Available online at www.sciencedirect.com

SCIENCE DIRECT

Polymer 46 (2005) 4950–4957

polymer

www.elsevier.com/locate/polymer

Theoretical analysis on the geometries and electronic structures of coplanar conjugated poly(azomethine)s

Cheng-Liang Liu[a], Fu-Chuan Tsai[a], Chao-Ching Chang[a], Kuo-Huang Hsieh[a,b], Jen-Liang Lin[c], Wen-Chang Chen[a,b,*]

[a]*Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan, ROC*
[b]*Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan, ROC*
[c]*Union Chemical Laboratories, Industrial Technology Research Institute, Hsinchu 300, Taiwan, ROC*

Received 5 January 2005; received in revised form 16 March 2005; accepted 16 March 2005
Available online 19 April 2005

Abstract

In this study, theoretical analysis on the geometries and electronic properties of various conjugated poly(azomethine)s is reported. The theoretical ground-state geometry and electronic structure of the studied poly(azomethine)s are optimized by the hybrid density functional theory (DFT) method treated in periodic boundary conditions at the B3LYP level of theory with 6-31G basis set. The geometry and electronic structure of poly(1,4-phenylenemethylidyneitrilo-1,4-phenylene-nitrilomethylidyne) (**PPI**) are compared with those of poly(*p*-phenylene vinylene) (**PPV**) or polyazine (**PAZ**). The theoretical results suggest the non-coplanar conformation of **PPI** but **PPV** and **PAZ** with a coplanar conformation. The electronic properties of **PPI** are in the intermediate between **PPV** and **PAZ**. The non-coplanar conformation of **PPI** could be released if the phenylene ring is replaced by the five-member ring of 3,4-ethylenedioxythiophene (**PEEI**), pyrrole (**PYYI**), thiophene (**PTTI**), furan (**PFFI**), or thiadiazole (**PThThI**). The theoretical E_g of **PEEI**, **PYYI**, **PFFI**, and **PTTI** are in the range of 1.11–1.67 eV, which is due to the coplanar configuration or donor–acceptor intrachain charge transfer. However, the large bond length alternation or lack of charge transfer characteristic makes the **PThThI** with a larger E_g of 2.47 eV than others. The trend on the IP or EA of the studied conjugated poly(azomethine)s are consistent with the electronic characteristic of the aromatic ring. The upper valence bandwidth of the studied five-member ring based poly(azomethine)s except **PThThI** is in the range of 562–613 meV, which is larger than that of **PPI** (247 meV) or **PPV** (373 meV). The results suggest that the electronic properties of conjugated poly(azomethine)s could be varied through various ring structure. The proposed new coplanar conjugated poly(zomethine)s can be potentially used as transparent conductors or thin film transistors.

Keywords: Poly(azomethine)s; Theoretical electronic properties; Planarity

1. Introduction

Conjugated polymers have been widely recognized as a new class of materials for electronic and optoelectronic devices, such as light emitting diodes [1], thin film transistors [2], and photovoltaic cells [3]. The intrinsic electronic properties of conjugated polymers governing the device performance are the ionization potential (IP), electronic affinity (EA), band gap (E_g), and band width (BW). The electronic and optoelectronic properties of conjugated polymers can be tuned through the following methodologies: [4,5] (1) donor (e.g. alkoxy) or acceptor (e.g. cyano) side group substitution; (2) incorporating heteroatoms (N, O, S, etc.) into the conjugated polymer backbone or ring structure (e.g. pyridine, pyrrole, furan, or thiophene); (3) solid state morphology [6,7].

Conjugated poly(azomethine)s have been widely studied for the last 20 years due to their excellent thermal, mechanical, electronic, optical, optoelectronic, and fiber-forming properties [8–14]. The general chemical structure of conjugated poly(azomethine)s is

---

[*] Corresponding author. Address: Department of Chemical Engineering, Polymer Science and Engineering, National Taiwan University, No1. Sec. 4, Roosevelt Rd, Taipei 106, Taiwan, ROC. Tel.: +886 2 23628398; fax: +886 2 23623040.
E-mail address: chenwc@ntu.edu.tw (W.-C. Chen).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.03.059

[–(Ar$_1$)–CH=N–(Ar$_2$)–N=CH–]$_n$. The C=N linkages of poly(1,4-phenylenemethylidyneitrilo-1,4-phenylenenitrilomethylidyne) (**PPI**) is isoelectronic with the C=C linkages of poly(*p*-phenylene vinlyene) (**PPV**). The incorporating the C=N linkage results in a non-planar conformation of **PPI** and thus the π-electronic delocalization is poor in comparison with **PPV** [8,9]. However, the C=N linkage also allows the complexation with acid or metal ion and thus could be used as fluorescence sensing device [15] or hole-transporting layer of light-emitting device [16]. A recent report on thiophene-based azomethine oligomers also shows that the C=N linkage considerably improves the self-assembly properties and thus high carrier mobility up to $\sim 10^{-2}\,\mathrm{cm^2\,V^{-1}\,S^{-1}}$ is achieved [17]. The control of conformation and their electronic structures are keys to the above technology applications. One strategy to improve the π-electron delocalization of **PPI** is to replace one of the phenylene rings by a thiophene ring, which has been reported by us [18] and other studies [10,13]. However, the development of coplanar conjugated poly(azomethine)s with the E_g less than 2.0 eV remains challenging, which can be potentially used as transparent conductors or thin film transistors.

