Quantum-Chemical Study of Geometrical and Electronic Structures of Thiophene-Based Bicyclic Polymers

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A quantum-chemical study was performed to investigate the geometrical and electronic structures of a variety of thiophene-based bicyclic polymers $[-(C_6H_2SX)_n-]$, where X = CH_2, SiH_2, C=O, C=S, or C=CH_2. These two (S and X) types of the bridging groups are different from each other in that S favors the aromatic form of a cyclic polymer and X the quinonoid form. Geometrical structures of the polymers were obtained from AM1 band calculations and the electronic properties from the modified extended Hückel band calculations. It is predicted that the bicyclic polymers with weak electron-donating groups (CH_2 and SiH_2 groups) are of the aromatic forms in the ground state and that the polymers with electron-withdrawing groups (C=O, C=S, and C=CH_2 groups) are of the quinonoid forms as observed in the thiophene copolymers, $-[(C_4H_2S)-(C_4H_2X)]_n-$. The band gaps (which correspond to the absorption peaks of $\pi-\pi^*$ band transition) of the bicyclic polymers in the ground state are estimated to be in the range of 1.4−1.9 eV. The band gaps were analyzed in terms of the bond-length alternation along the conjugated carbon backbone, the C1−C4 interactions, and the electronic effect of the bridging groups. In comparison with the contributions found in the thiophene copolymers, the contribution from the bond-length alternation to the band gaps decreases, and the contributions from the C1−C4 interactions and the electronic perturbation of S increase. As a result, the band gaps of the bicyclic polymers are about 0.2 eV smaller than those of the corresponding thiophene copolymers.

Introduction

During the last couple of decades, π-conjugated polymers have been extensively studied because of their characteristic electronic and optical properties which propound a variety of potentially technological applications of the polymers.[1] The electro-optical properties of a conjugated polymer are predominantly governed by its gap (E_g) between the valence and conduction bands. Therefore, recent research efforts[2−23] have focused on the design of small band gap polymers with $E_g < 1$ eV. Some strategies to achieve such a goal have emerged: (1) coupling of two polymeric chains−ladder polymers,[11,24−26] (2) fusion of conjugated rings onto heterocyclic polymers,[2,12,16,27] (3) insertion of a methine group between two heterocyclic rings,[3,7,13,28−30] (4) replacing heteroatoms of heterocyclic polymers with new bridging groups which are either electron acceptors or very weak electron donors,[18,20] (5) alternation of strong electron-donating and -accepting moieties,[8] (6) copolymerization of two different (aromatic and quinonoid) types of cyclic units,[6,10,15,21,23] and (7) fusion of cyclic units with electron-donating or -accepting groups.[4,5,9,17,19,22]

Recently, some tricyclic polymers fused with a combination of electron-donating and electron-withdrawing groups have been reported to possess small band gaps.[4,5,19,22] Lambert and Ferraris synthesized polycyclopentadithiophenes fused with electron-withdrawing groups: polycyclopenta[2,1-*b*:3,4-*b'*]dithiophene-4-one (PCDT)[4] and poly-4-dicyanomethylene-4*H*-cyclopenta-[2,1-*b*:3,4-*b'*]dithiophene (PCDM).[5] They reported that PCDT exhibited the absorption peaks at 740 nm (1.68 eV) and 425 nm (2.92 eV), and that the peak of the optical spectrum for PCDM appeared at 950 nm (1.31 eV) with the onset at ca. 0.8 eV. Neutral polycyclopenta[2,1-*b*:3,4-*b'*]dithiophenes were reported to show the optical absorption peaks of the neutral films

in the range of 545−680 nm (1.8−2.3 eV) and to display the conductivities of 200−400 S/cm[9]. Toussaint and Bredas demonstrated that the small band gap of PCDM would be mainly due to a strong stabilizing interaction between the lowest unoccupied molecular orbital (LUMO) of the carbon backbone and the LUMO of the electron-withdrawing group.[17]

Following the theoretical work on the effects of the bridging groups on the geometrical structures and the band gaps of five-membered ring polymers,[20,31,32] we have investigated the geometrical and electronic structures of heterocycle−nonheterocycle copolymers, $-[(C_4H_2X)-(C_4H_2Y)]_n-$.[21,23] According to the investigation, the copolymers exhibit the different isomeric structures depending on the bridging groups in the nonheterocycles and possess small band gaps (1.6−2.1 eV) due to the reduced electronic perturbation of the heteroatoms compared with that found in the heterocyclic polymers. Our recent study revealed that bithiophene polymers fused with nonheteroatoms maintain the small bond-length alternations and the enhanced C1−C4 interactions of the conjugated carbon backbones, resulting in the small band gaps (0.7−2.0 eV).[33] Therefore, it is interesting to look into the geometrical structures and electronic properties of the fused bicyclic polymers with a combination of heterocyclic and nonheterocyclic units and to compare them with those of the corresponding copolymers. Table 1 shows the summary of the effects of the briding groups in the homopolymers. To the best of our knowledge, only heteroaromatic bicyclic polymers have been investigated so far.[34−36] Poly(thieno[3,2-b]thiophene) (PTT) was reported to show an intrinsic conductivity ($\sim 10^{-6}$ S/cm) in the semiconductor region.[36]

