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# An *Ab Initio* Structural Analysis of Polythiophene Oligomers

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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 determines 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.*

## Introduction

A new class of polymers with conjugated π-electron backbones represents an important research area with diverse scientific problems of fundamental significance. They display unusual electronic properties such as low energy optical transitions, low ionization potentials, and high electron affinities [12 ].

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Mostly due to their high conductivity, polymers involving 5-member rings (eg. polythiophene, polypyrrole, etc.) have attracted a great deal of attention [4]. They have been studied extensively from both fundamental and application aspects because of their potential as materials for particle detectors [2].

Among these conjugated polymers, polythiophene (PT) has been thoroughly studied because it is one of the most attractive intrinsic conductive polymers; having 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].

There are a small number of theoretical attempts to compare 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 employing *ab initio* method by calculating the final energy of the oligomers.

## 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 molecular orbital (MO) calculations based upon the Schroedinger hamiltonian equation for a multi-electron molecule:

$$H\psi = E\psi \qquad (1)$$

where H is the Hamiltonian and $\Psi$ is the set of wavefunctions giving discrete energy solutions E for the system.

Since equation 1 eludes exact solution, a variety of schemes have been made to obtain approximate solutions. The form of the wavefunction $\psi$ varies with the level of approximation used. It is very common for the linear combination of atomic orbitals (LCAO) approximation to be used, where all $\psi$'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 eigenvalues form an orthonormal set according to:

$$\psi_i = \sum_{\mu=1}^{N} c_{\mu i}\Phi_\mu \qquad (2)$$

$$\Sigma c_\mu^2 = 1 \qquad (3)$$

$$\psi_i \psi_\mu d\tau = 0(i = \mu); (i \neq \mu) \qquad (4)$$

where $\psi_i$ are the basis functions and $c_{\mu i}$ are the expansion coefficients determined from the Roothaan and Hall matrix eigenvalue equation [11, 13].

If the many-electron Hamiltonian contains no electron spin operators, we can write the one-electron orbitals $\psi_i$ (j) as a product of spatial $\Phi_i(j)$ and spin [$\alpha(j)$ or $\beta(j)$] components to give, for a closed shell configuration of paired electrons,

$$\psi(1,2,3,\ldots n) = \left(\frac{1}{n!}\right)^{1/2} \begin{vmatrix} \Phi_1(1)\alpha(1) & \Phi_1(2)\alpha(2) & \Phi_1(3)\alpha(3) & \cdots & \Phi_1(n)\alpha(n) \\ \Phi_1(1)\beta(1) & \Phi_1(2)\beta(2) & \Phi_1(3)\beta(3) & \cdots & \Phi_1(n)\beta(n) \\ \Phi_2(1)\alpha(1) & \Phi_2(2)\alpha(2) & & & \vdots \\ \Phi_2(1)\beta(1) & \Phi_2(2)\beta(2) & & & \vdots \\ \vdots & \vdots & & \ddots & \\ \Phi_{n/2}(1)\beta(1) & \vdots & & & \Phi_{n/2}(n)\beta(n) \end{vmatrix}$$

where $\Phi_i(j)$ denotes the *i*th spatial containing the *j*th electron, and $\beta(j)$ and $\alpha(j)$ represent the electron spin functions for the *j*th electron,

respectively. In the two-electron system, the spin and spatial parts of the function separate [15].

Standard basis sets for electronic structure calculations used linear combinations of gaussian functions equation

$$g(\alpha, \vec{r}) = cx^n y^m z^l e^{-\alpha r^2} \qquad (5)$$

In this equation, $\alpha$ is a constant determining the size (radial extent) of the function. The exponential function is multiplied by powers (possibly 0) of x, y, and z, and a constant for normalization so that the integral of $g^2$ over all space is 1 (note that therefore c must also be a function of $\alpha$) [10].