Theoretical analysis on the electronic structures of various conjugated polymers has been extensively reported [19–26]. We have successfully used the hybrid density functional theory (DFT) method to predict conjugated poly(azomethine)s [18]. In this study, the theoretical analysis on the geometries and electronic properties of conjugated poly(azomethine)s (**1**,**2**), **PPV** (**3**), and polyazine (**PAZ, 4**) is reported, as shown in Fig. 1. The theoretical ground-state geometry and electronic structure of the studied poly(azomethine)s are optimized by the DFT method treated in periodic boundary conditions at the B3LYP level of theory with 6-31G basis set [19,24,25]. The geometry and electronic structure of **PPI** are compared with those of **PPV** and polyazine (**PAZ**) to address the role of the C=N linkage. Then, the effects of the π-electron donor or acceptor ring based backbone on the electronic properties of conjugated poly(azomethine)s were studied, including 3,4-ethylenedioxythiophene (**PEEI, 2a**), pyrrole (**PYYI, 2b**), thiophene (**PTTI, 2c**), furan (**PFFI, 2d**), and thiadiazole (**PThThI, 2e**). The effects of the ring structure on the conformation and electronic properties are discussed in this study.

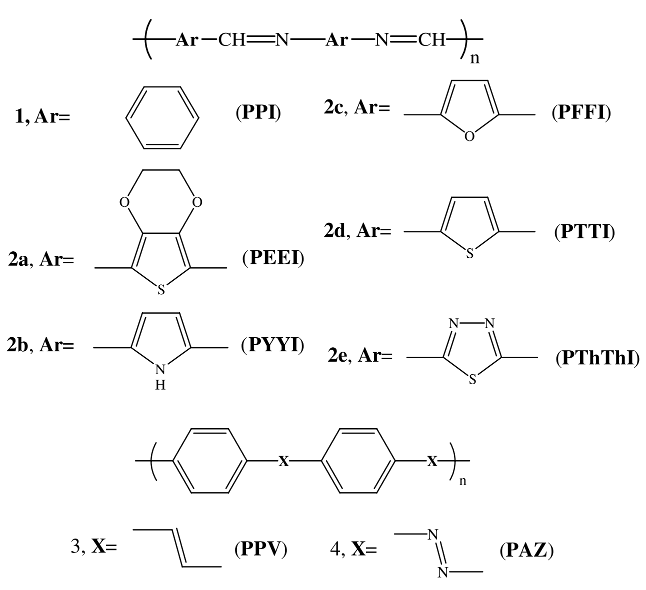

Fig. 1. Conjugated polymers for theoretical analysis.

2. Methodology

The ground-state geometry and electronic structure of the studied poly(azomethine)s are optimized by means of the hybrid density functional theory (DFT) method treated in periodic boundary conditions at the B3LYP level of theory (Becke-style 3-parameter density functional theory [27] using the Lee–Yang–Parr correlation functional [28]) with 6-31G basis set performed on Gaussian 03 program package [29]. This method B3LYP//B3LYP (started with B3LYP geometry optimization followed by B3LYP electronic structure calculation) is more reliable than other methodology when applied to the system where the equilibrium geometries deviate substantially from planar structures [19]. It has been reported in the literature [30] that the 6-31G basic set yields a similar result on the prediction of dihedral angle of conjugated materials as that of 6-31G* (6-31G basis set with added augmentation of polarization function). Since the calculation of B3LYP/6-31G* is time consuming for conjugated polymers, the 6-31G is chosen as the basis set for the present study. Besides, the theoretical electronic properties of **PPV** and **PPI** based on B3LYP/6-31G energy level are in a good agreement with those reported in the literature by other method or experimentally.

In this analysis, one full unit cell was used for the calculation of an isolated, infinite, and one-dimensional polymer in the gaseous phase, starting from the geometry of the central portion (two repeat units) of the corresponding polymer. Full geometry optimization was performed inside a given lattice length, and the lattice parameters were then varied to locate both the equilibrium lattice parameters and the lowest-energy structure in that unit cell.

3. Results and discussion

3.1. Influence of the linkage on the electronic structures: PPI, PPV, and PAZ

The optimized geometries and electronic structures of **PPI**, **PPV**, and **PAZ** are shown in Fig. 2 and Table 1. The bond length of the C=N linkage in **PPI** and that of the C=C linkage in **PPV** are 1.293 and 1.355 Å, respectively. Besides, the C–C bond length between the C=N linkage