In this study, we investigated the geometrical and electronic structures of various thiophene-based bicyclic polymers $[-(C_6H_2SX)_n-]$ in Figure 1: polythieno[3,2-*b*]cyclopentadiene (PTP), polythieno[3,2-*b*]silole (PTS), polythieno[3,2-*b*]oxocyclopentadiene (PTOP), polythieno[3,2-*b*]thiocyclopentadiene (PTTP), and polythieno[3,2-*b*]fulvene (PTF). Geometrical structures of

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TABLE 1: Effects of Various Bridging Groups on the Geometrical Structures and the Band Gaps of Five-Membered Ring Homopolymers in the Ground State[a]

bridging group	geometrical structure of the homopolymer	effect of the bridging groups on the band gaps
>S	aromatic form	increase (1.9 eV)[b]
>O	aromatic form	increase (3.0 eV)
>NH	aromatic form	increase (3.5 eV)
>CH$_2$	quinonoid form	decrease (−0.7 eV)
>SiH$_2$	quinonoid form	decrease (−0.1 eV)
>C=O	quinonoid form	increase (0.4 eV)
>C=S	quinonoid form	increase (0.5 eV)
>C=CH$_2$	quinonoid form	decrease (−0.3 eV)

[a] Data for the heteroatoms from ref 32. Data for the other bridging groups from ref 20. [b] Number in parentheses corresponds to the contribution from the electronic perturbation of the bridging group to the band gap of the corresponding homopolymer.
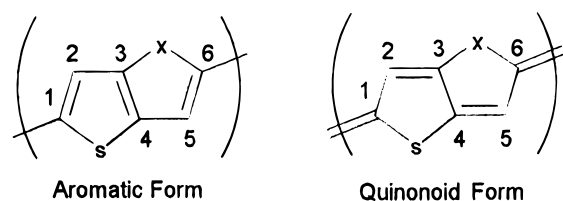
X : CH$_2$　polythieno[3,2-b]cyclopentadiene (PTP)

　: SiH$_2$　polythieno[3,2-b]silole (PTS)

　: C=O　polythieno[3,2-b]oxocyclopentadiene (PTOP)

　: C=S　polythieno[3,2-b]thiocyclopentadiene (PTTP)

　: C=CH$_2$　polythieno[3,2-b]fulvene (PTF)

Figure 1. Aromatic and quinonoid forms of the thiophene-based bicyclic polymers [−(C$_6$H$_2$SX)$_n$−] with two different types of bridging groups.

the polymers were optimized through AM1 band calculations[37] and their electronic properties were obtained from modified extended Hückel (MEH) band calculations.[38] Also, the band gaps of the polymers were analyzed in terms of bond-length alternation along the conjugated carbon backbone, C1−C4 interactions in the frontier orbitals, and the electronic effect of the bridging groups. The method for the band gap analysis will be described in detail in the next section.

Methodology for the Band Gap Analysis

Recently, we have successfully decomposed the band gaps of conjugated five-membered ring polymers using the following equation:[20,21,23,30−32]

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

Here $\Delta E^{\delta r}$ refers to a gap arising from bond-length alternation (δr) along the conjugated carbon backbone. Since E_g of *trans*-PA arises only from the bond-length alternation, the relationship between $\Delta E^{\delta r}$ and δr was derived from the calculated E_g and δr values for *trans*-PA as in eq 2.[32]

$$\Delta E^{\delta r} = 16.1 \text{ (eV/Å) } \delta r \tag{2}$$

ΔE^{1-4} corresponds to a contribution from the interactions between C1 and C4 atoms of a *cis*-PA-type conjugated carbon backbone. The interactions between C1 and C4 atoms in the frontier orbitals are different from each other: one is bonding and the other antibonding. These interactions increase the band gap of *cis-transoid*-PA ($\Delta E^{1-4} > 0$) and decrease the gap of *trans-cisoid*-PA ($\Delta E^{1-4} < 0$).[32] The contribution (ΔE^{1-4}) to E_g can be evaluated by subtracting $\Delta E^{\delta r}$ from the band gap (E_g') arising only from the carbon backbone of a conjugated polymer,