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,

$$\Psi_{GTO} = \sum c_k e^{a_k r^2} \quad . \qquad (6)$$

where $a_k$ is a constant determining the size (radial extent) of the function and $c_k$ the constant of normalization which depends on $a_k$. 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) [10, 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 gaussian functions. Furthermore, a larger basis set was employed with split valence (3-21G) by increasing the number of basis sets per atom. 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 programs 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 by imposing the CI Schoenflies symbol of the said group [8].

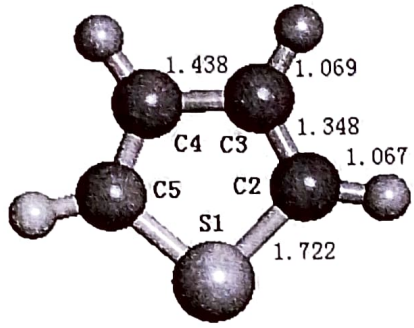
## Results and Discussion

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.

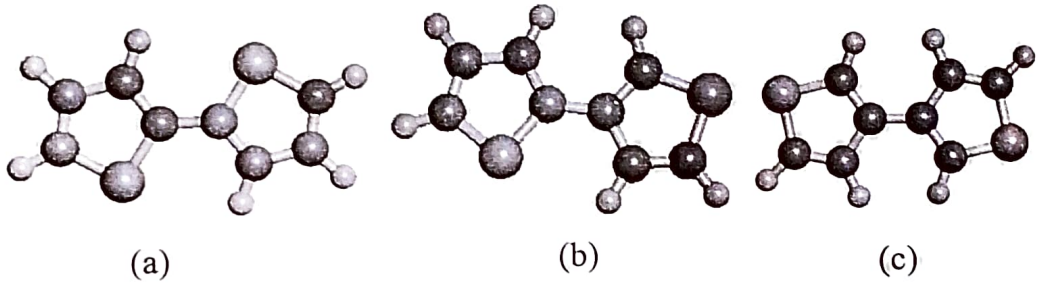
It turned out that the ground state of the resulting oligomers depend mainly on the number of α or β type terminating monomers but not on how they were ordered. For example, if one of the monomers was connected to the central one by its α carbon and the others through their β carbons, the other possible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

Finally, all calculations show that α-α bonding is the most stable and probable coupling and in good agreement with many previous experimental results [2,3,4].

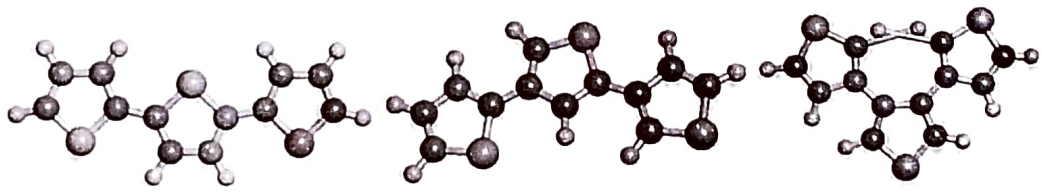



Bond angles
$\angle C_3C_2C_1=112.383°$
$\angle S_4C_3C_2=111.929°$
$\angle H_2C_1C_2=123.692°$
$\angle H_8C_3C_2=127.093°$

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



(a) (b) (c)



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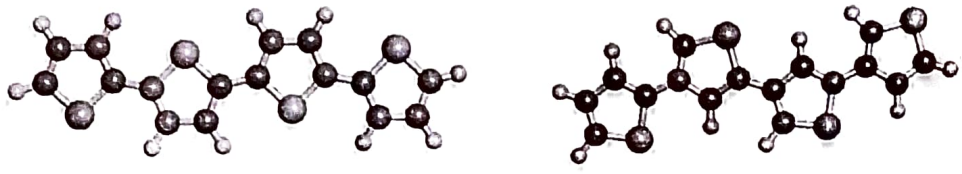

