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Conformations and Electronic Structures of New Conjugated Polymers Based on Poly(cyclopentadienylene) and Polysilole

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ABSTRACT: The conformations and electronic structures of several five-membered-ring polymers were investigated with the partial retention of diatomic differential overlap (PRDDO) method. Band structures of the polymers were calculated using the modified extended Hückel (MEH) method. The polymers considered in this study are analogous to heterocyclic polymers such as polythiophene, polyfuran, and polypyrrole; however, they have bridging groups of XY_2 (XY_2 = CH_2, CF_2, SiH_2, and SiF_2) instead of heteroatoms. The relative stability of the aromatic and quinoid forms of these polymers was examined through an oligomer approach. The evolution of the band gaps of these systems was analyzed in terms of bond-length alternations, changes in the C1–C4 distances, and the effects of pure electronic interactions between the polymeric backbone and the bridging groups. It was found that insertion of the bridging group into the polymeric backbone affects the band gap in two distinct ways. The decrease of the C1–C4 distance relative to that found in *cis*-polyacetylenes narrows the band gap of the aromatic form and widens the band gap of the quinoid form. On the other hand, electronic interactions tend to increase the band gap of the aromatic form and decrease the band gap of the quinoid form. The electronic effect of a CH_2 group on the band gap is small but not negligible (ca. 0.7 eV), and the resultant band gaps of both the aromatic and quinoid forms are comparable to those of polyacetylenes. The electronic interactions of the other bridging groups are so small that the quinoid forms became more stable in the ground state.

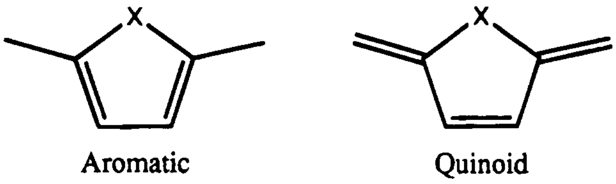
Introduction

In the last few decades conjugated polymers have been extensively studied, largely because of their unique electrical and optical properties.[1] Much progress has been made in synthesizing such polymers both chemically and electrochemically,[2] in characterizing their electro-optical properties in an ex-situ or in-situ way,[3] and in improving their environmental stability and processibility.[4] Recently, many experimental[5] and theoretical[6-8] efforts have focused on the design of new conjugated polymers with very small band gaps (E_g < 1 eV) that exhibit intrinsic conductivity or at least semiconducting properties. To be successful in designing such polymers, the evolution of the band gaps of conjugated polymers should be well understood, since the energy gap between the highest valence band and the lowest conduction band is a critical factor among the many factors affecting the electrical conductivity. In this respect, it is encouraging that theoretical work[7-10] has contributed toward elucidating the relationship between the band gap and the chemical structures of quasi one-dimensional conjugated polymers.

Owing to their potential environmental stability, conjugated polymers containing cyclic repeat units (phenyl, thiophene, furan, etc.) have been a major target for new conductive polymers. We have previously analyzed the evolution of the band gap of heterocyclic polymers with aromatic ground states, such as polythiophene (PT), polypyrrole (PPy), and polyfuran (PF), by viewing the polymers as derivatives of trans–cisoid polyacetylene (PA) and decomposing the band gaps according to the following equation.[10]

$$E_g = \Delta E^{\delta r} + \Delta E^{1-4} + \Delta E^{el} \qquad (1)$$

Here E_g is the band gap of a conjugated polymer with a repeat unit consisting of five-membered rings. $\Delta E^{\delta r}$, ΔE^{1-4}, and ΔE^{el} are the contributions arising from three distinct effects: bond-length alternations along the backbone (δr), change in the C1–C4 distances induced by a heteroatom which bridges these atoms, and the pure electronic effect of the heteroatom. Two of these contributions (ΔE^{1-4} and ΔE^{el}) are qualitatively different depending on whether the polymer is of the quinoid or aromatic type.



$\Delta E^{\delta r}$ is due to Peierls distortion of the polymeric backbone, and it is well-known that large values of δr lead to large band gaps for both the aromatic and quinoid forms.