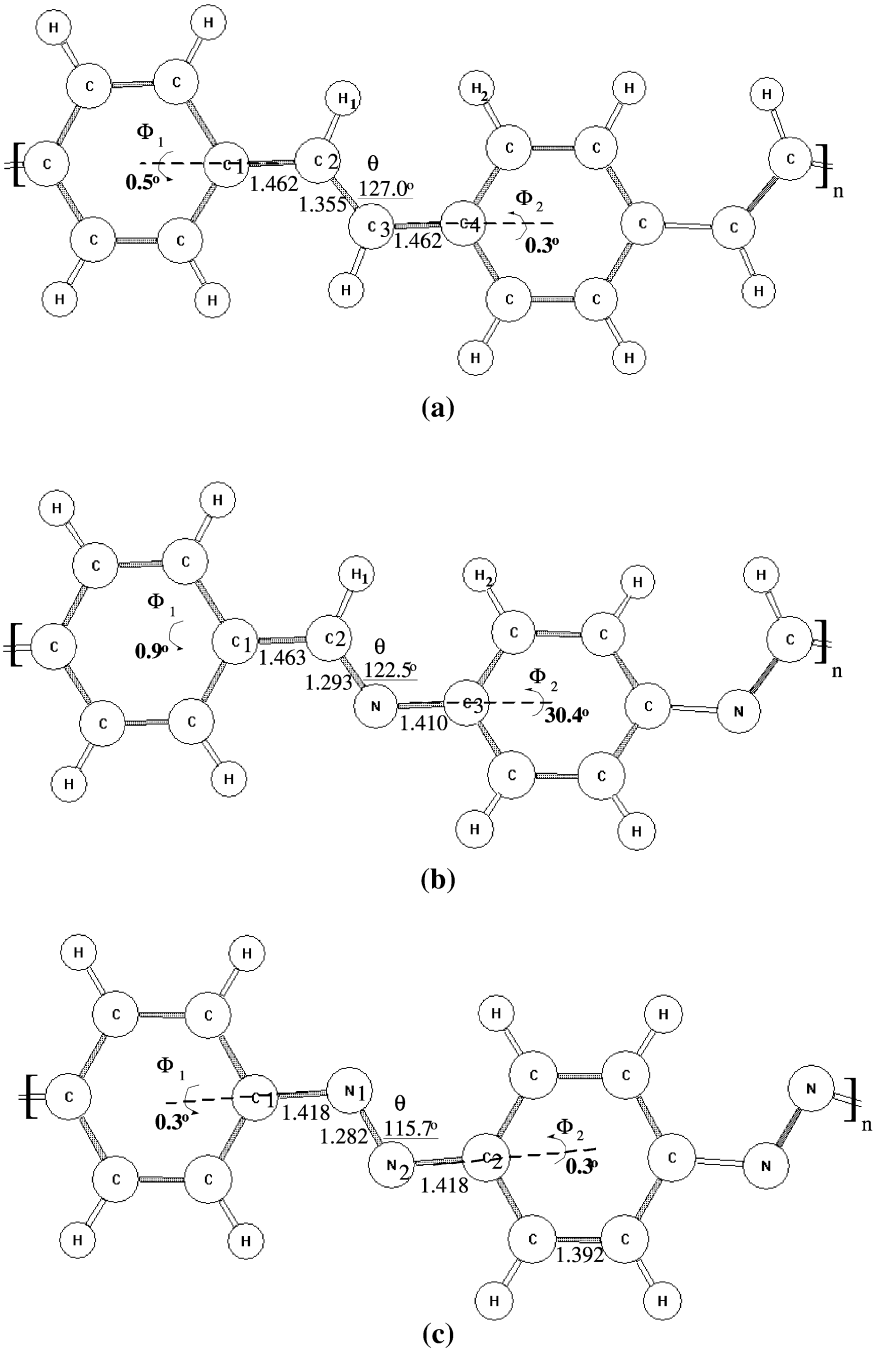

Fig. 2. Optimized geometries of (a) **PPV** (b) **PPI** (c) **PAZ**.

and the *N*-phenylene in **PPI** is 1.410 Å, while that between the C=C linkage and the phenylene in **PPV** is 1.462 Å. The shorter bond lengths of C=N and C–N than those of C=C and C–C are due to the larger electro-negativity of the nitrogen than carbon. If the bond length alternation (δ) is defined as the difference on the bond length between the double and single bond, it shows similar δ of **PPI** and **PPV**, as illustrated in Table 1. However, a significant difference is shown on the dihedral angles (Φ_1 and Φ_2) between aromatic ring and linkage. The dihedral angles (Φ_1 and Φ_2) in **PPV** are almost zero but Φ_2 of **PPI** is 30.4°, as shown in Fig. 2. The repulsion force between the adjacent hydrogen atoms on the C=N linkage and the *N*-phenylene of **PPI** results in a non-coplanar conformation. Besides, the bond angle θ shown in Fig. 2 is 122.4° for **PPI** and 127.0° for **PPV**. Both the differences of bond length and bond angle between **PPV** and **PPI** result in the distance between H_1 and H_2 much shorter in **PPI** than that in **PPV**. Consequently, it results in a much smaller (and negligible) H–H repulsion force for **PPV** than that of **PPI**. It explains why **PPV** is coplanar but **PPI** is twisted instead. The non-coplanar conformation of **PPI** was also verified from the X-ray diffraction results of small

Table 1
The optimized geometries and electronic properties of the studied conjugated polymers

