Tetrahedron Vol. 40, No. 20, pp. 3963 to 3970, 1984
Printed in the U.S.A.

0040–4020/84 $3.00 + .00

REACTIVITY/STRUCTURE CORRELATIONS FOR THE ELECTROPOLYMERIZATION OF PYRROLE: AN INDO/CNDO STUDY OF THE REACTIVE SITES OF OLIGOMERIC RADICAL CATIONS

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(*Received in USA* 10 *April* 1984)

ABSTRACT: INDO/CNDO molecular orbital methods applied to the oligomeric radical cations of pyrrole reveal that, during electropolymerization, the reactive sites in the intermediate oligomers become chemically inequivalent to those of the monomer. Thus, with increasing chain length, the unpaired electron becomes increasingly delocalized such that the α-positions, which are the most reactive sites in the monomer, no longer have the highest localization of the unpaired electron, which is taken as a measure of reactivity. In the trimer radical cation, the spin density at the 3,3''-positions (β-positions) is approximately equal to that of the α-positions, which are, therefore, about equally reactive. A torsional energy diagram of the trimer radical cation reveals that a coplanar anti conformation is energetically favored. Extensions of this concept predict that whereas initially the oxidative electropolymerization of pyrrole might result in a rather regularly α,α'-linked polymer, a more irregular connection pattern can be expected to result during later stages of the chain growth of polypyrrole. In particular, a number of linkages involving the β-positions are predicted to increase with increasing chain length.

INTRODUCTION

By now, a considerable variety of aromatic molecules (R) have been found to electropolymerize at the anode surface, thereby yielding semi-conducting polymers. R can include such molecules as pyrrole,[1] thiophene,[2] 2,2'-bithiophene,[2] azulene,[3,4] and indole,[2c,5] to name a few examples. Clearly, R itself may also be an oligomer, as evidenced by the facile electropolymerization of 2,2'-bithiophene.[2b] More importantly, electropolymerization is considered to depend on the presence of a reactive radical cation ($R^{\dot{+}}$) for chain propagation,[3-5] which is continuously formed *via* the anodic oxidation of the aromatic molecules at the anode surface. These radical cations can undergo a variety of reaction pathways, depending upon their intrinsic stability.[5] When $R^{\dot{+}}$ is relatively stable, it can diffuse away from the electrode surface and undergo reactions to form soluble products. If $R^{\dot{+}}$ is a highly unstable radical cationic species, it can rapidly undergo indiscriminate reactions with either the solvent or anions to yield soluble products. Between these two stability extremes $R^{\dot{+}}$ can undergo "electropolymerization," described previously as an $E(CE)_n$ reaction.[3] According to this concept, $R^{\dot{+}}$ initially undergoes radical coupling, *i.e.*, dimerization, with another $R^{\dot{+}}$ at the electrode surface, followed by deprotonation and reoxidation. The subsequent reaction sequences involve the combination of oligomeric radical cations with $R^{\dot{+}}$, followed by deprotonation, reoxidation, radical combination, and so on, to eventually lead to a polymeric film, coating the electrode surface. At each step of the electropolymerization reaction, chain propagation is dependent on the presence of $R^{\dot{+}}$ in the vicinity of the anode surface. This view is supported by the finding that in order to sustain film growth, the electrode potential (voltage) has to be maintained at the electrochemical oxidation potential of R.[6] Also, previous chronoabsorptometric data (for R=pyrrole) have revealed that polypyrrole films grow linearly with time t, and not $t^{1/2}$.[7] These data imply that the rate-limiting step during film growth is the radical coupling process itself, and not diffusion of the monomer to the electrode.[7] Such a condition will assure a surplus of $R^{+\cdot}$ at the electrode surface. Thus, it appears that the reactivity of the radical cation $R^{+\cdot}$ is a key parameter which determines whether electropolymerization of an aromatic molecule will occur. Accordingly, we have attempted to determine the reactivity parameters *via* INDO/CNDO molecular orbital calculations. For this purpose we have utilized a known[8] correlation between reactivity and the density of the unpaired electron, in particular with its degree of localization at a specific site of these important radical cation intermediates. As an illustrative example, we have chosen the electropolymerization reaction of pyrrole.

