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First-principles studies of some conducting polymers: PPP, PPy, PPV, PPyV, and PANI

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Abstract

We present results of first-principles calculations of the electronic properties of several conducting polymers containing either phenylene or pyridine rings. The applied density functional method employs linear muffin-tin orbitals (LMTOs) as basis functions. It has been explicitly constructed for calculating the electronic properties of infinite, periodic, helical, polymeric chains. We study poly(*p*-phenylene) (PPP), poly(*p*-phenylenevinylene) (PPV), poly(2,5-pyridine) (PPy), poly(2,5-pyridinevinylene) (PPyV) and polyaniline (PANI). The structural parameters were obtained either from experimental information or by applying semi-empirical methods. We find that by replacing a carbon atom by a nitrogen atom in the phenylene ring, an occupied *n*-band appears. Simultaneously, the first ionization potential is increased which can be related to the electronegativity of nitrogen compared to that of carbon. When a vinylene linkage separates the rings, steric effects between the rings are diminished and the rings may thus be coplanar. This increases the π -electron delocalization and produces a stabilization of the system. In contrast, by replacing the vinylene linkage by an amine group (resulting in PANI) a non-planar polymer is obtained which has a larger band gap and a smaller ionization potential. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: One-dimensional polymers; Density functional calculations; Polypyridine; Poly(*p*-phenylene); Polyaniline

1. Introduction

During the last two decades much research activity has been devoted to quasi-one-dimensional polymers having an extended π -electron system [1,2]. The investigation of these semiconductor polymers has become increasingly important because of their unusual combination of electronic, optical, and mechanical properties [1–3]. For these materials, a large intrinsic electrical conductivity and (hyper-) polarizabilities have been reported in cases where

they have particularly small band gaps [4,5]. Other conjugated polymers with larger band gaps have been reported to show electroluminescence [2,6]. The discovery (in 1990) of this property for poly(*p*-phenylenevinylene) has triggered a still growing interest in identifying other conducting polymers with similar properties that, accordingly, may be applied in light-emitting diodes (LEDs) [2,7].

Within this context one of the most studied conducting polymers is poly(*p*-phenylenevinylene) (PPV) because of its attractive physicochemical properties. PPV may be considered a copolymer of poly(*p*-phenylene) (PPP) and polyacetylene (PA) [2,6,11]. Therefore, one may suggest that, as a first approximation, its intrinsic electronic

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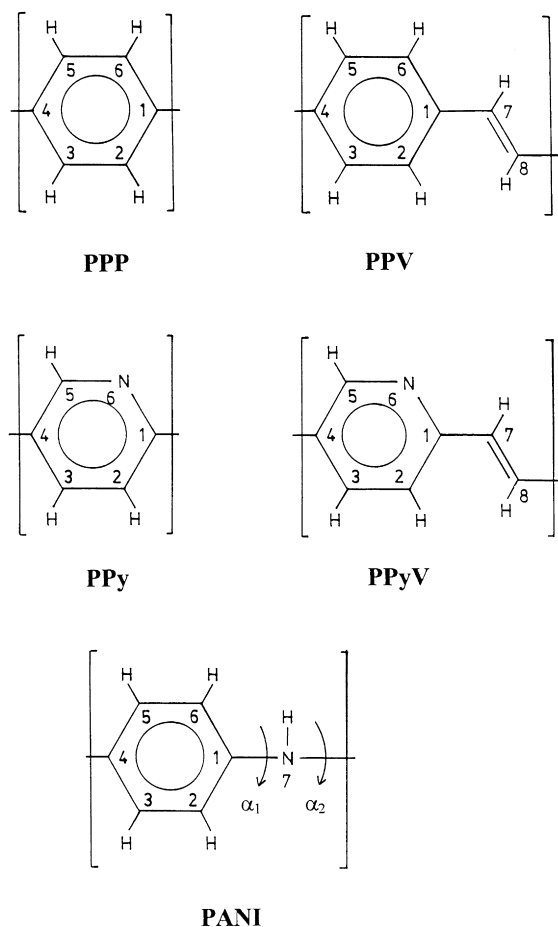


Fig. 1. Schematic representation of the unit cell of the studied polymers.

and optical properties are in between those of PPP and PA [8].

PPP is the structurally simplest conjugated polymer based on phenylene rings [9]. It is an insoluble and infusible dark brown material with poor conductivity. However, this material was one the first reported having blue electroluminescence (whereas that of PPV is greenish-yellow) [2,10,11].

