planar but with a twist torsional angle present between neighboring phenyl rings. Baudour *et al.*^{13–15} found an angle of 13° for *p*-terphenyl, for *p*-quaterphenyl a mean torsional angle of 17.1° between the external (the first or the fourth) and the adjacent internal (the second or the third) phenyl rings, and a mean angle of 22.7° between the two internal rings. Sasaki¹⁶ measured a torsional angle of almost 20° for *p*-quaterphenyl and Baker *et al.*¹⁷ obtained values between 20° and 30° . All of these measurements indicated that the oligomers crystallize in an alternately tilted structure: i.e., a structure in which all the odd numbered rings and all the even numbered rings are located in two planes tilted with respect to each other by the torsional angle. None of them found evidence that oligomers of the phenyl ring crystallize in a helical structure in which

the twist between connective neighboring rings always increases by the same torsional angle.

In crystalline PPP the structure is not so clear as in oligomers. Baudour¹⁸ found evidence for a high-temperature phase in which all phenyl rings are located in the same plane. However, such a planar configuration is most likely the result of an average of structures with different twist angles. At low temperature, PPP undergoes several phase transitions to nonplanar structures. Kawaguchi and Petermann¹⁹ assumed PPP to crystallize in an orthorhombic structure with four phenyl rings from two adjacent chains per unit cell. Their diffraction experiments could be interpreted in terms of the monoclinic space group $P2_1/n$. However, the monoclinic distortion was small or even zero, in which case the structure is orthorhombic. Shacklette *et al.*²⁰ could not conclude whether PPP was planar on the basis of their experiments. However, they inferred from data on oligomers that the torsional angle between the phenyl rings of PPP is 23° . Finally, Lenstra *et al.*²¹ also concluded that PPP is nonplanar on the basis of the conformation of oligomers.

Understanding the electronic and optical properties of PPP will be essential in taking full advantage of this material's potential technological applications in optical devices. Experimentally, the optical band gap has been determined by optical measurements^{6,22} and the ionization energy by x-ray (XPS)²³ and ultraviolet (UPS) photoelectron spectroscopy.²⁴ The electronic structure of oriented thin films of sexiphenyl was studied by angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) using synchrotron radiation by Narioka *et al.*²⁵ recently.

Only a limited number of theoretical studies have been reported, however. Cuff and Kertesz²⁶ made an analysis of

the intensity of the vibrational peaks in the Raman spectrum of oligomers based on *ab initio* Hartree–Fock (HF) calculations. Based on a comparison of their work with experimental results, they concluded that the most probable structure of PPP is nearly planar with an inter-ring torsional angle of less than 20° . Some of the earliest band structure calculations for PPP were performed by Brédas *et al.*^{27–30} They used the experimental values of the geometrical parameters and the torsional angle as input for HF calculations on an alternately tilted chain. Bakhshi and Ladik³¹ made an HF calculation of the ionization energy, electron affinity, and bandwidth values for both a planar and a helical PPP chain. Later, Ladik and co-workers^{32,33} did the same for HF calculations on a helical structure, and have also applied correlation corrections for the band structure using the electronic polaron model³⁴ and the inverse Dyson equation in its diagonal form.³⁵ They have calculated the self-energy using second-order Møller–Plesset perturbation (MP/2) theory.³⁶ More recently, Champagne *et al.*³⁷ carried out another *ab initio* HF study of the electronic properties of planar and nonplanar PPP and made an analysis of the polarizability of PPP as well as the inter-ring torsion effects upon the polarizability. Ambrosch-Draxl *et al.*³⁸ used a first-principles local density approximation (LDA) with a full potential linearized augmented plane wave (LAPW) as well as a pseudopotential method to calculate torsional angles of 22.7° in a single PPP chain and 17° in crystals. In that work, they concluded that the band gap and bandwidth value can be tuned by structural modifications.

In this article, an all-electron first principle calculation is carried out systematically on a single helical chain of PPP with several different inter-ring torsional angles. The LDA approximation is used with a Gáspár–Kohn–Sham term for the exchange and a Perdew–Zunger fit to the Monte Carlo results of Ceperley–Alder for the correlation energy of a homogeneous electron gas. Gaussian-type functions are used both to construct the wave functions and to fit the charge density and the exchange-correlation potential. Two main considerations encourage this work: (1) Our LDA approach using Gaussian orbitals has been successfully applied to plastic polymers such as polyethylene, polyfluoroethylene, etc., which have only the σ bands and localized electrons and obtained rather good results for both conformation and electronic structure (see Sec. II), and this article will be the first attempt of this approach on a conducting polymer, which has both π and σ bands and delocalized electrons. (2) Although several first principle calculations have been done for PPP in both a single chain and crystal state, the HF calculation used a Gaussian basis and the LDA only plane waves. So it is quite useful to fill in the gap by running a Gaussian basis LDA calculation and compare the results with both the other method and the different basis. Compared with Refs. 37 and 38 and other HF calculations, the internal coordinates of the polymer chain are optimized by an all electron calculation. The equilibrium conformation has a torsional angle of 34.8° . The band structure, especially the energy gap and bandwidths as well as the effect of torsion upon them, are investigated and compared to experimental data. Because of recent experimental interest in tailoring the electronic and optical properties of PPP by chemical modifications on the

structure, we have investigated in detail how specific elements of the band structure, especially the energy gap and bandwidths as well as the ionization energy, vary as a function of the internal coordinates. With the help of the first-order perturbation method, all the variations of the band structure corresponding to the changes of the geometry can be fully understood in terms of a simple tight-binding model. In the following sections, we will first describe the method we use and then report the results for the conformation and band structure. The possibilities of the tuning of the gap and bandwidths will be discussed at the end.

