

## Electronic Properties and Conformation of $\pi$ -Conjugated Molecules with Phenyl and Heterocyclic Group

Eunho Oh and Cheol-Ju Kim\*

Department of Chemistry, Chonbuk National University, Chonju 561-756, Korea

A quantum-chemical investigation on the conformations and electronic properties of *trans*(diphenyl-diheterocyclic) ethenes (*t*-PHEs) as building block for fully  $\pi$ -conjugated polymer are performed in order to display the effects of heterocyclic ring substitution. Structures for the molecules, *t*-PHEs were fully optimized by using semiempirical AM1, PM3 methods, and *ab initio* HF method with 6-31G basis set. The potential energy curves with respect to the change of single torsion angle are obtained by using *ab initio* HF/6-31G basis set. The curves are not similar shapes in the molecules with respect to heterocyclic rings. It is shown that the steric repulsion interactions between phenyl ring and heterocyclic ring are subjected to different type with the respect to each heterocyclic ring. Electronic properties of the molecules were obtained by applying the optimized structures and selected geometries to the extended Huckel method. To investigate the change of HOMO-LUMO gaps with respect to the torsion angle, we select the optimized structures. By using the results, the dependency of conjugation for the energy gaps is analyzed. For *t*-PPE the energy gap increase up to 0.52 eV compared with its planar structure. In the cases of *t*-PFE and *t*-PTE, the energy gap increase by 1.29 and 1.15 eV, respectively, compared with its planar structure.

**key words:** conformation analysis, potential energy curve, HOMO-LUMO gap, Heterocyclic, conjugation

### INTRODUCTION

It has been well-known that poly(p-phenylene vinylene) (PPV) derivatives were utilized as the materials for conductive polymers, light emitting devices (LED), and electro-optic devices [1-3]. They have a good properties of  $\pi$ -conjugated electronic structure in polymer backbone. Conformation and physical properties, such as electronic, photophysical, and photonic properties of PPV and its derivatives have been extensively studied to explain the structure-properties relationship [4-6]. Recently, the investigation of potential energy curves in methoxy-substituted PPVs were reported. It was focused that  $\pi$ -conjugation of polymer backbone are affected by steric repulsion of substituents and delocalization of  $\pi$  electrons for PPV derivatives [6, 7].

In conformational analysis, the investigations for one torsion angle change were extremely performed not only on PPV derivatives, but also on various conjugated systems, such as biphenyl, 2,2'-bithiophene, 2,2'-bifuran, and 2,2'-bipyrrole, etc. [8, 9]. For phenylene-hetero ring system, the study on the conformation of the thiophene analogs showed that the twisted isomers are more stable than the coplanar ones due to the steric repulsion of the pendant groups with the sulfur atom. In pyrrole analogs, the steric repulsion

between the methyl substituent and hydrogens in the pyrrole ring is strong enough to overcome the stabilization due to the delocalization of the  $\pi$  electrons [6, 7]. Many applications of density functional theory (DFT) in chemistry have utilized the useful tool in obtaining molecular properties, but Hartree-Fock (HF) method is useful for conformational analysis [7, 9]. The quantitative prediction of torsional potential curve in conjugated systems is difficult in experimental and theoretical point of view. In small molecules the predictions of the potential energy curves have investigated by using density functional method and HF method [7].

Recently, fully conjugated and soluble polyazomethines were synthesized by polycondensation of aromatic dialdehydes with two kind of diamines having a tetraphenylethylene structures [10]. It is expected that building block unit of polyazomethines experienced steric hinderance because of the repulsive interaction between adjacent phenylene groups. In the polymer, the degree of  $\pi$ -conjugation between vinylene and phenylene groups will only be restricted by the repulsion.

In this study, building blocks of polyazomethines with five membered heterocyclic groups, furan, pyrrole, and thiophene were chosen. The model systems are *trans*(diphenyl-diheterocyclic) ethenes (*t*-PHEs) as shown in Fig. 1 and have four torsion angle parameters. In many cases, the potential energy curves with respect to the change of single torsion angle have obtained. However, there is only a few study on the system with many torsion angle parameters. To investigate the potential energy curves with respect to the change of

\*To whom correspondence should be addressed.

E-mail : cjkim@moak.chonbuk.ac.kr

Received 15 May 2000; accepted 10 June 2000

single torsion angle, the quantum chemical calculations were employed. The potential energy curves have been obtained by using *ab initio* HF method for fully conjugated systems, *t*-PHEs. The HOMO-LUMO energy gaps with respect to conformational change were investigated by using the extended Hückel method [6, 11].

