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Growth mechanisms of polypyrroles

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The oligomerization mechanisms of several derivatives of pyrrole have been studied by quantum-mechanical methods. Different growth processes are compared from the point of view of thermodynamic stabilities to gain insight into the branching possibilities. For the simple polypyrrole, polymerization may proceed through either an α or a β carbon with equal probabilities. When an aldehyde group is attached to the nitrogen, β positions are definitely favoured owing to strong steric hindrance. For 2-pyrrole carboxaldehyde and 3-pyrrole carboxaldehyde, the most stable forms of the bonding are alternating ones that go through α–β pairs.

(Keywords: polypyrroles; growth mechanisms; quantum-mechanical modelling)

INTRODUCTION

Nowadays, with the vastly improved computational facilities available, it is possible to compute the electronic properties of molecules with considerable sizes. Employing both *ab initio* and semi-empirical quantum-mechanical methods, there have been a number of studies of the oligomerization mechanisms of conducting polymers. One of the earlier applications of the *ab initio* calculations on pyrrole dimers and polymer chains was carried out by Bredas and Street, who discussed the importance of the possibility of achieving a coplanar conformation upon doping[1]. The internal rotation barriers and conformational stabilities for 2,3′- and 3,3′-bipyrrole were examined using small STO-3G (Slater-type orbitals, three Gaussian) and 4-21G basis sets by Orti *et al.*[2], who also examined the conformational behaviour of 2,2′-bipyrrole by *ab initio* calculations[3]. Also there were reports on the structural, electronic and non-linear optical properties of pyrrole derivatives[4]. From the semi-empirical approaches we note the modelling of polypyrrole structures by MNDO (modified neglect of differential overlap) parametrization[5], the computation of the electronic properties of polypyrrole involving α–β linkages[6] and the polymerization process of pyrrole[7]. We have also reported our findings on the oligomerization mechanism of *N*-methacryloyl pyrrole, which was studied by extensive AM1 (Austin model 1) calculations[8]. In that work we presented optimized structures with various types of bondings, starting from monomer up to tetramers. In comparison of α–α, α–β and β–β type pyrrole–pyrrole linkages, it was found that β–β type bonding is the most stable form, and on average, the introduction of one α-type linkage requires about 5 kcal mol^{-1} of energy. One of us has also examined the configurational properties of simple polypyrrole chains employing the semi-empirically generated potential maps[9]. Isomeric states for torsional rotations were identified as the minimum-energy positions; statistical weights determined on this basis were then used in calculating the average dimensions of polypyrrole chains by the rotational isomeric state model and the matrix multiplication scheme.

In this study, we would like to report results on semi-empirical studies of the oligomerization mechanism of several substituted polypyrroles: pyrrole, *N*-pyrrole carboxaldehyde, 2-pyrrole carboxaldehyde and 3-pyrrole carboxaldehyde. We have fully optimized the structures of the monomers; then the stable forms of a large number of possible dimer, trimer and tetramer structures are studied and classified. Also some of the other electronic properties are analysed, which could help in our understanding of the statistical behaviour of long chains.

STRUCTURES OF OLIGOMERS

In order to facilitate a thorough search of potential maps of a large number of structures, we decided to use a semi-empirical quantum-mechanical approach. Our previous experience with similar calculations have shown that AM1 produced accurate structures and reasonable rotational properties, and in this work the AM1 option of MOPAC[10] is used again.

The structural analysis is carried out for the following polypyrroles: pyrrole, *N*-pyrrole carboxaldehyde, 2-pyrrole carboxaldehyde and 3-pyrrole carboxaldehyde. For simplification, we denote these monomers as P (pyrrole), PN (*N*-pyrrole carboxaldehyde), P2 (2-pyrrole carboxaldehyde) and P3 (3-pyrrole carboxaldehyde) (*Figure 1*). Throughout the discussion we employ the index α to identify a carbon atom at position 2 or 5 and similarly β represents a carbon atom at position 3 or 4.