Conjugated polymers that luminesce with blue light are difficult to obtain because most of them have band gaps too small to allow blue emission [2]. To date, the only conjugated polymer candidates are poly(alkyl-fluorenes), PPP, and pyridine-based polymers, such as poly(2, 5-pyridine) (PPy) and poly(2, 5-pyridinevinylene) (PPyV) [2]. Pyridine-based conjugated poly-

mers have, moreover, been shown to be promising candidates for LEDs [7,12,13]. Compared to the phenylene-based analogues, one of the most important features of the pyridine-based polymers is their higher electron affinity [14]. In addition, PPy has processability advantages over PPP as reported by Gebler et al. [15] PPy can be considered as obtained from PPP by replacing one CH unit per phenylene ring by a nitrogen atom; cf. Fig. 1. PPyV may be considered as a copolymer between PPy and PA and therefore, as a first approximation, it may be expected that its electronics properties be in between those of the two precursor polymers. Alternatively, PPyV may be obtained from PPV by replacing one CH unit per phenylene ring by an N atom.

Another – currently intensively studied – conjugated polymer that can be considered a derivative of PPP is polyaniline (PANI), which contains phenylene rings linked via amine groups [16–18]. This material has a very high electronic conductivity but its luminescence properties are not fully explored [4,5,16,17].

Comparing the different polymers (Fig. 1) it is obvious that they all are closely related and can be obtained from each other by either replacing CH groups by N atoms and/or by adding linkages between the rings. This variational freedom opens up the possibility to control the materials properties and to produce materials with pre-defined properties once the relations between composition and structure on the one side and property on the other is clearly understood. As a step in this direction we performed first-principles, density functional calculations on all the systems of Fig. 1 and shall here report the results of this study and, in particular, compare their electronic properties. In addition we shall compare their electronic properties with those of the simpler conjugated polymers polyacetylene and polycarbonitrile. We have applied a method that has been developed explicitly for polymeric systems. This method has proven to be an accurate tool for calculating the electronic properties of conjugated polymers [19–21].

The calculations were done for fixed structures. The structural parameters were taken either from crystallographic data obtained with X-ray diffraction [22–25] or from calculations with the Austin Model 1 (AM1) or Parameterization 3 (PM3) semi-empirical methods [26–28]. For most of the systems it was assumed that they have a planar conformation with,

Table 1

Selected structural parameters of PPP, PPy, PPyV, PPV and PANI. h denotes the unit-cell length (Å) and r denotes bond lengths (Å). The notation is as in Fig. 1

	PPP ^a	PPy ^b	PPV ^a	PPyV ^b	PANI ^c
h	4.375	4.350	6.413	6.488	5.249
$r_{C(1)-C(2)}$	1.411	1.401	1.397	1.403	1.412
$r_{C(2)-C(3)}$	1.413	1.391	1.336	1.387	1.386
$r_{C(3)-C(4)}$	1.411	1.396	1.373	1.399	1.415
$r_{C(4)-C(5)}$	1.413	1.404	1.384	1.403	1.412
$r_{C(5)-C(6)}$	1.411	—	1.387	—	1.386
$r_{C(6)-C(1)}$	1.413	—	1.394	—	1.412
$r_{C(1)-C(7)}$	—	—	1.469	1.460	—
$r_{C(7)-C(8)}$	—	—	1.318	1.341	—
$r_{C(5)-N(6)}$	—	1.345	—	1.345	—
$r_{C(1)-N(6)}$	—	1.365	—	1.365	—

^a Crystallographic data.

^b Data from PM3 calculations.

^c Data from AM1 calculations.

however, the exception that the torsion angles in PANI were set equal to $\alpha_1 = \alpha_2 = 30^\circ$ (see Fig. 1).

There are several theoretical studies of the electronic properties of these polymers, particularly on PPV; we should point out the studies carried on by Gomes da Costa et al. [29], where the electronic properties of a tri-dimensional polymeric arrangement is calculated. They have first proved the suitability of theoretical method based on DFT in order to calculate electronic properties of polymeric systems. The main goal of this work is to compare systematically the electronic properties of several member of a family of polymers, including PPV, by using a parameter-free method. We will employ a DFT based on method which uses the linear muffin-tin orbitals (LMTO) considering full potential in the interstitial region. This method was specifically adapted to calculate the electronic properties of helical polymers.

The paper is outlined as follows. In the next section we describe briefly our computational scheme. Subsequently, we describe our main results for the various polymers. Finally, these are compared and our conclusions are presented.

2. Methodology

The structural parameters we have used are listed in Table 1. For PPP and PPV we used information from

crystal structures of oligomers determined by X-ray diffraction [22–25]. Whereas we have optimized the structural data of PPy, PPyV and PANI using the semi-empirical AM1 method [28] for PANI [26,27] and PM3 method for PPy and PPyV on finite pentamers. The resulting structural data obtained with the AM1 and PM3 methods agree reasonably well with those determined by X-ray diffraction [30,31]. In the subsequent polymer calculations the structure was obtained by periodically repeating that of the central unit cell of the pentamers.

