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Theoretical study on the structural and electronic properties of new materials based on benzothiodiazole and pyrrole derivative

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ABSTRACT

The theoretical study on the ground state geometries and electronic properties of new conjugated compounds using benzothiadiazole and pyrole as substrates was carried out using density functional theory (DFT) method at B3LYP level with 6-31G basis set. The dihedral angle, bond length, electronic and UV-Visible absorption properties were determined. The coupling (of the donor and acceptor) and substituent effects on the geometry and electronic properties of these substrates were discussed.The results show that the geometries of the materials were significantly affected by the substituents. The substitution of the pyrrole ring with pyrrolium oxide destabilizes the HOMO, LUMO levels with a decrease in a band gap and results in a red shifting in the absorption spectrum. The theoretical results suggest that both the donor strength and the stable geometry contribute significantly to the electronic properties of alternating donor–acceptor conjugated copolymers. These electronic properties compared favourably with conjugated copolymers that had been used in optoelectroniv devices. Hence, these copolymers could have potential applications in transparent conductors, or photovoltaic devices.*

Key words: conjugated polymers; benzothiazole-pyrrole; electronic property; DFT

INTODUCTION

Conjugated polymers, a class of organic or novel molecular based conductors not only possess the optoelectronic properties of Si, Ge, group iii-iv and group ii-vi inorganic semi-conductors but also possess the processing advantages and mechanical properties of polymers (1), have attracted great interest for their use in transparent conductors, photovoltaic cells, light emitting diodes, and semi-conductor layers in field effect transistors (FET) [2]. A key feature of these novel semiconductors materials is that manipulation of the chemical structures allows control of the optical band gap [3]. Low band gap which is the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of conjugated polymers can afford intrinsic conductivity with enhanced nonlinear optical properties,and harvest more photon with long wavelength [4].

Many ways to design low band gap energy polymers have been reported in the literatures but this work will concentrate on donor–acceptor type of polymer, based on benzothiadiazole and pyrrole. 2,1,3-benzothiadiazole and its derivatives have been widely studied and has been incorporated in a growing number of low- band-gap materials in large part, due to the ease of preparation of 4,6-dibromo-2,1,3-benzothiadiazole(5). It is a wellknown electron-deficient molecule [6, 7] that can be conjugated with an electron-rich molecule to form oligomers or polymers with small energy band gaps. Several different polymers of this type have been synthesized for applications in light emitting diodes, solar cells [8] light-harvesting, and other optical or electronic functional devices.

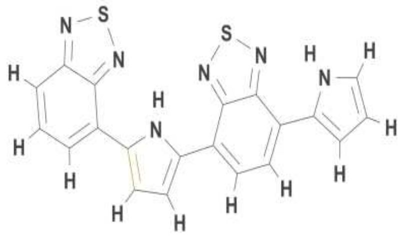
We are particularly interested in the alternating 2,1,3 benzothiadiazole donor–acceptor based copolymers since their electronic structure can be tuned efficiently by intramolecular charge transfer (CT) and due to their judicious structural modification and flexibility on the electrical properties for application devices.(9) However since the electronic properties of these donor–acceptor copolymers varied significantly with the arrangement and substitutent attachment, the knowledge of conformations and electronic structures will give a better understanding of the electronic and optical properties of these materials. Thus theoretical calculation will provide a lot of useful information that will help in building up a good relationship between stuctures and properties of these materials and a comprehensive understanding of the elctronic structure/properties of these benzothiadiazole based copolymers would help to futher develop this, and other classes of donor–acceptor copolymers for electronic applications.