## MATERIALS AND METHODS

Fully conjugated organic molecules are designed so that two phenyl and two heterocyclic groups are substituted at trans position of ethylene, respectively. The structures for the organic molecules, *trans*-(diphenyl-,diheterocyclic)ethylenes (*t*-PHEs) are shown in Fig. 1. The model systems for fully conjugated building block of polyazomethines may not be planar structure. To obtain the optimized structures of *t*-PHEs, semiempirical AM1, PM3 methods, and *ab initio* HF (6-31G basis set) method are employed [6, 12]. Structure of each molecule has optimized by starting from three initial structures. One of the input structures were planar between phenylene units and vinylene group ( $\psi_1 = \psi_2 = 0.0^\circ$ ) and nonplanar between heterocyclic groups and vinylene group ( $\psi_3 = -\psi_4 = 90.0^\circ$ ). Another structure was the conformation which phenyl groups were almost perpendicular to vinylene group ( $\psi_1 = \psi_2 = 90^\circ$ ) and the heterocyclic groups were planar with vinylene group ( $\psi_3 = -\psi_4 = 180^\circ$ ). The other structure was the conformation which phenyl groups were almost perpendicular to vinylene group ( $\psi_1 = \psi_2 = 90^\circ$ ) as well as the heterocyclic groups were planar with vinylene group ( $\psi_3 = -\psi_4 = 90^\circ$ ). The parameters of the optimized structures were summarized in Table 1.

To investigate the stable conformational structures for the polymers, *ab initio* HF calculations were carried out with the 6-31G basis set in the Gaussian 98 package [12]. To display the potential energy curves for a variety of *t*-PHEs, the torsional angles ( $\psi_1$  and  $\psi_2$ ) between the phenyl groups and the vinyl unit were fixed at optimized torsion angles. The torsion angles ( $\psi_3$  and  $\psi_4$ ) between the heterocyclic groups and the vinyl unit varies by 10 degree as shown in Fig. 1 and at each torsional angle the

geometrical parameters were fully optimized. During the geometrical optimizations, the heterocyclic units were restricted to the trans conformation with parallel geometry with respect to vinylene group.

Electronic properties of the molecules are obtained by applying the optimized structures and the selected geometries (maxima or minima) of potential curves to the extended Huckel (EH) method [11]. To investigate the change of HOMO-LUMO gaps with respect to the torsion angle, the optimized structures were selected. By using the results, the dependency of conjugation for the energy gaps is analyzed. The EH method has been shown to yield reliable electronic structures for a wide variety of conjugated polymers, including those with heterocyclic rings [4, 7, 8].

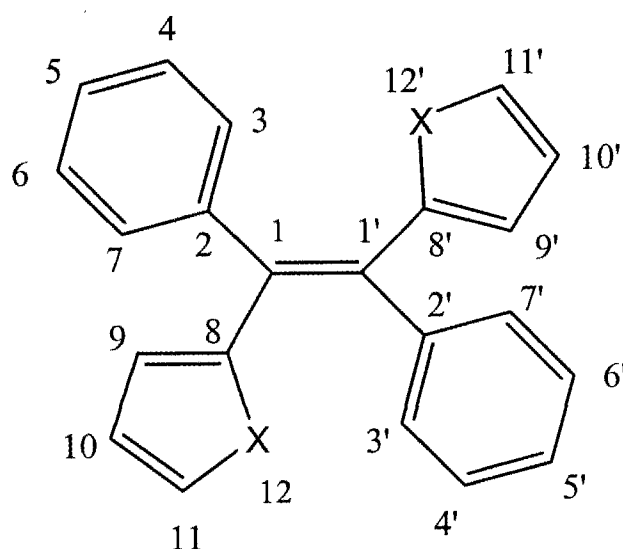


Figure 1. Structures of *t*-PHE, torsion angles ( $\psi_1$  and  $\psi_2$ ) of phenyl group with respect to vinylene group ( $\psi_1$ : C1'-C1-C2-C3,  $\psi_2$ : C1-C1'-C2'-C3') and torsion angles ( $\psi_3$  and  $\psi_4$ ) of heterocyclic group with respect to vinylene group ( $\psi_3$ : C1-C1'-C8'-C9',  $\psi_4$ : C1'-C1-C8-C9).  
*t*-PPE= *trans*-(1,2-diphenyl)-1,2-di(2-pyrrolyl) ethene(X=NH),  
*t*-PFE= *trans*-(1,2-diphenyl)-1,2-di(2-furanyl) ethene(X=O),  
*t*-PTE= *trans*-(1,2-diphenyl)-1,2-di(2-thiophenyl) ethene(X=S).

