

Structural Studies of Polythiophenes: An *Ab Initio* Evaluation of Coupling Through α and β Carbons

A. C. Alguno¹, R. V. Bantaculo², R. M. de Asis³, R. M. Venquizo²,
A. A. Castillon⁴, A. S. Dahili², H. Miyata⁵, and A. M. Bacala²

¹College of Arts and Sciences, NORMISIST, Ampayon, Butuan City, Philippines

²Department of Physics, MSU-IIT, Iligan City, Philippines

³College of Arts and Sciences, Ateneo de Zamboanga, Zamboanga City, Philippines

⁴College of Arts and Sciences, SJIT, Butuan City, Philippines

⁵Department of High Energy Physics, Niigata University, Japan

alguno@physics.msuiit.edu.ph; rolando@physics.msuiit.edu.ph;

rdea@physics.msuiit.edu.ph; rey@physics.msuiit.edu.ph; ann_cast@eudoramail.com;

allen@physics.msuiit.edu.ph; bacala@msuiit.msuiit.edu.ph; miyata@hep.sc.niigata-u.ac.jp

INTRODUCTION

Extensive studies have been done both fundamentally and practically on conducting polymers like polythiophene (PT). Once positively doped, PT is relatively stable in air, due in part to the resonance effect of the sulfur which acts to stabilize a carbonium ion on the polymer chain (Yang & Chien, 1995). The drastic changes in electrical, optical and magnetic properties upon doping (Castillon, 2000) have attracted much attention from both theoretical and practical physicists.

In the undoped state, polythiophene is an insulator with a band gap of about 2.0 eV (Castillon, 2000) and can be used as heterojunction together with polypyrrole (PPy). Their combination exhibits excellent rectifying characteristics (Castillon, 2000). PT stable films can be prepared by either an electrochemical, or a chemical method (Roncalia, 1992).

Like polypyrrole, the neutral polythiophene as observed in the infrared (IR) and a Carbon¹³ NMR spectrum has shown that α - α' carbon linkages predominate (Roncalia, 1992; Yurtsener, 1999). Thus, the commonly accepted structure of PT is a linear chain of monomers bonded by α - α' carbons.

This paper investigates the most probable carbon coupling during polymerization. The thermodynamical probabilities of linking α and β carbons in dimers

through pentamers of polythiophenes were determined employing *ab initio* method.

METHODOLOGY

All semi-empirical calculations were carried out using HYPERCHEM program running in Windows NT for initializations. The output files were then fed to BABEL software running in turbo Linux for conversion as input files to General Atomic and Molecular Electronic Structure System (GAMESS) suite of programs. Semi-empirical and *ab initio* calculations were running at SUN sparc station and Beowulf cluster at physics, MSU-IIT.

Fig. 1 summarizes the methods and approaches employed in this study. Geometry optimizations were done at the Restricted Hartree-Fock (RHF) level of theory using PM3, STO and 3-21G.

RESULTS

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 Fig 2. As observed, pure α - α' linkages showed a planar conformation and linear

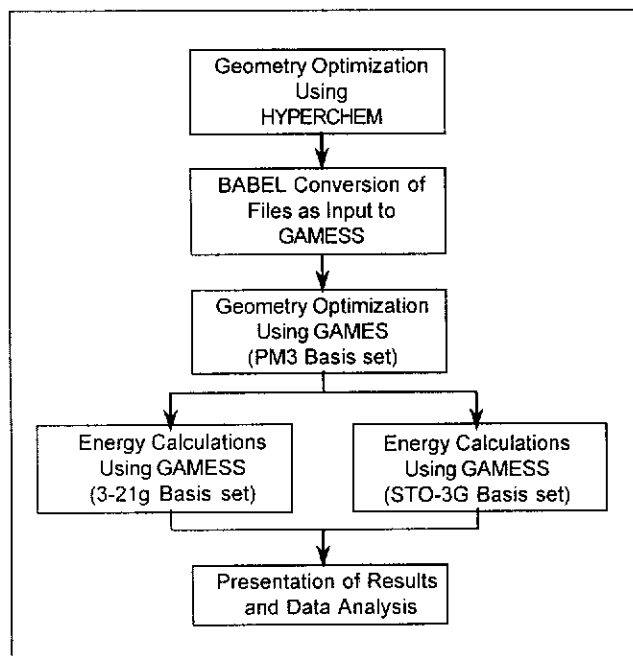


Fig. 1. Schematic diagram employed in this study.