The ΔE^{1-4} effect in the aromatic form arises as follows. When bridging atoms are introduced into the backbone, the C1–C4 distance decreases. This increases the antibonding character between π-orbitals of C1 and C4 in the highest occupied crystal orbital (HOCO) and pushes the energy of the HOCO up (Figure 1). On the other hand, the lowest unoccupied crystal orbital (LUCO) energy level is almost unchanged, since the antibonding character due to the second-neighbor interactions (C1–C3 an C2–C4) in the LUCO increases while the corresponding bonding character between C1 and C4 increases. Therefore, the geometrical relaxation due to insertion of bridging atoms into the trans–cisoidal polyacetylene backbone leads to a lowering (ca. −0.7 eV) of the band gap. The narrow band gap becomes again widened by the electronic perturbation of the bridging atom, since by symmetry the p orbital

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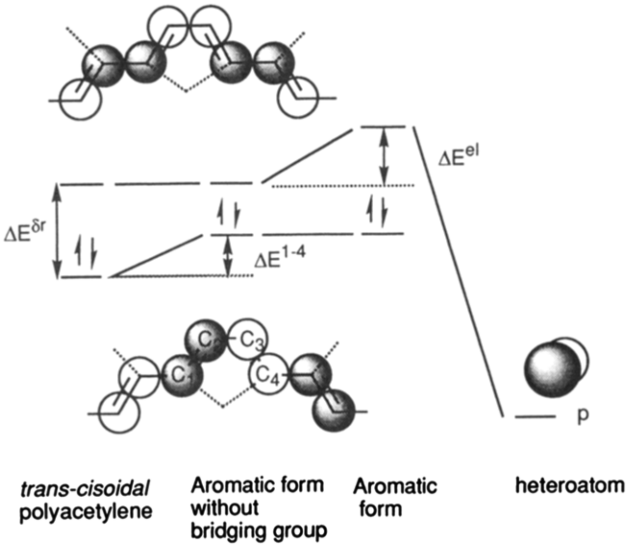

Figure 1. Schematic representation of the variation of the HOCO and the LUCO of the aromatic form of the polymer as a function of the C1−C4 distance and the electronic perturbation of the heteroatom.

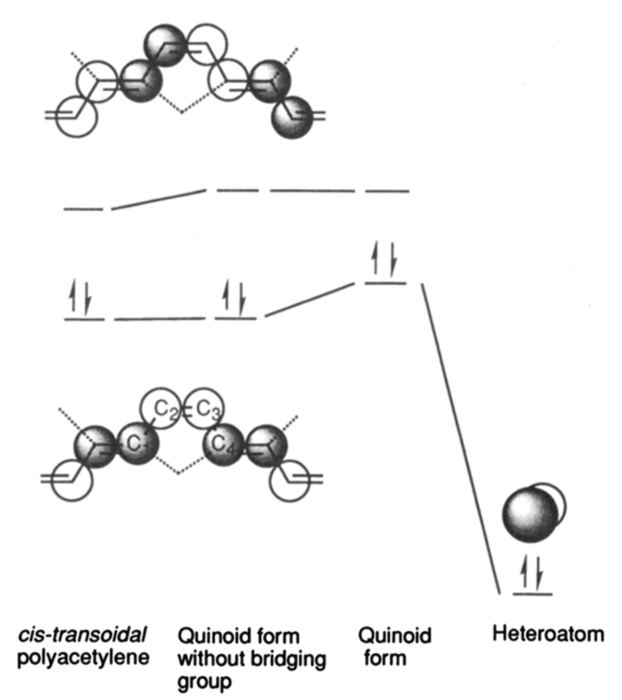

Figure 2. Schematic representation of the variation of the HOCO and the LUCO of the quinoid form of the polymer as a function of the C1−C4 distance and the electronic perturbation of the heteroatom.

of the bridging atom interacts only with the LUCO of the polymeric backbone (Figure 1).

In the quinoid form, the ΔE^{1-4} and ΔE^{el} terms contribute to the band gap differently. Reduction of the C1−C4 distance does not affect the HOCO energy, because the increase in the bonding C1−C4 interaction is balanced by the increase of the antibonding C1−C3 and C2−C4 interactions (Figure 2). However, decreasing the C1−C4 distance increases the antibonding C1−C4, C1−C3, and C2−C4 interactions in the LUCO. Therefore, the band gap increases. Introduction of the heteroatom, which mixes with the HOCO but not the LUCO, now decreases the band gap.