Monomers

First of all, the structures of the monomers of the above-mentioned compounds are determined by optimizing all internal coordinates. In *Table 1*, the heats of formation, geometrical parameters and electronic properties such as bond orders or charges are given for chemically interesting parts of the molecules. The heats

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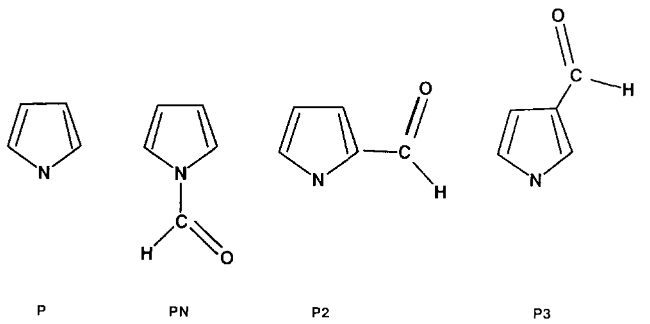

Figure 1 Pyrrole monomers: P, pyrrole; PN, *N*-pyrrole carboxaldehyde; P2, 2-pyrrole carboxaldehyde; P3, 3-pyrrole carboxaldehyde

Table 1 Thermodynamic and structural results for monomers[a]

	P	PN	P2	P3
ΔH (kcal mol^{-1})	39.9	13.7	8.2	6.7
Internal coordinates				
$r(NC_\alpha)$ (Å)	1.39	1.41	1.38	1.40
$r(C_\alpha C_\beta)$ (Å)	1.40	1.39	1.41	1.40
$\theta(C_\alpha NC_\beta)$ (deg)	109.0	108.0	108.6	108.8
Bond orders				
NC_α	1.18	1.09	1.23	1.15
$C_\alpha C_\beta$	1.55	1.65	1.50	1.59
C_aN		0.97		
C_aC			0.97	0.98
q_N	−0.45	−0.43	−0.46	−0.46

[a] C_a aldehyde carbon

of formation of substituted pyrroles are much lower than that of the unsubstituted one and the stability order can be written as P3 > P2 > PN > P. A quick look at the bond lengths and bond angles points out that the geometry of the pyrrole ring seems not to be seriously affected by the addition of an aldehyde group. As expected, the N–C bond of the ring weakens by substitution at nitrogen, whereas the double bond becomes stronger to compensate that effect. A similar but weaker effect is observed for substitution at position 3, and in contrast to these observations, substitution at position 2 strengthens the N–C single bond. The variation of the charge on nitrogen is relatively small, producing a slightly less electronegative nitrogen for PN and more negative nitrogen for P2 and P3.

Dimers

Starting with these structures, we proceed to search through all possible binding types for dimers. In the case of dimers, there are three distinct bonding types, which are denoted as α–α, α–β and β–β. In this notation, as an example, α–β is used to identify a linkage between an α carbon of the first monomer and the β carbon of the second monomer. The dimer structures were first obtained by full optimization. However, the changes in the ring structures were so small that we decided to employ vibrationally frozen pyrrole rings throughout the complete study. The aldehyde groups are always allowed to bend and rotate, so that repulsions between different molecules are minimized, especially when oligomers start to deviate from planarity to a large extent.

From the heat of formations of P (*Table 2*), we see that there are no significant differences between α–α, α–β and β–β type bondings, i.e. the bonding can be through any position. Even though simple polypyrroles are mostly thought to be composed of α–α linkages, the energy differences from other types of bondings are so small that we believe a more appropriate structure should involve a large number of branches from the main chain. This point will be stressed again when we discuss larger oligomers. Obviously the situation is different for the substituted pyrroles. There is an almost 6 kcal mol^{-1} energy difference between the α–α (having the highest heat of formation) and β–β (having the lowest heat of formation) bonds in the case of PN, and α–β type lies in between for the stability ordering. P2 displays a parallel behaviour but with a smaller difference in energy, which is about 2 kcal mol^{-1}. In the case of P3, both α–α and β–β type bondings are equally probable and surprisingly α–β is higher in energy than both of them. The explanation of this somewhat different behaviour lies in the steric hindrance of aldehyde groups. Even though the structures are highly optimized, especially for PN, α–α bonding is difficult owing to the repulsion of two aldehyde groups which lie very close to each other. In *Figure 2* the structures of the most stable forms are presented. The bond length for connecting two monomers varies slightly from 1.42 Å (β–β type) to 1.44 Å (α–α type) for all dimers and the bond order remains constant as 1.0.