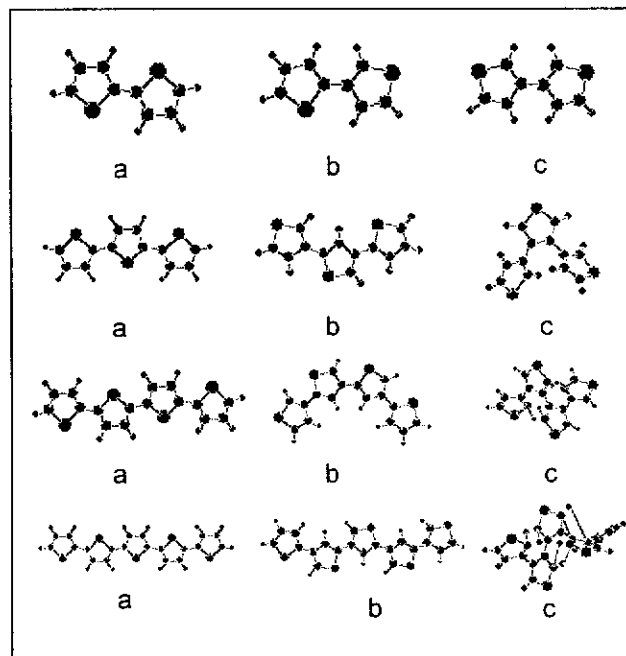
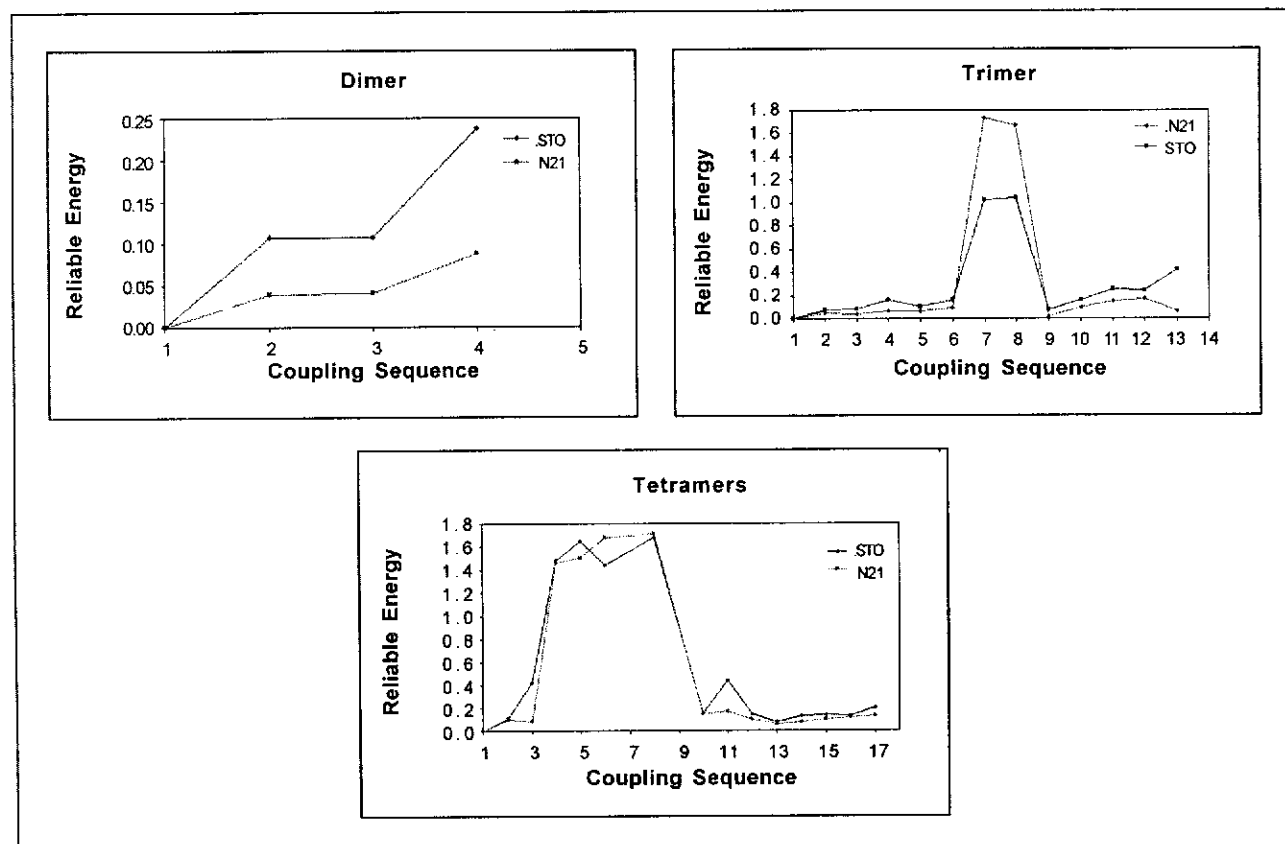
Fig. 2. Optimized geometry structure of (a) α -linear; (b) $\alpha\beta$ -planar (c) $\beta\beta$ -kink dimers, trimers, tetramers, pentamers.

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

chains, α - β' bondings showed slightly linear but purely planar and β - β' couplings showed a kink structure.

As shown in Fig. 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 $\alpha\alpha$ - $\alpha\beta$, $\beta\alpha$ - $\alpha\alpha$ - $\alpha\alpha$ and $\alpha\alpha$ - $\alpha\alpha$ - $\alpha\beta$ - $\alpha\alpha$

It turned out that the ground state of the resulting oligomers depends 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.

CONCLUSIONS

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.

ACKNOWLEDGMENTS

We thank the MSU-IIT Chemistry Department, especially Dr. Edgar Ignacio, Engr. Wilfredo Chung, and Prof. Ronald Pascual, for many fruitful discussions and suggestions. Likewise, thanks are due to MSU-IIT Computer Center, especially to Mr. Dante D. Dinawanao, for all their help.

REFERENCES

Castillon, A., 2000. Study on the New Organic Semiconductor Radiation Detector (unpublished), Master's Thesis, MSU-IIT, Iligan City.

Roncalia, J., 1992. Conjugated poly(thiophenes): synthesis, functionalizations, and applications. *Chem Rev.* 97:711-738.

Yang, X. & J. Chien, 1995. Autooxidation and stabilization of undoped and doped polyacetylenes. *Journal of Polymer Science: Polymer Chemistry Edition*, 23: 856-878.

Yurtsener, M. & E. Yurtsener, 1999. Structural studies of polypyrroles: an *ab initio* evaluation of bonding through *a* and *b* carbons. *Synthetic Metals* 98:221-227.