In this article, the theoretical analysis on the geometries and electronic properties of conjugated copolymers based on benzothiadiazole, pyrrole and its derivative are reported (as shown in fig.1) using DFT method. The DFT (density functional theory) gives satisfactory results with experiment by costing low computational demands compared to the computational methods developed for the calculation of the electronic structure and excitation energies of molecular systems [10]

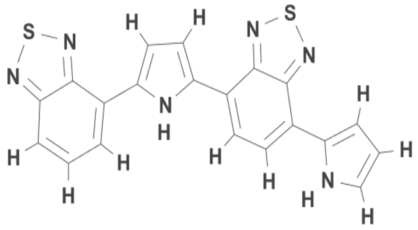
THEORETICAL METHODOLOGY

The computational method used to study the electronic properties of the polymers is the density functional theory (DFT) for which the energy of a system is described as a function of the electronic density. The density that uniquely minimizes that functional determines the system ground state. We use the Spartan 08 program package to run our calculations with the Becke, three parameter, Lee-Yang- Parr (B3LYP) exchange- correlation method. It has been shown that this method gives an accurate description of carbon-based materials.[11, 14] The Spartan 08 program package uses molecular orbitals as basis set to construct the wave function of the system. In order to obtain an accurate description of the physical system, we used the large 6-31G* basis set for the electronic properties of the model compounds. It has been shown that B3LYP/6-31G* gives decent ground state structures of conjugated polymers[12]. In the case of the model compounds, (DFT/ B3LYP/6-31G*) were used in the analysis. The molecules are built from the scratch as show in figure 1 below.

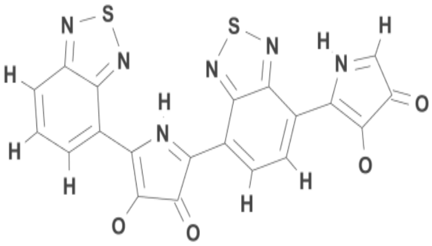
CIS BT-PY OLIGOMER



TRAN BT-PY OLIGOMER



BT-PYO OLIGOMER



BT-TH OLIGOMER

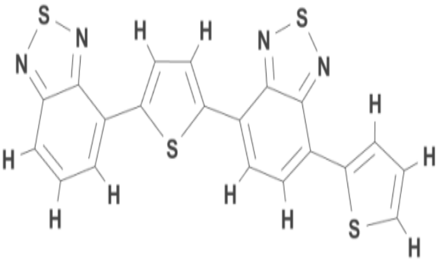
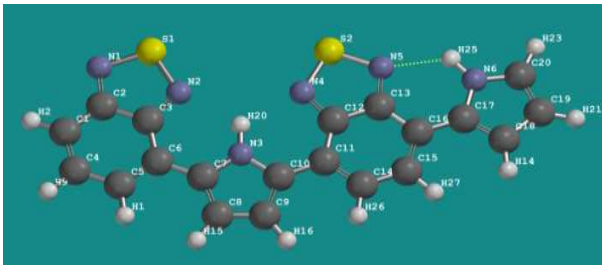
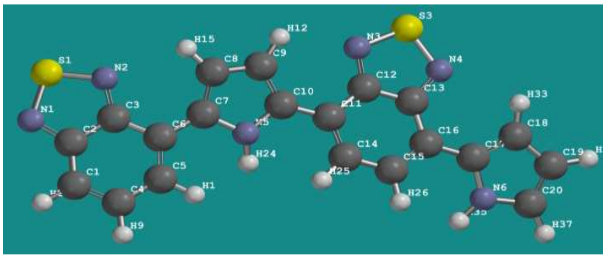
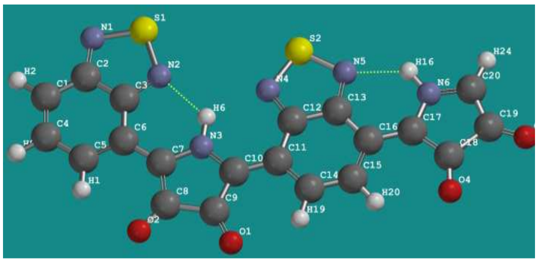