	$R_{C1–C2}$ (Å)	$R_{C2=N}$ (Å)	$R_{C3–N}$ (Å)	δ^a (Å)	$\Phi_1{}^b$ (°)	$\Phi_2{}^b$ (°)	Valence bandwidth (meV) and effective mass	Conduction bandwidth (meV) and effective mass	IP (eV)	EA (eV)	E_g (eV)
1 (PPI)	1.463	1.293	1.410	0.021	0.9	30.4	247 ($0.742m_e$)	298 ($0.688m_e$)	5.47	2.64	2.83
2a (PEEI)	1.414	1.314	1.345	0.023	0.2	0.6	613 ($0.233m_e$)	644 ($0.223m_e$)	4.25	3.14	1.11
2b (PYYI)	1.427	1.309	1.371	0.006	1.8	12.1	562 ($0.406m_e$)	552 ($0.403m_e$)	4.40	2.73	1.67
2c (PFFI)	1.424	1.309	1.348	0.025	0.3	0.1	590 ($0.376m_e$)	556 ($0.343m_e$)	4.89	3.33	1.56
2d (PTTI)	1.423	1.308	1.357	0.018	0.3	0.3	572 ($0.278m_e$)	583 ($0.275m_e$)	5.03	3.61	1.42
2e (PThThI)	1.436	1.296	1.363	0.040	0.6	0.8	318 ($0.530m_e$)	287 ($0.504m_e$)	7.19	4.72	2.47
3 (PPV)	1.462^c	1.355^d	1.462^e	0.025	0.5	0.3	373 ($0.466m_e$)	392 ($0.446m_e$)	4.78	2.31	2.47
4 (PAZ)	1.418^f	1.128^g	1.418^h	0.020	0.3	0.3	347 ($0.474m_e$)	405 ($0.464m_e$)	5.92	3.61	2.31

[a] Average bond length alternation.
[b] Φ_1 and Φ_2 are defined in Figs. 1 and 2.
[c] $R_{C1–C2}$.
[d] $R_{C2=C3}$.
[e] $R_{C3–C4}$.
[f] $R_{C1–N1}$.
[g] $R_{N1=N2}$.
[h] $R_{N2–C2}$.

molecule *trans*-*N*-benzylideneaniline [31], in which the C=N plane twists 55° from the *N*-phenylene and 10° from the benzylidene ring in the opposite direction. It leads to the conjugation between the C=N nitrogen lone-pair electrons and π-electrons on the *N*-phenylene, which suggests the twisted nature of **PPI**. For the case of **PAZ**, both the dihedral angles (Φ_1 and Φ_2) are almost zero since there is no H–H repulsion force as shown in Fig. 2(c). The very small dihedral angles suggest that both **PPV** and **PAZ** exhibit the coplanar conformation.

The calculated electronic properties of **PPI**, **PPV**, and **PAZ** are shown in Table 1. The calculated (IP, EA, E_g) of **PPI**, **PPV** and **PAZ** are (5.47, 2.64, 2.83) eV, (4.78, 2.31, 2.47) eV, and (5.92, 3.61, 2.31) eV, respectively. Note that the experimental (IP, EA, E_g) of **PPI** and **PPV** are (5.12, 2.60, 2.52) eV and (5.11, 2.71, 2.40) eV, respectively [9]. It indicates that the (IP, EA) is underestimated in the coplanar **PPV**, while that is overestimated in the non-coplanar **PPI**. The deviation between the experimental and theoretical results might be due to the polymer packing in solid state or the condition of cyclic voltammetry measurements. However, the trend on the order of calculated electronic properties is in agreement with that of the experimental results.

The effect of the linkage between the phenylene rings on the electronic structures can be further illustrated by the HOMO and LUMO energy levels of Fig. 3. The (IP, EA) of **PPI** is intermediated between **PPV** and **PAZ**. It shows the asymmetric stabilization of the HOMO and LUMO levels when the C=C linkage in **PPV** is replaced by the C=N linkage. This stabilization is attributed to not only the electron-withdrawing C=N linkage but also the twisted conformation of **PPI**. It is known that the substitution of an electron-withdrawing group can lead to the stabilization of frontier orbitals [4,5]. However, the twisted conformation would result in the stabilization of the HOMO level but the

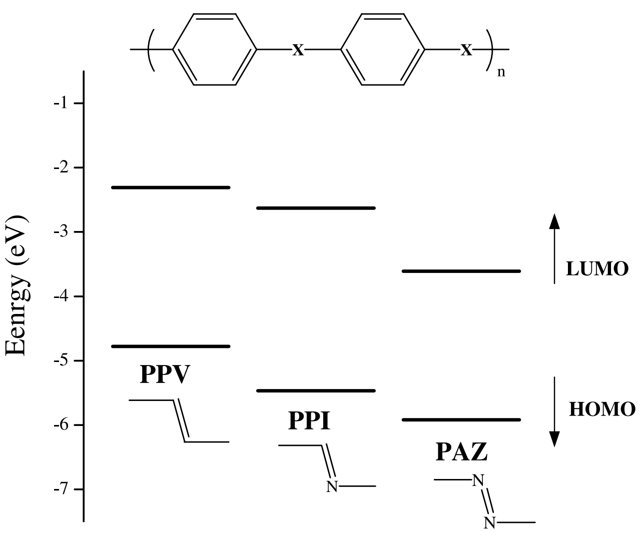

Fig. 3. Effect of linkage between the phenylene rings on the HOMO and LUMO energy levels.