II. THEORY

In this work we use the local-density functional approach based on a linear combination of Gaussian-type orbital (LCGTO) originally developed for molecular systems,^{39,40} and extended to two-dimensionally periodic systems⁴¹ and chain polymers,^{42,43} to calculate the total energies and electronic structures of helical chain polymers.^{44–46} The local density approximation is used with a Kohn–Sham exchange term⁴⁷ and a Ceperley–Alder correlation term,⁴⁸ using the Perdew–Zunger analytic fit.⁴⁹ The helicity of the polymer system is described by a screw operator \hat{S} . The one-electron wave functions transform under \hat{S} according to Bloch’s theorem.^{44,46} These wave functions are constructed from a linear combination of products of nuclear-centered Gaussian type orbitals with real solid spherical harmonics. Furthermore, the exchange-correlation potential and the charge density in the Coulomb potential are fitted with a linear combination of Gaussian-type functions,⁴⁴ a procedure originally developed for molecular systems.^{39,40} Details of the theory can be found in the references given above.

The contracted Gaussian orbitals and the auxiliary functions used in this calculation are those optimized for LDF calculations by Godbout *et al.*⁵⁰ Using Huzinaga’s notation,⁵¹ the orbitals for the hydrogen atom have a (41/1*) contraction pattern and for carbon a (7111/411/1*) contraction pattern. The Gaussian functions used to fit the density and the exchange potential (auxiliary functions) for the carbon atoms consist of four *s* functions and four sets of *s*, *p*, and *d* functions, all of them with the same exponents, and are denoted as (4,4;4,4) while a (3,1;3,1) auxiliary basis is used for the hydrogen atoms.

III. RESULTS

A. Conformation

Using the approach described above, the total energy and band structure of a single helical PPP chain for different inter-ring torsional angles are calculated for a unit cell containing one phenyl ring; each phenyl ring is rotated relative to the previous phenyl ring in the chain by a constant torsional angle. Only torsional angles smaller than 90° were considered because of the planar reflection symmetry of each phenyl ring. The internal coordinates, l_1 , l_2 , d , h , and θ are defined in Fig. 1. According to HF calculations^{26,28} as well as x-ray reflection experiments^{13,14,16} the difference between the bond lengths l_1 and l_2 within a ring is about 0.02 \AA which is

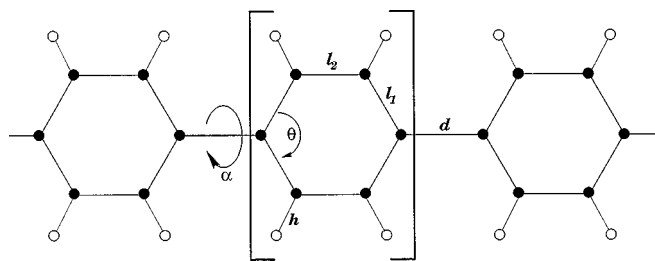


FIG. 1. Definition of structural parameters in the PPP chain. The unit cell is shown in the square bracket. Carbons are denoted by the filled circles and hydrogens denoted by the open circles.

much smaller than the difference between either in-ring bond length l_1 or l_2 and the inter-ring bond length d . For computational convenience then, we have only considered a single bond length l within the ring, which largely reduces the computational effort. The geometry parameters l , d , h , and θ together with the torsional angle α are optimized and listed in Table I, together with other reported theoretical and experimental results. The value of our calculated bond lengths and bond angles are within the range of values of the different experimental results and agree well with other theoretical predictions. The crystallographic data on oligomers indicate that the difference between the bond length within the rings and between rings is about 0.1 Å. Our corresponding value is about 0.08 Å which is smaller than the HF results of Cuff and Kertesz²⁶ on oligomers but larger than the pseudopotential LDA value of 0.06 Å of Ref. 38. The calculated bond angle of 120.95° indicates a modest deformation of the phenyl ring, caused in large part by the interaction between the hydrogen atoms in the ortho positions of neighboring phenyl rings.

We depict in Fig. 2 the total energy per phenyl ring relative to the planar PPP conformation for several different torsional angles α . The absolute minimum occurs at a torsional angle of 34.8° with a well depth of 1.7 kcal/mol relative to the planar conformation. The nonzero torsional angle is the result of two competitive effects: on one hand the steric repulsion between the hydrogen atoms in the ortho positions of neighboring phenyl rings which favors nonplanarity, and on the other hand the conjugation of p orbitals on the carbon atoms which delocalizes the π electrons and favors a planar structure. The x-ray data of crystalline PPP as well as its oligomers¹⁷ show that the adjacent rings are