Table 2 The heats of formation (kcal mol^{-1}) of various pyrrole dimers

Dimers	P	PN	P2	P3
α–α	80.6	34.2	19.7	16.4
α–β	80.3	32.2	18.1	18.5
β–β	80.9	28.4	17.9	16.6

In *Figure 3*, we plot the rotational potentials of dimers. These potential functions are obtained by rotating the second pyrrole ring with increments of 10° around the monomer–monomer bond. At each step the internal

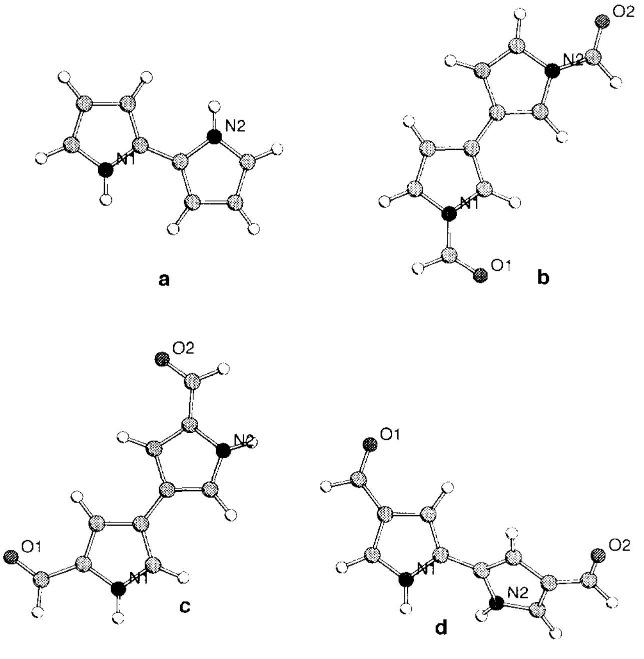

Figure 2 Ball-and-stick models of the optimized geometries of dimers of (a) P, (b) PN, (c) P2 and (d) P3

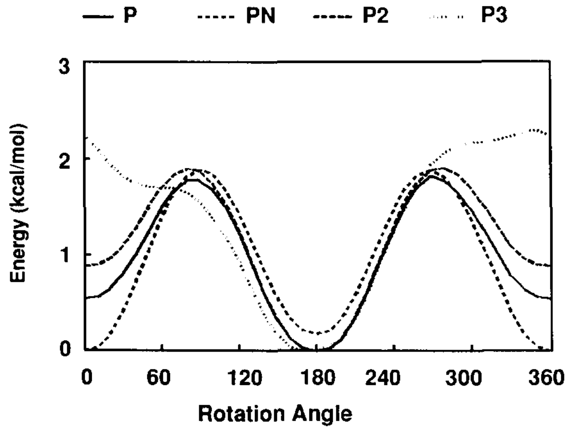

Figure 3 Variation of the potential energy as a function of the torsional angle between the planes of two monomers. Energies are shifted so that the energy of the most stable form is zero

structures are kept frozen but the angular conformations of the aldehyde groups are optimized to minimize the steric hindrance. These rotational potentials provide information for the statistical interpretation of the chain behaviour. The number of minima and their positions determine the possible structures from a thermodynamic viewpoint whereas the barriers point to the probabilities of transitions between these multiple minima. In all cases the absolute minima are at 180° corresponding to structures where the two rings lie on the same plane but in opposite directions. The second minima are at 0° for P, PN (which is degenerate with the absolute minimum) and P2. However P3 seems to have an inflection point at small angles. In all cases, the rotational barriers are less than 2 kcal mol^{-1}.