E_g' being calculated by removing the atomic orbtials of the briding groups from the Hamiltonian and overlap matrices. The contribution from ΔE^{1-4} is small in *cis*-PA (0.2 eV) but becomes significant as the C1−C4 distance becomes shorter. In a five-membered ring system this effect amounts to 0.2−0.7 eV, depending on the size of the bridging atom.[20,32] This effect together with ΔE^{el} is in some cases crucial in determining the relative stability of aromatic vs quinoid forms of conjugated cyclic polymers.[31] ΔE^{el} is due to the electronic interaction between a conjugated carbon backbone and moieties such as a bridging atom or group, pendent groups, and fused rings. Finally, ΔE^{el} is calculated by deducting E_g' from the estimated E_g of the polymers. This electronic effect corresponds to the second-order energy correction which is proportional to the square of the overlap between the frontier molecular orbitals of the carbon backbone and moiety orbitals and which is inversely proportional to the energy difference between the levels corresponding to these orbitals. The ΔE^{el} of heteroatoms in heterocyclic polymers is so large that it dominates the band gaps of the polymers and induces the aromatic forms to being more stable.[31,32] Since the thiophene-based bicyclic polymers in Figure 1 have two different bridging groups (S and X), the total electronic effect of the bridging groups is separated to estimate the contribution from each bridging group: $\Delta E^{el} = \Delta E^{el}(S) + \Delta E^{el}(X)$.[21,23] $\Delta E^{el}(S)$ can be estimated in two different ways as follows:

$$\Delta E^{el}(S) = E_g(S) - E_g' \tag{3}$$

or

$$\Delta E^{el}(S) = E_g - E_g(X) \tag{4}$$

Here $E_g(S)$ corresponds to the band gap of the polymeric backbone which possesses only S in one of the rings and no X in the other ring, and vice versa for $E_g(X)$. $\Delta E^{el}(X)$ can be calculated using the same equations where S and X are transposed. Eqs 3 and 4 are, however, not equivalent but complement each other since the electronic effects of S and X are not independent but strongly correlate to each other. ΔE^{el}-(S) in eq 3 refers to the electronic effect of S on the band gap of the backbone which possesses only S in one of the rings as a bridging group while $\Delta E^{el}(S)$ in eq 4 corresponds to the effect of S on the band gap of the backbone which is already perturbed electronically due to the presence of the X group. Therefore, if we assume that S atoms go into the polymeric backbone to form five-membered rings ahead of the X groups, we have to calculate the electronic effect of S using eq 3 and the effect of the X group using eq 4 where S and X are transposed. In the reverse case, we have to use eq 4 to estimate the electronic effect of S and eq 3, where S is replaced with X, to compute the effect of the X group. However, the same value of the total electronic effect, ΔE^{el}, is produced regardless of the way we choose to calculate the individual electronic effect of the bridging groups. Therefore, we take the average of the values calculated, using both eqs 3 and 4, to determine the separate electronic effect of the bridging groups.

Geometrical Structures

Several quantum-chemical methods (ab initio and semiempirical techniques such as modified neglect of diatomic overlap [MNDO] and complete neglect of differential overlap [CNDO] types) have been used to obtain the ground-state geometries of polymers. Because of computational time, the ab initio method may not be suitable for an infinite chain. To our knowledge, only *trans*-PA was studied through ab initio crystal orbital

TABLE 2: Heats of Formation (kcal/mol of Unit Cell) of the Isomers of the Thiophene-Based Bicyclic Polymers [−(C₆H₂SX)ₙ−] in Figure 1

	PTP	PTS	PTOP	PTTP	PTF
aromatic	68.96	56.01	52.98	115.27	97.11
quinonoid	70.32	58.29	50.85	113.28	96.83

calculations.[39,40] It was also reported that ab initio calculations with small basis sets are subject to overestimating the bond-length alternation and, thus, quite large basis sets are required to produce reasonable results. Therefore, an oligomeric approach has been widely employed to extract a polymeric structure from the optimized central unit of the corresponding oligomer such as a trimer or a tetramer. However, one should be careful when adopting this approach for determining the ground-state geometries of conjugated polymers and for estimating the relative stabilities of the aromatic and quinonoid structures since these properties strongly depend on the types of terminal groups of an oligomer.[16,18,41]

