Electronic Structures of Heterocyclic Ladder Polymers; Polyphenothiazine, Polyphenoxazine, and Polyphenoquinoxaline

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Geometrical and electronic structures of three heterocyclic ladder polymers, polyphenothiazine (PTL), polyphenoxazine (POL), and polyphenoquinoxaline (PQL), were investigated with the extended Hückel crystal orbital method. Fully optimized geometries were obtained by total energy calculations using the solid-state version of the modified neglect of diatomic overlap (MNDO) method. Two types of bandgaps were found: one at the Brillouin zone edge arising from a Peierls distortion and the other at the center of the Brillouin zone ($k = 0$) due to heteroatomic perturbations. The bandgap at the Fermi level, E_F, is due to Peierls distortion and is small, 0.3–0.5 eV, which reflects the experimentally observed substantial conductivity (10^{-6}–10^{-5} Ω^{-1} cm^{-1}) of pristine PTL. At high doping levels (charge transfer of around ±0.8e/unit cell), the Peierls gaps are predicted to disappear, but the gaps due to heteroatoms are essentially unchanged. Therefore, the heteroatoms are responsible for certain experimental observations: short electron delocalization lengths in ladder polymers as determined by ^{14}N electron nuclear double resonance measurements, and only a small (2–4 orders of magnitude) increase in conductivity and spin concentrations of doped PTL. From the assignments of band symmetries, it is found that a transition between highest occupied band and lowest unoccupied band is IR active in a high-frequency region (>ca. 3000 cm^{-1}) and that two direct optical transitions ($B_g \leftarrow A_u$) from the Fermi level to the higher conduction bands can occur in the visible range as observed experimentally from the quinoid form of triphenodithiazine.

Introduction

Since the discovery[1] that polyacetylene (PA) can achieve metallic conductivity upon doping with electron donors (such as alkali metals) or acceptors (such as I_2 or AsF_5), highly conjugated polymers have been the subject of major research activity. Moreover, the findings of enhanced conductivities (by 10–13 orders of magnitude upon doping) of poly-*p*-phenylene (PPP),[2] poly(*p*-phenylene sulfide) (PPS),[3] polypyrrole (PPy),[4] and polythiophene (PT)[5] accelerated the research effort to create new materials which combine good electrical conductivity with good stability in air. In this regard, ladder polymers constructed by linking two PA chains have attracted interest and a lot of theoretical work[6] has been done concerning the geometrical and electronic structures of a prototypical ladder polymer, polyacene (PAc) in Figure 1. To our knowledge, Pac has not been synthesized as of yet. However, several heterocyclic ladder polymers such as polyphenoquinoxaline (PQL),[7] polyphenothiazine (PTL),[8] and polyphenoxazine (POL)[8] were recently synthesized (L stands for ladder). In spite of substantial conductivity (around 10^{-5}–10^{-6} Ω^{-1} cm^{-1})[8] of pristine PTL, it was observed that doping of PTL with AsF_5 or with protonic acids such as H_2SO_4 and $ClSO_3H$ increases conductivities[9,10] by only 2–4 orders of magnitude and spin concentrations[10] by a factor of only 2.3–4.6.

The bandgaps of conjugated polymers are determined by several competing factors. Geometrical relaxation due to the coupling of electron orbitals around the Fermi level is very important in many cases.[6] It is well-known that pristine PA has a bandgap[11] of ~1.5 eV at the Fermi level due to a dimerized structure[12] with alternating short and long bonds (Peierls distortion[13]). The ground states of PPP, PPy, and PT are predicted to be aromatic with bandgaps greater than those of their quinoid forms.[14] Another important factor is the perturbation of heteroatoms as pointed out by Rice and Mele.[15] The effect of heteroatoms on bandgaps of conjugated polymers was intensively investigated by Kafafi and Lowe.[16] The effect of topology such as rings fused to a main chain were also

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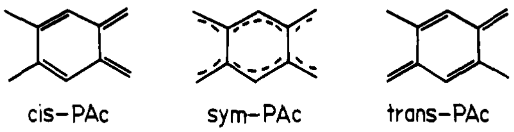

Figure 1. Three isomers of polyacene (PAc).