In this study, we explore a scheme aimed at designing new promising conductive polymers. Our goal is to depress the electronic effects of bridging groups (ΔE^{el}) by taking as bridging groups moieties such as CH_2, CF_2, SiH_2, and SiF_2. These groups all have HOMOs which are much lower in energy than the p orbitals of heteroatoms, resulting in less mixing with the π-system of the backbone. However, the C1−C4 distance will still decrease and ΔE^{1-4} contributions will still be negative in the aromatic form. These bridging groups lead to the following polymers: poly(cyclopentadienylene) (PPD), poly(1,1-difluorocyclopentadienylene) (PFPD), polysilole (PS), and poly(difluorosilole) (PFS), respectively. Geometrical structures of both the aromatic and quinoid forms of the polymers in Figure 3 were obtained from partial retention of diatomic differential overlap (PRDDO) calculations.[11] The relative stability of the quinoid and aromatic forms was investigated, since it has been demonstrated that the band gaps of similar systems depend strongly on the detailed structural parameters of the backbone.[7,8,12] We employed the modified extended Hückel (MEH) method[10] to calculate the electronic structures of the polymers, and we analyzed the electronic properties of the polymers according to eq 1 to deduce the effects of bridging groups on the band gaps of the polymers.

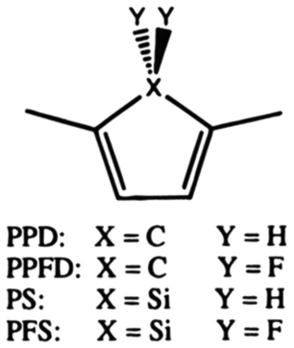

Figure 3. Aromatic and quinoid forms of poly(cyclopentadienylene) (PPD), poly(cyclodifluoropentadienylene) (PFPD), polysilole (PS), and poly(difluorosilole) (PFS). The numbering is the same for the quinoid forms.

Geometrical Structures and the Relative Stability of the Aromatic and Quinoid Structures

An oligomeric approach was employed for estimating the polymer structures in Figure 3. That is, the geometrical structures of the trimers were obtained by performing full PRDDO optimizations, except for the C−H bond lengths. The aromatic forms were modeled by attaching one hydrogen at each terminal C atom, while the quinoid forms were terminated with two hydrogens. The $C(sp^3)-H$ and $C(sp^2)-H$ bond lengths were fixed at 1.10 and 1.08 Å, respectively. All the conformers were considered to be anti-coplanar. Polymeric structures were extracted from the optimized structures of the central unit of the trimers and are presented in Table 1. It was found that insertion of the bridging groups into *cis*-PA backbones decreases the C1−C4 distances by 0.4−0.7 Å but results in only minor changes in the bond-length alternation parameter δr. Note that the predicted δr are quite large compared to the semiempirical predictions.[13] However, our MEH band structure calculations (see below) are parametrized to reproduce experimental band gaps with both PRDDO and semi-empirical geometries. A detailed discussion of the effect of δr on the calculated band gap may be found elsewhere.[10]

Table 1. Geometrical Parameters (Å and deg) Employed for the MEH Band Calculations[a]

geometrical params	PPD A	PPD Q	PFPD A	PFPD Q	PS A	PS Q	PFS A	PFS Q
1−2	1.318	1.460	1.317	1.454	1.333	1.465	1.324	1.467
2−3	1.440	1.307	1.456	1.313	1.469	1.318	1.471	1.318
1−X	1.499	1.504	1.541	1.533	1.816	1.810	1.804	1.793
X−Y	1.100	1.100	1.375	1.377	1.393	1.398	1.574	1.581
4−1′	1.444	1.323	1.440	1.320	1.449	1.310	1.437	1.311
1−2−3	110.3	111.8	110.9	111.8	116.3	117.4	116.5	117.0
2−1−X	108.0	105.7	108.0	107.0	106.9	105.1	106.1	105.3
2−3−H	123.6	125.4	123.5	126.0	119.6	123.4	119.2	123.5
1−X−Y	111.9	111.6	112.2	112.2	113.1	112.8	114.6	114.5
3−4−1′	128.6	129.2	129.1	128.5	125.0	124.3	125.2	124.1
2−1−X−Y	120.7	121.1	120.3	120.5	117.0	117.3	119.8	120.1
δr[b]	0.124	−0.145	0.131	−0.138	0.126	−0.151	0.130	−0.153
1−4[c]	2.354	2.389	2.397	2.391	2.649	2.668	2.654	2.652