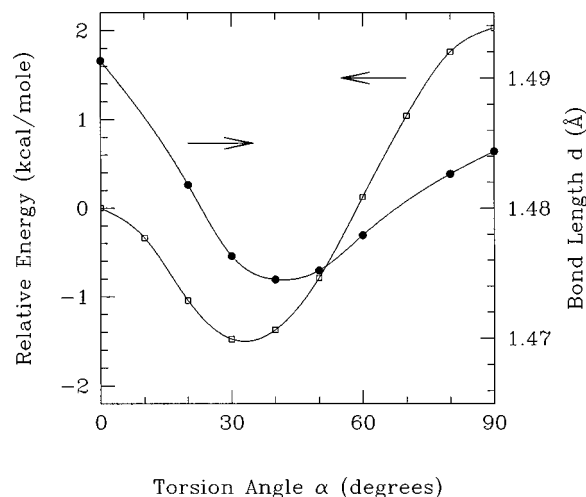


FIG. 2. Torsional potential energy (open squares for the calculated values), given in kcal/mol, and inter-ring bond length d (full circles), given in angstrom versus torsional angle. For each angle the C–C bond length between neighboring phenyl rings is optimized while the C–C bond length within a ring, l , and the C–C–C angle, θ , are kept constant and equal to the values obtained for the dihedral angle of 34.8°.

twisted with respect to one another by torsional angle values between 20° and 30°, slightly smaller than our calculated result. However, this can be understood by the fact that the interchain interaction between different chains in a three-dimensional material favors a less buckled structure. This effect is also the reason that crystalline PPP has a tilted structure. In the single PPP chain where the π electrons are delocalized, the interaction between next-nearest-neighboring rings is small so that the torsional energy of both the helical and tilted structures are going to be about the same. Our calculated torsional angle of 34.8° is slightly larger than the other LDA result using LAPW of 27.4°.³⁸ The C–C bond length between two neighboring rings has been optimized for different torsional angles to see how torsion affects the other geometrical parameters, and this is also depicted in Fig. 2. From this figure, we notice the strong correlation between the bond length and the energy curve although the minimum occurs at about 40° which is slightly larger than the minimum of the energy curve. Again as for the energy, the bond-length curve is the global result of the repulsion between hydrogen atoms and π conjugation of the p orbitals.

TABLE I. Optimized geometry parameters using the PZ local-density approximation, in comparison with another LDF pseudopotential calculation and HF calculated geometry parameters on phenyl oligomers as well as experimental results. For the definition of parameters, see Fig. 1.

| | LDA ^a PPP | LDA (Ref. 38) PPP | HF (Ref. 26) Oligomer | Experiment (Refs. 13, 14, and 16) |
|--------------------|-------------------------|----------------------|--------------------------|--------------------------------------|
| l_1 (Å) | 1.394 | 1.378 | 1.382 | 1.356–1.409 |
| l_2 (Å) | 1.394 | 1.399 | 1.388 | 1.371–1.425 |
| d (Å) | 1.473 | 1.456 | 1.492 | 1.469–1.505 |
| h (Å) | 1.098 | 1.100 | 1.074 | 0.960–1.129 |
| θ (degrees) | 120.95 | 121.2 | 120.3 | 104–128 |
| α (degrees) | 34.8 | 27.4 | 53.22 | 20–27 |

^aPresent calculation.

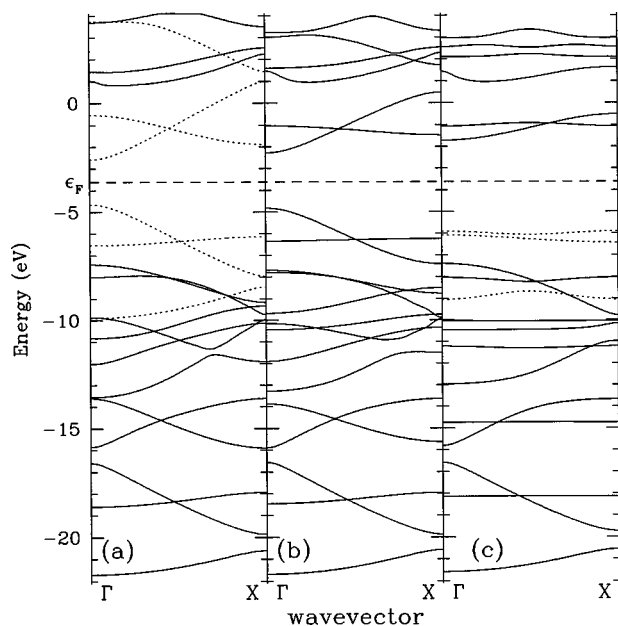


FIG. 3. Band structure of PPP for (a) the planar conformation, (b) a 34.8° twisted structure, and (c) 90° twisted structure. The π bands for the planar conformation are given by dotted lines in (a), the corresponding occupied π bands are given by dotted lines for the 90° twisted conformation in (c).