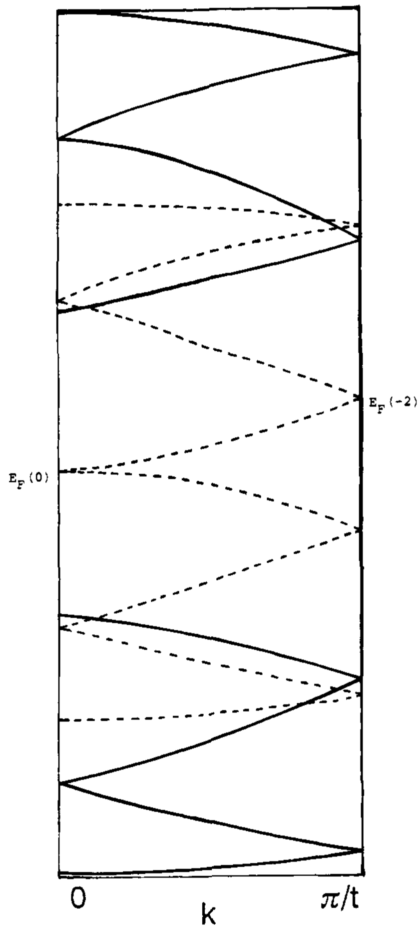

Figure 2. Energy band structure of the π-electrons of *sym*-PAc for a 16 C atom unit cell ($E_F(q)$ is explained in the text).

studied with respect to the bandgaps of several PPy- and PT-based systems.[14]

In this study we investigate the geometrical and electronic structures of heterocyclic ladder polymers and their modifications upon charge transfer, aiming at elucidating the experimental observations of high intrinsic conductivity but lack of significant increase in conductivity and spin concentrations of PTL upon doping.

The electronic structures of ladder polymers have not been extensively studied with the exception of polyacene, PAc. PAc is expected to be a small-gap system, although it should undergo a (second order) Peierls distortion.[6] The π-electron band structure of the equidistant form (sym-PAc in Figure 1) is given in Figure 2. This band structure is represented in a Brillouin zone corresponding to 16 C atoms (16 π-electrons, 16 π-orbitals) in order to facilitate the comparison with the title polymers. In the alternative representation with 4 C atoms in the repeat unit there are four bands only, two of which are degenerate at the Fermi level, $E_F(0)$. These two bands are represented by dashed lines, the other two π-bands by solid lines in Figure 2. $E_F(-2)$ corresponds to a negatively charge PAc with 2 electrons per unit cell, i.e., poly($C_{16}H_8^{2-}$), which is isoelectronic to the title compounds. The degeneracy at $E_F(0)$ is accidental and is lifted if one goes beyond a simple Hückel approach.[6]

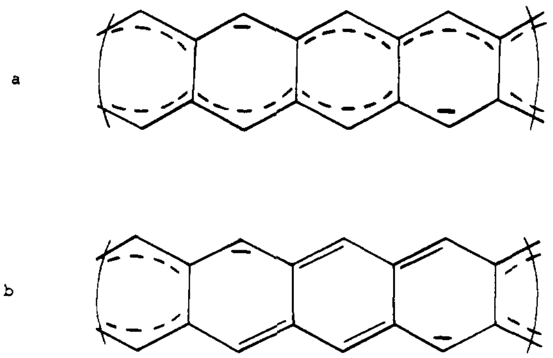

Figure 3. Two alternative bond arrangements for poly($C_{16}H_8^{2-}$), a negatively charge polyacene which is isoelectronic to the title compounds.

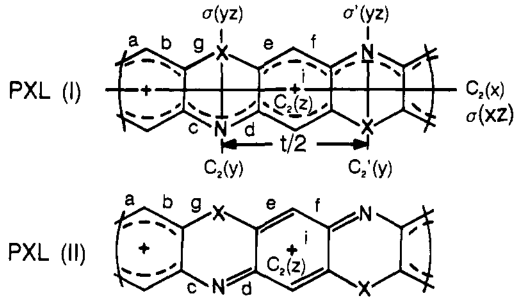

Figure 4. Two isomers of the heterocyclic ladder polymers (PTL, X = S; POL, X = O; PQL, X = NH) with symmetry elements. Optimized geometrical parameters are listed in Table I.

Figure 3 shows two alternative structures for poly($C_{16}H_8^{2-}$). The main difference with respect to the title compounds will be that the two X atoms in the unit cell contribute two π-electrons shifting E_F to the ninth band. Furthermore, these heteroatoms will also produce strong perturbations leading to several bandgap openings in the band structure.