[a] See figure 3 for the definition of the geometrical parameters. [b] An average value of the bond-length alternation, defined as $\delta r = [R(1-2) - R(2-3) + R(3-4) - R(4-1')]/2$. Corresponding values for trans−cisoidal and cis−transoidal polyacetylenes are −0.145 and −0.154 Å, respectively. [c] Corresponding values for trans−cisoidal and cis−transoidal polyacetylenes are 3.065 and 3.111 Å, respectively. [d] MNDO PM3 values of δr for the aromatic and quinoid forms are 0.095 and 0.114 Å, respectively.[13]

Table 2. Relative Stabilities (kcal/mol) of the Aromatic vs Quinoid Forms for the Titled Polymers as a Function of the Chain Length[a]

	XY_2			
chain length	CH_2	CF_2	SiH_2	SiF_2
1	10.69	0.85	8.57	5.54
2	3.86	−2.14	2.90	0.61
3	2.22	−2.86	0.71	−1.34
4	1.56	−3.06	−0.36	−1.78
5	0.93	−3.35	−1.00	−2.29
6	0.51	−3.55	−1.43	−2.61
∞[b]	−1.15	−3.93	−3.68	−4.31

[a] All geometrical optimizations were performed at the PRDDO level. [b] Second order and $N = 6$.

To examine the relative stability of the aromatic vs quinoid forms, the total energy for the oligomers up to the hexamers was calculated with the structures extracted from the trimer optimizations. We approximate[8,12] the energy difference between the two forms *in the absence of end groups* as a function of the chain length (N) according to eq 2. Here E_q and E_a are the

$$\Delta E_{qa}^{N} = E_{q}^{N} - E_{a}^{N} - 2E_{H} + 2E_{CH} \qquad (2)$$

total energies of the quinoid and aromatic forms, respectively. E_H is the hydrogen atomic energy, −0.4712 au (corresponding to a 1s orbital exponent of 1.24), and E_{CH} is the average C−H bond dissociation energy, 90.3 kcal/mol. Finally, we extrapolate the energy difference per chain length, $\Delta E_{qa}^{N}/N$, using eq 3. The relative stability of the two forms of the infinite polymer is given by a_0 (aromatic forms are energetically favored if $a_0 > 0$). For the detailed scheme, the reader is referred to refs 8 and 12. In Table 2, calculated $\Delta E_{qa}^{N}/N$ values for the oligomers are shown, along with the values extrapolated to the infinite chain limit ($N = \infty$). The geometrical structures of PFPD, PS, and PFS are all predicted to be quinoid in the ground state. There is very little previous theoretical work on these systems. For PS, we predict that the two forms are within ~4 (kcal/mol)/repeat unit. This prediction is consistent with MNDO PM3 band calculations[13] which predicted that the quinoid form is more stable by ~2 (kcal/mol)/repeat unit. Also, ab initio calculations with the molecular structures modeled after polysilole showed that both forms are nearly isoenergetic.[14] Because of the extremely small energy difference between the aromatic and quinoid forms of PPD, the ground-state geometry of this polymer is unclear. We expect that both forms of PPD are nearly equivalent in energy and we will show below that the two forms have very similar electronic properties.

$$\Delta E_{qa}^{N}/N = a_0 + a_1/N + a_2/N^2 \qquad (3)$$

Electronic Structures

It is well-known that Hartree−Fock (HF) level calculations overestimate the band gaps of conjugated polymers.[20,21] Non-HF based models, such as the extended Hückel or modified extended Hückel method, do not explicitly include electron correlation, but can be parametrized to yield reasonable band gaps in comparison to experimental values. The electronic structures of the polymers considered here were obtained by performing MEH band calculations[10] with the geometrical parameters in Table 1. The MEH method adopts a new form for the off-diagonal elements which has an additional distance-dependent empirical factor. This approach has been shown to yield remarkably reliable band structures for a wide variety of conjugated polymers.[10,15] The atomic parameters used for Si were 1.75 for the valence orbital exponents[16] and 8.15 eV for the valence-state ionization potentials of the 3p orbitals.[17] It is important to note that the MEH method is designed to reproduce band gaps defined as the λ_{max} for the π to π^* transition, and not the band edge, as is often used to define the gap experimentally. Typically, the band edge is about 0.5 eV lower than λ_{max}.