B. Band structures

The band structure of PPP chains with torsional angles of 0°, 34.8°, and 90° are depicted in Fig. 3. The 28 valence electrons on each phenyl ring will result in 14 filled bands. For the planar PPP conformation whose band structure is depicted in Fig. 3(a), the structure will have a point group symmetry that commutes with the helical operation (the translation operator in this case) of C_{2v} . This means that the bands in Fig. 3(a) can be labeled with the irreducible representations of C_{2v} . Like benzene this structure possesses a mirror reflection in the plane of the atoms, and the bands can be thought of as σ and π bands. In Fig. 3(a) we have denoted these π bands with dotted lines. In benzene the 6 π molecular orbitals would split into four energy levels: the nondegenerate lowest energy occupied state, a doubly degenerate occupied set of states, a doubly degenerate unoccupied pair of states, and a nondegenerate unoccupied state of highest energy. Within an sp^3 tight-binding model (or a Hückel model), the doubly degenerate levels would have energies of $\pm V_{pp\pi}$ and the nondegenerate levels would have energies of $\pm 2V_{pp\pi}$, where $V_{pp\pi}$ is the Slater–Koster matrix element for π bonding between adjacent atoms. Making a chain of phenyl rings breaks the D_{6h} point group symmetry in benzene and breaks the degeneracy present in the orbital energies. The highest and lowest energy nondegenerate levels in benzene will belong to the a_2 representation of the C_{2v} group present in planar PPP. Each degenerate energy level in benzene will split into two nondegenerate levels, one belonging to the a_2 representation in C_{2v} and the other belonging to the b_2 representation. As Champagne *et al.*³⁷ have noted, the a_2 state will have no contribution from the atoms at the end points of the bonds between phenyl rings. Within a nearest-neighbor tight-binding model, this a_2 band would show a total lack of dispersion, but with longer-range contributions

included in the first-principles calculations we find that the interactions between monomers cause the band to be weakly bonding with it rising in energy slightly from Brillouin zone center to zone edge. The crossing of π bands in three can occur because one of them belongs to the a_2 and the other one to the b_2 representation of the c_{2v} point group. The crossings of the σ bands has similar reasons. Within a Hückel model, the PPP planar conformation has particle–hole symmetry, thus leading to the occupied and unoccupied π bands being symmetric across the Fermi level. We see in Fig. 3(a) that this relationship remains a good approximation for our first-principles results. For the topology of the orbitals at high symmetry points of the Brillouin zone, several other discussions are also available.^{52,53}

We also depict the band structures for the 34.8° and 90° torsion-angle PPP conformations in Figs. 3(b) and 3(c). The band structures in Fig. 3(b) are seen to exhibit only modest changes from those of the planar conformation depicted in Fig. 3(a). Because of diminished π coupling between phenyl rings as the torsion angle is twisted from the planar conformation, the π band widths decrease with increasing torsion angle. This effect is accompanied by a corresponding increase in the band gap. This effect is dramatically enhanced in the extreme case of a torsion angle of 90°, where the band gap enlarges from 1.99 eV for the planar conformation to 4.31 eV for the 90° twisted conformation. From Table II it can be found that the band widths of the valence and the conduction bands for 90° twisted PPP are 0.41 and 1.16 eV, respectively, indicating that these two bands are rather flat in this extremely nonconjugated conformation.

Rotating the torsion angle from the planar conformation removes the reflection plane, and reduces the highest point group symmetry that commutes with the helical operator to C_2 , with the bands now labeled with the irreducible representations a and b of the C_2 group. This will allow some mixing between the σ and π bands present in the planar conformation. For the extreme case of a 90° torsion angle, we again have a mirror reflection plane present, and the C_{2v} point group is a subgroup of the total symmetry group of the polymer chain, but we note that the C_{2v} point group here does not commute with the helical operation equivalent to a translation combined with a C_4 rotation. Because the helical operator commutes with the full C_{2v} group acting on the set of functions belonging to the a representation of the C_2 group, we can further label these bands by whether they belong to the a_1 or a_2 representations of this group for the 90° torsion angle. The a_2 representation will have no contribution on the carbon end points of the inter-ring bond as in the planar case. The b representation can only have π orbitals that are orthogonal to the local phenyl ring and originate from the carbon end points of the bonds connecting phenyl rings, and these π orbitals will likewise be orthogonal to each other. This results in very little dispersion in any of the a_2 or b bands, with only significant dispersions in four occupied bands in Fig. 3(c).

The valence and conduction bandwidths, band gaps, and valence band maxima are given in Table II and compared with other reported theoretical and related experimental results. The calculated band gap for our equilibrium conforma-

TABLE II. The calculated valence band (VB) maxima, valence band widths, conduction band (CB) widths, and band gaps compared with another LDA (Ref. 38) and HF (Refs. 31 and 33) calculations as well as experimental results. All the values are expressed in units of eV. α is the torsional angle between the neighboring phenyl rings.

| | α | VB max | VB width | CB width | Gap |
|-----------------------------|----------|--------|----------|----------|------------------|
| LDA(PZ) ^a | 0.0° | -4.71 | 3.38 | 3.77 | 1.99 |
| LDA(PZ) ^a | 34.8° | -4.93 | 2.58 | 2.86 | 2.54 |
| LDA(PZ) ^a | 90.0° | -6.00 | 0.41 | 1.16 | 4.30 |
| LDA(LAPW) (Ref. 38) | 0.0° | ... | 3.20 | 3.5 | 3.4 ^b |
| HF (Ref. 31) | 22.7° | -6.95 | 4.91 | ... | ... |
| HF (Ref. 33) | 22.7° | -8.85 | 4.91 | 5.60 | 8.24 |
| HF+/MP2 (Ref. 33) | 22.7° | -7.71 | 4.12 | 5.22 | 4.88 |
| Expt. (UPS solid) (Ref. 25) | | -5.65 | 3.5 | ... | 2.8 |
| Expt. (UPS gas) (Ref. 25) | | -6.95 | 2.9 | ... | 3.4 |

^aPresent calculation.