We employed the solid-state version of the MNDO method (MOSOL) with AM1 Hamiltonians to obtain geometrical structures of the thiophene-based bicyclic polymers in Figure 1. The geometric parameters of the polymers were obtained through full optimization of the parameters with an assumption of the planar structures. Since the conjugated cyclic polymers are nondegenerate in the ground state and, thereby, two types of isomers are possible, both isomeric structures of the polymers were obtained and their heats of formation were compared to figure out the ground-state geometry. Note that depending on the starting geometry, the optimized structure is either of an aromatic or of a quinonoid form since there are usually two minima on the potential energy surface of a cyclic polymer which represent the aromatic and quinonoid forms, respectively.[20,21,23,32]

Table 2 presents the heats of formation of the aromatic and quinonoid forms of the thiophene-based bicyclic polymers. It is estimated that the aromatic forms of PTP and PTS are the more stable of the two isomeric structures in the ground state while the quinonoid forms of PTOP, PTTP, and PTF are the more stable. Therefore, it is deduced that the preference of the bridging S atom for the aromatic form of a cyclic polymer overwhelms that of > CH₂ and > SiH₂ groups for the quinonoid form, but not that of the electron-withdrawing groups, >C=O,

>C=S, and >C=CH₂. The same trend was observed in the heterocycle−nonheterocycle copolymers.[21,23] However, the energy differences between the aromatic and quinonoid forms of the bicyclic polymers are small compared with those of the corresponding copolymers. The difference is only 1.36 kcal/mol of unit cell in PTP and two isomeric structures of PTF are estimated to be nearly isoenergetic. Optimized structural parameters for both aromatic and quinonoid forms of the polymers are listed in Table 3. In the aromatic forms, the short bonds are longer and the long bonds shorter compared with the corresponding bonds of the thiophene copolymers. Particularly, the C3−C4 bond, which is shared by two different rings, is much longer than the corresponding bonds of the thiophene copolymers. Therefore, the bond-length alternation of the aroamtic forms decreases by about 0.02 Å, which leads to the reduction of the band gaps as much as 0.3−0.4 eV, according to eq 1. In contrast, in the quinonoid forms, the short bonds are shorter and the long bonds longer than those of the corresponding thiophene copolymers. As a result, the bond-length alternations of the quinonoid forms of the bicyclic polymers increase by 0.014 Å over those of the thiophene copolymers, corresponding to the band gap increment of 0.2 eV.

The inter-ring distances of the aromatic forms are slightly shorter than the corresponding value (1.44 Å) obtained from the recent X-ray diffraction study[42] of single crystals of unsubstituted sexithiophene. The increase (0.02 Å) in the inter-ring distance enlarges the bond-length alternation by 0.006 Å. The band gap is expected to subsequently increase by 0.1 eV according to eq 2.

Electronic Properties

It is well-known that Hartree−Fock (HF) level calculations greatly overestimate the band gaps of conjugated polymers and the calculated E_g at the HF level must be scaled down to compare with experimental values.[40,43,44] One may think of a simple scaling scheme to estimate the actual E_g of a conjugated polymer from a calculated one at the HF level. But, transferability of a scaling factor from one polymeric system to another is limited since the band gap of a conjugated polymer usually arises from various factors. In fact, the CNDO/2 calculations have shown that a scaling factor obtained from the *trans*-PA

TABLE 3: Optimized Geometrical Parameters for the Thiophene-Based Bicyclic Polymers [−(C₆H₂SX)ₙ] in Figure 1 (Bond Lengths in Angstroms and Bond Angles in Degrees): Aromatic (A) and Quinonoid (Q) Forms

	PTP		PTS		PTOP		PTTP		PTF	
	A[a]	Q	**A**	Q	A	**Q**	A	**Q**	A	**Q**
1−2	1.386	1.463	1.389	1.469	1.390	1.468	1.387	1.462	1.385	1.460
2−3	1.421	1.351	1.415	1.345	1.417	1.351	1.419	1.354	1.418	1.351
3−4	1.409	1.486	1.399	1.476	1.409	1.487	1.412	1.488	1.409	1.485
4−5	1.441	1.353	1.451	1.356	1.452	1.352	1.448	1.353	1.445	1.354
5−6	1.377	1.472	1.359	1.453	1.373	1.474	1.380	1.480	1.385	1.483
3−X	1.497	1.495	1.776	1.774	1.489	1.484	1.471	1.467	1.470	1.468
4−S	1.649	1.668	1.666	1.693	1.641	1.669	1.643	1.670	1.651	1.672
>C=Y[b]					1.223	1.227	1.533	1.539	1.333	1.335
6-1′	1.422	1.342	1.420	1.340	1.420	1.343	1.424	1.348	1.427	1.347
1−2−3	111.0	112.3	112.6	113.8	110.5	111.6	111.0	112.0	111.3	112.4
2−3−4	111.9	113.1	111.6	112.9	112.3	113.5	112.1	113.3	112.5	113.7
3−4−5	110.0	110.9	116.8	117.7	110.2	111.4	109.2	110.4	109.0	110.1
4−5−6	108.3	109.3	113.8	115.0	108.7	109.2	108.5	108.9	108.7	109.4
S−4−3	111.9	110.5	111.2	109.5	111.9	110.3	111.8	110.2	111.2	109.6
X−3−4	108.7	107.6	107.0	105.3	107.8	106.5	108.7	107.4	108.6	107.4
5−6−1′	125.4	124.0	130.2	128.7	125.9	124.2	124.7	123.0	124.2	123.0
1−4	2.444	2.487	2.464	2.513	2.439	2.485	2.448	2.490	2.461	2.506
3−6	2.357	2.370	2.632	2.656	2.379	2.379	2.350	2.351	2.347	2.358
δr[c]	0.037	0.125	0.046	0.119	0.039	0.128	0.037	0.125	0.037	0.125