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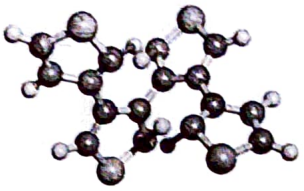

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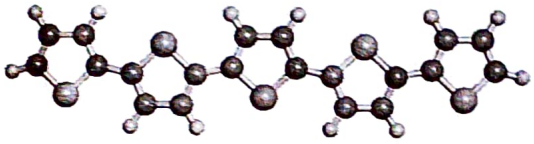
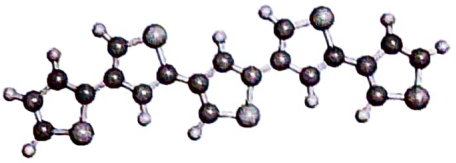


(a)



(b)

(c)

*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**

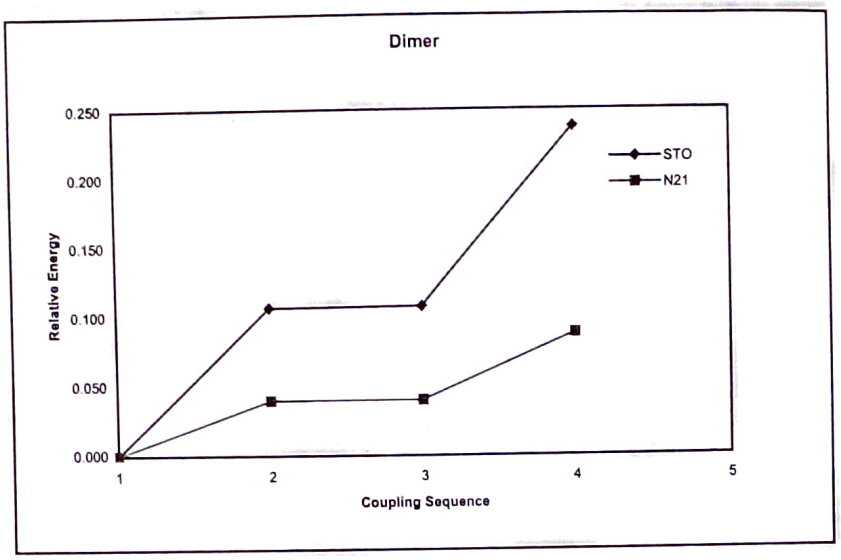
| No. | Coupling Sequence | *STO-3G* | 3-21G |
|---|---|---|---|
| **1** | αα - αα | 0.000 | 0.000 |
| **2** | αα - αβ | 0.074 | 0.043 |
| **3** | αα - βα | 0.088 | 0.037 |
| **4** | αα - ββ | 0.155 | 0.062 |
| **5** | αβ - αα | 0.098 | 0.065 |
| **6** | αβ - αβ | 0.159 | 0.097 |
| **7** | αβ - βα | 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 | 0.000 | 0.000 |
| 2 | αβ - αα - αα - αα | 0.122 | 0.143 |
| 3 | αα - αβ - αα - αα | 0.089 | 0.105 |
| 4 | αα - αα - αβ - αα | 0.086 | 0.102 |
| 5 | αβ - αβ - αα - αα | 0.111 | 0.101 |
| 6 | αβ - αβ - αβ - αβ | 0.135 | 0.074 |
| 7 | ββ - ββ - ββ - ββ | 0.949 | 0.508 |
| 8 | βα - ββ - ββ - ββ | 0.671 | 0.297 |
| 9 | ββ - βα - ββ - ββ | 0.591 | 0.094 |
| 10 | ββ - ββ - βα - ββ | 0.688 | 0.259 |
| 11 | ββ - ββ - ββ - βα | 0.945 | 0.496 |
| 12 | βα - βα - ββ - ββ | 0.411 | 0.032 |
| 13 | βα - βα - βα - ββ | 0.161 | 0.037 |
| 14 | βα - βα - βα - βα | 0.125 | 0.010 |
| 15 | βα - αα - αα - αα | 0.060 | 0.079 |
| 16 | βα - βα - αα - αα | 0.082 | 0.055 |
| 17 | βα - βα - βα - αα | 0.104 | 0.033 |
| 18 | αβ - ββ - ββ - ββ | 0.945 | 0.495 |
| 19 | αβ - αβ - ββ - ββ | 0.671 | 0.283 |
| 20 | αβ - αβ - αβ - ββ | 1.543 | 1.543 |
| 21 | αα - αα - αα - βα | 0.087 | 0.105 |
| 22 | ββ - ββ - ββ - αβ | 0.487 | 0.112 |
| 23 | αα - αα - βα - αα | 0.089 | 0.105 |
| 24 | αα - βα - αα - αα | 0.086 | 0.102 |
| 25 | αα - αα - βα - βα | 0.110 | 0.082 |
| 26 | αα - βα - βα - βα | 0.129 | 0.057 |
| 27 | ββ - ββ - αβ - ββ | 0.613 | 0.126 |
| 28 | ββ - αβ - ββ - ββ | 0.688 | 0.259 |
| 29 | ββ - ββ - αβ - αβ | 0.401 | 0.108 |
| 30 | ββ - αβ - αβ - αβ | 0.172 | 0.101 |