Table 1. Optimized geometric parameters. Bond lengths(Angstrom) and torsion angles(degree).

Molecules	Methods	C1-C1'	C1-C2	C1-C8	$\psi_1$	$\psi_2$	$\psi_3$	$\psi_4$
<i>t</i> -PPE	HF/6-31G	1.349	1.468	1.476	58.4	-121.7	42.0	-149.6
	AM1	1.355	1.468	1.463	50.3	-50.3	103.0	-102.1
	PM3	1.349	1.476	1.463	77.3	-77.3	87.2	-87.2
<i>t</i> -PFE	HF/6-31G	1.345	1.502	1.469	80.1	-79.1	27.2	-27.7
	AM1	1.354	1.468	1.456	51.3	-51.2	86.7	-83.6
	PM3	1.346	1.476	1.464	77.3	-77.3	106.7	-107.2
<i>t</i> -PTE	HF/6-31G	1.346	1.497	1.478	57.8	-131.8	55.2	-131.8
	AM1	1.355	1.471	1.454	59.2	-59.1	93.7	-93.7
	PM3	1.349	1.475	1.463	75.2	-75.1	87.3	-87.3

## RESULTS AND DISCUSSION

### Conformational Analysis of *t*-PHEs.

In optimized structures, the torsion angles between phenylene and vinylene group as well as between heterocyclic group and vinylene group are displayed various values, but not planar. The *p*-orbitals of phenylene carbons are perpendicular to the *p*-orbitals of vinylene carbons, so that the resonance structure between phenylene and vinylene carbons may not be expected. In the case of unsubstituted stilbene, Lohst *et al.* reported that the potential energy curve is flat up to the torsion angle of  $30^\circ$  by using 3-21G basis set [13]. For dimethoxy PPVs, it was reported that the optimal torsion angles are in the range 20-30 and the energy difference between the planar and the twisted conformations varies from 0.2 to 1.0 kcal/mol by using 6-31G(D) basis set [6]. In our model, the pyrrole group substituted to vinylene increases torsion angle between phenylene and vinylene group because of the steric repulsion [7, 9].

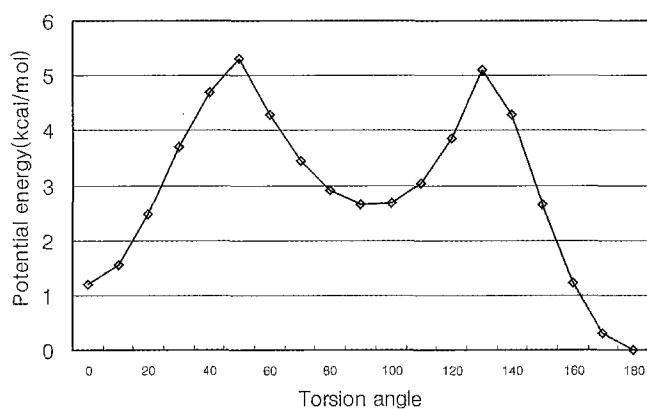


Figure 2. *Ab initio* 6-31G potential energy curve for *t*-PPE. Torsion angles of phenyl group with respect to vinylene group are fixed ( $\psi_1=58.4^\circ$ ,  $\psi_2=-121.7^\circ$ ) and torsion angles of pyrrole ring with respect to vinylene group are varied with  $\psi_3=-\psi_4$ .

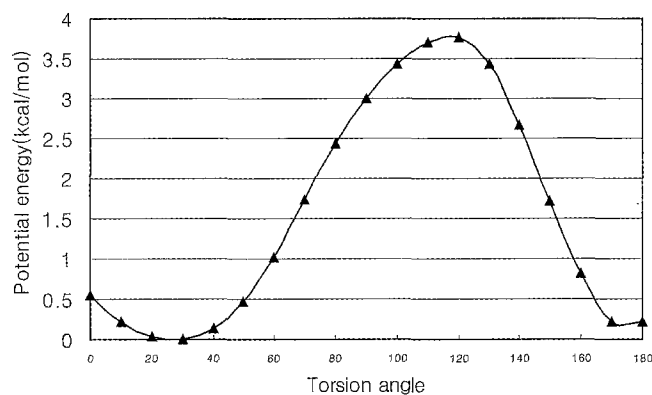


Figure 3. *Ab initio* 6-31G potential energy curve for *t*-PFE. Torsion angles are fixed ( $\psi_1=80.1^\circ$ ,  $\psi_2=-79.1^\circ$ ) and torsion angles of furan ring with respect to vinylene group are varied with  $\psi_3=-\psi_4$ .