[a] Bold type indicates the more stable forms of the isomers. [b] Y = O, S, or CH₂. [c] Average value of the bond-length alternation, defined as $\delta r = |R(1{-}2) - R(2{-}3) + R(3{-}4) - R(4{-}5) + R(5{-}6) - R(6{-}1')|/3$.

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TABLE 4: Valence Shell Atomic Parameters Used in the Modified Extended Hückel Band Calculations[a]

atom	n	l	IP	ζ	n	l	IP	ζ
H	1	0	13.60	1.300				
C	2	0	21.40	1.625	2	1	11.40	1.625
Si	3	0	17.30	1.750	3	1	8.15	1.750
S	3	0	20.00	2.117	3	1	13.30	2.117
O	2	0	32.30	1.975	2	1	14.80	1.975

[a] n and l are the principal and angular momentum quantum numbers, respectively. Ionization potential is represented by IP (in eV), Slater orbital exponent by ξ (in au).

system cannot be used for the polyfuran system.[45] Therefore, lower level approaches such as the valence effective Hamiltonian (VEH),[46] Hückel, and extended Hückel[47] methods have been widely used for predicting the E_g of one-dimensional conjugated polymers. Though non-HF-based models do not explicitly include electron correlation, the success of these models comes from parametrizations that yield reasonable band gaps in comparison to experimental values.

We adopted the MEH method to calculate the electronic properties of the polymers using the geometrical parameters optimized through AM1 band calculations. The MEH method was parametrized to reproduce band gaps defined as λ_{max} for the $\pi-\pi^*$ transition of conjugated polymers and not the band edge as is often used to define the gap experimentally.[38] This approach has been shown to yield remarkably reliable band structures for a wide variety of conjugated polymers, including those with heteroatoms.[38,48] MEH parameters used in the calculations are listed in Table 4.

The predicted electronic properties of the thiophene-based bicyclic polymers are presented in Table 5. The corresponding properties of the thiophene copolymers are given in parentheses for comparison. *Note that the band gap we report here corresponds to the $\pi-\pi^*$ absorption peak, not to the band edge whose value is typically about 0.5 eV lower than the peak value.* It is again confirmed that the more stable form of the isomers possesses the larger band gap than does the less stable one as observed in other cyclic systems.[20,21,23,32] The band gaps of the polymers in the ground state were estimated to be in the range of 1.36−1.92 eV, being less than those of the homopoly-

mers and thiophene copolymers. Among the bicyclic polymers, PTF shows the smallest E_g of 1.36 eV and PTTP exhibits the largest E_g of 1.92 eV with an indirect gap of 1.21 eV. PTTP is found to have the largest ionization potential (IP), implying the greatest stability against oxidation. It is predicted that all the bicyclic polymers show similar electron affinities (EAs), though PTP shows the slightly small EA, and possess similar highest valence bandwidths. The electron-withdrawing groups produce the relatively flat lowest conduction band (LCB). Particularly, PTOP exhibits the very flat LCB whose width is only 0.13 eV. Compared with the corresponding thiophene copolymers, the bicyclic polymers possess smaller IPs by 0.4−0.5 eV and smaller EAs by 0.3 eV, but relatively larger bandwidths. Therefore, the bicyclic polymers are expected to be more susceptible to oxidation and less susceptible to reduction than the corresponding thiophene copolymers.