Dimer
0.250
0.200
0.150
0.100
0.050
0.000
Relative Energy
STO
N21
1
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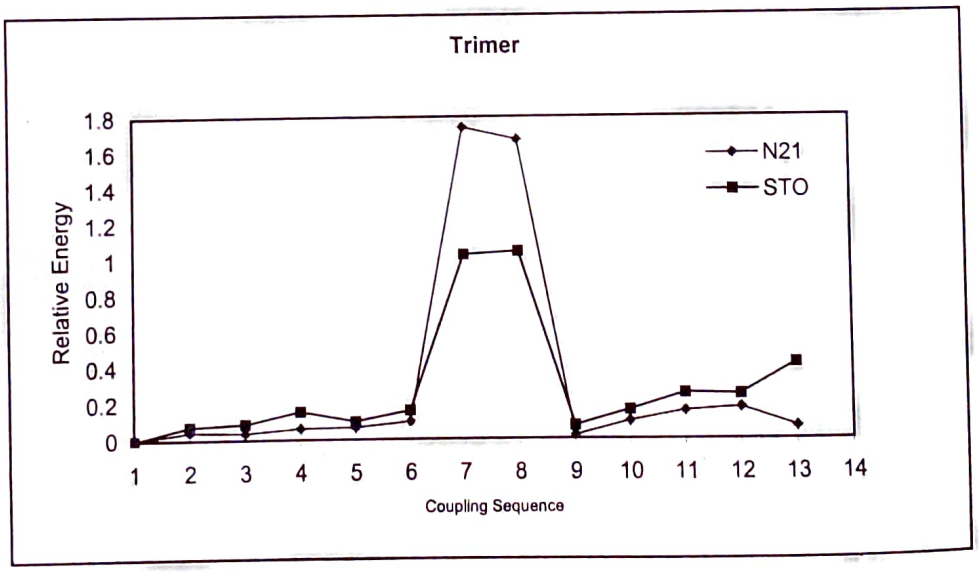
5
Coupling Sequence