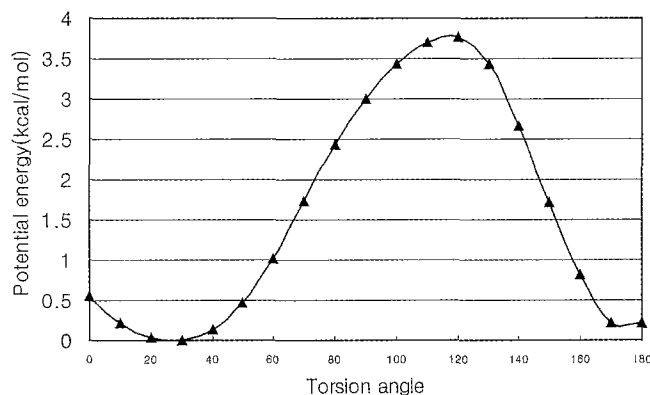


Figure 4. *Ab initio* 6-31G potential energy curve for *t*-PTE. Torsion angles are fixed ( $\psi_1=57.8^\circ$ ,  $\psi_2=-131.8^\circ$ ) and torsion angles of thiophene ring with respect to vinylene group are varied with  $\psi_3=-\psi_4$ .

According to the conformation analysis of *t*-PHEs, the twisted conformers are more stable than the coplanar ones because of the steric repulsion of the adjacent phenyl groups. The optimized conformations of *t*-PHEs are displayed in Table 1. In the case of semiempirical AM1 and PM3 methods, the optimized structures are exactly parallel (eclipse form) between two phenyl groups as well as two hetero cyclic groups. For the molecules (*t*-PHE) the torsion angles between phenylene and vinylene group are near  $50^\circ \sim 60^\circ$  and the torsion angles between phenylene and vinylene group are near  $86^\circ \sim 106^\circ$ . Phenyl groups are more flat than hetero cyclic groups with respect to vinylene unit. However, by using *ab initio* HF/6-31G basis, the structures are not symmetric torsion angles. Two phenyl groups as well as two hetero cyclic groups are similar to staggered form. There are many torsion angle parameters in the molecules. In the fully conjugated polyazomethene, PPV units are backbone of the polymer [10]. To obtain the potential energy curves for the polymer we fixed the two torsion angles  $\psi_1$  and  $\psi_2$  at optimized angles and adjusted the rest two angles so that hetero cyclic rings have parallel geometry, that is,  $\psi_3=-\psi_4$ . The torsion angles between the hetero cyclic groups and the vinyl unit varies by 10 degree. The potential energy curves for *t*-PHEs are shown in Figs. 2~4. The potential energy curves are not similar shapes each other. It is shown that the repulsion interactions between phenyl ring and heterocyclic ring are subjected to different type with the respect to each heterocyclic ring (pyrrole, furan, and thiophene).

In conformational analysis of *t*-PPE, the torsion angles between vinylene and phenyl groups are fixed at  $\psi_1=58.4^\circ$  and  $\psi_2=60.3^\circ$ . According to the rotation of the pyrrole ring units, the minimum position in the potential curve is planar structure ( $\psi_3=-\psi_4=180^\circ$ ) and the other minimum is near  $\psi_3=-\psi_4=90^\circ$ . The planar structure is more stable than perpendicular structure and the rotational barrier is calculated to be 5.10 kcal/mol. The maxima of potential curve are at  $\psi_3=-\psi_4=50^\circ$  and  $\psi_3=-\psi_4=130^\circ$ . At these torsion angles, the closest distances between

phenyl hydrogen and the hydrogen attached to the pyrrole nitrogen are 2.02 and 2.09 Å. These distances are shorter than the sum of the van der Waals radii (2.40 Å) [14]. Therefore, the maxima of potential energy curve arises from the consequences of steric repulsion between the hydrogens. However, at the torsion angle 90°, the distance between the hydrogens is 2.5 Å, which is larger than the sum of the van der Waals radii. At the planar geometry these distances between the hydrogens are 2.50 and 2.45 Å, respectively. Therefore, the steric repulsion between the hydrogens does not dominant and the planar structures are stable. The corresponding furan and thiophene systems do not have such repulsions because of the absence of a hydrogen on the oxygen and sulfur [7]. The systems behave in a remarkably different fashion.