The calculated electronic properties of the polymers are summarized in Table 3. As is well-known,[7,8,12] more stable forms of similar polymers generally have larger band gaps, lower energy levels of HOCOs, higher energy levels of LUCOs, and narrower bandwidths. Given the fact that the near energetic degeneracy of the PPD conformers makes an assessment of the ground-state structure difficult, it is gratifying that both conformers have very similar electronic properties (Figure 4). All other systems in this study show significant differences between the aromatic and quinoid band gaps. The only system for which related experimental data are available is PS, for which the dibutyl derivative, $-(C_4H_2SiBu_2)_n-$, exhibits an experimental UV absorption peak[18] at 2.0 eV, closer to our predicted band gap for the aromatic form (1.88 eV) than the quinoid form (2.61 eV) of the parent polysilole polymer. Note, however,

Table 3. Comparison of the Predicted Electronic Properties (eV) of the Titled Polymers

polymers[a] (XY_2)	E_g	E_{HO}	highest valence bandwidth	E_{LU}	lowest conduction bandwidth
PPD (A)	2.23	−11.16	4.03	−8.93	6.01
(CH_2) (Q)	2.17	−11.07	4.08	−8.90	6.00
PFPD (A)	1.81	−11.25	3.92	−9.43	6.08
(CF_2) (Q)[b]	2.65	−11.60	3.48	−8.95	5.12
PS[c] (A)	1.88	−11.39	3.87	−9.51	5.95
(SiH_2) (Q)	2.61	−11.65	3.71	−9.04	5.44
PFS (A)	1.84	−11.41	3.99	−9.57	5.97
(SiF_2) (Q)	2.79	−11.81	3.52	−9.02	5.02
trans−cisoidal PA	2.14	−11.70	5.08	−9.55	10.79
cis−transoidal PA	2.60	11.89	4.90	−9.29	10.65

[a] All geometrical parameters were obtained from the PRDDO optimizations. [b] The most stable conformer is underlined, except for the case of CH_2 where the aromatic and quinoid forms are essentially equal in energy. [c] UV maximum absorption peak for $-(C_4H_2SiBu_2)_n-$ is located at 2.0 eV.[18]

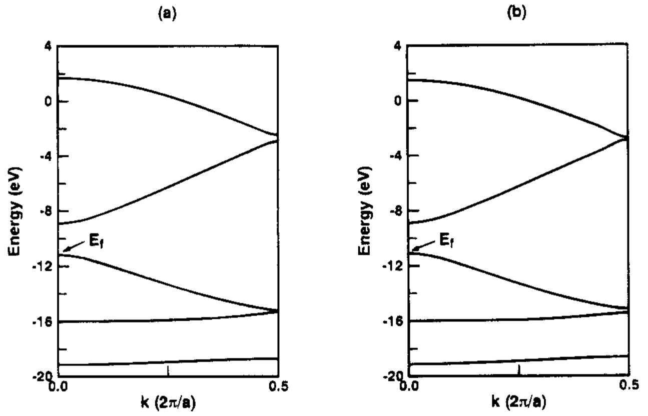

Figure 4. π-Band structures of the (a) aromatic and (b) quinoid forms of poly(cyclopentadienylene).

Table 4. Analysis of the Band Gap Evolution of the Titled Polymers (eV)[a]

polymers (XY_2)	E_g	E_g'	$\Delta E^{\delta r}$	ΔE^{1-4}	ΔE^{el}
PPD (A)	2.23	1.59	2.03	−0.44	0.64
(CH_2) (Q)	2.17	2.89	2.38	0.51	−0.72
PFPD (A)	1.81	1.74	2.15	−0.41	0.07
(CF_2) (Q)	2.65	2.77	2.26	0.50	−0.12
PS (A)	1.88	1.81	2.07	−0.26	0.07
(SiH_2) (Q)	2.61	2.73	2.48	0.25	−0.12
PFS (A)	1.84	1.90	2.13	−0.23	−0.06
(SiF_2) (Q)	2.79	2.76	2.51	0.25	0.03
trans−cisoidal PA	2.14		2.38	−0.24	
cis−transoidal PA	2.60		2.53	0.07	

[a] Analysis was performed according to eq 1. [b] E_g' is the band gap of the corresponding polymeric backbone without the bridging group XY_2.

that there is some ambiguity[13,14,18,19] in the structure of $-(C_4H_2SiBu_2)_n-$. Specifically, it is uncertain whether this polymer is of the poly(diethynylsilane) type, which has four-membered rings, or of the polysilole type, which has five-membered rings. Additionally, the effects of the Bu groups on the conformation of the backbone, and thus the band structure, may be substantial.