Doping with various electron donors and acceptors is known to affect electronic structures of quasi-one-dimensional conjugated polymers by modifying their geometries through the strong coupling of the electrons at E_F to the "amplitude modes",[6c] for instance the bond length alternation patterns shown in Figure 1 for polyacene. The trends of geometrical changes in the bond distances of the skeleton of the polymer upon charge transfer (CT) are often predictable from the bonding and antibonding patterns of the highest occupied and lowest unoccupied crystal orbitals of the undoped ground state as demonstrated in refs. 17 and 18. Peierls distortion of *trans*-PA becomes depressed as CT occurs and finally bond equalization is achieved at CT of around ±0.1 e/CH unit.[17] Also conjugated polymers with nondegenerate ground states such as PPP, PPy, and PT were predicted to modify their aromatic structures toward quinoid-like forms upon doping with electron donors or acceptors.[14,18]

Methods and Models

Two types of structures for the heterocyclic ladder polymers, PXL (PTL, X = S; POL, X = O; PQL, X = NH), can be constructed based upon poly($C_{16}H_8^{2-}$) of Figure 3, which are shown in Figure 4. Reflection along the lines connecting heteroatoms in the same ring and

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Table I. Heats of Formation (kcal/mol of Unit Cell) and Geometrical Parameters (Å) of the Heterocyclic Ladder Polymers[a] PXL

	PTL (X = S)		POL (X = O)		PQL (X = NH)	
	I	II	I	II	I	II
H_f	96.80	88.14	28.92	20.49	103.06	95.76
a	1.446	1.417	1.440	1.413	1.437	1.413
b	1.385	1.408	1.392	1.414	1.394	1.414
c	1.352	1.405	1.356	1.407	1.356	1.403
d	1.352	1.307	1.356	1.311	1.356	1.313
e	1.385	1.363	1.392	1.370	1.394	1.373
f	1.446	1.479	1.440	1.470	1.437	1.466
g	1.685	1.686	1.366	1.367	1.398	1.398
t	9.97	9.98	9.56	9.57	9.69	9.70

[a] Geometrical parameters are defined in Figure 4.

2-fold rotation symmetries perpendicular to the polymer plane were imposed on PXL(I) and only 2-fold rotation symmetry on PXL(II). According to the line group theory,[19] which takes into account one-dimensional translation symmetry, PXL(I) is isomorphous with the D_{2h} point group and PXL(II) with C_{2h}. PXL(I) is expected to be a highly delocalized π-electronic structure[7] with lower symmetry PXL(II) being the likely ground state.[8] Complete in-plane geometrical optimizations were performed on the basis of the tight-binding self-consistent-field crystal orbital (SCF-CO) method at the level of the modified neglect of diatomic overlap (MNDO) approximation.[14,20] The unit cells of ladder polymers employed for the calculations are illustrated in Figure 4. Six wave vectors were chosen from 0 to π/t (t is the length of the translation vector) with regular intervals. Up to third nearest neighboring unit cells were taken into account in the lattice sums.

Since the SCF Hartree–Fock methods (e.g., ab initio, MNDO, ect.) greatly overestimate bandgaps,[23] we employed the extended Hückel (EH) method[24,25] to produce approximate electronic structures of the ladder polymers. The EH method is known to yield reasonable band structures sometimes underestimating bandgap values if bond length alternation effects dominate the bandgap.[25] Heteroatom effects are represented in a well-balanced manner. Optimized structures of the ladder polymers were obtained by the MNDO method as described above and were used as input in the EH band structure calculations.

Geometrical Structures

The calculations found indeed the PXL(II) structure to be more stable than the more symmetrical PXL(I) structure by 7.3–8.7 kcal/mol of unit cell, depending on the heteroatoms. The heats of formation and optimized geometrical parameters of the three materials are presented in Table I. The predicted structures of ladder polymers in their ground states are similar to the structures suggested by Kim[8] from the IR spectrum study of PTL and POL and by Casa et al.[21] from the IR spectrum study of the quinoid (Q) form of triphenodithiazine (TPDT). These structures have two types of carbon rings; one ring has a benzenoid-like structure with almost identical C–C bond lengths along the chain and the other one is quinoid-like with C–C bonds alternating in length by about ±0.05 Å along the edge "chains" of the macromolecules. Also two types of C–N bonds exist in PXL(II), the difference between the two types of C–N bond lengths is about 0.1 Å. The two types of C–X bond lengths are almost identical regardless of types of the structures. In the more symmetrical structure, PXL(I), the difference in bond lengths of the C–N bonds disappear and the two carbon rings become identical. These carbon rings have two different adjacent C–C bonds along the chain differing by as much as about 0.06 Å.