For conformational analysis of *t*-PFE, the torsion angles between vinylene and phenyl groups are fixed at  $\psi_1=80.1^\circ$  and  $\psi_2=101.0^\circ$ . The phenyl groups are almost perpendicular to vinylene unit. For the rotation of the furan rings, the minimum energy structure is obtained at  $\psi_3=-\psi_4=30^\circ$  and the maximum potential energy is in  $\psi_3=-\psi_4=120^\circ$  conformation. The rotational barrier is calculated to be 3.77 kcal/mol. The rotational barrier is considerably smaller than pyrrole and thiophene systems. The small rotational barrier results from the absence of considerable steric repulsion because of phenyl group geometries, which are almost perpendicular to vinylene unit. However, at torsion angle 120°, the distance between oxygen in furan ring and the hydrogen attached to phenyl group is about 2.79 Å, which is close to the sum of van der Waals radii (2.70 Å) [14]. This implies that the destabilization due to conjugation is dominant rather than the steric repulsion.

From the optimized structure of *t*-PTE, the torsion angles between vinylene and phenyl groups are at  $\psi_1=57.8^\circ$  and  $\psi_2=55.6^\circ$ . To investigate the potential energy curve with respect to the rotation of thiophene ring, these torsion angles are fixed. With respect to rotation of thiophene rings, the minimum energy structure is obtained at  $\psi_3=-\psi_4=90^\circ$  and thiophene units are perpendicular to the vinylene. The maxima of potential energy are near  $\psi_3=-\psi_4=20^\circ$  and  $\psi_3=-\psi_4=140^\circ$ . The rotational barrier is calculated to be about 7.00 kcal/mol. Actually, it seems that the rotational barrier is too high to change conformation. In conformational analysis *t*-PTE, the potential energy curve is mainly affected by steric repulsion between sulfur in thiophene and carbon in phenyl ring due to large sulfur atom [7]. The sum of van der Waals radii is 3.25 Å. At the torsion angles 20° and 140°, the closest distances between two atoms are 3.04 and 3.05 Å, respectively. On the other hand, at the torsion angles 90°, the distance has the value of 3.66 Å. It is the reason why the potential energy curve is minimum at the torsion angle.

### Electronic Properties of *t*-PHEs.

Table 2. EH results for electronic properties of *t*-PHEs for structures by using *ab initio* HF/6-31G.

Molecules	torsion angle (degree)	E (HOMO) (eV)	E(LUMO) (eV)	energy gap (eV)
<i>t</i> -PPE	opt.	-11.36	-8.91	2.45
	50	-11.54	-8.75	2.79
	90	-11.69	-8.61	3.08
	140	-11.42	-8.85	2.57
	180	-11.30	-9.04	2.56
<i>t</i> -PFE	opt.	-11.45	-9.12	2.33
	30	-11.46	-9.09	2.35
	90	-11.78	-8.33	3.45
	120	-11.72	-8.50	3.22
	180	-11.40	-9.24	2.16
<i>t</i> -PTE	opt.	-11.58	-8.89	2.69
	20	-11.38	-9.32	2.06
	90	-11.86	-8.68	3.18
	150	-11.45	-9.20	2.25
	180	-11.38	-9.35	2.03

The calculated electronic properties of *t*-PHEs are given in Table 2. The planarity between vinylene and heterocyclic rings is affected to produce changes in electronic properties [4, 6, 7]. HOMO-LUMO gaps are small by increasing the planar structures of heterocyclic rings. At a torsion angle of 90°, the energy gaps of the *t*-PHEs increase to maximum due to the reduced  $\pi$  overlap between the heterocyclic rings and the vinylene unit. Since the interaction between the heterocyclic rings and the vinylene unit is antibonding in HOMO and bonding in the LUMO, the reduction of  $\pi$  overlap stabilizes the HOMO level, but destabilizes the LUMO level. The degree of the stabilization of the HOMO energy level is smaller in energy than the destabilization of the HOMO energy level [6, 7]. The EHT  $\lambda_{\max}$  values according to change of conformations are predicted as shown in Table 2. For optimized structures of *t*-PPE, *t*-PFE, and *t*-PTE, the predicted HOMO-LUMO energy gaps are obtained as 2.46, 2.33, and 2.69 eV, respectively. The energy gaps are absolutely depend on the torsion angle between vinylene and heterocyclic rings. In the optimized structures for *t*-PPE, *t*-PFE, and *t*-PTE as shown in Table 1, the torsion angles,  $\psi_3$  (and  $\psi_4$ ) are 42.0° (-149.6°), 27.2° (-27.7°), and 55.2° (-131.8°), respectively. It is shown that electronic properties of *t*-PHE strongly depend on the planarity of heterocyclic groups and vinylene group. For *t*-PPE structure with  $\psi_3=90^\circ$ , the energy gap increase by 0.52 eV compared with its planar structure. In the cases of *t*-PFE and *t*-PTE with  $\psi_3=90^\circ$ , the energy gap increase by 1.29 and 1.15 eV, respectively, compared with its planar structure.