2.1. Density functional method for helical polymers

Our density functional method has been described in detail elsewhere [21] and shall therefore only briefly be described here. It is based on the density functional formalism of Hohenberg and Kohn [32] in the single-particle formulation of Kohn and Sham [33]. The resulting Kohn–Sham single-particle equations

$$\hat{H}_{KS}\psi_i(\mathbf{r}) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (1)$$

are solved by expanding ψ_i in a basis of linearized muffin-tin orbitals (LMTOs) which have the form

$$h_l^{(l)}(\kappa|\mathbf{r} - \mathbf{R}_k|)Y_L(\mathbf{r} - \mathbf{R}_k) \quad (2)$$

in the so-called interstitial region (outside all atom-centered, non-overlapping, so-called muffin-tin spheres). Inside the spheres each of these functions is augmented continuously and differentiable with numerical functions obtained from Eq. (1) by replacing $V_{\text{eff}}(\mathbf{r})$ by its spherically symmetric part. In Eq. (2), $L \equiv (l, m)$ describes the angular momentum, \mathbf{R}_k is the position of the k th atom, κ is a purely imaginary number whose absolute value is a decay constant, and $h_l^{(l)}$ is a spherical Hankel function. It shall be stressed that the full potential is used in the calculations and not only its muffin-tin part. Finally, for the exchange-correlation part of $V_{\text{eff}}(\mathbf{r})$ we used the local approximation of von Barth and Hedin [34].

The method has been specifically designed for calculations on infinite, periodic polymers. The periodicity is used in constructing Bloch waves from equivalent basis functions of different unit cells i.e. from the j th basis function of the n th unit cell χ_{jn} , the

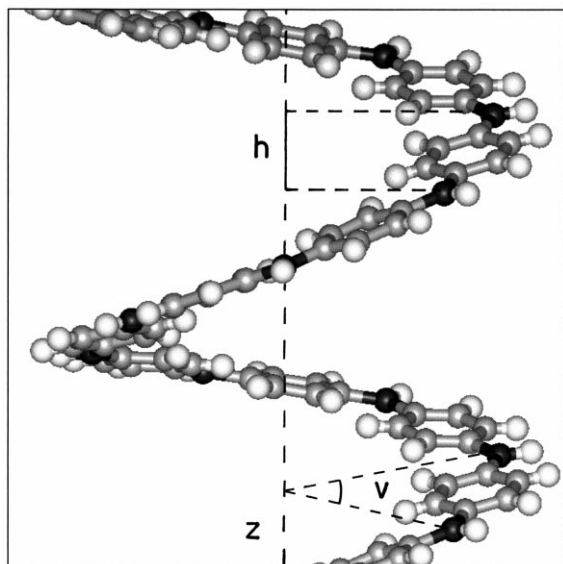


Fig. 2. Schematic representation of a polyaniline helix.

Bloch waves are defined as follows:

$$\chi_j^k = \lim_{N \rightarrow \infty} \frac{1}{\sqrt{2N+1}} \sum_{n=-N}^N \chi_{jn} e^{ikn\pi} \quad (3)$$

where j is a compound index describing the site at which the basis function is centered, its angular dependence, as well as any other dependence that distinguishes the basis functions.

By using that the Hamilton operator of Eq. (1) possesses the full symmetry of the system, the following equations are obtained:

$$\langle \chi_{j_1}^k | \chi_{j_2}^k \rangle = \lim_{N \rightarrow \infty} \frac{1}{2N+1} \sum_{n_1, n_2=-N}^N e^{ik\pi(n_2-n_1)} \langle \chi_{j_1 n_1} | \chi_{j_2 n_2} \rangle \quad (4)$$

$$\langle \chi_{j_1}^k | \chi_{j_2}^k \rangle = \lim_{N \rightarrow \infty} \sum_{n=-N}^N e^{ikn\pi} \langle \chi_{j_1 0} | \chi_{j_2 n} \rangle \quad (5)$$

and, equivalently,

$$\langle \chi_{j_1}^k | \hat{H}_{KS} | \chi_{j_2}^k \rangle = \lim_{N \rightarrow \infty} \sum_{n=-N}^N e^{ikn\pi} \langle \chi_{j_1 0} | \hat{H}_{KS} | \chi_{j_2 n} \rangle \quad (6)$$

In the actual calculations, the infinite summations in Eqs. (4)–(6) are carried through with N so large that they can be considered converged.

We used a basis set consisting of two subsets of s , p , and d functions on all sites. The two subsets differ in the decay constants κ of the Hankel functions.

By other way, in order to calculate specifically a polymer system we shall define it as being infinite in one dimension and finite in the other two. Therefore, we will consider it as being an infinite, periodic, isolated and helical chain with a straight helical axis (see Fig. 2). In a global coordinate system, we can describe the position of the i th atom of the n th unit cell by,

$$x = r_i \cos u_{ni} \quad y = r_i \sin u_{ni} \quad z = u_{ni}/v \cdot h + z_i \quad (7)$$

with

$$u_{ni} = n \cdot v + \phi_i. \quad (8)$$

The parameters r_i , ϕ_i , and z_i are internal coordinates that are unique for the i th atom whereas h and v describe the size of the unit cell as well as the primitive symmetry operation that maps the system onto itself (a combined translational h and rotational v). Finally, the zig-zag symmetry is a special case of the helical geometry. For more details about the method, the reader is referred to Refs. [19–21,35].