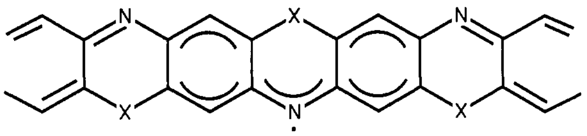

Figure 5. Solitonic defect in a ladder polymer (spin = $^1/_2$, charge = 0).

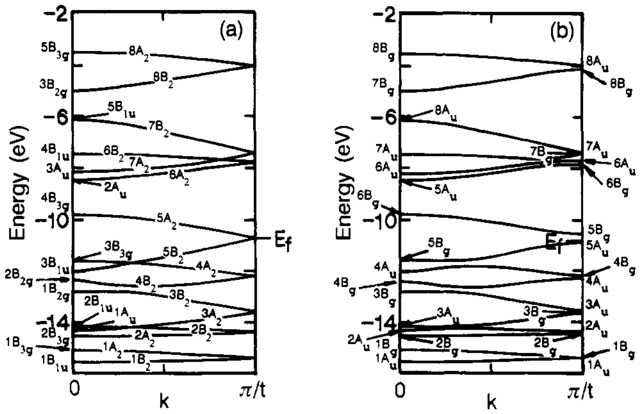

Figure 6. Extended Hückel π-band structure of (a) PTL(I) and (b) PTL(II). Symmetries which are not shown at π/t for PTL(I) and between $0 < k < \pi/t$ for PTL(II) are all A″.

Since the PXL(II) structure has an alternating pattern with two types of carbon rings connected to each other by heteroatoms, two energetically equivalent resonance forms can be derived by interchanging carbon rings, and thus topological solitons are possible mobile defects similar to the case of neutral and lightly doped *trans*-PA[22]. At the center of such a soliton the structure is similar to PXL(I) where two carbon rings and two C–N bonds are identical, respectively, as shown in Figure 5.

Electron Counting

The translational unit cell consists of 12 carbon atoms and two nitrogen atoms each contributing one π-electron. The two X groups (–S–, –O–, or –NH–) contribute two π-electrons each, a total of 18 π-electrons per unit cell leading to 9 occupied bands out of the total of 16 π-bands. Should we attempt to derive the properties of the title polymers from those of PAc, there appear three major obvious differences: (1) the unit cell is 4 times larger, the bands of PAc shown in Figure 2 correspond to such an enlarged cell; (2) the presence of the N and X heteroatoms leads to gaps at the zone edges; (3) the filling is higher than in PAc by two electrons per 16 non-hydrogen atom unit.

Consequently, the particular alternation patterns shown in Figure 1, although important for neutral polyacene, have

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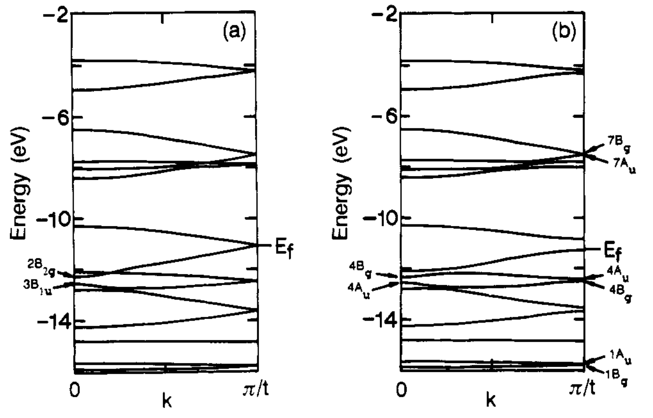

Figure 7. Extended Hückel π-band structure of (a) POL(I) and (b) POL(II). Symmetries, except those labeled, are the same as those for PTL in Figure 6.