In summary, the potential energy curves are not similar shapes in fully conjugated polymers, including the heterocyclic rings and phenyl groups. It is shown that the steric

repulsion interactions between phenyl ring and heterocyclic ring are subjected to different type with respect to each heterocyclic ring (pyrrole, furan, and thiophene). Although we can synthesize the fully conjugate molecules,  $\lambda_{\max}$  values according to change of conformations will variously changed because of the steric repulsion interaction and the difference of  $\pi$ -conjugation.

*Acknowledgement* – This paper was supported by research funds of Chonbuk National University.

## REFERENCES

1. Bradley, D. D. D (1993) Conjugated Polymer Electroluminescence. *Synth. Metals* **54**, 401-415.
2. Kraft, A., A. C. Grimsdale, and A. B. Holmes (1998) Electroluminescent Conjugated Polymers. *Angew. Chem. Int. Ed.* **37**, 402-428.
3. Song, S. Y. and H. K. Shim (2000) Synthesis of poly(phenylene-alt-thiophene) polymer and characterization of its light emitting properties. *Synth. Metals* **111-112**, 437-439.
4. Meyers, F., A. J. Heeger and J. L. Bredas (1992) Fine tuning of the band gap in conjugated polymers via control of block copolymer sequences. *J. Chem. Phys.* **97**, 2750-2778.
5. Belletete, M., L. Mazerolle, N. Desrosiers, M. Leclere and G. Durocher (1995) Spectroscopy and Photophysics of some Oligomers and Polymers Derived from Thiophenes. *Macromolecules* **28**, 8587-8597.
6. Hong, Sung Y. (1999) Quantum-chemical Study of Effects of Alkoxy Substitution on the Conformations and Electronic Properties of Poly(p-phenylenevinylene). *Bull. Korean Chem. Soc.* **20**, 42-48.
7. Hong, Sung Y. and D. S. Marynick (1992) Theoretical Study of the Conformations and Electronic Structures of Phenylene-Pyrrole and Phenylene-Furan Copolymers. *Macromolecules* **25**, 3591-3595.
8. Peri, J., W. L. Yu, W. Hwang and A. J. Heeger (2000) A novel series of efficient thiophene-based light emitting conjugated polymers and application in polymer light-emitting diodes. *Macromolecules* **33**, 2462-2471.
9. Karpfen, A., C. H. Choi and M. Kertesz (1997) Single-Bond Torsional Potentials in Conjugated Systems: A Comparison of ab initio and Density Functional Results. *J. Phys. Chem. A* **101**, 7426-7433.
10. Matsumoto, T., F. Yomada and T. Kurosaki (1997) Fully Conjugated and Soluble Polyazomethines, *Macromolecules* **30**, 3547-3552.
11. Ren, J., W. Liang and M.-W. Whangbo (1998) *Crystal and Electronic Structure Analysis Using Caesar*, Prime-Color Software, Inc.
12. Foresman, J. B. and A. Frisch (1996) Geometry Optimization, In *Exploring Chemistry with Electronic Structure Methods*. Gaussian Inc. p.p.39-59.
13. Lhost, O. and J. L. Bredas (1992) Conformational analysis of Stilbene Derivatives. *J. Chem. Phys.* **96**, 5279-5286.
14. Weast, R. E. (1990) *Handbook of Chemistry and Physics*; 70th Ed. CRC Press Inc.: Boca Raton, Florida, U.S.A., D-190.
15. Han J. H., Y. S. Lee, K. S. Nahm, E. H. Cho, S. B. Ko, C. J. Kim, I. C. Jeon, W. H. Lee, E. K. Suh and Y. H. Lee (1999) Correlation between Energy Transfer and Phase Separation in Emissive Polymer Blends. *Bull. Korean Chem. Soc.* **20**, 1093-1096.