We found that the aromatic forms of these systems tend to have smaller band gaps than trans−cisoid PA, while the quinoid forms are inclined to have larger band gaps than cis−transoid PA. To analyze the effects of bridging groups, we decomposed the band gap according to eq 1, and the results are shown in Table 4. The decomposition was performed as follows. Since the band gap of *trans*-PA arises exclusively from Peierls distortion, a standard value of $\Delta E^{\delta r}/\delta r$ was computed from the predicted band gap (2.25 eV) and δr (0.137 Å) for *trans*-PA. The δr value was computed from PRDDO optimizations of the pentamer *trans*-PA. This procedure yields an estimated value of $\Delta E^{\delta r}/\delta r$ of 16.4 eV/Å. Then, the $E^{\delta r}$ for each polymer was estimated by multiplying the standard $E^{\delta r}/\delta r$ value for a conformer by the δr value of each polymer. For each polymer, ΔE^{1-4} amounts to $E_g' - \Delta E^{\delta r}$, where E_g' is the band gap calculated from the corresponding polymeric backbone without the bridging groups. Finally, ΔE^{el} was evaluated by applying eq 1 and solving for ΔE^{el}. As shown in Table 4, the electronic effects of the bridging groups on the band gap are greatly suppressed, resulting in small band gaps for the aromatic forms of these polymers. We have previously reported[10] the values of ΔE^{el} for polythiophene, polypyrrole, and polyfuran (which are all aromatic in the ground state) to be 2.2, 3.4, and 3.0 eV, respectively, much larger than the values found in the current work.

The band gaps of the polymers result primarily from bond-length alternations, because the ΔE^{1-4} and ΔE^{el} values are uniformly smaller than $\Delta E^{\delta r}$, and generally of opposite sign. As shown in Figures 1 and 2 and Table 4, the aromatic forms generally have negative ΔE^{1-4} values and positive ΔE^{el} values, while the opposite situation is found for the quinoid forms. Such tendencies become much weaker when large Si atoms and/or electronegative F atoms are employed as the bridging group. This is because the large Si atom does not decrease the C1−C4 distance sufficiently and the 3p orbital of Si is too diffuse to effectively overlap with the π-orbitals of the polymeric backbone. Also, fluorine atoms lower the energy levels of molecular orbitals of the bridging groups, and the resultant MOs do not mix strongly with the π-orbitals of the polymer backbone.

Conclusions

We have investigated the conformations and electronic structures of four new conjugated cyclic polymers, poly(cyclopentadienylene), poly(1,1-difluorocyclopentadienylene), polysilole, and poly(difluorosilole). These polymers consist of five-membered rings which have CH_2, CF_2, SiH_2, or SiF_2 as bridging groups. We found that the ground-state geometries of all of these polymers, except possibly PPD, are quinoid. The aromatic and quinoid forms of PPD are calculated to be nearly degenerate, and the band structures are very similar. The bridging groups affect the band gaps in two principle ways: by decreasing the C1−C4 distance and by pure electronic effects. Decreasing the C1−C4 distance decreases the band gap of the aromatic form but increases the gap of the quinoid form. On the other hand, the electronic interactions between the bridging groups and the π-orbitals of the polymeric backbone increase the band gap of the aromatic form and decrease the band gap of the quinoid form. The electronic effects of CH_2, CF_2, SiH_2, and SiF_2 are much smaller than those of S, NH, and O. Therefore, contrary to the cases of PT, PPy, and PF, the band gaps of these polymers arise mainly from the effects of bond-length alternations, leading to smaller band gaps for these new conjugated polymers. The band gap of poly(cyclopentadienylene) is calculated to be comparable to those of polyacetylenes.

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