

Dimerization of Pyrrole

Mine YURTSEVER

*İstanbul Technical University,
Chemistry Department, İstanbul - TURKEY*

Ersin YURTSEVER

*Koç University, Chemistry Department,
80860 İstinye, İstanbul - TURKEY*

Received 04.11.1997

Accurate ab-initio quantum mechanical calculations of pyrrole dimers are reported. The thermodynamical stabilities of dimers with $\alpha - \alpha$, $\alpha - \beta$, and $\beta - \beta$ type linkages are compared in order to predict the possibilities of branching in polypyrroles. Calculations employing large basis sets and including electron correlation effects predict the $\alpha - \alpha$ dimers as the most stable form. However, an $\alpha - \beta$ type bonding requires only 1.5-2.0 kcal/mol, and the energy necessary to introduce a $\beta - \beta$ type bond is 3.6-4.0 kcal/mol. These values show that a high degree of branching is possible even at room temperatures.

Introduction

Polypyrroles form an interesting field of study mostly due to their high conductance upon doping. They are usually prepared by electrochemical means or by chemical oxidation. The resulting material is highly insoluble and unsuitable for a detailed structural analysis. Various attempts have been made to understand the structures of polypyrroles using FTIR¹, Raman², Scanning Tunneling Microscopy³, X-ray Diffraction⁴ and Solid State ¹⁵N NMR⁵; however the different experimental conditions do not allow conclusive evidence on its structure. The high insolubility implies a strong degree of branching which probably involves bonding through β carbons.

Theoretical approaches form another alternative for obtaining information on the bonding of such complex structures. In fact, a number of attempts have been made employing semi-empirical quantum mechanical calculations on geometries and rotational barriers of oligomers⁶⁻⁸, effective valence Hamiltonian approximations on band structure⁹ and small basis ab-initio calculations again on small oligomers of pyrroles and their derivatives^{10,11}. The semiempirical calculations offer a great deal of understanding of reaction mechanisms, especially for organic compounds; however, they usually cannot give accurate quantitative answers due to their parametric nature. On the other hand, ab-initio calculations are more reliable, but the computational times could be very prohibitive for applications involving large molecules. They also suffer from inherent errors of small basis sizes and/or exclusion of electron correlation effects.

In this study, we present accurate results on the thermodynamical stabilities of $\alpha - \alpha$, $\alpha - \beta$, and $\beta - \beta$ dimers of pyrrole. By increasing the basis size and calculating electron correlations using density functional theory and Moller-Pleset perturbation techniques, we were able to find the relative stabilities of these three

dimers and predict the probability of branching through β carbons to be quite high. We are currently in the process of carrying out a large set of calculations on trimer and tetramers including branched forms so that reliable force fields can be generated to study the branching in long chains.

Calculations

The calculations were carried out by Gaussian 94¹² package running at SGI Challenge server with 4 R10000 CPU. We first optimized the structure of the monomer. We were able to produce the most accurate results ever presented¹³. In Table 1 we present the energy and the geometrical parameters of the monomer for basis sizes from STO-3G to 6-311**, including polarization functions on all atoms.

Table 1. Energy and bond lengths of pyrrole

Basis	Energy	N-C α	C α -C β	C β -C β	N-H	C-H
STO 3G	-206.227120	1.3886	1.3509	1.4317	1.0201	1.0773
4-31G	-208.507447	1.3711	1.3580	1.4273	0.9882	1.0650
6-31G	-208.730135	1.3728	1.3626	1.4296	0.9891	1.0663
6-311G	-208.770675	1.3720	1.3612	1.4295	0.9862	1.0648
6-31G*	-208.807851	1.3630	1.3582	1.4269	0.9824	1.0703
6-31G**	-208.819703	1.3629	1.3580	1.4267	0.9911	1.0705
6-311G*	-208.848766	1.3628	1.3580	1.4274	0.9891	1.0703
6-311G**	-208.860412	1.3627	1.3579	1.4273	0.9907	1.0703

We then proceeded to optimize the geometries of the three dimers again using the same series of increasing basis sets. In all calculations, the $\alpha - \alpha$ dimer was found to be the most stable form. This is quite different from the semiempirical results⁸ in which the $\alpha - \beta$ dimer was found to be the most stable with only negligible differences from the other two. In Table 2, the energies and relative stabilities with respect to the $\alpha - \alpha$ linkage are given. The formation of an $\alpha - \beta$ bond requires 1.50-1.65 kcal/mole more energy than that of $\alpha - \alpha$. Similarly, the linkage of two β carbons requires 3.50-3.80 kcal/mole energy relative to the $\alpha - \alpha$. During optimization, individual pyrrole rings remain very close to planar structure. Critical geometrical parameters are given in Table 3. In general, the intermonomer distance increases slightly going from $\alpha - \alpha$ to $\beta - \beta$ type dimers. The torsional angle varies between 143 to 151 degrees. The electron correlation effects are computed by carrying out density functional theory and Moller-Plesset perturbations of second order. These calculations require extensive computation times running up to two days for single structure, only a small sample was attempted. The geometrical structures of dimers do not change significantly for the correlated wave functions. The basic difference between the SCF and post-SCF results is that the energy differences between $\alpha - \alpha$ and $\alpha - \beta$ bondings increase to 2.0 kcal/mole, whereas the relative stabilities of $\alpha - \beta$ to $\beta - \beta$ type dimers remain around 2.1 kcal/mol. The minimum basis set of STO-3G produces very similar results to semiempirical ones which predict planar dimer structures. Upon using split basis sets, we observe several qualitative changes, the most important one being that rings do not lie on the same plane but rather at a tilt angle of 30-35°. In higher basis sets, even the quantitative results do not change. The rotational potential functions for all three dimers for the basis set of 4-31G are given in Fig. 1a-1c. These plots are qualitatively different from those obtained from STO-3G, but very similar to those obtained from higher basis sets. They all show an asymmetric double-well behavior where the actual minimum is around 145° (both nitrogens point out to opposite directions) and there exists another one at 35 - 40°. The largest