3. Results

Starting with PPP as a reference system, those considered here (see Fig. 1) have been obtained

- (i) by addition of a vinylene linkage between the rings giving PPV, or
- (ii) by replacing one carbon atom of each phenylene ring by a nitrogen atom leading to PPy, or
- (iii) by applying both modifications (i) and (ii) simultaneously resulting in PPyV, or, finally,
- (iv) by adding an amine group between the rings giving PANI.

All systems, in particular PPV and PANI, have been the subject of many previous experimental or theoretical studies but there exist only few detailed comparative studies of their electronic properties as obtained with first-principles methods.

3.1. Poly(*p*-phenylene) (PPP)

The (near-)planarity of *p*-hexakisphenyl oligomers

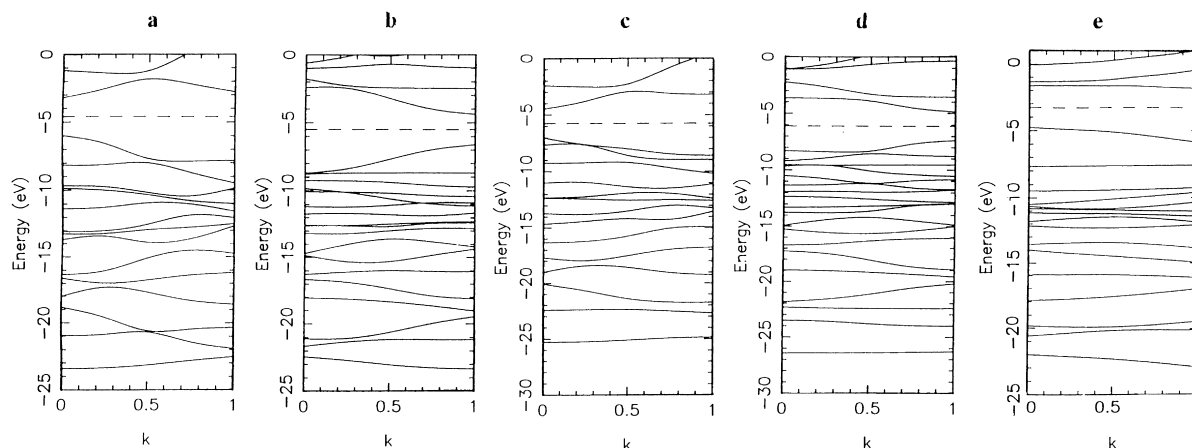


Fig. 3. Calculated band structures (a) PPP, (b) PPV, (c) PPyV and (e) PANI. Dotted line indicates the Fermi level. $k = 0$ and $k = 1$ correspond to the center and edge of the first Brillouin zone, respectively and the dashed lines mark the Fermi level.

can be understood in terms of a competition between intramolecular (*ortho*-hydrogen) repulsion and intermolecular (packing) interactions [25]. Accordingly, the torsion angle between neighboring rings has been determined as 20° – 30° in solution whereas it, in the crystalline phase, decreases to 0° – 10° [25,36]. In our calculations we assumed that the polymer is planar which should be a fair approximation. The structural parameters of one unit cell have been taken from Ref. [25] (see Table 1). The main changes in the electronic properties when passing to a non-planar PPP would result in an overall narrowing of the electronic bands.

Fig. 3(a) shows our calculated band structures of PPP. There are three occupied π bands as well as three π^* bands above the Fermi level. These are equivalent to the π and π^* levels of the benzene molecule. The highest occupied and the lowest unoccupied bands correspond to a π and a π^* band, respectively (see Fig. 4). A very flat π band crosses the highest occupied band. The orbitals of this are antisymmetric with respect to reflection in the mirror plane perpendicular to that of the nuclei and vanish therefore on the carbon atoms in *para* positions. This flat band produces a sharp peak in the density of states (DOS) which should dominate photoelectron spectra.

The bandwidth of the highest occupied band is 3.5 eV, the band gap is 2.8 eV, and the ionization potential, IP, is 6.0 eV. All these values are in good agreement with those determined experimentally by

Grem et al. [10,11] and Shacklette et al. [37]. In a theoretical study using the VEH method, Brédas et al. found a band gap of 3.5 eV and an IP of 5.6 eV [38], once again in good agreement with our values. Our calculated band structures agree also well with the recent *ab initio* Hartree–Fock band structures of Champagne et al. [39] except for the fact that the Hartree–Fock bands are overall wider than the density-functional bands. This is a common difference between results of Hartree–Fock and those of density functional calculations.

3.2. Poly(*p*-phenylenevinylene) (PPV)

For PPV we used an older structural data from X-ray diffraction experiments on *trans*-stilbene (see Table 1) [22–24]. We add that more recent experimental data [39–41] indicate a somewhat reduced bond length alternation of the vinylene linkage. For the present purpose these differences should, however, be of only secondary importance.