Trimer
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Relative Energy
N21
STO
1
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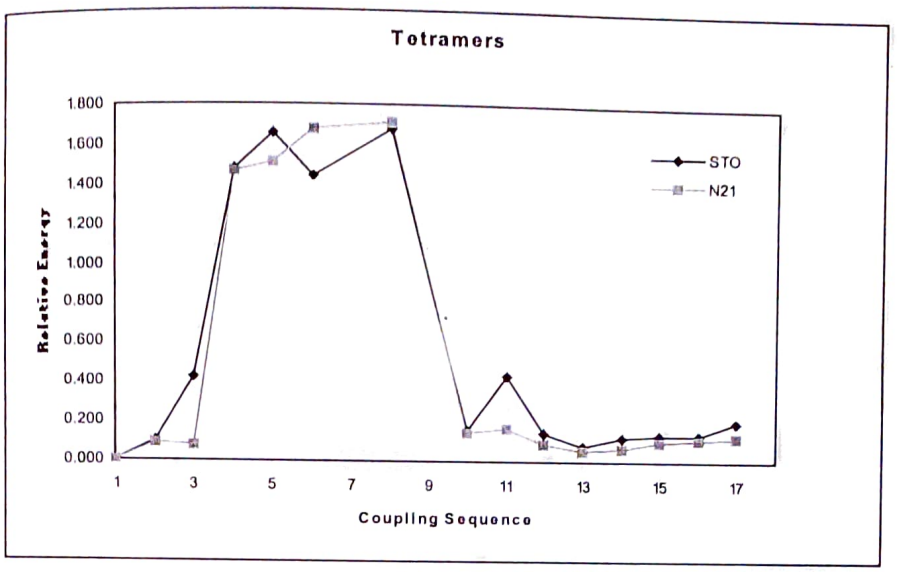
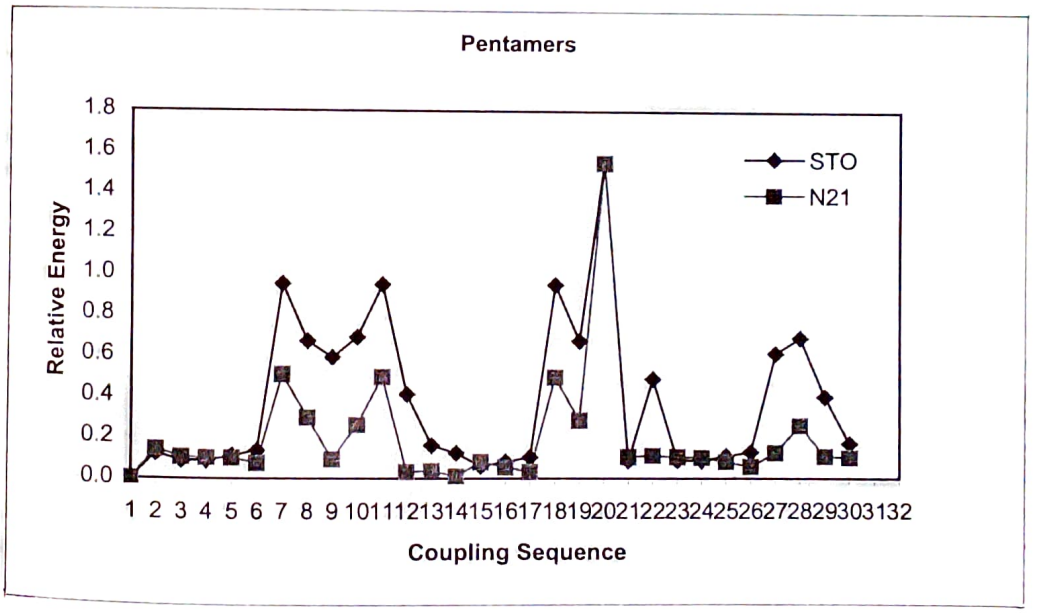
Coupling Sequence




***Figrure 3.*** *Plot of relative energy vs coupling sequence of dimer, trimer, tetramer, and pentamer*

## Conclusion

We have studied the geometrical and energetics of polythiophene oligomers up to pentamers employing *ab initio* quantum mechanical calculations. Minimum basis set of slater-type-orbital (STO-3G) containing the minimum number of basis functions and a larger basis set with split valence (3-21G) had been extensively studied. Geometrical parameters can also be obtained from these calculations.

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 $\alpha$ - $\alpha'$ coupling has the lowest final energy among the thiophene oligomers; thus it is the most stable coupling.

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