A STRUCTURAL STUDY OF POLYTHIOPHENE COUPLING THROUGH α AND β CARBONS: AN *AB INITIO* EVALUATION

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ABSTRACT – **Detailed *ab initio* quantum mechanical calculations of a number of polythiophene oligomers are carried out to ascertain relative stability of structures bonding through α and β carbons. Energetics of dimers, trimers, tetramers, and pentamers with all possible linkages types are obtained from fully optimized geometries. This will determine the relative energy of α and β carbons linkages of the oligomers. Final energy of the oligomers is calculated using different ab-initio basis sets (3-21G and STO-3G) of the polythiophene geometry. Geometrical structures and energetics of thiophene oligomers are presented.**

KEY WORDS -- Polythiophene, α and β coupling, *ab initio,* basis set.

1. Introduction

Academic and industrial research groups around the world have shown great interest in conjugated polymers particularly polythiophene (PT) as an important class of electronic material [2]. Early studies had shown that these materials exhibit high electrical conductivities.

High conductivities, corrosion resistance, and low density are among their properties that are beginning to find applications in the fields of battery materials, electrochromic displays, electromagnetic shielding, sensor technology, non-linear optics, and molecular electronics [2, 3, 5].

Recently, a collaborative study between Niigata University of Japan and MSU-IIT of the Philippines conducted a study on the search of new semiconductor radiation detector by fabricating a radiation detector prepared through electrochemical synthesis using polythiophene doped with tetraflouroborate [4].

Silicon (Si) has been commonly used as radiation detectors [4]. It serves as vertex detectors of the interaction point and decay point of short-lived elementary particles in B-factory experiments in Kou Enerugi Kenkyushuo (KEK), Tsukuba, Japan and other major experiments in the USA and Europe. Since Si is very expensive to make into large silicon semiconductor detector, they tried to study other potent conducting polymers particularly polythiophene and polypyrrole as radiation sensors. The films produced by these polymers are strong, flat, thin, stable in the electron beam, easy to process, and entails very cheap fabrication cost compared to silicon.

Among these conjugated polymers, PT has been extensively studied because it is one of the most attractive intrinsic conductive polymers. It has good mechanical properties and environmental stability in both doped and pristine form [4]. PT films can be easily prepared through electropolymerization process. During the process coupling occurs primarily through the α carbon atoms of the heterocylic ring since these are the positions of highest unpaired electron π spin density and hence reactivity [3].

Theoretically, there are a small number of attempts to comapare α-α, α-β and β-β and they are carried out mostly in dimers of thiophene. Non α - α′ linkages (e.g. α-β′ and β-β′ couplings) can occur to variable extends, causing breaks in conjugation and hence, reduction in film conductivity. Such linkages are more profound in the later stages of electropolymerization where the unpaired electron π spin density of the *α* carbon atom of the oligomer approaches that of the *α* carbon atom. [3].

Like polypyrrole (PPy), the neutral polythiophene as observed in the IR in carbon ^{13} NMR spectra has shown that α-α′ carbon linkages predominate [1, 6]. Thus, it is assumed that the most probable coupling occurred during the electrochemical polymerization is α-α′ coupling [4]. This study aims to investigate the assumptions previously presented by experiments *via* computational analysis

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employing *ab initio* method by calculating the final energy of the oligomers.

2. Computational Details

Intrinsic thiophene oligomers from dimer up to pentamer were investigated using *ab initio* quantum mechanical method. The *ab-initio* quantum mechanical method involves the molecular orbital calculations that employs Molecular Orbital (MO) methods based upon the Schroedinger hamiltonian expression for a multi-electron molecule (equation 1). This expression eludes exact solution, hence a variety of schemes have been made to obtain approximate solutions. For the hamiltonian H, a set of wavefunctions ψ exists that gives discrete energy solutions *E* for the molecular system. This is a classic eigenvector-eigenvalue problem, where the MO wavefunction eigenvectors correspond to the MO energy eigenvalues [11].

$$H\psi = E\psi \tag{1}$$

The Hamiltonian [12], H is the total energy operator for a system, and is written as the sum of the kinetic energy of all the componenents of the system and the internal potential energy. For a single molecule, the total Hamiltonian can be written as follows:

$$H = -\sum_{i}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A}^{M}\sum_{i}^{N}\frac{Z_A}{r_{iA}} + \sum_{i>j}^{N}\frac{1}{r_{ij}} - \sum_{A}^{M}\frac{1}{2M_A}\nabla_A^2 + \sum_{A>B}^{M}\frac{Z_A Z_B}{r_{AB}} \tag{2}$$