RESULTS AND DISCUSSION

It has previously been shown for a series of oligomers derived from pyrrole and benzene that the peak oxidation potentials of the members decrease as a function of chain length.[6a] These data suggest a decreasing reactivity and thus increasing stability of the oligomeric radical cations with increasing chain length, which is probably due to more efficient delocalization of the unpaired electron. A direct method of estimating the stability of such oligomeric radical cations starts from their electronic structure. It was pointed out by Adams in 1969 that the spin density of a radical cation is a valid reactivity index.[8] The spin density data can be obtained directly *via* electron spin resonance (ESR) spectrometry, or estimated *via* molecular orbital calculations. ESR studies, for example, reveal that the stability of the radical cations derived from the oligomeric series benzene, p-biphenyl and p-quaterphenyl, increase with increasing chain length; because the benzene and p-biphenyl radical cations are very reactive, they can only be observed *via* ESR at low temperatures (ca. −103°C or lower) when they are trapped in rigid isolation matrices.[9,10] Higher temperatures preclude observation of the unstable (*i.e.*, reactive) benzene radical cation. On the other hand, biphenyl dimerizes rapidly upon electrooxidation at higher temperatures, upon which it gives rise to the more stable radical cation of p-quaterphenyl, *i.e.*, the quatermer of the p-phenylene series.[11] The radical cations of the latter can be observed by ESR in the liquid phase above 0°C. Comparison of the ESR data of this series of oligomers reveals decreasing spin densities at the reactive p-positions with increasing chain length (Figure 1). Thus, the radical cation of benzene would be expected to be the most reactive, while that of the quatermer should be the most stable. This is in accord with the experimental findings.[9-11] For comparison, the spin densities calculated *via* the HMO method for

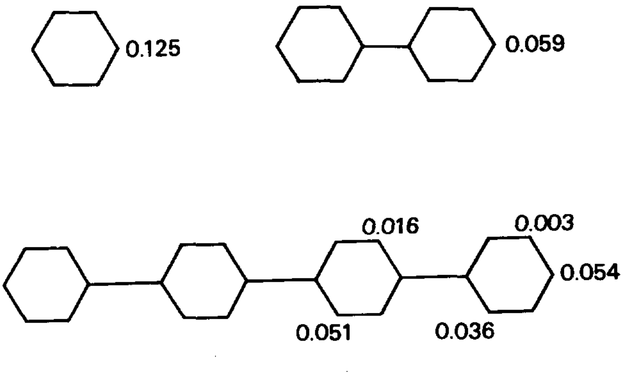


Figure 1. Spin density distribution of the radical cations derived from some p-benzenes, *i.e.*, poly(p-phenylenes). The values for p-quaterphenyl were taken from Ref. 11. For benzene and p-biphenyl, the hyperfine splitting constant values from Ref. 9 were used to calculate the spin densities, using Q=35.7 (see Ref. 11).

p-quaterphenyl[11] are in good agreement with the experimental results (Figure 1). Thus, the spin density distribution of radical cations can indeed serve as a useful reactivity parameter. A similar application of molecular orbital calculations to other homologous series of polyaromatics could allow insights into the electropolymerization reaction of other types of molecules R mentioned above. This would allow extrapolation to their hypothetical polymer structure, thereby facilitating the characterization of these polymers. These aspects are considered below using R=pyrrole as an illustrative example.