^b3D value.

tion of PPP of 2.54 eV is somewhat smaller than that suggested by optical measurements of 2.8 eV²² and 3.4 eV⁶ for solid phase and gas phase PPP, respectively. Because of the presence of exciton bands, these experimental results, especially the solid-phase results, represent a lower bound to the fundamental gap. In comparison, Ambrosch-Draxl *et al.*³⁸ predicted a gap value of 3.0 eV for three-dimensional (3D) crystalline PPP, while we made an estimation based on their Fig. 12 of 4 eV for the one-dimensional (1D) gap at a torsion angle of 34.8°. The valence effective Hamiltonian (VEH) calculation performed by Brédas *et al.*²⁸ yielded a 3.5 eV gap for PPP and a 4.3 eV gap for quaterphenyl. Ladik *et al.* reported a HF band gap value of 8.24 eV and after correlation corrections a value of 4.88 eV.³³

Mobility of charge carriers in a solid is closely related to the bandwidth of the band containing the charge carriers. The calculated width of the highest filled band is 2.58 eV and that of the lowest unfilled band 2.86 eV. The relatively large bandwidths of these π bands indicate the extent of the delocalization of the π electrons. The calculations of Ambrosch-Draxl *et al.*³⁸ gave for the highest filled band a width of about 3.2 eV and for the lowest unfilled one a width of about 3.5 eV. The HF results presented by Ladik *et al.* are much larger,³³ 4.91 eV for the valence band width and 5.60 eV for the conduction bandwidth. Correlation corrections reduce the valence and conduction bandwidths to 4.12 and 5.22 eV, respectively.³³ The restricted HF calculation by Champagne *et al.*³⁷ gave a valence bandwidth of 4.45 eV which is similar to the results of Ladik *et al.* The ultraviolet photoelectron spectroscopy (UPS) study carried out on solid and gaseous sexiphenyl reported for the valence bandwidths values of 3.5 and 2.9 eV, respectively.²⁴ Of course to obtain an estimate of mobility, one has to take into account inter-chain hoppings which may even be dominant. To obtain an estimate to them, one has to perform at least two-dimensional (2D) calculations which we plan to do. The 1D band structure can still give an insight for the mobility along the chain.

The ionization potential of the polymer will be given to good approximation by the energy at the top of the valence band, and this quantity will be a reasonable guide of the sensitivity of the material to oxidation. Our LDA result for

the ionization potential is 4.93 eV whereas the XPS²³ and UPS²⁴ results are 6.5 and 5.65 eV, respectively. The HF and HF plus correlation correction results reported by Ladik *et al.*³³ yielded ionization energy values of 8.85 and 7.71 eV, respectively. Another HF calculation carried out by Champagne *et al.*³⁷ using a split-valence 3-21G basis set predicted an ionization energy of 7.16 eV.

C. Conformation dependence of band structure

To study the effects of structural modifications resulting from chemical substitution of the hydrogens in PPP in more detail, we have calculated the band structures of a single PPP chain for ten different torsional angles. The valence and conduction bandwidths, the band gaps, and the ionization potentials are shown in Fig. 4. These curves are all strongly cor-

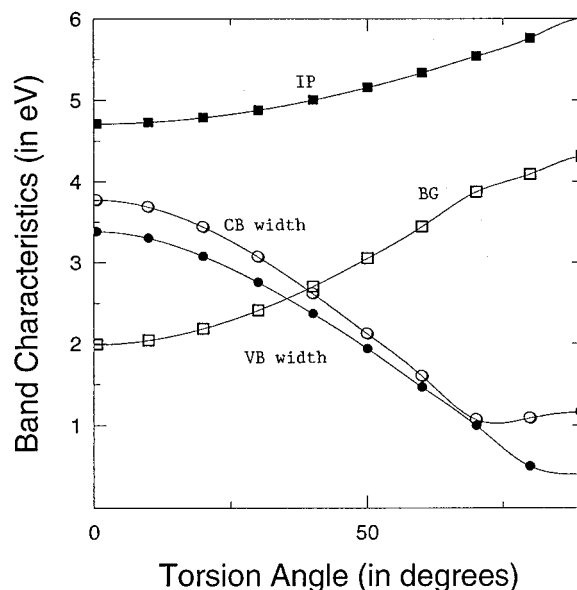


FIG. 4. Variation in bandwidths of the valence bands (VB) and the conduction bands (CB), band gaps (BG), and the ionization potentials (IP) of a single chain of PPP as a function of the torsion angle. The closed and open circles denote the calculated values of the valence and the conduction bandwidths, respectively, whereas the closed and open squares represent the calculated values of the ionization potentials and band gap, respectively.