Fig. 3(b) shows our calculated band structures of PPV. These possess four occupied π bands of which three are related to the benzene π system (as for PPP) whereas the fourth (the energetically highest) has a large contribution from the vinylene π functions. The frontier orbitals are shown in Fig. 5 where the large contribution from the vinylene linkage can be recognized. The single-particle band gap of PPV corresponds to a $\pi \rightarrow \pi^*$ transition. Our calculated

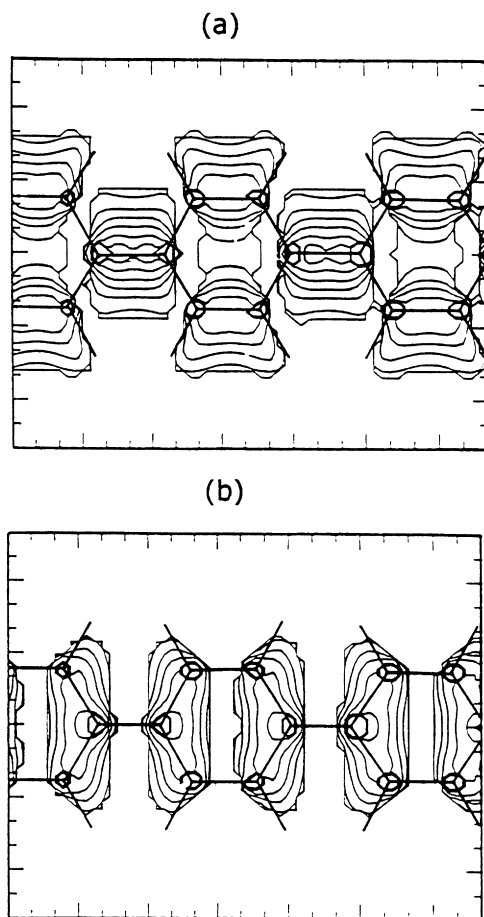


Fig. 4. Pattern of the frontier band of PPP at $k = 0$. (a) lowest unoccupied band and (b) highest occupied band. The plots are shown in a plane parallel to that of the nuclear backbone (whose structure is also shown).

value for its size, 2.0 eV, fits reasonably well with the one determined experimentally, i.e. about 2.4 eV. The underestimate is consistent with the general tendency of density functional methods to underestimate band gaps of semiconductors by 0.5–1 eV.

Our results agree well with those obtained by Gomes da Costa et al. on PPV using another parameter-free density functional method [42]. In particular, as we do, they found a pair of a very flat and a steeper π band both just above and just below the Fermi level that pairwise almost meet at $k = 0$. Also their lowest valence band is very flat but their total valence-band width is slightly larger than ours. The difference may, however, be related to differences in

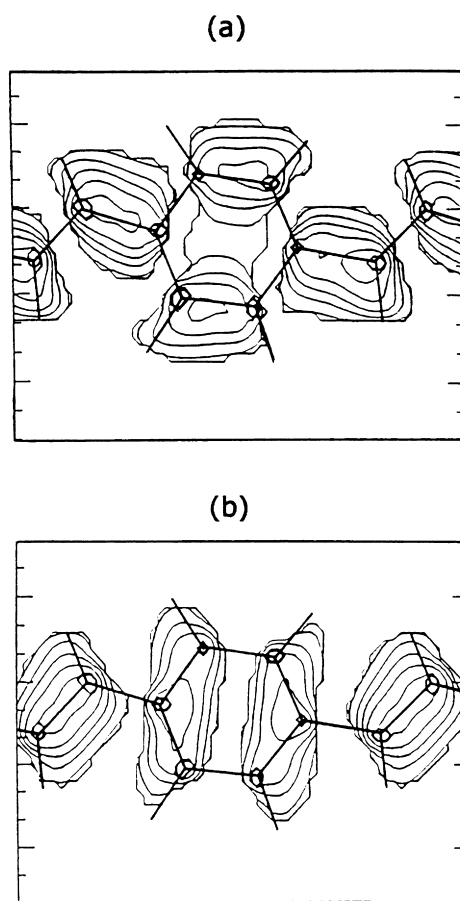


Fig. 5. Pattern of the frontier band of PPV at $k = 1$. (a) lowest unoccupied band and (b) highest occupied band. The presentation is as in Fig. 3.

the structure of the polymers as well as the difference between a crystalline material and an isolated chain.

As in PPP, the very flat π valence-band should dominate the photoelectron spectra of this material. A detailed comparison between our density of states and with the experimental XPS and UPS spectra of PPV obtained by Obrzut et al. [43] and Fahlman et al. [44], respectively, shows that our results agree well with the experimental ones.