The molecular spin orbitals $\chi_i(x)$ satisfy the eigenequation such that the Hartree Product wavefunctions are products of occupied spin orbitals, and thus an energy which is a sum of individual orbital energies, as

$$\Psi = \chi_i(x_1)\chi_j(x_2)\chi_k(x_3)\cdots\chi_n(x_n) \tag{3}$$

$$\langle \Psi \mid H \mid \Psi \rangle = \varepsilon_i + \varepsilon_j + \ldots + \varepsilon_\eta = E. \tag{4}$$

and the generalized wavefunction to give the N electron Slater determinant is,

$$\Psi = (N!)^{-1/2}\begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_\eta(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_\eta(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_\eta(x_N) \end{vmatrix} \tag{5}$$

Roothan's [13] contribution is to use a set of basis functions to expand the molecular wave function in terms of a set of basis functions to recast the integro-differential equations into a set of algebraic equations. These basis functions must span Hilbert space and be physically adequate. Thus the wave function looks like;

$$\vartheta_i = \sum c_{i\mu}\chi_\mu(\vec{r}_i) \tag{6}$$

$$\sum c_{i\mu}{}^2 = 1 \tag{7}$$

$$\vartheta_i\vartheta_j d\tau = 0(i \neq j);1(i = j) \tag{8}$$

where φ_j are the basis functions and $c_{i\mu}$ are the expansion coefficients.

Now minimize the total energy with respect to the variational parameters $c_{i\nu}$ subject to orthonormality of the total wave function $\langle \chi_\mu \mid \chi_\nu \rangle = \delta_{\mu\nu}$. This constraint appears as Lagrange multipliers, written as $\varepsilon_{\mu\nu}$, in the minimization plus the expansion in terms on Hilbert Space basis functions, gives the Hartree-Fock-Roothan (HFR) algebraic equations to solve for the variational parameters $c_{i\nu}$, written as,

$$\sum_{\nu}(F_{\mu\nu} - \varepsilon_i S_{\mu\nu})c_{i\nu} = 0 \tag{9}$$

where the Fock matrix $F_{\mu\nu}$ and $D_{\mu\nu} = \sum c_{i\lambda}c_{i\sigma}$, is the density matrix and $S_{\mu\nu}$ is the overlap matrix which arises from the non-orthogonality of the basis functions [13].

In matrix form, the HFR equations are of the following form,

$$FC = SCE \tag{10}$$

where C is he expansion coefficient matrix $c_{i\nu}$ and E is the energy. To solve equation 10, transform to a standard eigen value problem, solve, and then transform back [13].

The types of integrals needed are, one electron integrals giving the overlap between different states, χ_μ and χ_ν,

$$S_{\mu\nu} = \int \chi_\mu^*(\vec{r})\chi_\mu(\vec{r}_i)d\vec{r}_i \tag{11}$$

one electron kinetic energy integrals,

$$T_{\mu\nu} = \int \chi_\mu^*(\vec{r}_i)[-\frac{1}{2}\nabla_1^2]\chi_\mu(\vec{r}_i)d\vec{r}_i \tag{12}$$

coulomb attraction between a single electron and the nuclei,

$$V_{\mu\nu} = \int \chi_\mu^*(\vec{r}_1)[\sum\frac{Z_A}{r_{1A}}]\chi_\nu(\vec{r}_1)d\vec{r}_1 \tag{13}$$

and two electron integrals, one for the coulomb repulsion and one for the quantum mixing due to indistinguishability of particles.

$$V_{\mu\nu} \equiv (\mu\mu \mid \lambda\sigma) = \int \chi_\mu^*(\vec{r}_1)\chi_\nu^*(\vec{r}_2)\frac{1}{|\vec{r}_{12}|}\chi_\lambda(\vec{r}_1)\chi_\sigma(\vec{r}_2)d\vec{r}_1 d\vec{r}_2 \tag{14}$$

The system of HFR equations are solved iteratively and might be outlined as follows [13]:

(a) make an initial guess for c_i
(b) calculate $F_{\mu\nu}$ and $S_{\mu\nu}$

(c) solve HFR equations for ε_i and $c_{\mu\nu}$

(d) repeat steps (a)-(d) until ε_i and/or c_i converge.

The form of the wavefunction ψ varies with the level of approximation used. It is very common for the linear combination of atomic orbitals (LCAO) approximation to be used, such as all ψ's are made by combinations of Atomic Orbitals (AOs) from the constituent atoms of the molecule. The set of AOs used to make up the MOs is called the basis set. Linear combinations of the AOs give a number of MOs equal to the number of basis set orbitals, where the MO eigenvectors form an orthonormal set according to the equations (equations 6, 7, 8) [11].