Fig.l. Structure of the studied compound







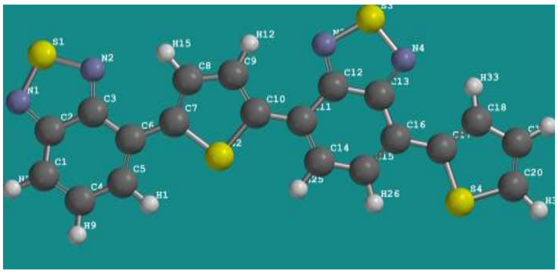
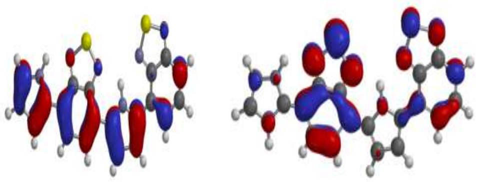


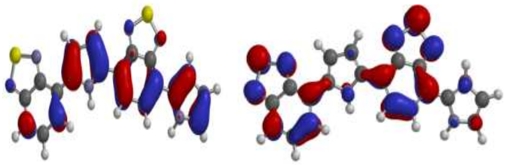
Fig.II. optimized structures of the studied oligomers

HOMO **LUMO**

Cis BT-PY

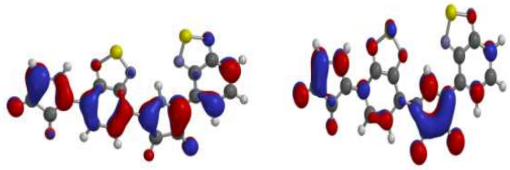


Trans BT-PY



HOMO **LUMO**

BT-PYO



BT-TH

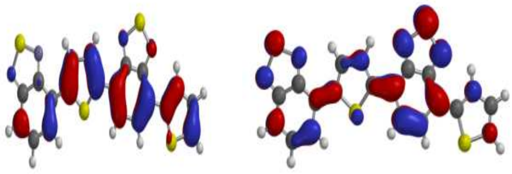


Fig.iii Electron distribution in HOMO(left figure) and LUMO(right figure) orbital

RESULTS AND DISCUSSION

3.1 Geometric properties

For all molecules, geometrical parameter were obtained after total optimization by B3LYP/6-31G*.These parameters were justified by comparing with the experimental results reported in the literature. In investigating the effect of substituent, the optimized structure and electronic properities of zwitterionic copolymer of benzothiadiazole- pyrrole were compared with those of trans BT-TH and ladder type BT-PY. On the other hand, investigation of the effect of change in the arrangnment(conformation and ring structure) of the back bone on the geometries and electronic properties, the optimized structures of coplymer pyrrole and benzothiadiazole were compared with the the modeled trans benzothiadiazole- pyrrole copolymer. For each model, three dihedral angles ɵi (with i=1, 2, or 3) , which greatly contribute to the internal energy were compared in table I. The bond length and dihedral angle of the experimental electron diffraction data for the BT-PY copolymer were compared with the theoretical result. The oligomer structures are shown in fig.II

The almost zero dihedral angle of copolymer BT-PY and BT-PYO suggest nearly a coplanar conformation which could enhance the delocalization of π-electrons from the pyrrole and pyrrolium oxide to benzothiadiazole. For the BT-PY the B3LYP/6-31G* calculation predict that the dihedral angle are θ_1= 0.14, θ_2=0.40, θ_3=0.29 . The effect of the recoupling (from cis to trans) which induced an additional hydrogen bonding in the arrangment of the molecule is clearly seen. A large reduction of dihedral angle θ_i is noticed. The effect is more marked in the case of BT-PYO (θ_1= 0.08, θ_2 =0.28, θ_3=0.34). These modifications may explain the gap variation i.e the change in band gap of the polymers found in table 3. It can also be explained that the conjugation across benzothiadiazole and pyrrole ring is increased due to hydrogen bonding formation in cis- BT-PY and BT-PYO when compared with tran-BT-PY. On the other hand , the replacement of the pyrrole ring in trans-BT-PY by the thiophene ring unit (BT-TH) leads to a smaller dihedral angle θ_i . The $\theta_1, \theta_2, \theta_3$ of BT-TH are 7.79, 0.42, 4.58 respectively, which are also larger than those of BT-PY and BT-PYO. This indicates that the thiophene ring substitution significantly enhances the planarity of the trans-oligomeric structure. The bridged bond length (L_B) between BT and PY in a (BT-PYO copolymers is reduced when compare with corresponding trans/cis BT-PY and BT-TH copolymers. This indicates an enhancement of double-bond character due to their increasing π-electron delocalization[2]. However, the bond length value obtained for pyrrole substitution with with thiophene in back bone does not change these parameters significantly as seen in Table 1