Trimers

In trimerization, there exist a number of chain growth possibilities. Similar to dimers we have to employ a symbolic notation to distinguish between various types of bondings. Here $\alpha\beta$–$\beta\beta$ denotes a bond between an α position of the first pyrrole and a β of the second and the second bond connects a β carbon of the second ring to a β carbon of the third monomer. Although there are 10 possibilities for growth mechanisms, of course for some monomers not all 10 structures are possible owing to the substitutions at these positions. In *Table 3*, heats of formation are given. For P, except for the $\beta\beta$–$\beta\beta$ isomer, all structures are very close energetically. Since it does not make any difference whether polymerization goes through either an α carbon or a β carbon in pyrrole, trimerization through α carbons had been the initiation step for the formation of pyrrole tetramer.

Table 3 The heats of formation (kcal mol^{-1}) of various pyrrole trimers

Trimers	P	PN	P2	P3
$\alpha\alpha$–$\alpha\alpha$	121.7	56.5	–	26.6
$\alpha\alpha$–$\alpha\beta$	121.3	54.9	–	22.9
$\alpha\alpha$–$\beta\alpha$	121.5	51.3	–	–
$\alpha\alpha$–$\beta\beta$	121.8	49.6	31.5	–
$\alpha\beta$–$\alpha\beta$	120.9	52.5	27.8	20.1
$\alpha\beta$–$\beta\alpha$	120.9	51.6	–	–
$\alpha\beta$–$\beta\beta$	121.1	52.4	–	–
$\beta\alpha$–$\alpha\beta$	121.0	49.9	–	–
$\beta\alpha$–$\beta\beta$	121.5	44.9	–	–
$\beta\beta$–$\beta\beta$	124.4	45.8	31.9	–

In the case of *N*-pyrrole carboxaldehyde, there is less than 1 kcal mol^{-1} energy difference between $\beta\alpha$–$\beta\beta$ and $\beta\beta$–$\beta\beta$ types. In order to be able to carry out systematic studies we decide to accept that trimerization propagating through $\beta\beta$–$\beta\beta$ type linkage is going to be the best possibility for the formation of a tetramer of *N*-pyrrole carboxaldehyde. In addition, we also note that, if it proceeds through $\beta\alpha$–$\beta\beta$, then for tetramers the number of linkage possibilities is going to be automatically restricted.

In contrast to these, trimerization propagates by means of $\alpha\beta$–$\alpha\beta$ type bonding for both P2 and P3, which is actually expected since one side of each monomer has already been blocked by the aldehyde group. To summarize our findings with trimers in a simplified manner, we proceed to identify the most stable forms as $\alpha\alpha$–$\alpha\alpha$ and $\alpha\beta$–$\alpha\beta$ for P, $\beta\beta$–$\beta\beta$ for PN, and $\alpha\beta$–$\alpha\beta$ for both P2 and P3.

A thorough study of the configurational statistics of long chains requires the definition of the so-called 'force fields', which are approximations to the changes in the potential functions by the rotation of monomers around the backbone structure (of course, for a more detailed job, one needs to consider the effects of the stretching and bending motions). One can then construct possible configurations and compute statistical properties. The rotational functions we have presented for dimers represent the relative orientations of adjacent rings; however, they do not determine the three-dimensional growth of a polymer chain. To search for possibilities of the coiling of such chains, one needs to construct two-dimensional potential maps. In this case, three successive rings are taken and their total energy is computed as functions of two adjacent torsional angles. Trimers that have the lowest heats of formation are taken as input and matrices are formed by changing each angle by 10° increments.