Let us discuss the evolution of the band gaps of the bicyclic polymers in terms of the bond-length alternation, the C1−C4 interactions and the electronic effect of the bridging groups, particularly in comparison with those of the thiophene copolymers. Figure 2 depicts the evolution of the band gap of the aromatic form of PTP. In the aromatic forms of the bicyclic polymers, the $\Delta E^{\delta r}$ values fall in the range of 0.60−0.75 eV, being smaller by 0.3−0.4 eV than those found in the copolymers due to the smaller δr as already mentioned in the Geometrical Structures section. Moreover, due to the additional C3−C6 interactions of the carbon backbone, the C1−C4 interactions which reduce the band gaps increase by 0.2 eV. In PTS, the total effect of the C1−C4 interactions is relatively small due to the large atomic size of Si, which connects C3 and C6 atoms. Consequently, the effect of the bond-length alternation of the band gap is almost counteracted by the effect of the C1−C4 interactions, resulting in nearly degenerate states of the highest occupied molecular orbital (HOMO) and the LUMO of the carbon backbone as shown in Figure 2. It is found that the ΔE^{el} contributions in PTP and PTS mainly come from S whose effect (1.2−1.3 eV) is about two thirds of $\Delta E^{el}(S)$ estimated in PT. The effect of CH_2 and SiH_2 groups are similar to that found in the corresponding copolymers and are very small. Accordingly, the band gaps of the aromatic forms of PTP and PTS are

TABLE 5: Electronic Properties[a] and Band Gap Decomposition[b] of the Thiophene-Based Bicyclic Polymers [−(C₆H₂SX)ₙ−] in Figure 1 (in eV): Aromatic (A) and Quinonoid (Q) Forms

	PTP		PTS		PTOP		PTTP		PTF	
	A[c]	Q	**A**	Q	A	**Q**	A	**Q**	A	Q
E_g	1.53	1.02	1.60	0.96	0.87	1.72	0.61	1.92[d]	0.97	1.36
	(1.70)[e]	(0.87)	(1.55)	(1.08)	(0.60)	(1.90)	(0.17)	(2.09)		
$\Delta E^{\delta r}$	0.60	2.01	0.75	1.92	0.63	2.06	0.60	2.01	0.60	2.01
	(0.92)	(1.80)	(1.00)	(1.79)	(1.01)	(1.84)	(0.97)	(1.80)		
ΔE^{1-4}	−0.65	0.60	−0.45	0.40	−0.61	0.57	−0.66	0.61	−0.67	0.60
	(−0.42)	(0.40)	(−0.32)	(0.26)	(−0.41)	(0.38)	(−0.43)	(0.40)		
ΔE^{el}	1.58	−1.59	1.30	−1.36	0.85	−0.91	0.67	−0.70	1.04	−1.25
	(1.20)	(−1.33)	(0.87)	(−0.97)	(0.00)	(−0.32)	(−0.37)	(−0.11)		
$\Delta E^{el}(S)$	1.24	−1.22	1.28	−1.31	1.35	−1.25	1.35	−1.16	1.17	−1.09
	(0.87)	(−0.95)	(0.85)	(−0.92)	(0.62)	(−0.74)	(0.53)	(−0.65)		
$\Delta E^{el}(X)$	0.34	−0.37	0.02	−0.05	−0.50	0.34	−0.68	0.46	−0.13	−0.16
	(0.34)	(−0.38)	(0.03)	(−0.05)	(−0.62)	(0.42)	(−0.90)	(0.54)		
IP	10.36	10.02	10.62	10.21	10.50	10.71	10.55	10.91	10.38	10.36
	(10.75)	(10.22)	(10.87)	(10.54)	(10.81)	(11.24)	(10.78)	(11.44)		
EA	8.83	8.99	9.02	9.25	9.63	8.99	9.94	8.99	9.41	9.00
	(9.05)	(9.35)	(9.32)	(9.47)	(10.20)	(9.34)	(10.61)	(9.87)		
HVBW	2.76	3.12	2.66	3.10	2.85	2.65	2.67	2.33	2.53	2.58
	(2.12)	(2.34)	(2.21)	(2.22)	(2.11)	(1.31)	(2.11)	(1.10)		
LCBW	3.23	3.43	3.06	3.30	0.95	0.13	0.39	0.71	1.32	0.82
	(2.32)	(2.62)	(2.36)	(2.51)	(1.17)	(0.23)	(0.80)	(0.52)		