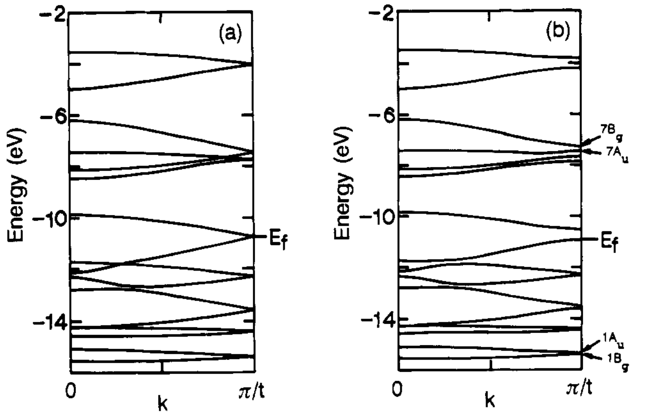

Figure 8. Extended Hückel π-band structure of (a) PQL(I) and (b) PQL(II). Symmetries, except those labeled, are the same as those for PTL in Figure 6.

no major role in determining the geometrical and electronic structures of the title polymers. However, PAc corresponding to the electron count of the title compound, i.e., poly($C_{16}H_{16}^{2-}$) should exhibit a Peierls-type symmetry lowering distortion similar to the one shown in Figure 3.

Electronic Structures

From the EH band structures of the polymers only π-bands are shown in Figure 6 for PTL, Figure 7 for POL, and Figure 8 for PQL. The band symmetries are assigned according to the line group theory.[19] Nine of the 16 π-bands are filled. The highest occupied crystal orbital (HOCO) and lowest unoccupied crystal orbital (LUCO) of PXL(I) are degernerate at the Fermi level. These 2p orbitals of PTL(I) are indicated in Figure 9 (the atomic orbitals with very small coefficients are not depicted). Similar orbital features were obtained for POL(I) and PQL(I). The interactions of S and N atoms with neighboring C atoms at the Fermi level are antibonding on one side and almost nonbonding on the other side. Therefore, shifting the S and N atoms, as indicated by small arrows in Figure 9, removes the degeneracy by stabilizing the HOCO and destabilizing the LUCO at the Fermi level. However, shift of the S atoms is not favorable because of lone-pair electrons in a π-type p orbital. In PXL(II), shift of N and C atoms results in small bandgaps, 0.32 eV for PTL, 0.41 eV for PQL, and 0.46 eV for POL. These values are quite smaller than that of *trans*-polyacetylene (about 0.96 eV by EH calculations,[25] while the experimental value[11] is 1.5 eV) and comparable to the predicted value of *trans*-polyacene.[6b] Such small bandgaps (relative to polyacetylene) may reflect the experimentally observed substantial conductivities[8] of pristine PTL (10^{-5} Ω^{-1} cm^{-1}) and POL (10^{-8} Ω^{-1} cm^{-1}). A transition between the HOCO and the LUCO at $k = \pi/t$ is allowed and is expected to occur in the high-frequency part of the infrared region. In fact, an FTIR spectrum of PTL shows a broad peak around 2600 cm^{-1} (0.3 eV).[8] From the band symmetry assignments, it is clear that two further direct optical transitions from the Fermi level ($5A_u$) to the higher conduction bands ($6B_g$ and $7B_g$) are possible. These transitions are expected to correspond to experimental observations,[21] two broad and strong absorption peaks at 521 nm (2.38 eV) and 556 nm (2.23 eV), from the UV–vis measurement of the Q form of TPDT. EH band calculations predicted these transitions with absorption energy of 3.02 and 3.44 eV for PTL, 3.28 and 3.81 eV for POL, and 3.07 and 3.68 eV for PQL.

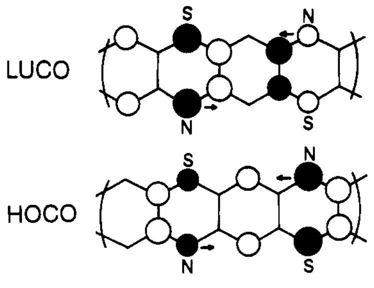

Figure 9. Degenerate π-type crystal orbitals of PTL(I) at the Fermi level. N and S indicate nitrogen and sulfur positions, respectively. Small arrows indicate the shift of N atoms to remove degeneracy.