For the rotation map of pyrrole, we observe that the absolute minimum is at the position 180°–180° (*Figure 4a*). This specifies a completely planar structure with alternating directions of dipoles. In contrast, *N*-pyrrole carboxaldehyde (*Figure 4b*) has a maximum at the same orientation. The inspection of the 3D models for this geometry reveals a strong overlapping of aldehyde groups, explaining the maximum. The qualitative behaviour of the rotational maps of PN and P2 are very similar, relatively shallow minima being at 150°–150° for PN and at 140°–160° for P2 (*Figure 4c*). Finally, for P3, the minimum point is observed at 160°–210° (*Figure 4d*).

Tetramers

The lowest-energy structures in trimers are then used to generate tetramers. For the formation of tetramers, we consider the addition of the fourth monomer in two different ways such that:

(a) they form a linear chain;
(b) they form a branched chain through either an α carbon or a β carbon.

Therefore, for each tetramer we investigate three possibilities: a linear chain and branching through two different carbons.

For unsubstituted pyrrole tetramers, the energy

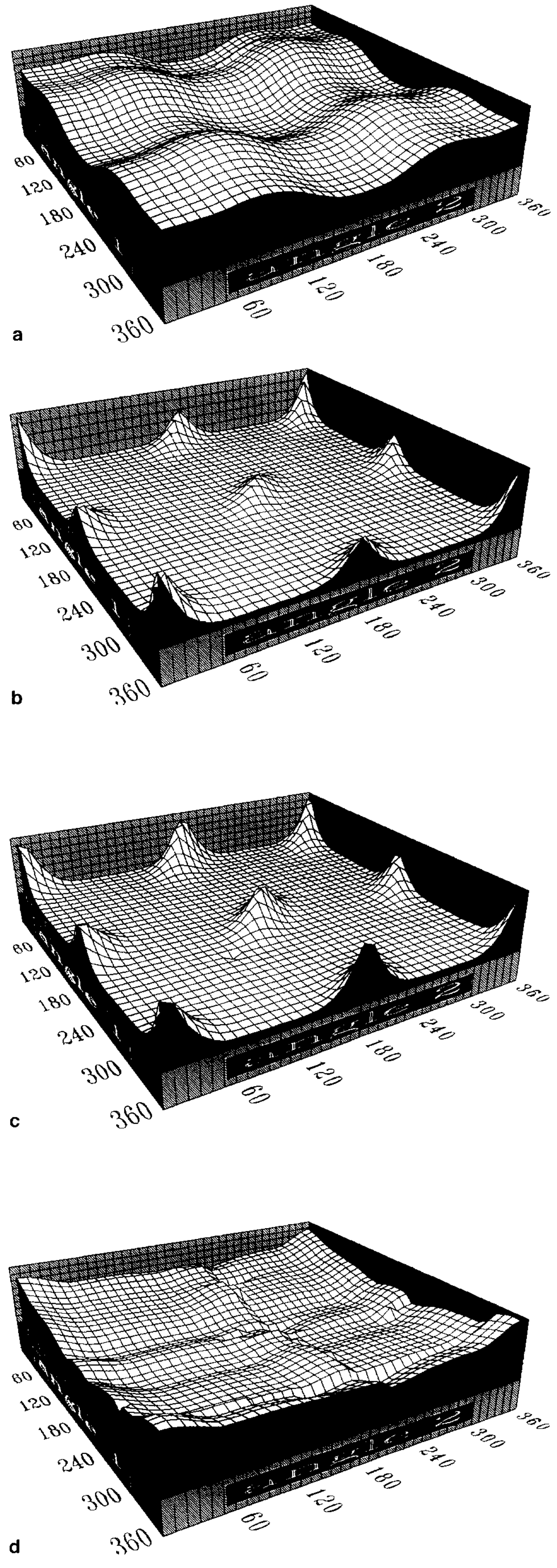

Figure 4 Rotational potential maps for trimers of (a) P, (b) PN, (c) P2 and (d) P3. The angles 1 and 2 are the torsional angles between monomer pairs 1–2 and 2–3 respectively. An angle of 0° denotes a conformation where both rings are in the same plane and nitrogen atoms are on the same side of the monomer–monomer bond