However, the actual mathematical treatment is more general than this, and any set of appropriately defined functions may be used. The basis set is a mathematical description of the orbitals within a system (which in turn combine to approximate the total electronic wavefunction) used to perform the theoretical calculations. Standard basis sets for electronic structure calculations used linear combinations of gaussian functions equation

$$g(\vec{r}) = cx^n y^m z^l e^{-\alpha r^2} \tag{15}$$

to form the orbital equation [10]

$$\varphi_i = \sum_{\mu=1}^{N} c_{\mu i}\chi_\mu . \tag{16}$$

For *ab initio* Molecular Orbital (MO) calculations, the minimal level of basis set (termed single-zeta) uses both core and valence AOs. For ease of computational integration, almost all modern *ab initio* computations approximate AOs as summations of gaussian type orbital (GTO) functions (equation 17). For higher-level work, complex basis sets have been devised, using two or more shells composed of summations of gaussian functions in order to simulate each occupied shell of an atom (and often even the higher-lying empty shells) [11]

$$\psi_{GTO} = \sum c_k e^{a_k r^2} . \tag{17}$$

The rationale behind using complex basis sets for *ab-initio* computations is that *any* approximate set of MO eigenvectors ψ_i will yield a molecular energy that lies above the "*true*" energy. This is due to the variational theorem, which states that E_{approx} is greater than E_{actual} in (equation 1) for nonapproximate hamiltonian expressions H (in this case the nonrelativistic, time-independent hamiltonian is appropriate). The greater the flexibility of the basis set, the greater the flexibility in the approximate MOs ψ_i, and the closer E_{approx} will come to E_{actual}. The cost for this greater level of accuracy is an increase in the time required to run a computation, and an increased complexity in interpreting the final result. These time constraints can be very substantial for either medium to large molecules, or for large basis set computations. Therefore, *ab initio* theory is practically usable only for certain types of problems in materials chemistry, even with the present state of the art of fast programming algorithms and ever-faster computers to run them [11].

In this study, a minimum basis set of STO-3G was initially carried out. This minimal basis set contains the minimum number of basis functions needed for each atom [10]. It is used to fixed-size atomic-type orbitals with three gaussians primitives per basis function of this Slater-type-orbital that approximates with gaussian functions. Furthermore, a larger basis set was employed with split valence (3-21G) by increasing the number of basis sets per atom. It allows orbitals to change size, but not to change the shape of the oligomers. Larger basis sets more accurately approximate the orbitals by imposing fewer restrictions on the locations of the electrons in space [10].

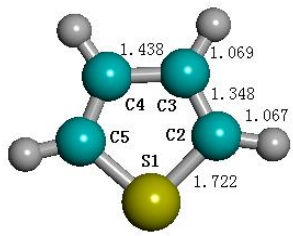
All calculations were initially calculated on semi-empirical method using HyperChem [7] suite of program and finally carried out using GAMESS [8] system of programs running at Sun Sparc station and Beowulf cluster. Molecular symmetry was applied throughout the entire program.

3. Results and Discussion

Geometries for thiophene monomer, dimers, trimers, tetramers and pentamers have been optimized at Hartree-Fock level using STO-3G and 3-21G basis sets. Some of the different types of coupling from dimer up to pentamer are shown in Figure 2. As observed, pure α-α′ linkages showed a planar conformation and linear chains, α-β′ bonding showed slightly linear but purely planar and β-β′ couplings showed a kink structure.

As shown in Figure 3, the coupling involving linear α-α′ structures manifested the lowest energy structure and linkages involving α-β′ and β-β′ in all oligomers showed a higher energy structure. However, some of the structures were almost energetically degenerate to the lowest energy, for example αα - αβ, βα - αα - αα and αα - αα - αβ - αα.

It turned out that the ground state of the resulting oligomers depend mainly on the number of α or β type terminating monomers but not on how they were ordered. For example, if one of the monomers was connected to the central one by its α carbon and the others through their β carbons, the other possible combinations were almost energetically degenerate.



Bond angles
$\angle C_3C_2C_1$=112.383°
$\angle S_4C_3C_2$=111.929°
$\angle H_2C_1C_2$=123.692°
$\angle H_8C_3C_2$=127.093°

Figure 1. Structures of thiophene monomer optimized using 3-21G-basis set. Bond distances are given in angstrom (Å).