barrier is observed for the $\alpha - \alpha$ dimer around 3.00 kcal/mol with a 1.00 kcal/mol barrier between two minima. The double well becomes almost symmetrical for $\beta - \beta$ due to the considerably reduced repulsion between the lone pairs of nitrogens.

Table 2. Ground state energies (in a.u.) and relative stabilities of dimers (in kcal/mol)

Basis	$E(\alpha\alpha)$	$E(\alpha\beta)$	$E(\beta\beta)$	$\alpha\beta - \alpha\alpha$	$\beta\beta - \alpha\alpha$
STO 3G	-411.329866	-411.327493	-411.324140	1.49	3.59
4-31G	-415.870936	-415.868542	-415.865114	1.50	3.65
6-31G	-416.315688	-416.313349	-416.310058	1.47	3.53
6-311G	-416.395170	-416.392653	-416.389061	1.58	3.83
6-31G*	-416.471850	-416.469272	-416.465930	1.62	3.71
6-311G*	-416.551262	-416.548618	-416.545152	1.66	3.83
6-311G**	-416.570155	-416.567665	-416.564385	1.56	3.62
4-31G MP2	-416.793404	-416.791142	-416.788112	1.42	3.32
6-311G*MP2	-417.963211	-417.960239	-417.956877	1.86	3.97
4-31G*DFT	-418.598404	-418.595253	-418.591903	1.98	4.08
6-311G*DFT	-419.242297	-419.239224	-419.236028	1.93	3.93

Table 3. Intermonomer distances R (in Å) and torsional angles θ

	$\alpha\alpha$	$\alpha\beta$	$\beta\beta$
R	1.4487	1.4542	1.4591
θ	149.0	144.0	150.0

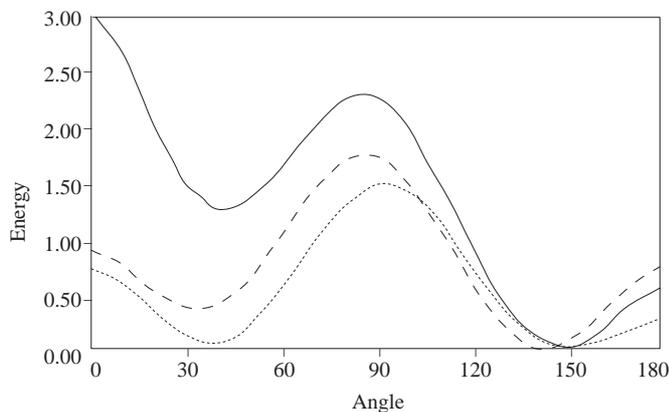


Figure 1. Rotational potentials as functions of the torsional angle between planes (in kcal/mol)

— $\alpha\alpha$ - - - - $\beta\beta$ $\alpha\beta$

These calculations show that both semi-empirical and minimum basis ab-initio calculations give qualitatively incorrect results. However, even a relatively small split basis set of 4-31G is able to predict correct energetic and geometry. We are currently using this basis set to generate a large database of energetic of trimers, tetramers and pentamers so that a kinetic growth type of approach may be used to predict the branching in polypyrroles.

References

1. H. Kato, O. Nishikawa, T. Matsui, S. Honma and H. Kokado, *J. Phys. Chem.* 95, 6014 (1991).
2. G. Zerbi, M. Veronelli, S. Martina, A.D. Schlter and G. Wegner, *J. Chem. Phys.* 100, 978 (1994).
3. R. Yang, W.H. Smyrl, D.F. Evans and W.A. Hendrickson, *J. Phys. Chem.* 96, 1428 (1992).
4. C. Petrillo, S. Borra, R. Cagnolati and G. Ruggeri, *J. Chem. Phys.* 101, 11004 (1994).
5. H. Kurosu, M. Kikuchi, and I. Ando, *J. Polym. Sci. B*, 33, 769 (1995).
6. K. Tanaka, T. Shichiri, and T. Yamabe, *Synt. Met.* 14, 271 (1986).
7. K. Tanaka, T. Shichiri, M. Toriumi, and T. Yamabe, *Synt. Met.* 30, 271 (1989).
8. P.S. Sargn, L. Toppare, and E. Yurtsever, *Polymer*, 37, 1151 (1996).
9. J.L. Bredas, G.B. Street, B. Themans, and J.M. Andre, *J. Chem. Phys.* 83, 1323 (1985).
10. E. Orti, J. Sanchez-Marin, and F. Tomas, *Theor. Chim. Acta* 69, 41 (1986).
11. F. Meyers, C. Adant, J.M. Toussaint, and J.L. Bredas, *Synt. Met.* 41, 3559 (1991).
12. Gaussian 94, Revision C.3, M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzales, and J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
13. E.D. Simadiras, N.C. Handy, and R.D. Amos, *J. Phys. Chem.* 92, 1739 (1988).