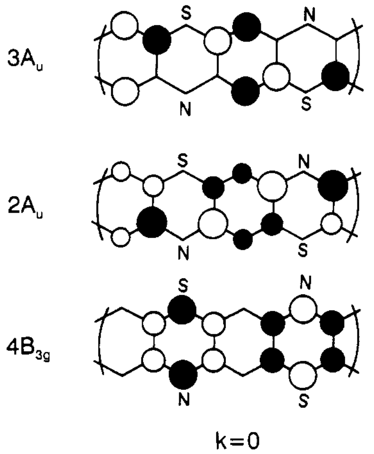

Figure 10. π-type $4B_{3g}$, $2A_u$, and $3A_u$ crystal orbitals of PTL(I) at k = 0. N and S indicate nitrogen and sulfur positions, respectively.

The band structures of the ladder polymers in question are broken up into narrow bands with relatively large gaps at the center of the Brillouin zone (k = 0) These band separations are still persistent in the highly symmetrical structure, PXL(I). The separations between the lowest unoccupied band and the next higher conduction band amount to about 1.3 eV for PTL, 1.4 eV for PQL, and about 1.9 eV for POL which can be traced using orbital arguments to perturbations of heteroatoms. For example, $4B_{3g}$ has nodal planes on carbon atoms, and $2A_u$ and $3A_u$ have nodal planes on heteroatoms as seen in Figure 10. The effect of heteroatoms on bandgaps was also discussed by Kafafi and Lowe.[16] The most trivial case is the gap opening due to heteroatoms in regular poly(methineimine), $(CHN)_x$, which is equal, at the simple Hückel (π-only tight binding) level, to the difference in the Coulomb integrals

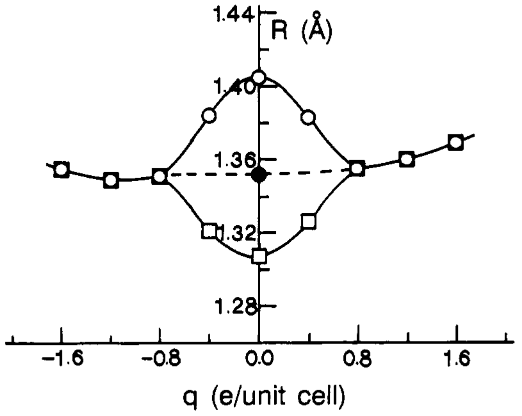

Figure 11. Variation of the C–N bond lengths of PTL(II) upon charge transfer q. ○ represents long bond lengths, □ short bond lengths, and ● the C–N bond length of PTL(I).

of nitrogen and carbon. In EH calculations, Coulomb integrals essentially correspond to atomic valence state ionization potentials (VSIP) and the VSIP of p orbitals of C, N, S, and O are −11.4, −13.4, −13.3, and −14.8 eV, respectively. Understandably, S and N lead to the similar gaps in size, about 2 eV, and O to even larger gaps. Therefore, heteroatoms with large electronegativities (relative to carbon) localize the π electrons in accordance with the observed ^{14}N electron nuclear double resonance (ENDOR) measurements[7] of ladder polymers.

Since the interactions of N atoms with neighboring C atoms are antibonding in the $4B_{3g}$ orbital and nonbonding in the $2A_u$ orbital at $k = 0$, the geometrical shift of N atoms to one side does not change the energy levels of the $4B_{3g}$ and $2A_u$ orbitals. The interactions of the edge C atoms are nonbonding with neighboring C atoms in $4B_{3g}$, and bonding with one C atom and antibonding with the other in $2A_u$. However, the geometrical shift of the edge C atoms stabilizes one ring and destabilizes the other in $2A_u$, effectively cancelling each other. Therefore, the geometrical distortion does not affect the gap opening at $k = 0$. EH calculations also indicate no essential difference in the gap sizes between PXL(I) and PXL(II) at $k = 0$.

Charge-Transfer Effects

Since a quasi-one-dimensional polymer undergoes significant geometrical changes upon charge transfer (CT), the electronic structure of an undoped polymer may be not suitable to interpret the behavior of the doped polymer. In our earlier work,[17b] CT was simulated in such a way that the amount of CT was equal to the empty or occupied parts of k space for the highest occupied or lowest unoccupied band. With the same scheme, we optimized the geometries of PXL(II) with CT up to ±1.6 e/unit cell (up to ±0.1 e/heavy atom in the chain).