Table 4 The heats of formation (kcal mol^{-1}) of various pyrrole tetramers

Tetramers	P	PN	P2	P3
Linear	162.7	62.9	41.2	32.3
Branching with α carbon	162.7	68.9	38.1	32.4
Branching with β carbon	163.6	67.6	39.6	35.8

differences between these three types are very small (*Table 4*). This suggests that growth of polypyrrole chains is almost a random process, i.e. branch formations or linear growth through α or β carbons are equally likely. The shapes of the long polypyrrole chains are then mostly determined by simple excluded-volume arguments and not from thermodynamic stabilities. On the other hand, for PN the linear chain ($\beta\beta$–$\beta\beta$–$\beta\beta$) seems to be more stable than branched ones to the order of 5–6 kcal mol^{-1}. For P2, again the branched forms are more stable than the linear one, especially if it grows through an α carbon. For P3, the branched form through β carbon is more difficult as we would expect, but the difference between linear growth and α bonding is negligible, implying both are equally likely.

For both trimers and various tetramers, the inter-monomer bonding remains fairly constant with the distance at 1.42–1.44 Å and the bond strength of 1.0 irrespective of the monomer type, the size of the oligomer or the bonding type. The lowest-energy structures are presented in *Figure 5*.

One final piece of information to be extracted from semi-empirical calculations is the separation between occupied and empty energy levels. Even though the

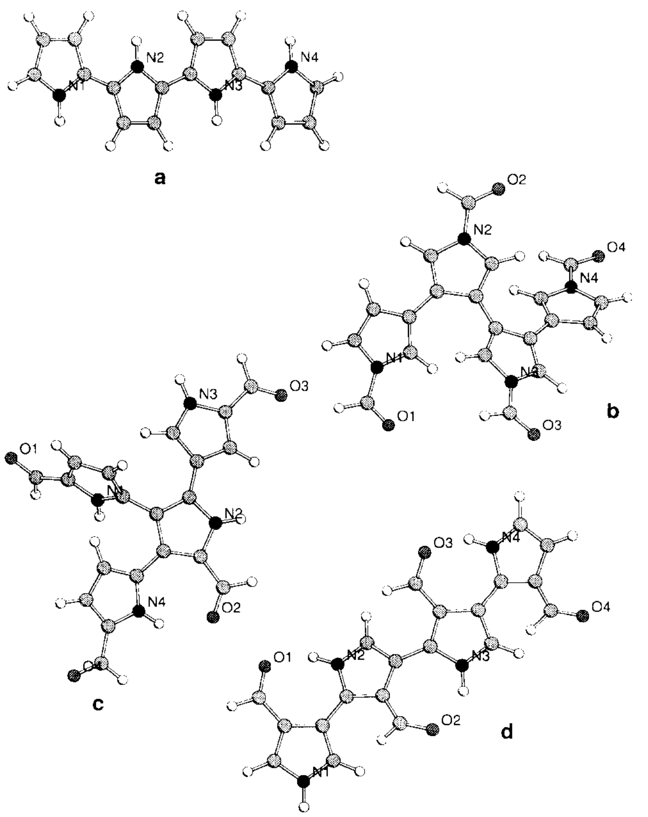

Figure 5 Ball-and-stick models of the optimized geometries of tetramers of (a) P, (b) PN, (c) P2 and (d) P3