TABLE I: Geometric parameters (bond length in Å) of studied oligomers as obtained B3LYP/6-31G*

METHOD	*DFT/B3LYP/631G**				*EXP*
Bond length	L(BT-PY)	BT-PY	BT-PYO	BT-TH	BT-PY
C15-C16	1.39	1.388	1.404	1.387	1.390
C16-C13	1.44	1.442	1.442	1.443	1.440
C13-N5	1.339	1.336	1.337		1.339
C13-C12	1.457	1.458	1.451	1.461	1.457
C17-C18	1.397	1.394	1.475	1.381	1.397
C18-C19	1.412	1.415	1.588	1.422	1.412
C19-C20	1.386	1.382	1.439	1.368	1.386
C20-N6	1.364	1.369	1.353		1.364
N10-C11	1.382	1.388	1.362		1.382
C16-C17	1.449	1.451	1.442	1.457	1.447
C12-C11	1.438	1.442	1.423	1.444	1.447
C11-C10	1.449	1.45	1.423	1.455	
C10-C9	1.404	1.397	1.474	1.383	
C9-C8	1.399	1.407	1.575	1.414	
C8-C7	1.403	1.396	1.456	1.382	
C10-N3	1.373	1.383	1.362		
C7-N3	1.375	1.384	1.371		
C7-C6	1.45	1.45	1.443	1.458	

[a]L(BT-PY) = ladder benzothiadiazole- pyrrole, [b]BT-PYO= benzothiadiazole- pyrrolium oxide, [c]BT-TH= benzothiadiazole- thiophene, [d]BT-PY benzothiadiazole- pyrrole respectively; Exp = Experimental value.

TABLE II Geometric parameters (dihedral angles (Θ) in degrees) of studied oligomers as obtained B3LYP/6-31G

ANGLES	*L(BT-PY)*	*BT-PY*	*BT-PYO*	*BT-TH*
$\Theta_1(C_3-C_6-C_7-C_8)$	0.14	17.42	0.08	7.79
$\Theta_2(C_9-C_{10}-C_{11}-C_{14})$	0.40	13.28	0.28	0.42
$\Theta_3(C_{15}-C_{16}-C_{17}-C_{18})$	0.29	16.50	0.34	4.58