As CT occurs, the lattice is predicted to be modified toward the PXL(I) structure. The behavior of C–N bonds upon CT is very similar to that of C–C bonds of *trans*-PA.[17b] As shown in Figure 11, the long and short C–N bonds of PXL(II) become shorter and longer with CT, respectively, and finally bond equalization occurs at CT of around ±0.8 e/unit cell (amounts to ±0.05 e/heavy atom). The plus sign corresponds to donor doping. This behavior can be understood by considering the properties of the orbitals at the Fermi level in Figure 12. The withdrawal of electrons from orbital $5A_u$ reduces the antibonding interactions of the long C–N bonds, invoking the shift of N atoms as indicated by small arrows in Figure 12. Similarly, putting electrons into orbital $5B_g$ leads to the development of the antibonding interactions of the short C–N bonds, which in turn shifts the N atoms to the same direction, diminishing the degree of C–N bond length alternation.

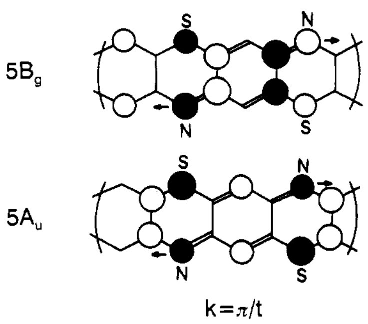

Figure 12. π-type crystal orbitals of PTL(II) at the Fermi level. N and S indicate nitrogen and sulfur positions, respectively. Small arrows indicate the shift of N atoms when electrons are withdrawn from $5A_u$ orbital and when put into $5B_g$ orbital.

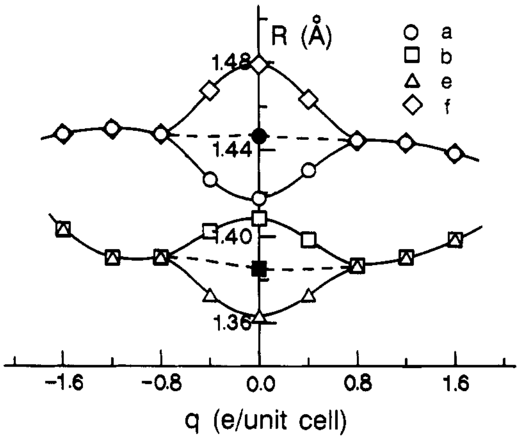

Figure 13. Variation of the C–C bond lengths of PTL(II) upon charge transfer q. See Figure 4 for notations of the geometrical parameters. Filled symbols represent the corresponding bond lengths of PTL(I).

The two carbon rings become identical at the same level of CT as seen in Figure 13, but the difference in length of two C–C bonds within the rings still remains up to high level of CT. Similar orbital arguments hold also for C–C bond variations. The variation of the lattice spacing, t, shows a trend similar to that found for *trans*-PA.[17b] When doped with acceptors, the lattice spacing is predicted to slightly decrease by about 0.1% up to $q = -0.8$ e and to increase by about 0.3% at large CT ($q = -1.6$ e). Doping with electron donors increases t slowly at small CT (about 0.2% at $q = 0.8$ e) and more steeply at larger CT (about 1.0% at $q = 1.6$ e).

Using the optimized structures at CT of ±1.6 e/unit cell, the electronic structures of PTL(II) are shown in Figure 14. As expected from the geometric structure similar to that of PTL(I), the band gaps at $k = \pi/t$ are closed, but at the center of the Brillouin zone are almost unchanged. The same features were obtained for PQL and POL. As discussed above, the bandgaps at $k = 0$ come from the perturbation of heteroatoms. Therefore, CT is not found to affect these bandgaps significantly. However, the Peierls bandgap is strongly affected by CT. The large gaps between the lowest unoccupied band and the next higher conduction band may be responsible for the slight increase in conductivity[9,10] and spin concentration[10] of highly doped PTL.

Conclusions

The family of PTL-type heterocyclic ladder polymers has a Peierls distorted ground state with alternating C–N

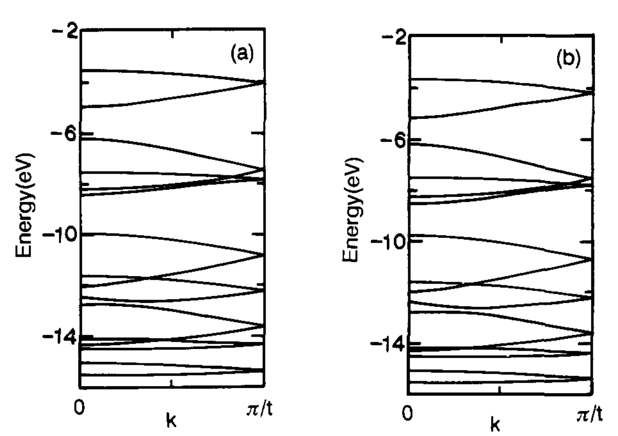

Figure 14. Extended Hückel π-band structure of PTL(II) at (a) $q = 1.6$ e and (b) $q = -1.6$ e. Symmetries are same as those for PTL(I) in Figure 6.