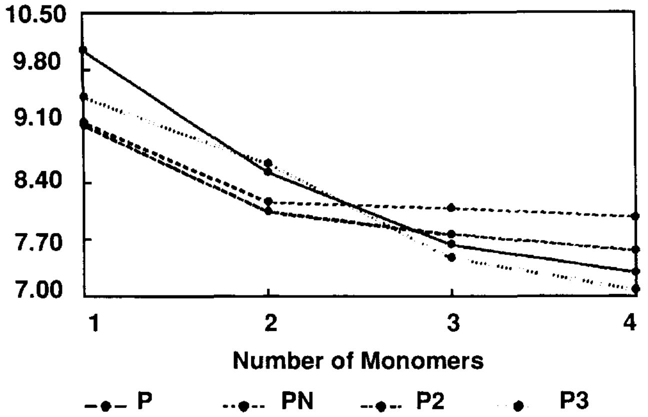

Figure 6 The variation of the HOMO–LUMO energy difference as a function of the number of monomers

conduction mechanisms and the factors defining the mobility of electrons are not well understood, one simply likes to correlate the energy level separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The obvious reasoning is that a small separation allows the excitation of electrons from lower bands to higher empty ones. However, an accurate computation of band gaps for polymers composed of highly unsymmetric units is an extremely difficult task and one can hope that the trend in the energy level separation for small systems may provide some information on the behaviour of large systems. For this purpose we present the HOMO–LUMO energy gaps (*Figure 6*) as functions of the number of units in the oligomer using the energetically most stable forms of each structure. The general trend is that the energy gap decreases as the number of monomer units increases. Without overemphasizing this point, we would like to state that these findings do not contradict experimental results.

CONCLUSION

We have presented structural and thermodynamic information on growth mechanisms of various pyrroles. The errors associated with the semi-empirical quantum-mechanical calculations are usually of the order of 1–2 kcal mol^{-1}. However, these error estimates are absolute values, and when one compares similar molecules energy fluctuations of 0.5 kcal mol^{-1} could also be significant. In our interpretations any two structures with energy difference less than 0.5 kcal mol^{-1} are treated as equivalent structures. From these extensive computations we deduce that, for unsubstituted polypyrroles, the choice of the α or β carbon for the binding site does not affect the thermodynamic stability of the oligomer. The general structure seems to be planar with nitrogens pointing in opposite directions. Upon branching, we also do not note any significant change from the linear structure as long as the bonding is through an α position. This implies that polypyrroles could easily form a branched structure as well as a linear one. For PN the linear form is more stable than branched structures; however, we notice exactly the opposite behaviour for P2. Similar to polypyrrole, P3 can also form linear and branched forms equally probably. For the growth mechanisms, we see that the bonding in polypyrrole can be through any carbon, for PN the bonding is almost exclusively through a β carbon, and for both P2 and P3 an alternating $\alpha\beta$–$\alpha\beta$ type bonding is the most probable mechanism. The bond distances between successive monomer units are fairly constant for all cases studied. The HOMO–LUMO differences of each monomer decrease as more monomer units are attached to the backbone, which does not contradict the simplified description of the conductivity of polymers.

REFERENCES

1 Bredas, J. L., Street, G. B., Themans, B. and Andre, J. M. *J. Chem. Phys.* 1985, **83**(3), 1323
2 Orti, E., Marvin, J. S. and Thomas, F. *J. Mol. Struct.* 1985, **124**, 307
3 Orti, E., Marvin, J. S. and Thomas, F. *Theor. Chem. Acta* 1986, **69**, 41
4 Meyers, F., Adant, C., Toussaint, J. M. and Bredas, J. L. *Synth. Met.* 1991, **41–43**, 3559
5 Orchard, B. J., Freidenreich, B. and Tripath, S. K. *Polymer* 1986, **27**, 1533
6 Tanaka, K., Shichiri, T. and Vamabe, T. *Synth. Met.* 1986, **14**, 271
7 Tanaka, K., Shichiri, T., Toriumi, M. and Vamabe, T. *Synth. Met.* 1989, **30**, 271
8 Yurtsever, E., Toppare, L. and Hallensleben, M. L. *J. Mol. Struct. (Theochem)* 1993, **280**, 1
9 Yurtsever, E. and Erman, B. *Polymer* 1993, **34**(18), 3887
10 MOPAC version 5.00, *Quantum Chem. Program Exch.* 455