3.3. Poly(2,5-pyridine) (PPy)

During the last 50 years, pyridine and systems based on pyridines have been intensively studied because of their photochemical properties (in

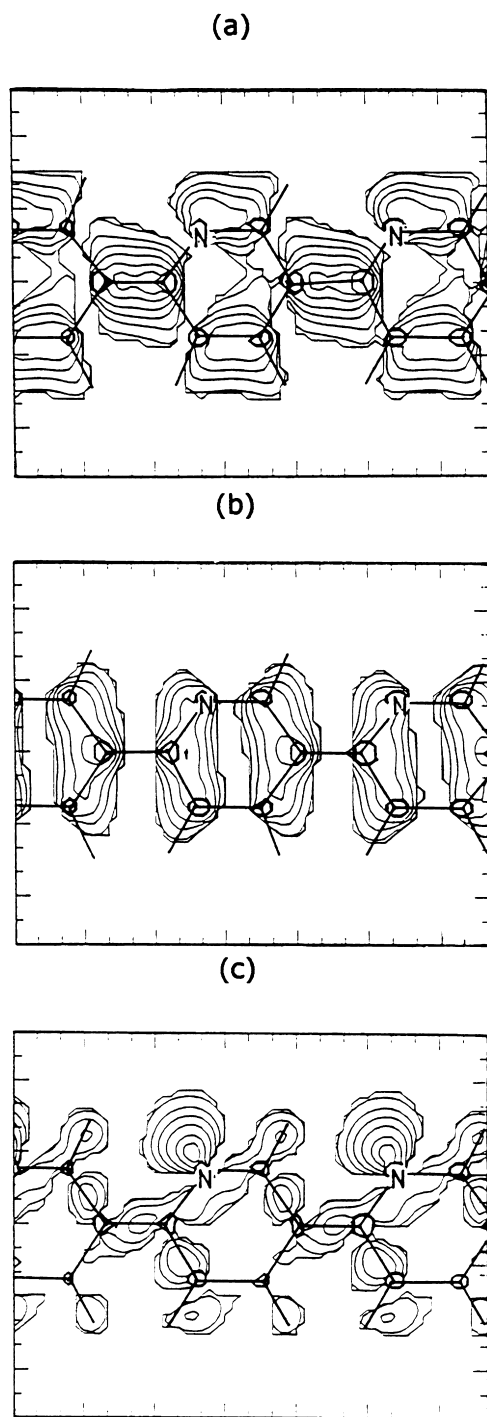


Fig. 6. Pattern of the frontier band of PPy at $k = 0$. (a) lowest unoccupied band, (b) highest occupied band and (c) highest - 1 occupied band. The presentation is as in Fig. 3.

particular, phosphorescence). The low-energy excitations include a $\pi \rightarrow \pi^*$ transition and an $n \rightarrow \pi^*$ transition. Owing to their unusual luminescence of blue light, polymers based on pyridine have been a subject of a major research activity [2,13,15,45].

Fig. 3(c) shows our calculated band structures of PPy. They include three occupied π bands and the three lowest unoccupied π^* bands. The most remarkable feature is the appearance of a very flat band just below the Fermi level. It originates from the n lone pairs of the nitrogen atoms (see Fig. 6). This finding agrees well with the previous reported orbital diagrams of pyridines and pyridine oligomers [46,47] as well as with previous density functional results on polycarbonitrile [48]. The band gap of PPy is slightly smaller than that of PPP, in agreement with experimental results [15]. Moreover, the Fermi energy of PPy is lower than that of PPP.

The energy of the lowest $n \rightarrow \pi^*$ transition relative to the lowest singlet $\pi \rightarrow \pi^*$ transition is extremely important for luminescence in a molecule containing n electrons. In fact, molecules in which an $n \rightarrow \pi^*$ transition is below the lowest singlet $\pi \rightarrow \pi^*$ transition generally fluoresce only weakly. From our calculations we find an $n \rightarrow \pi^*$ transition around 3.2 eV and a $\pi \rightarrow \pi^*$ transition around 2.5 eV. The latter value is in good agreement with the experimental value of about 3 eV [15], when taking the common band gap underestimate of density functional calculations into account. Blatchford et al. [31] calculated the lowest electronic transition energy of PPy by extrapolating oligomer results obtained by using the semi-empirical PM3 + SCI Hartree–Fock method. They found that, for PPy, the difference between the two lowest transition energy ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) is around 0.8 eV, remarkably similar to our results of 0.6 eV.

Finally, the ionization potential of PPy shows an increase of around 1 eV compared to PPP. This difference indicates that this system is significantly more stable against oxidation.

3.4. Poly(2,5-pyridinevinylene) (PPyV)

We optimized the structure of one unit cell of PPyV using the semi-empirical PM3 method. Our obtained results agree well with those reported by Blatchford et al. for oligomers [31].