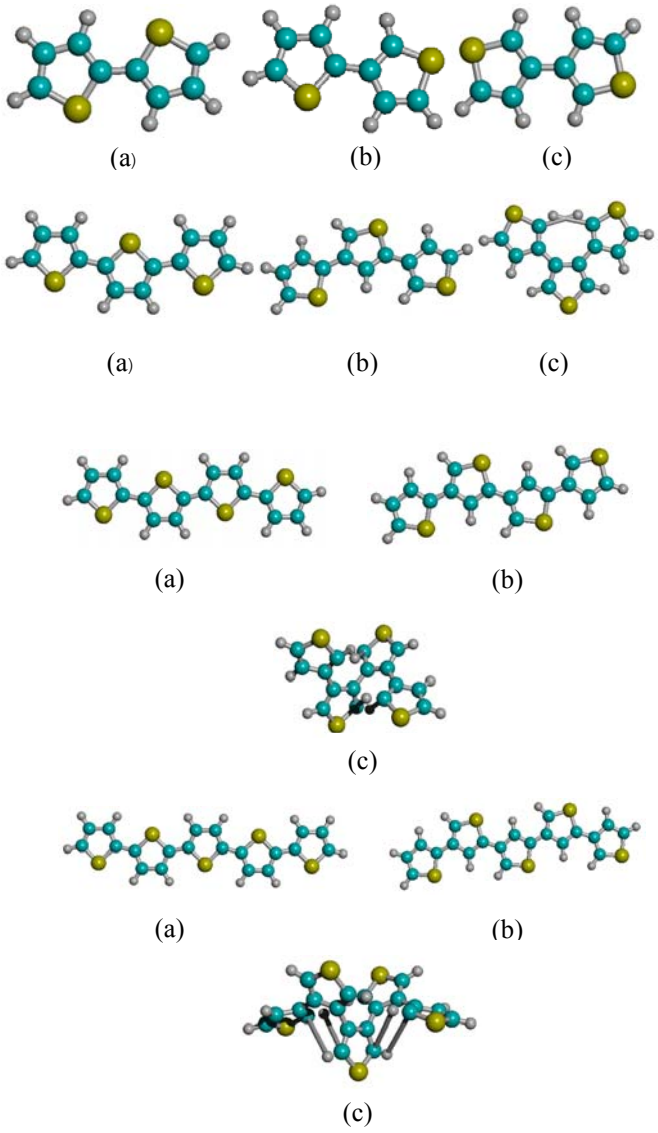


Figure 2. Optimized geometry structure of (a) αα-linear (b) αβ-planar (c) ββ-kink for dimers, trimers, tetramers, pentamers.

Table 1. Relative energies (in eV) of linear combination of dimer, trimer, tetramer and pentamer ground states.

Dimer

No.	Coupling Sequence	STO-3G	3-21G
1	αα	0.000	0.000
2	αβ	0.107	0.040
3	βα	0.108	0.040
4	ββ	0.237	0.088

Trimer

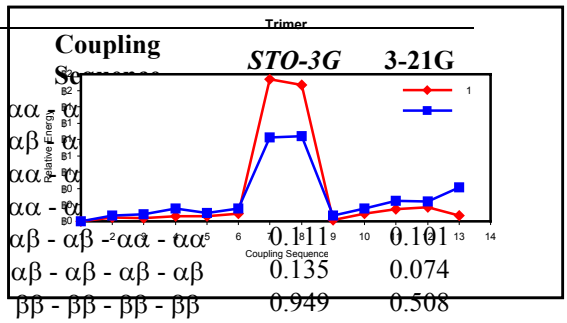
No.	Coupling Sequence	*STO-3G*	3-21G
1	αα - αα	0.000	0.000
2	αα - αβ	0.074	0.043
3	αα - βα	0.088	0.037
4	αα - ββ	0.155	0.062
5	αβ - αα	0.098	0.065
6	αβ - αβ	0.159	0.097
7	αβ - βα	1.024	1.738
8	αβ - ββ	1.041	1.669
9	βα - αα	0.071	0.017
10	βα - βα	0.159	0.097
11	βα - ββ	0.250	0.152
12	ββ - αα	0.244	0.171
13	ββ - ββ	0.418	0.067