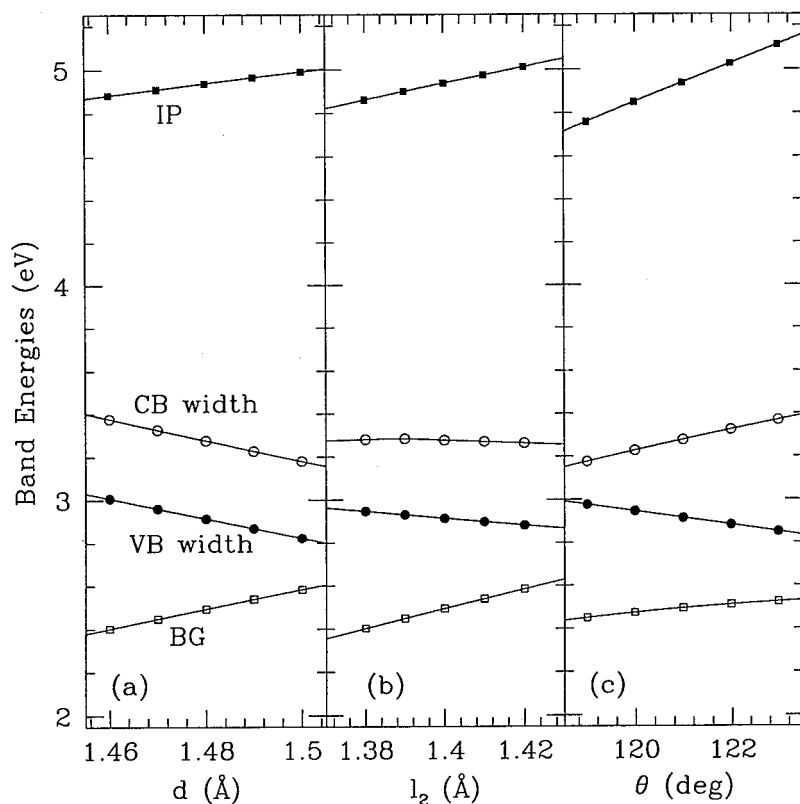


FIG. 5. Variation in bandwidths of the valence bands (VB) and the conduction bands (CB), band gaps (BG), and the ionization potentials (IP) of a single chain of PPP as a function of internal coordinates (a) d , (b) l_2 , and (c) θ . The closed and open circles denote the calculated valence and conduction bandwidths, respectively, whereas the closed and open squares represent the calculated ionization energy and band gap, respectively.

related with each other, and the general trends can be well understood within the framework of a tight-binding model.⁵⁴ In particular, the increased torsion angle leads to decreased π conjugation between phenyl rings, resulting in decreased bandwidths and increased band gaps with the frontier states at the extreme case of a 90° torsion angle being analogous to those in benzene. For optical applications such as in light-emitting diodes, the important characteristics of the material will be the carrier recombination efficiency and the carrier mobility, with the latter directly related to the carrier bandwidth. We thus see that any structural modifications that increase the PPP backbone torsion angle will result in a blue-shifted band gap, but at the expense of decreased carrier mobility. Given the small increase in ionization potential, we would also expect any such chemically modified structure to be at least as chemically resistant to oxidation as pristine PPP, if not more so. Besides the changes of the band gap and bandwidths, the shape of the bands also varies with the change of the torsional angle especially around the extreme case of 90° . At the torsion angle around 80° the bottom of the conduction band changes from the point of $\kappa=0$ to that of $\kappa=\pi$ while the top of the valence band keeps staying at $\kappa=0$. Therefore the band gap changes from a direct to an indirect gap. But at the torsion angle of 90° , the states in the valence bands at the center and at the edge of the Brillouin zone have the same energy, so that the direct gap at $\kappa=0$ and the indirect gap between $\kappa=0$ and $\kappa=\pi$ are degenerate.

Besides the torsional angle, chemical modification can lead to structural modification of the internal coordinates of the PPP chain. To investigate these effects, we have carried out several sets of calculations separately varying the inter-

ring carbon-carbon bond distance d , the ring carbon-carbon bond distance l_2 , and the phenyl ring bond angle θ with all other internal coordinates kept fixed. The equilibrium parameters in these calculations were taken to be averaged values of the experimental data,^{13,14,16} i.e., $l_1=1.38$ Å, $l_2=1.40$ Å, $d=1.48$ Å, and $\theta=118.04^\circ$. Note that, as for the fixed internal coordinates, the experimental value of the torsion angle for the stable configuration (22.7°) was chosen. Changes of the order of 2% in the parameters l_2 , d , and θ but not l_1 are considered because the steric effects of replacing the hydrogens in the phenyl ring with other side groups will predominantly influence only these parameters. Similar to our results for torsion angle changes, we depict our results for the valence bandwidths, conduction bandwidths, band gaps, and ionization potentials in Fig. 5. We have also carried out analogous calculations for the two extreme cases of torsion angles of 0° and 90° .

For small changes in the inter-ring bond distance d depicted in Fig. 5(a), the trends are the same as with the changes in torsion angle depicted in Fig. 4. As can be seen, the band gap and ionization energy increase almost linearly with the bond length while the widths decrease. For planar PPP the results are similar, while for the 90° torsion angle conformation the lack of conjugation between phenyl rings leads to very little change in any of these properties with changes in the inter-ring bond distance d . For a bond length variation from 1.46 to 1.5 Å we calculate a change in band gap from 2.4 to 2.6 eV. In Fig. 5(b), the variation of the characteristics with respect to the intra-ring C-C length l_2 , is shown. These results are quite similar to the previous results except that the bandwidths are less sensitive to small

changes in l_2 than in d , and the band gap and ionization energy both decrease with l_2 for the 90° twisted conformation whereas they increased at 22.7° . Finally in Fig. 5(c), the effects of changes in the bond angle θ , of less than 2%, are depicted. Again the changes in those features are similar to those arising from changes in d or l_2 except that the conduction bandwidth increases with increasing angle instead of decreasing as in the two previous cases.