destabilization of the LUMO level, and increases the E_g consequently [32]. Therefore, the degree of the stabilization of the HOMO level is more than that of the LUMO level when the C=C linkage in **PPV** is replaced by the C=N linkage, leading to the larger bandgap of **PPI**. The replacement of C=C linkage by N=N linkage leads to the asymmetric stabilization of the HOMO and LUMO levels since the N=N linkage is an electron-withdrawing segment. Therefore, the IP and EA of the **PAZ** are larger than those of **PPV**. Besides, the calculated E_g of **PPV** and **PAZ** are 2.47 and 2.31 eV, respectively. The smaller E_g of **PAZ** is probably attributed to the intrachain charge transfer from the electron-withdrawing N=N linkage and the electron-donating phenylene ring. The bond length alternation of **PPI**, **PPV**, and **PAZ** shows an insignificant variation but not in the case of electronic properties. It suggests that the dihedral angle plays a major role on the electronic properties of poly(azomethine)s.

3.2. Influences of the electron donor/acceptor five-member ring on the electronic properties of conjugated poly(azomethine)s

As mentioned previously, the six-membered ring based poly(azomethine)s, **PPI**, has a non-coplanar conformation and affects its electronic properties significantly. If the phenylene ring is replaced by the five-member heterocyclic ring in the backbone of conjugated poly(azomethine)s, the geometries and electronic structures would change dramatically. The optimized geometries and calculated electronic properties of conjugated poly(azomethine)s, **PEEI** (**2a**), **PYYI** (**2b**), **PFFI** (**2c**), **PTTI** (**2d**), and **PThThI** (**2e**) are shown in Table 1, respectively. Fig. 4 shows the calculated geometries of **PEEI** (**2a**), **PTTI** (**2d**), and **PThThI** (**2e**). The five-member ring based conjugated poly(azomethine)s show a very small dihedral angle(Φ_1 or Φ_2), which suggests a coplanar conformation. It is attributed to the absence of the repulsion force between the adjacent hydrogen atoms on the C=N linkage and the *N*-substitued phenlyene. The planar configurations are in agreement with a recent report on a model compound of thiophene-based monazomethine, as evidenced by X-ray crystal analysis [33]. The bond length alternation of the studied five member ring based conjugated poly(azomethine)s are in the range of 0.006–0.040 Å, in which **PThTh** with the largest of 0.040 Å.

The electronic properties (IP, EA, E_g) of **PPI** are also significantly modified by the five-member ring based conjugated poly(azomethine)s, as shown in Table 1. The HOMO and LUMO energy levels of the studied coplanar conjugated poly(azomethine)s are illustrated in Fig. 5. As shown in Table 1 and Fig. 5, the calculated IP increases in the following order: **PEEI** < **PYYI** < **PFFI** < **PTTI** < **PPI** < **PThThI**, while the order of calculated EA is **PPI** < **PYYI** < **PFFI** < **PEEI** < **PTTI** < **PThThI**. The smallest IP of **PEEI** is as expected since 3,4-ethylenedioxythiophene shows stronger π-donating strength than the others. Similarly, the largest EA of **PThThI** is due to the better π-accepting ability of thiadiazole, which indicates **PThThI** might be more stable in the n-doped form [25]. The relative order on IP/EA of **PYYI**, **PFFI** and **PTTI** is consistent with the electron donating ability of the heteroatom. The smallest IP and EA of **PYYI** among three above conjugated polymers indicate that pyrrole might be sensitive in the neutral form and stable in the p-doped form since nitrogen shows less electro-negativity than sulfur and oxygen [24]. Weaker donor strength of heteroatom (sulfur compared to oxygen) [34] leads to a larger IP of **PTTI** than that of **PFFI** by 0.14 eV.

The calculated E_g of the studied conjugated poly(azomethine)s increases in the following order: **PEEI** < **PTTI** < **PFFI** < **PYYI** < **PThThI** < **PPI**. The five-membered ring heterocyclic poly(azmothine)s is almost coplanar and thus the calculated E_g is much smaller (0.3–1.7 eV) than that of **PPI**. Besides, the electron-withdrawing imine group, C=N could have a significant intramolecular charge transfer with the electron-donating heterocyclic rings (3,4-ethylenedioxythiophene, pyrrole, furan and thiophene) and thus result in a very small band gap [34]. The 3,4-ethylenedioxythiophene based conjugated poly(azomethine)s, **PEEI**, has a E_g of 1.11 eV, which is among the smallest among poly(azomethine)s. The small E_g of **PEEI** is also close to other classes of small bandgap polymers reported in the literature, including poly(isothianaphthene)s [35,36], poly(thiophene methine)s. Hence, they could have the potential applications as transparent conductors [37,38]. Although the thiadiazole based conjugated poly(azomethine)s, **PThThI**, also shows a coplanar structure, the E_g is much larger (about 1 eV) than the other five-member ring based polymers. It might be due to the large bond length alternation or lack of the intrachain charge transfer as that of polymers **2a**–**2d**. The charge transfer ability could be investigated by calculating total atomic Mulliken charge [39]. As for the case of **PThThI**, the calculated net orbital atomic charge on the electron-rich thiadiazole and electron-deficient imine moiety amount 0.131 and $-0.131e$, respectively. However, the corresponding values are 0.231 and $-0.231e$ for those of **PTTI**. The smaller charge values on the alternating donor–acceptor unit indicate less intrachain charge transfer ability for **PThThI** than that for **PTTI**. **PYYI** has a larger bandgap among these four electron-donating heterocyclic ring based polymers since **PYYI** shows a small torsional angle (12.1°) between the imine linkages and pyrrole group.