[a] IP = ionization potential, EA = electron affinity, HVBW = highest valence bandwidth, and LCBW = lowest conduction bandwidth. [b] E_g is a band gap corresponding to the $\pi-\pi^*$ absorption peak of a spectrum. See eq 1 in the text for the components of a band gap. [c] Bold type indicates the more stable forms of the isomers. [d] An indirect transition is predicted to occur at 1.21 eV. [e] The numbers in parentheses are the values for corresponding thiophene copolymers.
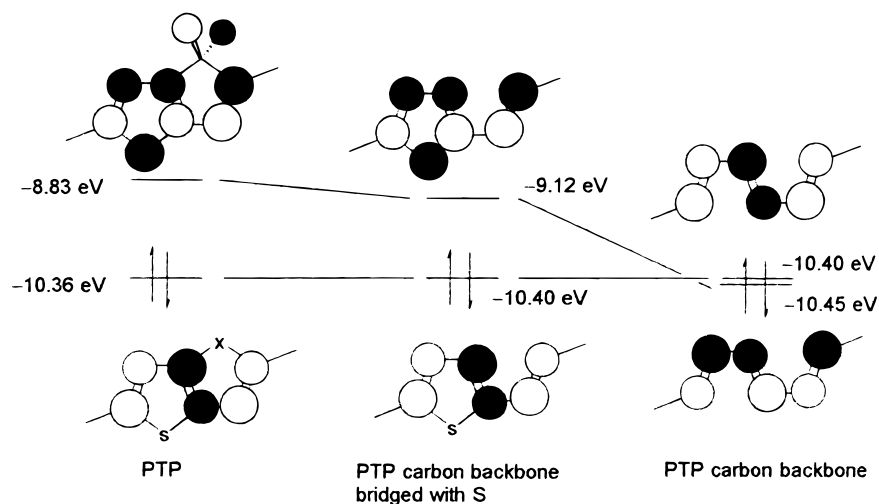
Figure 2. Evolution of the band gap of the aromatic form of polythieno[3,2-*b*]cyclopentadiene.
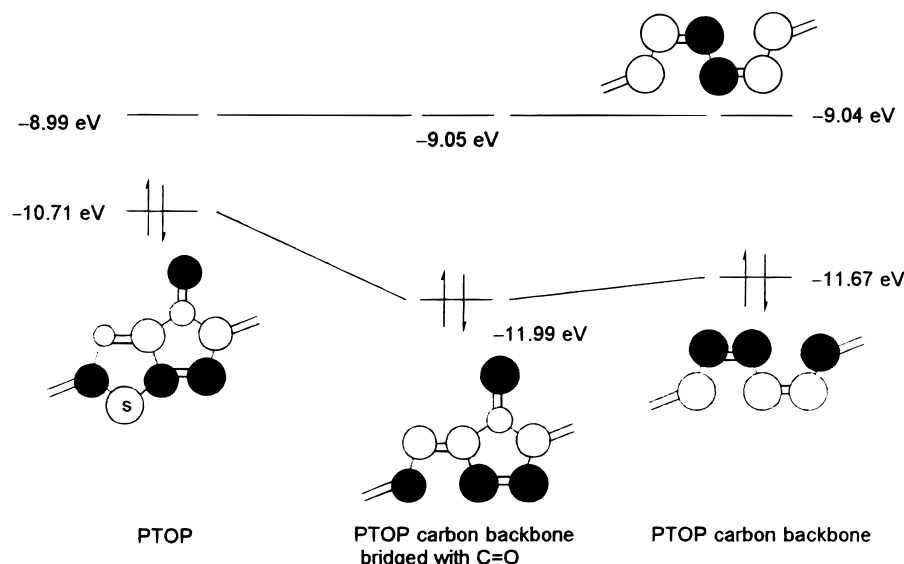

Figure 3. Evolution of the band gap of the quinonoid form of polythieno[3,2-*b*]oxocyclopentadiene.

revealed to mainly arise from the electronic perturbation of S. Therefore, it is concluded that the smaller band gaps of PTP and PTS are due to the smaller $\Delta E^{el}(S)$ compared to those values in PT. Compared with poly(thienylene cyclopentadienylene) (PThPD), the band gap of PTP decreases by 0.2 eV due to the smaller bond-length alternation and the enhanced C1−C4 interactions although the ΔE^{el} value of PTP is estimated to be larger by about 0.4 eV. In the quinonoid forms of PTOP, PTTP, and PTF, the bond-length alternation and the C1−C4 interactions increase the band gaps by as much as 2 and 0.6 eV, respectively. Therefore, it is understood that the band gaps mainly arise from the bond-length alternation of the carbon backbone. These gaps are reduced by the effect of the bridging groups, mainly S. Among the bridging groups, S and C=CH$_2$ groups decrease the band gaps through the antibonding interaction between the HOMO of the carbon backbone and the π-type orbital of the bridging groups while C=O and C=S groups increase the gaps through the bonding interaction as illustrated in Figure 3 for the evolution of the band gap of the quinonoid form of PTOP. Compared with the corresponding thiophene copolymers, the larger bond-length alternation contributes 0.2 eV more and the enhanced C1−C4 interactions increase the band gap by 0.2 eV. However, the contribution from the electronic perturbation of S increases, leading to the reduction of the band gaps by as much as 0.6 eV. As a result, the band gaps of PTOP and PTTP become 0.2 eV smaller than the gaps

of the corresponding thiophene copolymers due to the enhanced electronic effect of S.