In order to understand the changes of the band characteristics versus the bond lengths, d and l ($l_1=l_2=l$), a tight binding (TB) model⁵⁴ is constructed by using only nearest-neighbor interactions and universal coupling constants as determined by Harrison.⁵⁵ The molecular π orbitals are those of a perfect benzene ring. However, in order to consider the influence of the changes of l_2 within the rings, one can go one step further and calculate the orbitals of a deformed benzene molecule with $l_1 \neq l_2$ by a first-order perturbation approach and use them to construct the Bloch basis functions.

The procedure to construct the Hamiltonian submatrix is similar to that in Ref. 47, except that the orbitals of a deformed benzene molecule with energies $\epsilon_p - 2V_l - 2/3V'_l$,

$\epsilon_p + 2V_l + 2/3V'_l$, $\epsilon_p - V_l + 1/3V'_l$, $\epsilon_p + V_l - 1/3V'_l$, $\epsilon_p - V_l - V'_l$, $\epsilon_p + V_l + V'_l$ are used instead of the orbitals of the original benzene ring, where ϵ_p , with the value of -8.97 eV, is the energy of the carbon p_z orbitals, V_l ($V_l = V_{l_1}$) are the coupling coefficients $V_{pp\pi}$ within the phenyl ring, and V'_l is the difference between the coupling coefficient V_{l_2} of a deformed benzene molecule with its undeformed value ($V'_l = V_{l_2} - V_l$). If the orbitals of the original benzene ring are denoted by $\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6$, in the same sequence as the energies above, the orbitals of the deformed benzene ring are then $\phi_1 - a\phi_4, \phi_2 - a\phi_3, \phi_3 + a\phi_1, \phi_4 + a\phi_1, \phi_5, \phi_6$, where a is equal to $\sqrt{2/9}V'_l/V_l$. A 6×6 Hamiltonian matrix can be obtained by using the Bloch functions constructed from the above orbitals. Because all six π bands are monotonic, the band characteristics such as the bandwidths, the ionization energy, and the band gap can be obtained by solving the matrix only at the high symmetry points in the Brillouin zone, $\kappa=0$ and $\kappa=\pi$. At these points the Hamiltonian matrix reduces to two 2D and two 1D submatrices. After some algebra, we get the eigenvalues E_j at $\kappa=0$:

$$E_{1,4}^{\kappa=0} = \epsilon_p - \frac{V_l}{2} - \frac{V'_l}{2} - \frac{V_d}{3} \cos \alpha \mp \frac{3V_l}{2} \sqrt{\left(1 - \frac{8}{81} \frac{V_d}{V_l} \frac{V'_l}{V_l} \cos \alpha + \frac{1}{9} \frac{V'_l}{V_l}\right)^2 + \frac{8}{81} \left(\frac{V_d}{V_l} \cos \alpha\right)^2},$$

$$E_{2,3}^{\kappa=0} = \epsilon_p + \frac{V_l}{2} + \frac{V'_l}{2} + \frac{V_d}{3} \cos \alpha \pm \frac{3V_l}{2} \sqrt{\left(1 - \frac{8}{81} \frac{V_d}{V_l} \frac{V'_l}{V_l} \cos \alpha + \frac{1}{9} \frac{V'_l}{V_l}\right)^2 + \frac{8}{81} \left(\frac{V_d}{V_l} \cos \alpha\right)^2}. \tag{1}$$

For $\kappa=\pi$, the results can be obtained by just reversing the sign of the terms which contain $\cos \alpha$ in the above equations. These eigenvalues are different from the ones given by formula (4.3) in Ref. 38. The present results reproduce the molecular eigenvalues for $V_d=0$ and are not degenerate at π and $V_d=V_l$.

Because the bond lengths d , l_1 , and l_2 are close to each other, the values of V_d , V_{l_1} , and V_{l_2} are close to each other. So the terms $8/81(V_d/V_l)^2$ and $8/81(V'_l/V_l)^2$ as well as $1/9V'_l/V_l$ are considerably smaller than one and as a reasonable approximation the terms under the square root can be reduced to 1. By taking this approximation, we obtain for:

$$E_g = E_3(\kappa=0) - E_4(\kappa=0) \approx -2V_l + \frac{V'_l}{2} + \frac{2V_d}{3} \cos \alpha,$$

(2) the ionization energy:

$$I = -E_4(\kappa=0) \approx -\epsilon_p - V_l + \frac{V'_l}{4} + \frac{V_d}{3} \cos \alpha,$$

(3) the bandwidths:

$$W = |E_i(\kappa=0) - E_i(\kappa=\pi)| = -\frac{2V_d}{3} \cos \alpha.$$

Notice that V_d , V_l , and V'_l are less than zero.