Fig. 6 shows the one-dimensional band structure along the polymer chain of **PPI** and **PEEI**. The bandwidths (BWs) and electron effective mass of the studied conjugated polymers are also summarized in Table 1. The BW values (or electron effective mass) were calculated on the upper valence band and lower conduction band, which are good parameters for predicting the hole and electron transporting ability, respectively [40–42]. The effective mass of the charge carriers (m^*) at the edge of the lower conduction or

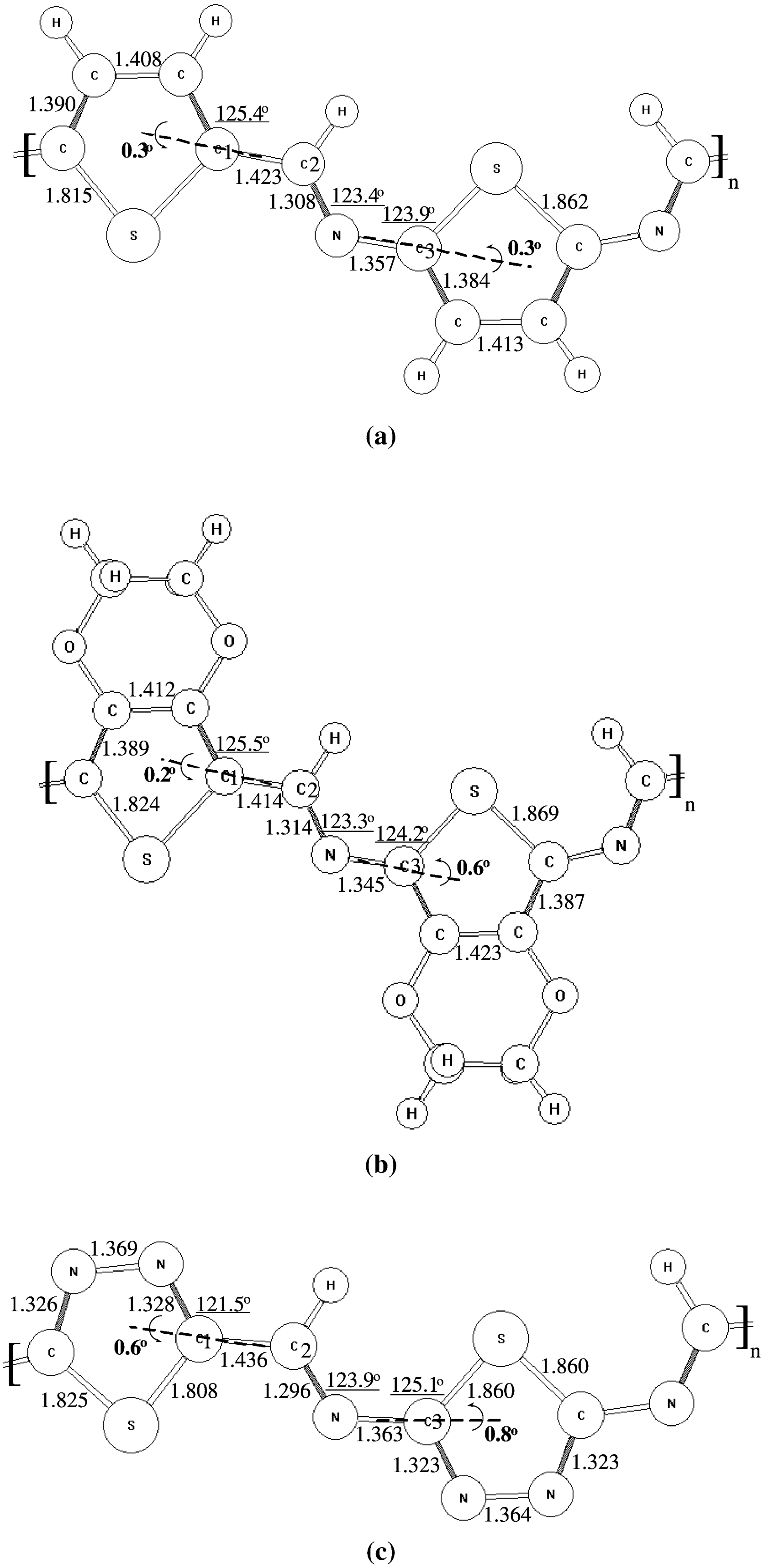

Fig. 4. Optimized geometries of (a) **PTTI** (b) **PEEI** (c) **PThThI**.