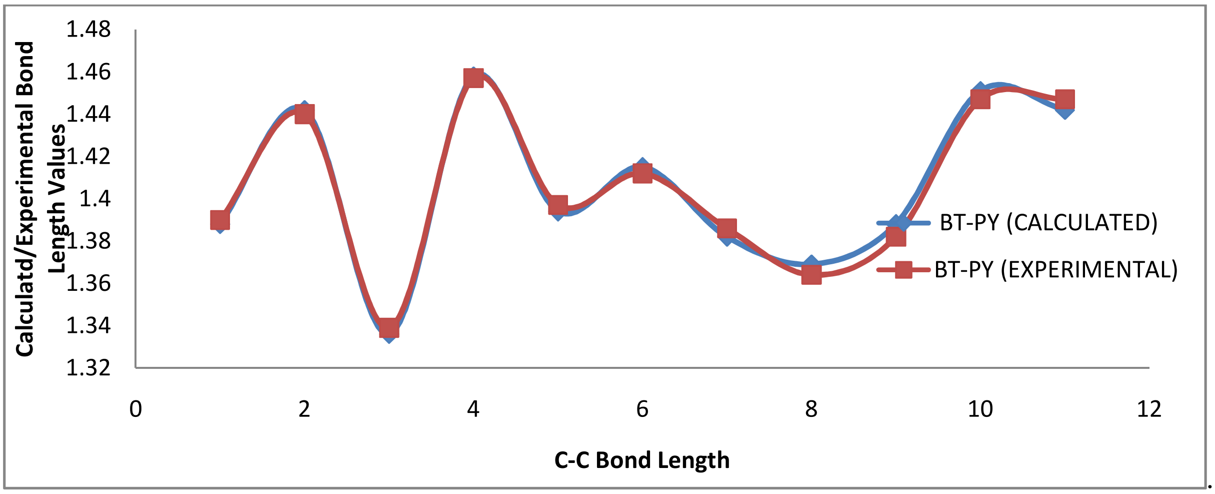


Figure IV. Graphical presentation showing both the theoretical calculated bond length and experimental bond bond for BT-PY where 1= C15-C16, 2= C16-C13, 3= C13-N5, 4= C13-C12, 5= C17-C18, 6= C18-C19, 7= C19-C20, 8= C20-N6, 9= N10-C11, 10= C16-C17,11= C12-C11 on bond length axis

2.2 Opto-electronic properties

The results obtained from our calculation certainly confirms that the band gap in conjugated oligomers is governed by their chemical structures. The theoretical calculations of the oligomers were measured in the gas phase, while experiments were performed in dilute solutions. The first factor responsible for the deviations is the fact that the predicted band gaps were measured from an isolated condensed phase chain while the experimental band gaps are measured in liquid phase, where environmental influence may be involved. The good agreement between our calculation and experiment could be an indication that the solvent has little impact on the electronic properties of the systems studied.

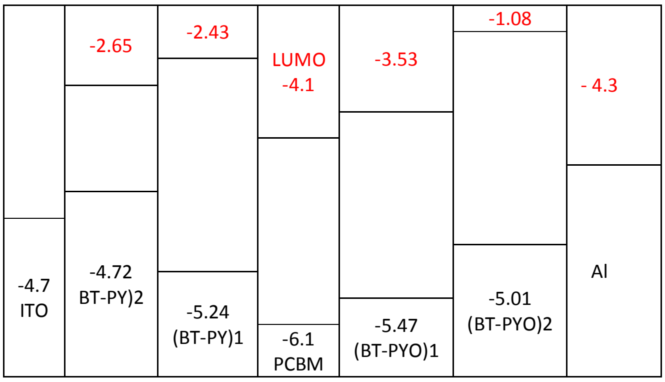
Table 3 lists the theoretical electronic calculations of the studied conjugated polymers. The electronic parameters (HOMO, LUMO Eg(energy band gap)) of the compounds BT-PYO is -5.01, -3.94, 1.08. This compound exhibit distabilizaion of the HOMO and LUMO levels in comparison with those of cis BT-PY, trans BT-PY and BT-TH which are (-4.72, -2.65, 2.07),and (-4.87, -2.55, 2.32) due to the oxygen substitution effect on the pyrrole group. Similarly the LUMO of cis BT-PY and trans BT-PY, exhibit destabilization as a result of the replacement of the pyrrole ring with the thiophene ring. This suggests that the coupling arrangement between electron rich and electron deficient in the backbone of polymer can result in an effective reduction in the band gap of the polymer. Therefore the correlation between the chemical structures of BT-PY based and BT-TH based copolymers suggest that the pyrrole unit is more effective in lowering the band gap than thiophene donor.