The band characteristics at ten different torsion angles are calculated from the above equations and are given in Fig. 6. As is seen from the expressions above, all the band characteristics change with the torsion angle as a cosine function, which is consistent with the LDA results, in most of the regions except around the extreme case of torsion angle 90° . In this conformation, the neighboring rings are perpendicular to each other and so the p_z orbitals are. The increase of the coupling between the p_z orbitals and the sp^2 hybrids of the neighboring carbon atom, which are now in the same plane, invalidate the TB model. As soon as this coupling becomes effective, one may expect the bandwidths to increase again. This increase can be seen in the LDA calculation above 70° (see Fig. 4). Note that the ionization energy curve calculated in the TB model (Fig. 6) is similar in shape to the LDA result (Fig. 4). However, the value at 0° in the TB model is 10.83 eV whereas the LDA result is 4.71 eV. In order to compare all the curves of band gap, bandwidths, and ionization energy in the TB model with the LDA calculation, the ionization energy curve in the TB has been shifted by -6 eV.

Furthermore, because the derivatives of the energy gap and the ionization energy with respect to the coupling coefficient and the derivative of the coupling coefficients with respect to the bond length between the neighboring rings, d , are positive, while the derivatives of bandwidths with respect to the coupling coefficient are negative, it is easy to conclude that when the bond length between the neighboring phenyl

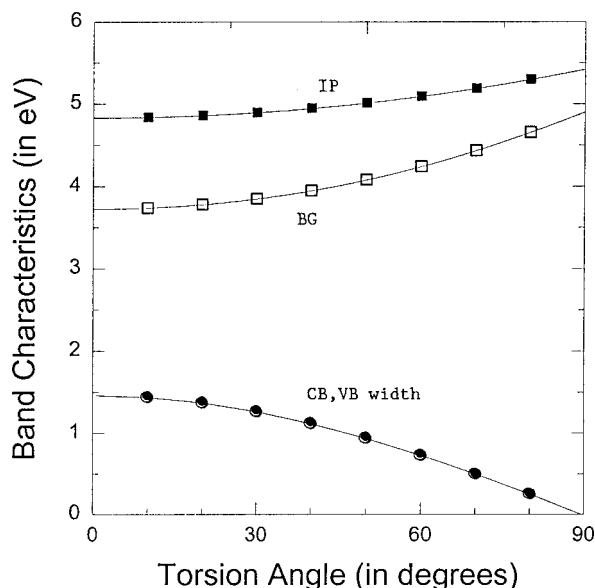


FIG. 6. The tight-binding bandwidths of the valence bands (VB) and the conduction bands (CB), band gaps (BG), and the ionization potentials (IP) of a single chain of PPP as a function of the torsion angle. The closed and open circles denote the calculated values of the valence and the conduction bandwidths, respectively, whereas the closed and open squares represent the calculated values of the ionization potentials and band gap, respectively. For clarity, the energy scale is the same as that of Fig. 4 and the ionization energy curve has been shifted by -6 eV. According to the TB bandwidth equation (Sec. III C), the valence and the conduction bandwidths are equal with each other at any α value.

rings increases, the band gap and the ionization energy increase while the bandwidths decrease. For a small deformation of the bond length, a linear dependence is expected. The case is similar to the change of bond length, l_2 , except that the bandwidths are independent of the bond length. We can see in Figs. 5(a) and 5(b) that the bandwidth changes are much smaller for changes in l_2 than d as expected. The changes of the bands versus the other parameter, θ , cannot be explained by our simple tight-binding model. Because of the deformation of the sp^2 hybrids, it is necessary to consider orbitals other than p_z , which makes the model much more complex.

It should be pointed out that Ambrosch-Draxl *et al.* (see Ref. 38) also did a TB calculation, starting from TB model conditions as the present authors for the case $l_1 \neq l_2$. However, their final equations for the band energies fail to yield the energy levels for the benzene molecule when $t_{22}=0$ and $t_{11}=t_{12}$ and give degenerate states at $\kappa=0$ and $\kappa=\pi$ of the Brillouin zone when $t_{11}=t_{12}=t_{22}$. This degeneracy does not appear in our results.

Changes in these geometrical parameters could be achieved by applying external stress or by substituting the hydrogen by other side groups. In general we find that substitutions that increase the band gap would lead to a decrease in conduction and valence bandwidths, with a resulting decrease in carrier mobility. Some possibilities for tailoring the properties of PPP still remain. For example, substitutions of the phenyl hydrogens that increase the sp^3 character of their bonding would tend to decrease the carbon's ring bond angles between l_1 and l_2 , leading to an increase in bond

angle θ . This would tend to increase the band gap while increasing the conduction bandwidth. Also, any chemical substitutions that lengthen l_2 without increasing d could potentially increase the band gap without making major changes to the bandwidths.

IV. CONCLUSIONS

A first-principles density functional calculation of the conformation and electronic structure of a single chain PPP is presented by using a local-density approximation and a Perdew-Zunger fit to the correlation energy. The parameters in the equilibrium conformation are optimized and found to be in rather good agreement with the experimental results. A torsion angle of 34.8° is predicted and the well depth relative to the planar conformation is 1.7 kcal/mol. The C-C bond length between the neighboring phenyl rings varies with the torsion angle in a similar way as the total energy. The calculated band gap value is 2.54 eV. The bandwidths and the ionization energy are in reasonable agreement with the experimental data. The effects of structural modifications on the electronic properties have been examined, and some structural modifications were found that allow an increase of the band gap with no significant decrease of the bandwidths.

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