bonds and two types of carbon rings. Since these are 2-fold degenerate, solitons can be expected as defects in the neutral form and at low doping levels. The electronic structures of these ladder polymers show two types of bandgaps; small gaps at the Brillouin zone edge arise from the Peierls distortion and large gaps at the center of the Brillouin zone, which are due to the perturbation of the heteroatoms in the chain. The bandgap at the Fermi level originates from Peierls distortion and is small, 0.3–0.5 eV, which may reflect the experimentally observed substantial conductivity of undoped pristine PTL. The heteroatoms lead to band separations into several narrow bands. Therefore, short carrier delocalization lengths in the heterocyclic ladder polymers, as observed from ^{14}N ENDOR measurements,[7] can be explained by the narrow bandwidth of the uppermost valence band. At around ±0.8 e CT/unit cell, the ladder polymers become highly symmetric and consequently, the bandgaps at the Brillouin zone edge become closed. However, bandgaps due to perturbation of heteroatoms still remain fundamentally unchanged, even up to CT of ±1.6 e/unit cell. This effect may be responsible for the experimental observations that there is only a small increase in conductivity and spin concentrations in doped PTL. An entirely different kind of ladder polymer, BBL (benzimidazobenzophenanthroline-type ladder polymer) will be investigated in a forthcoming publication.[26]

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Tin-Sulfur and Tin-Selenium Phenylated Ring Systems as Organometallic Precursors to Tin Sulfide and Tin Selenide

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Group 14–16 six-membered rings, $(Ph_2EX)_3$ (E = Si, Sn; X = S, Se), were synthesized in 49–61% yield from Ph_2ECl_2 and anhydrous Na_2X made from elemental Na and X with a catalytic amount of naphthalene in THF. Pyrolysis of the tin-containing rings, $(Ph_2SnS)_3$ and $(Ph_2SnSe)_3$, at temperatures over 300 °C in a helium atmosphere yielded microcrystalline black powders identified as SnS or SnSe by X-ray diffraction. Scanning electron micrographs show the powders to consist of agglomerates of crystals having platey (SnS) or prismatic (SnSe) habits.

Introduction

Progress in the synthesis of group 13–15 semiconductors, such as GaAs and InP, by organometallic chemical vapor deposition (OMCVD) of single-source precursors[1] has prompted an extension of the technique to prepare group 14–16 analogues as well. Pyrolysis of compounds of the type $R_kE_lX_mR'_n$ (R, R′ = C_{1-4} alkyl groups; E = group 14; X = group 16; $k = 0$–6; $l = 1$–2; $m = 1$–4; $n = 0$–4)[2] or metal selenolates, $[R_2NC(Z)Se]_nM^{n+}$ or $[ROC(Z)Se]_nM^{n+}$ (R = C_{1-10} alkyl group; M = metals; Z = O, Se; $n = 1$–5),[3] at 250–450 °C gave composite metal sulfides and selenides useful for semiconductor devices and solar cells.

The traditional synthetic approach toward group 14–16 semiconductors through utilization of the OMCVD process involves mixing a tetraalkyl group 14 compound with H_2S or H_2Se (e.g., eq 1).[4] Single-source precursors offer some

$$Me_4Sn + H_2S \xrightarrow[625\ ^{\circ}C]{} SnS + CH_4 + ... \qquad (1)$$

important advantages over the traditional methods. These advantages include increased stability toward air and moisture and better hydrocarbon solubility. For the most part, the single-source precursors studied thus far possess small alkyl groups which depart when heated. Compounds with aryl substituents have largely been ignored.

We have begun an investigation in which organometallic systems containing aryl groups are employed to produce potential semiconducting compounds by OMCVD or condensed phase pyrolysis. The most common methods used to synthesize binary compounds by a solid-state approach are sintering the elements at high temperatures and long reaction times[5] and by mixing an alkali-metal chalcogenide

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