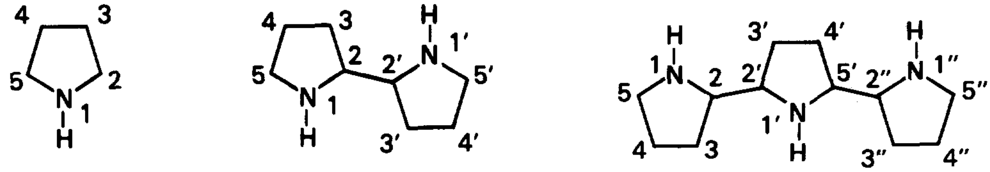
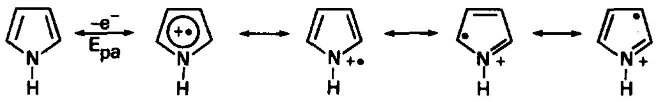


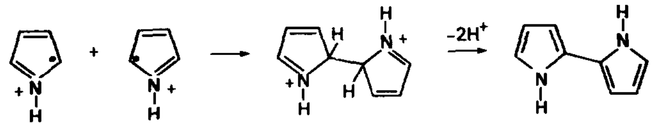
Figure 2. The numbering scheme of pyrrole oligomers.

Electronic Structure

The electrooxidation of monomeric pyrrole at an electrode surface gives rise to a delocalized radical cation. Our INDO[12] molecular orbital calculations reveal that, as expected, the delocalized pyrrole[13] monomer radical cation [1] has the highest spin density at its equivalent α-positions (Figure 3). Thus, among the resonance forms [2], [3] and [4] shown, [3] is clearly the most important. Accordingly, in the dimerization of two monomer pyrrole radical cations, radical coupling can be expected to occur at the α-positions. Indeed, dimerization to the dihydrodimer [5] proceeds with great facility, followed by loss of two protons to yield the neutral 2,2'-dimer [6]. The driving force for deprotonation is stabilization of the positive charges by return to aromaticity.



[1] [2] [3] [4]



[5] [6]

The E(CE)$_n$ reaction at the anode surface continues with the electrooxidation of the dimer [6] to its radical cation [7]. Since the loss of an electron is now accommodated by two monomer units, the oxidation potential of [6] is lower than that of the monomer, and is, therefore, readily electrooxidized at the applied voltage. The spin density distribution of the coplanar anti form [7] is given in Figure 3. As with the monomer radical cation counterpart, the positions with the highest spin density remain at the α-positions, namely the 5,5'-positions. However, because the unpaired electron is distributed over two monomer units, delocalization dilutes the spin density (*i.e.*, reactivity) of the α-positions in the dimer, similar to the example given above for the p-phenylene series. Conversely, the β-positions have acquired more spin density, indicative of a different type of spin distribution in the dimer radical cation. A resulting consequence is stabilization and thus decreased reactivity of [7]. This may well account for the difficulty found in producing thick, continuous, free-standing polypyrrole films from the electrooxidation of either 2,2'-bipyrrole or 2,2':5',2''-terpyrrole,[6a] although it is reported to be possible.[14] Among the resonance forms shown for the dimer radical cation, INDO calculations (Figure 3) predict [9] to be the predominant structure. The dimer radical cation can, therefore, be expected to continue to react primarily at the α-positions. Thus, at this stage of the electropolymerization process, the surplus of monomer radical cations [3] at the electrode surface assures further predominance of α,α'-coupling, to yield the dihydrotrimer [11], which upon deprotonation forms the neutral trimer, *i.e.*, 2,2':5',2''-terpyrrole [12]. Subsequent electrooxidation yields the radical cation thereof [13], for which the spin density distribution predicted by the INDO calculations is given in Figure 3. The radical cation [13] in its coplanar

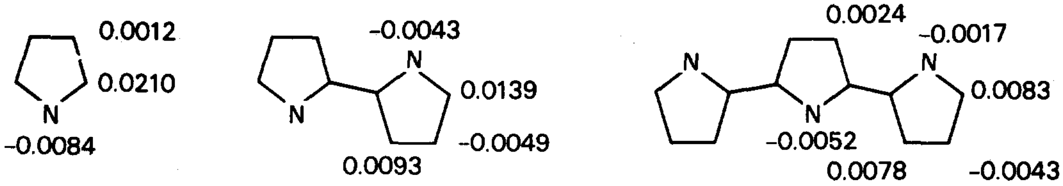
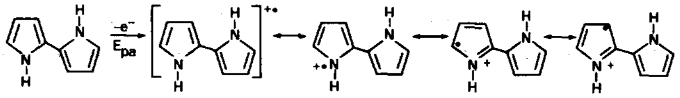
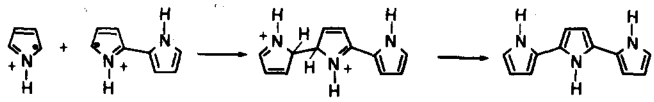