TABLE III Theoretical electronic parameters showing the values of HOMO, LUMO band gap energies (Eg) and maximum absorption wave length obtained by B3LYP/6-31G* of the studied molecules

MOLECULE	*E_{HOMO} (eV)*	*E_{LUMO}eV*	*E_geV*	*λ (nm)*
PBT-PY)	-4.72	-2.65	2.07	659
TP(BT-PY)	-4.87	-2.55	2.32	580
P(BT-PYO)	-5.01	-3.94	1.08	767.03
P(BT-TH)	-5.25	-2.81	2.46	543

These results can be further comfirmed by the calculated frontier molecular orbital shown in fig ii because the relative ordering of the occupied and virtual orbital provides a reasonable indication of excitation properties. Frontier orbital of the HOMO, spread over the whole backbone of the pyrrole and thiophene copolymers, demonstrating that strong interactions between the HOMO energy levels of BT and that of PY/Th. The LUMO orbitals have similar shapes of bonding character between two linking carbon atoms of inter-ring. This is because thiophene and pyrrole have similar energy levels of their LUMO orbitals. Figure v. display the resulting energy band diagram in relation to the relative energy levels of the most most widely used acceptors in organic solar cells; PCBM and the work function of indium tin oxide (TIO) and aluminium (Al) which are usually employed as electrodes in polymer solar cells. The HOMO of (BT-PY)$_2$ and (BT-PYO)$_1$ are distinctively higher in energy than that of PCBM. (fig. v). However, not the HOMO energy level but the relative position of the donor LUMO and the acceptor LUMO are important for the intending charge transfer. The difference between the LUMO of BT-PY)2 (BT-BYO)$_1$ and PCBM are around 1.67ev and 0.57ev respectively. The difference of the latter (BT-BYO)$_1$ is the same as the value reported for the differences between the LUMO of dithocarbamate and PCBM which is sufficiently high to allow for an unrestricted and direct charge transfer.

Figure v. Energy band gap diagram with HOMO/LUMO levels of modified BT-PY copolymer and PCBM in relation to the work function of ITO and Al



The absorption wave length of the studied copolymer compounds in the gaseous phase is shown Table 3. The peak of absorption wave length (λ_{max}) of cis BT-PY is about 659.68nm. This value compared favourably with the experimental value reported in literature [14]. The difference of 60nm between the theoretical and experimental values can be attributed to the environmental effect and the state of the polymer chain in solution [15]. Trans BT-PY exhibits a blue shift of about 79nm in the UV region, when compared to cis BT-PY. This difference can, to some extent be attributed to the planarizing power of the intramolecular hydrogen bonds. Thus we can say that the coupling arrangment of electron donor and electron acceptor affect the effective expansion of the light absorption range. To investigate the effect of substitution on the absorption properties, the value of λ_{max} of (BT-TH) and BT-PYO were compared with the absorption wave length of BT-PY copolymers. It was noted that the λ_{max} shows almost equal values but in opposite direction. BT-PYO exhibits a red shift by 107.40nm relative to the cis BT-PY while BT-TH exhibits a blue shift by 116.63nm. The comparison suggests that the optical absorption property λ_{max} increases as the strength of the donor increases.

The maximum absorption of the corresponding copolymers cis and trans BT-PY (580nm, and 659nm respectively) compared to the absorption maximum of the homopolymers reported in the literature, suggest, however, that these copolymers are promising small band gap materials. More also, the combination of zwitterionic pyrrole derived as the donor and benzothiadiazole as the acceptor gives the most promising values.

CONCLUSION

The electronic structure and properties of benzothiadiazole (BT) based alternating donor–acceptor conjugated copolymers were systematically studied using density functional studies to know the effect of ring structure and ring substitution on the backbone of the copolymer molecules. The geometries of the materials were significantly affected by the substituent attached to the chain. The substitution of the pyrrole ring with pyrrolium oxide destabilizes the HOMO, LUMO levels with a decrease in a band gap and results in a red shifting in the absorption spectrum. Hence, these two copolymers could have potential applications in transparent conductors, or photovoltaic devices, . The theoretical results suggest that both the donor strength and the stable geometry contribute significantly to the electronic properties of alternating donor–acceptor conjugated copolymers.

From an application perspective, the results from energy band gap, together with the results of the UV- absorption spectroscopy suggest these materials ((BT-PY and BT-PYO) to be excellent candidates for electronic and optoelectronics applications.

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