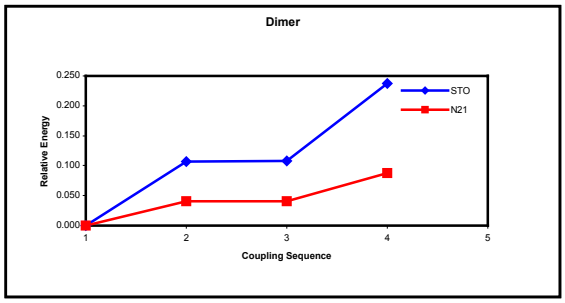
Tetramer

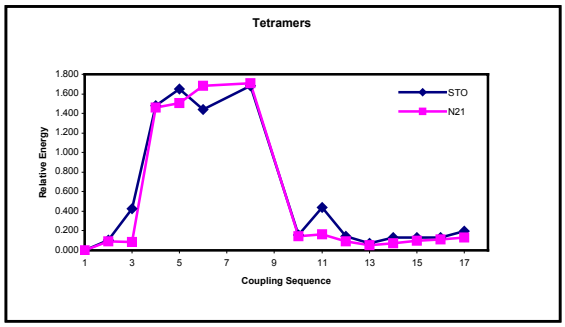
No.	Coupling Sequence	*STO-3G*	3-21G
1	αα - αα - αα	0.000	0.000
2	αα - βα - αβ	0.103	0.093
3	αα - ββ - βα	0.427	0.083
4	αβ - βα - αβ	1.480	1.462
5	αβ - ββ - αα	1.650	1.505
6	αβ - βα - αα	1.440	1.682
7	αβ - ββ - αβ	1.680	1.711
8	αα - ββ - αα	0.156	0.144
9	αα - ββ - ββ	0.438	0.166
10	αβ - αβ - αβ	0.147	0.092
11	βα - αα - αβ	0.073	0.054
12	βα - αβ - αβ	0.128	0.072
13	βα - βα - αβ	0.133	0.098
14	ββ - αα - αα	0.130	0.112
15	ββ - αα - ββ	0.197	0.128

Pentamer

No.	Coupling Sequence	*STO-3G*	3-21G
1	αα - αα - αα - αα	0.111	0.101
2	αβ - αα - αα - αα	0.135	0.074
3	αα - αα - αα - αβ	0.949	0.508
4	αα - αα - αα - βα	0.671	0.297
5	αβ - αβ - αα - αα	0.591	0.094
6	αβ - αβ - αβ - αβ	0.688	0.259
7	ββ - ββ - ββ - ββ	0.945	0.496
8	βα - ββ - ββ - ββ	0.411	0.032
9	ββ - βα - ββ - ββ	0.161	0.037
10	ββ - ββ - βα - ββ	0.125	0.010
11	ββ - ββ - ββ - βα	0.060	0.079
12	βα - βα - ββ - ββ	0.082	0.055
13	βα - βα - βα - ββ	0.104	0.033
14	βα - βα - βα - βα	0.945	0.495
15	βα - αα - αα - αα	0.671	0.283
16	βα - βα - αα - αα	1.543	1.543
17	βα - βα - βα - αα	0.087	0.105
18	αβ - ββ - ββ - ββ	0.487	0.112
19	αβ - αβ - ββ - ββ	0.089	0.105
20	αβ - αβ - αβ - ββ	0.086	0.102
21	αα - αα - αα - βα	0.110	0.082
22	ββ - ββ - ββ - αβ	0.129	0.057
23	αα - αα - βα - αα	0.613	0.126
24	αα - βα - αα - αα	0.688	0.259
25	αα - αα - βα - βα	0.401	0.108
26	αα - βα - βα - βα	0.172	0.101
27	ββ - ββ - αβ - ββ		
28	ββ - αβ - ββ - ββ		
29	ββ - ββ - αβ - αβ		
30	ββ - αβ - αβ - αβ		







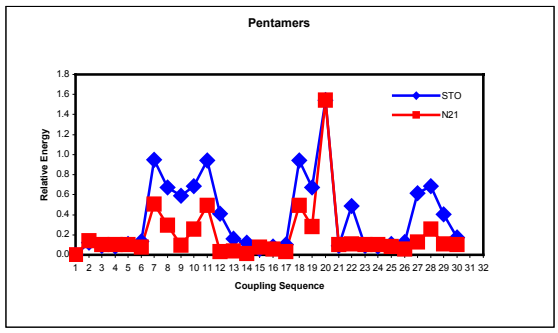


Figure 3. Plot of the relative energy vs coupling sequence of dimer, trimer, tetramer and pentamer

4. Conclusion

The addition of a thiophene to a polythiophene backbone can be achieved in a large number of ways depending on the position along the chain as well as the orientation of the monomer. The relative energies of the possible structures can then be predicted by counting the types of thiophene rings. Finally, it was observed that α - α′ coupling has the lowest final energy among the thiophene oligomers; thus it is the most stable coupling**.**

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