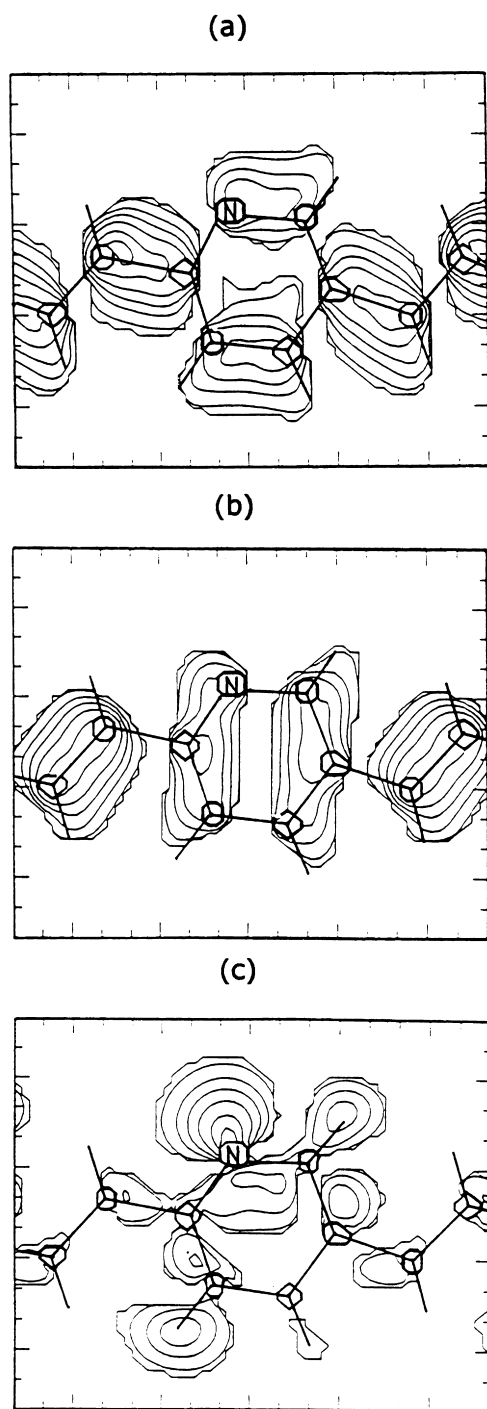


Fig. 7. Pattern of the frontier band of PPyV at $k = 1$. (a) lowest unoccupied band, (b) highest occupied band and (c) highest - 1 occupied band. The presentation is as in Fig. 3.

PPyV may be considered as a copolymer between PPy and PA. It is, in addition, the analogue of PPV but contains pyridine instead of phenylene rings. However, while PPV to a good approximation possesses a charge-conjugation symmetry, this symmetry is broken for PPyV. Our calculated band structures, shown in Fig. 3(d), contain four occupied π bands and four unoccupied π^* bands. As for PPy, a very flat band from the nitrogen lone pairs appears in the uppermost part of the valence bands.

The frontier orbitals of PPyV are shown in Fig. 7. The first electronic transition corresponds to a $\pi \rightarrow \pi^*$ transition, for which the π orbital has a large contribution from the p orbitals of carbon atoms from the vinylene linkage. The band just below the highest occupied one is the nitrogen lone-pair band and it gives rise to a low-energy $n \rightarrow \pi^*$ transition.

As for PPy, the relative energies of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are very important. Our results show, for PPyV, an $n \rightarrow \pi^*$ transition at around 3.8 eV and a $\pi \rightarrow \pi^*$ transition around 2.5 eV. The latter is in excellent agreement with the experimental value for the $\pi \rightarrow \pi^*$ transition, i.e. around 2.6 eV [12,13]. In their semi-empirical study, Blatchford et al. [31] obtained a difference between these two transitions of about 1.4 eV, absolutely consistent with our result of 1.3 eV (see Table 2).

Similar to PPy, PPyV also has a higher ionization potential than PPV. This polymer also should therefore be more resistant against oxidation.

3.5. Polyaniline (PANI)

We studied the electronic properties of PANI only in its reduced form. Previous experimental and theoretical works have shown that PANI has a large band gap in the reduced state (around 3.6 eV) which diminishes for the oxidized state [49].

In our calculations, a non-planar helical geometry was assumed having the internal coordinates of one aniline unit, predetermined from semi-empirical AM1 calculations (see Fig. 1). Fig. 3(e) shows our calculated band structures. We obtain an energy gap of 3.0 eV, which is (accidentally), in better agreement with experiment than the one obtained by Brocks et al. using another first-principles density functional method [50]. The fact that the bands are fairly flat and that the band gap is relatively large agrees with

Table 2

Electronic properties of PPP, PPV, PPy, PPyV and PANI, compared with those of polyacetylene (PA) and polycarbonitrile (PCN) (values between parenthesis corresponds to experimental ones, they have been taken from the references indicated in the footnote)

	PPP	PPV	PPy	PPyV	PANI	PA	PCN
Fermi level (eV)	– 4.65	– 5.10	– 5.75	– 6.12	– 3.29	– 4.88	– 4.17
$n \rightarrow \pi^*$ transition (eV)	—	—	3.16	3.81	—	—	2.48
$\pi \rightarrow \pi^*$ transition (eV)	2.77 (2.7 ^a –2.8 ^b)	2.03 (2.4) ^b	2.53 (3.00) ^c	2.50 (2.60) ^d	2.95 (3.60) ^e	0.67	1.24
Ionization potential (eV)	6.03	6.12	7.02	7.37	4.76	5.21	4.79
Total valence-band width (eV)	17.38	18.30	18.27	19.04	20.14	15.98	18.99
Total π valence-band width (eV)	5.38	6.01	5.29	5.93	6.21	4.11	5.31

^a Refs. [9,10].