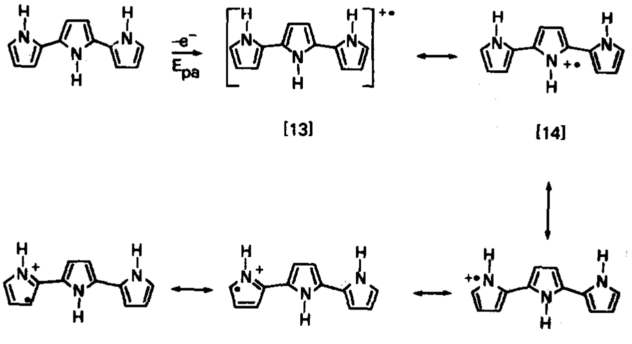
Figure 3. INDO molecular orbital calculations of the spin density of pyrrole, and coplanar anti 2,2'-bipyrrole and 2,2':5',2''-terpyrrole radical cations.



[7] [8] [9] [10]



[11] [12]



[13] [14]

[17] [16] [15]

anti-configuration is predicted to be well-delocalized, with much of the spin density residing at the 2',5'-, 5,5"- and 3,3"-positions. It is interesting to note that here the α-positions, namely the 5,5"-positions, are no longer the positions with the highest spin density. They are comparable in magnitude of their spin densities to those predicted for the 2',5'- and 3,3"-positions. The 2',5'-positions should be sterically inaccessible to monomer radical cation attack. Conversely, the 5,5"-positions can be easily attacked by the monomer radical cations, thereby propagating α,α-linkages still further. However, β-coupling at the 3- or 3"-position is somewhat sterically hindered, and therefore the monomer radical cation would have to couple with the oligomer radical cation in a non-planar configuration. The steric crowding caused by a planar configuration arises from the short interatomic distances encountered by the non-bonding H-atoms, in particular, between the 1- and 1"-hydrogens for the structure shown in Figure 4, or when twisted 180°, the 1- and 3"-hydrogens. However, a CNDO torsional potential diagram of 2,2':3',2"- terpyrrole, reveals that a twist angle of approximately 135° results in a minimum energy configuration (Figure 5). Thus, our INDO calculations predict that monomer radical cations could in principle undergo radical coupling reactions at either the 5,5"-positions (*i.e.*, α-positions), or the 3,3"-positions (*i.e.*, β-positions!) of these oligomeric radical cations. Reaction at the latter positions have certainly been rated unfavorable above for both the monomer and dimer radical cations. However, while competitive β-coupling is assumed when the reactivity of the pyrrole oligomer depends solely on the spin density distribution at those positions, if α-coupling continues to predominate, then other parameters such as steric constraints must limit reaction of the β-positions. Nevertheless, the INDO calculations reveal an important

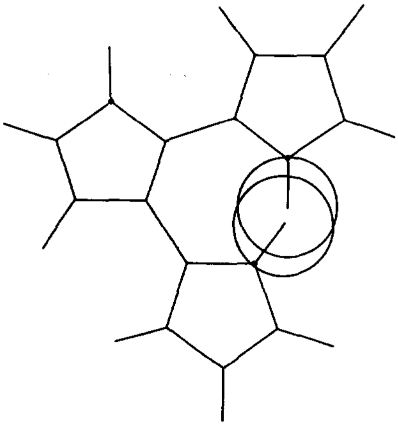
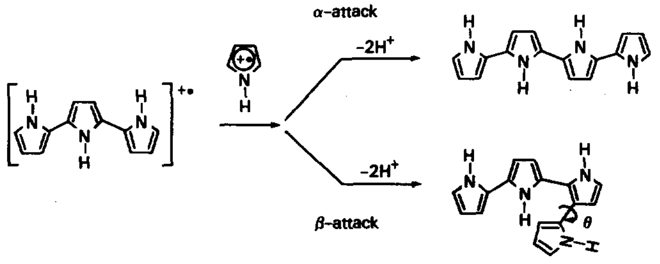