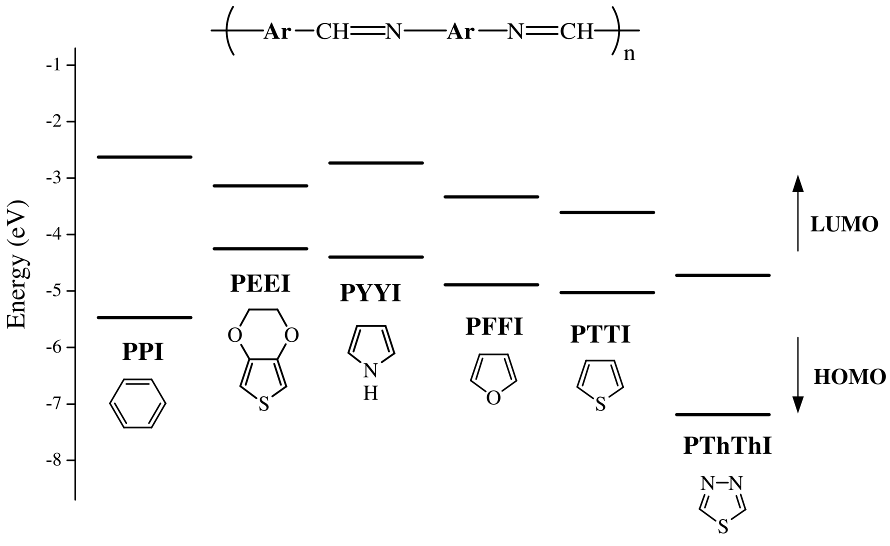

Fig. 5. Effects of the ring structure on the HOMO and LUMO energy levels of conjugated poly(azomethine)s.

upper valence band is defined as

$$\frac{1}{m^*} = \frac{1}{\eta}\left(\frac{\partial^2 E(k)}{\partial k^2}\right) \tag{1}$$

The larger curvature of the energy with the function of momentum reaches a maximum at the inflection point corresponding to diverging mass and thus decreases the effective mass. The kinetic model of mobility (μ) is given by the Drude form [40,43],

$$\mu = \frac{e\tau}{m^*} \tag{2}$$

When the BW is larger, the effective mass of hole (or electron) should be smaller leading to a higher carrier mobility. Specifically, the effective mass equals the free hole or electron mass at the broad band [44]. The calculated upper valence BW of poly(azomethine)s (**2a**–**2d**) is 562–613 meV, which is higher than that of **PPI** with 246 meV or **PPV** with 373 meV. Besides, the calculated effective mass of valence band edge of poly(azomethine)s (**2a**–**2d**) which is lower than that of **PPI** and **PPV** is consistent with the trend of the upper valence BW. Thus, the hole mobility of the coplanar p-type poly(azomethine)s (**2a**–**2d**) is expected to be higher than that of non-coplanar **PPI**. The high bandwidths (small electron effective mass) of the proposed conjugated poly(azomethine)s could have the potential applications as thin film transistors for organic electronics. The high mobility of thiophene based azomethine oligomers reported in the literature [17] also suggested the above prediction.

4. Conclusions

In this study, the theoretical geometries and electronic properties of varies aromatic ring based conjugated poly(azomethine)s are investigated. The comparison on the geometry of **PPI** with those of **PPV** and **PAZ** reveals that the non-coplanar conformation of **PPI** is resulted from the repulsion force between the adjacent hydrogen

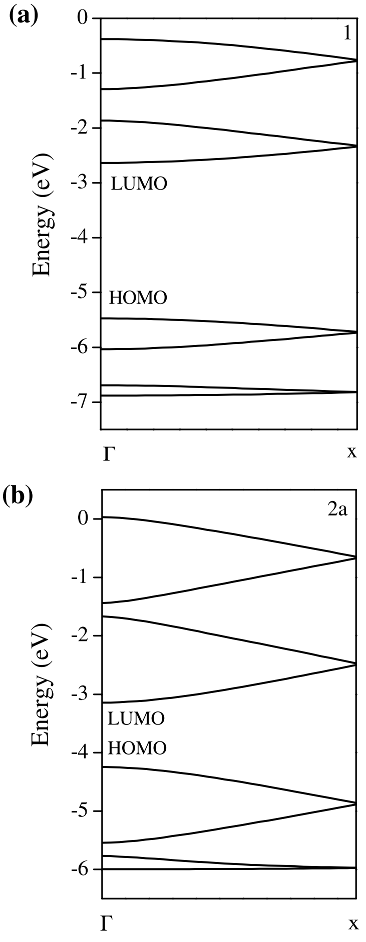

Fig. 6. Band structure of (a) **PPI** and (b) **PEEI** along the polymer axis.

atoms on the C=N linkage and N-phenylene. The electronic properties of **PPI** are in the intermediate between **PPV** and **PAZ**. The non-coplanar conformation of **PPI** could be overcome by the five member ring based conjugated poly(azomethine)s, including 3,4-ethylenedioxythiophene (**PEEI**), pyrrole (**PYYI**), or thiophene (**PTTI**), furan (**PFFI**), and thiadiazole (**PThThI**). The coplanar configuration or donor–acceptor intrachain charge transfer resulted in small E_g of **PEEI PYYI**, **PFFI**, and **PTTI**. The trend on the IP or EA of the studied conjugated poly(azomethine)s are consistent with the ring characteristic. The upper valence bandwidth of the studied five-member ring based poly(azomethine)s except **PThThI** is larger than that of **PPI**. The results suggest that the electronic properties of conjugated poly(azomethine)s could be varied through various ring structure and can be potentially used as transparent conductors or thin film transistors.