^b Ref. [45].

^c Ref. [7].

^d Ref. [14].

^e Ref. [27].

the low conductivity determined experimentally by Abell et al. [51]. The Fermi level is located around – 3.2 eV relative to the vacuum level.

The highest occupied and the lowest unoccupied bands of PANI are π -like bands. The orbitals of the lowest unoccupied band have nodes on the nitrogen atoms (as also observed by Libert et al. [52] from VEH calculations on the infinite polymer and by Sjögren and Stafström [53] from semi-empirical calculations on a monomer), which breaks the conjugation path. This fact is the main reason for the flatness of the bands closest to the Fermi level. Also, our further results agree well with previous reported results obtained with the VEH and extended Hückel methods [36].

4. Discussion and conclusions

Table 2 summarizes our calculated values for some of the key quantities and compares them with similar results for polyacetylene (PA) [54] and polycarbonitrile (PCN) [48]. Before discussing those in detail we add that our calculation scheme may suffer from rigid shifts of all bands when passing from one material to another. This means that the Fermi level and the ionization potential may be less accurate than the bandwidths and band gaps.

Of the systems of Table 2, three (PPP, PPV, and PA) contain only carbon and hydrogen atoms. For these, the valence-band widths (both the total and

the π valence-band width) increase when passing from PA, via PPP, to PPV. In order to analyse this, we first consider the simplest single-particle Hückel Hamiltonian for the π electrons. Setting all nearest-neighbour hopping integrals equal to t , the total π bandwidth becomes $4t$ for PA, whereas it is $4.83t$ for PPP and $4.61t$ for PPV. The differences, because of the differences in the number of carbon neighbours per carbon atoms, explain thus why the π bands are broader for PPV and PPP than for PA, but does not explain the difference between the former two. That may accordingly be owing to more subtle effects than those of the simplest Hückel model (e.g. different hopping integrals t for different bonds, different on-site energies ε for different carbon atoms because of different chemical surroundings, etc.).

In general, the substitution of some of the CH groups by N atoms leads to larger bandwidths as also is evident from Table 2. For PA and PCN (polycarbonitrile) this difference is most easily analysed. The Hückel model shall in this case be modified by having different on-site energies for the two types of atoms (C and N) of the backbone. Denoting this difference $\Delta\varepsilon$, the total π valence-band width of PCN becomes $2[(\Delta\varepsilon)^2 + 4t^2]^{1/2}$, i.e. larger than for PA. Similar effects are observed when passing from PPP to PPy or from PPV to PPyV.

Adding a vinylene linkage between the rings leads to only modest changes in the band structures. Most noticeable is the occurrence of more bands as well as (for PPP compared with PPV) less band crossings

owing to a reduction of the symmetry. Some of those (including some of the bands closest to the Fermi level) have large contributions from the vinylene linkages, so that substitution at these carbon atoms may be a way of modifying the electronic properties. In contrast, the incorporation of the vinylene linkages reduces steric effects between the rings, so that a planar geometry with more delocalized π electrons will be more stable. Accordingly, the gross features of the band structures of PPV (PPyV) are largely described as a superposition of those of PPP (PPy) and PA. This indicates also that one may add more vinylene linkages between the rings leading to only modest changes in the band structures.

A comparison between the orbitals of the equivalent systems (i.e. Figs. 4 and 6, and Figs. 5 and 7) shows that the orbitals are very similar for the substituted and unsubstituted systems with only modest polarization effects of the different orbitals due to the presence of the N atoms. Thus, the most significant difference is the occurrences of the extra lone-pair bands for the N-containing materials, that are absent for those without N atoms. As, although indirectly, can be seen in Table 2, these bands occur only slightly (about 1 eV) below the highest occupied bands.

The situation is slightly different for the reduced form of PANI, which was the only form of the polymer that was considered here, where the N atoms are in the electronic pathway, giving a more pronounced effects for PANI. For instance, in this case the inclusion of an amine group leads to a reduction of the π and π^* bandwidths compared with, e.g. PPP. In addition, the N atoms in this case do not occur as single N atoms, but as NH groups, which have a tetragonal symmetry forcing the chain be out of planarity, with also a direct consequence on the bandwidths.

The replacement of a phenylene ring by a pyridine ring produces an overall lowering of the whole band structures, although the two rings are isoelectronic. In fact, the Fermi level of PPy and PPyV are shifted around 1 eV (because of the above-mentioned computational inaccuracies, this number shall only be considered a rough estimate) to more negative values compared with their analogues PPP and PPV. This fact can be explained by considering the electronegativity of nitrogen.

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