The band gap of the aromatic form of PTP with the inter-ring distance of 1.44 Å was calculated to be 1.62 eV, which is greater by only 0.1 eV than that with the inter-ring distance of 1.42 Å, as estimated in the Geometrical Structures section. The HOMO and LUMO levels were pushed down and up by ca. 0.05 eV, respectively. The slight increase in the inter-ring distance is found not to affect the other electronic properties at all.

The absorption peak (2.83 eV) of PTT was experimentally observed at a slightly higher energy than the peak (2.7 eV) of PT.[34] This optical measurement seems inconsistent with the conductivity measurement[36] which showed a semiconductive character of PTT. PTT is analogous to our polymeric system, but has two S atoms in the unit cell. Therefore, it is expected from the comparison of the band gaps of the bicyclic polymers and the corresponding copolymers that PTT possesses a band gap smaller than PT by about 0.2 eV which is a special case of copolymers with two identical monomers in the unit cell. To support our conjecture, we calculated the band gap of PTT whose geometrical structure was optimized through an AM1 band calculation. The predicted band gap of PTT is 2.01 eV, being 0.3 eV smaller than the gap[32] of PT. Therefore, our result supports the conductivity measurement rather than the optical measurement. The discrepancy between these two measure-

ments may be due to structural disorder of the prepared samples: mainly α−α′ linkages or non α−α′ linkages depending on the polymerization method as pointed out by Pelter et al.[49] The analysis of PTT band gap reveals that the $\Delta E^{el}(S)$ contribution amounts to 2.06 eV, and the $\Delta E^{\delta r}$ and ΔE^{1-4} contributions correspond to 0.52 and −0.57 eV, respectively.

Conclusions

We have investigated the geometrical and electronic structures of a variety of thiophene-based bicyclic polymers $[-(C_6H_2\text{-}SX)_n-]$, where X = CH_2, SiH_2, C=O, C=S, or C=CH_2. These two (S and X) types of the bridging groups are different from each other in that S favors the aromatic form of a cyclic polymer and X the quinonoid form. AM1 band calculations demonstrate that the bicyclic polymers with weak electron-donating groups (CH_2 and SiH_2 groups) are of the aromatic forms in the ground state and that the polymers with electron-withdrawing groups (C=O, C=S, and C=CH_2 groups) are of the quinonoid forms as observed in the thiophene copolymers $-[(C_4H_2S)-(C_4H_2X)]_n-$. Therefore, it is concluded that the preference of the bridging S atom for the aromatic form of a cyclic polymer overwhelms that of the >CH_2 and >SiH_2 groups for the quinonoid form, but not that of the electron-withdrawing groups, >C=O, >C=S, and >C=CH_2. The modified extended Hückel band calculations estimate the band gaps (which correspond to the absorption peaks of $\pi-\pi^*$ band transition) of the bicyclic polymers in the ground state to be in the range of 1.36−1.92 eV, being smaller than those of the corresponding thiophene copolymers as well as PT. According to the band gap analysis, the band gaps of aromatic PTP and PTS largely come from the electronic perturbation of S, and those of quinonoid PTOP, PTTP, and PTF mainly evolve from the large bond-length alternations. In comparison with the thiophene copolymers, it is revealed that the contribution from the bond-length alternation to the band gaps decreases, and the contributions from the C1−C4 (including C3−C6) interactions and the electronic perturbation of S increase. As a result, the aromatic form of PTP exhibits a small band gap due to the small bond-length alternation and the additional C3−C6 interactions; on the other hand, the quinonoid forms of PTOP, PTTP, and PTF show small band gaps due to the large electronic perturbation of S atoms. In fact, the band gaps of the bicyclic polymers are estimated to be about 0.2 eV smaller than those of the thiophene copolymers. It is also found that the band gap of aromatic PTP is 0.8 eV smaller than that of PT primarily due to the smaller electronic effect of S in PTP.

In conclusion, we provide the information on how to modulate the geometrical structure and electronic properties of a thiophene-based bicyclic polymers by adopting two different types of bridging groups and on how the band gap arises through the analysis of the gap in terms of the bond-length alternation, C1−C4 interactions, and the electronic effect of the bridging groups.

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