Acknowledgements

We thank the financial supports of the National Science Council, Industrial Technology Research Institute, and the Ministry of Economic Affairs of Taiwan for this work.

References

[1] Gross M, Müller DC, Nothofer HG, Scherf U, Neher D, Bräuchle C, et al. Nature 2000;405:661.
[2] Sirringhaus H, Tessler N, Friend RH. Science 1998;280:1741.
[3] Yu G, Gao J, Hummelen JC, Wudl F, Heeger AJ. Science 1995;270:1789.
[4] Roncali J. Chem Rev 1997;97:173.
[5] Lu HF, Chan HSO, Ng SC. Macromolecules 2003;36:1543.
[6] Chen SH, Su AC, Chou HL, Peng KY, Chen SA. Macromolecules 2004;37:167.
[7] Lin WJ, Chen WC, Wu WC, Niu YH, Jen AKY. Macromolecules 2004;37:2335.
[8] Yang CJ, Jenekhe SA. Chem Mater 1995;7:1276.
[9] Yang CJ, Jenekhe SA. Macromolecules 1995;28:1180.
[10] Wang C, Shieh S, Legoff E, Kanatzidis MG. Macromolecules 1996;29:3147.
[11] Thomas O, Inganas O, Andersson MR. Macromolecules 1998;31:2676.
[12] Olinga TE, Destri S, Botta C, Porzio W, Consonni R. Macromolecules 1998;31:1070.
[13] Destri S, Pasini M, Pelizzi C, Porzio W, Predieri G, Vignali C. Macromolecules 1999;32:353.
[14] Krebs FC, Jorgensen M. Synth Met 2004;142:181.
[15] Giuseppone N, Lehn JM. J Am Chem Soc 2004;126:11448.
[16] Kimoto A, Cho JS, Higuchi M, Yamamoto K. Macromolecules 2004;37:5531.
[17] Kiriy N, Bocharova V, Kiriy A, Stamm M, Kreb FC, Adlder HJ. Chem Mater 2004;16:4765.
[18] Tsai FC, Chang CC, Liu FC, Chen WC, Jenekhe SA. Macromolecules 2005;38:1958.
[19] Yang S, Olishevski P, Kertesz M. Synth Met 2004;141:171.
[20] Cornil J, dos Santos DA, Beljonne D, Brédas JL. J Phys Chem 1995;99:5604.
[21] Choi CH, Kertesz M, Karpfen A. J Chem Phys 1997;107:6712.
[22] Logdlund M, Salaneck WR, Meyers F, Brédas JL, Arbuckle GA, Friend RH, et al. Macromolecules 1993;26:3815.
[23] Cornil J, Gueli I, Dkhissi A, Sancho-Garcia JC, Hennebicq E, Calbert JP, et al. J Chem Phys 2003;118:6615.
[24] Salzner U, Lagowski LB, Pickup PG, Poirier RA. Synth Met 1998;96:177.
[25] Kwon O, McKee ML. J Phys Chem A 2000;104:7106.
[26] Hutchison GR, Ratner MA, Marks TJ. J Phys Chem A 2002;106:10596.
[27] Becke AD. J Chem Phys 1993;98:5648.
[28] Lee C, Yang W, Parr RG. Phys Rev B 1998;37:785.
[29] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Peterssonp GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA. Gaussian Inc., Pittsburgh PA; 2003.
[30] Lin BC, Cheng CP, Lao ZP. J Phys Chem A 2003;107:5241.
[31] Manecke G, Wille WE, Kossmehl G. Makromol Chem 1972;160:111.
[32] Brédas JL, Street GB. J Chem Phys 1985;83:1323.
[33] Skene WG. Polym Prepr 2004;45:253.
[34] Yamamoto T, Zhou ZH, Kanbara T, Shimura M, Kizu K, Maruyama T, et al. J Am Chem Soc 1996;118:10389–99.
[35] Wudl F, Kobayashi M, Heeger AJ. J Org Chem 1984;49:3382.
[36] Meng H, Wudl F. Macromolecules 2001;34:1810.
[37] Chen WC, Jenekhe SA. Macromolecules 1995;28:465.
[38] Chen WC, Liu CL, Yen CT, Tsai FC, Tonzola CJ, Olson N, et al. Macromolecules 2004;37:5959.
[39] Delgado MCR, Hernandez V, Navarrete JTL, Tanaka S, Yamashita Y. J Phys Chem 2004;108:2516.
[40] Haddon RC, Siegrist T, Fleming RM, Bridenbaugh PM, Laudise RA. J Mater Chem 1995;5:1719.
[41] Cornil J, Calbert JP, Brédas JL. J Am Chem Soc 2001;123:1250.
[42] Cheng YC, Sibley RJ, da Silba Filho DA, Calbert JP, Brédas JL. J Chem Phys 2003;118:3764.
[43] Beleznay FB, Bogar F, Ladik J. J Chem Phys 2003;119:5690.
[44] Karl N. Synth Met 2003;133–134:649.