Figure 4. The configuration of 2,2':3',2"-terpyrrole from a molecular coordinate program, illustrating the steric crowding of a coplanar arrangement. The circles represent the van der Waals radius (1.1 A) of the H-atom.



trend, namely, that as oligomerization proceeds from monomer to dimer to trimer radical cations, delocalization of the unpaired electron causes the spin density distribution to be decreased in the α-positions, concomitant with an increase at the β-positions, *i.e.*, the 3,3''-positions. Extension of this trend suggests that as the oligomer progressively increases in chain length, the extensive π-delocalization which sets in will delocalize the unpaired electron over the entire oligomer, such that further radical coupling would not be overwhelmingly favored at any single position. If the INDO results are taken literally, β-linkages would be much more prevalent in polypyrrole than previously appreciated, and the simple picture of a regularly α,α'-bonded polypyrrole would thus be grossly incomplete. Indeed, recent XPS studies of polypyrrole by Pfluger *et al.*[15] reveal that as many as one in three pyrrole rings is affected by structural disorder. Secondly, the poor crystallinity of polypyrrole[16] could in part be explained in terms of β-linkages. Thus, β,β'-dimethylpyrrole, which has both β-positions blocked with methyl groups, should contain none or few β-linkages, and indeed yields a much more crystalline polymer.[16] Lastly, the β-linkages could be an important source of defect sites, since they affect conjugation and thus the degree of π-spin density delocalization.

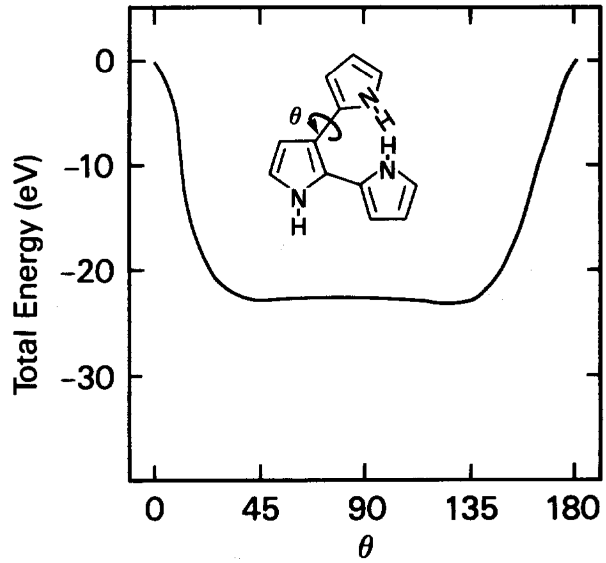


Figure 5. CNDO torsional potential diagram of 2,2':3',2''-terpyrrole.

Conformational Constraints

According to our hypothesis, the oligomeric radical cations which form during the $E(CE)_n$ electropolymerization reaction are the key intermediates which determine whether chain propagation continues, or termination results. These oligomeric radical cations require positions with appreciably localized spin density in order to undergo radical coupling with the reactive monomer radical cations. Because these oligomers are highly conjugated, it is not unreasonable to expect their stability to be sensitive not only to chain length, but also to deviations from planarity, which again affects the degree delocalization.

The spin density distribution in the 2,2'-bipyrrole radical cation [7], was given previously in Figure 3. INDO calculations of the torsional dependence of the spin density distribution in [7] predict that the 5,5'-positions have the highest spin density when the monomer units are coplanar, 0.0139 and 0.0140 for the anti and syn configurations, respectively (Figure 6). When the two monomer units are twisted by 90°, the spin density at the α-positions suffer little, to a minimum value of 0.0112. The spin density distribution at the other positions remain about the same. Thus, even with severe inter-ring twisting, the α-positions still remain the most reactive. However, because of the extensive delocalization operative in the dimer radical cation, INDO calculations predict a large torsional energy of 1.8 eV (Figure 6). The energy penalty associated with small deviations from planarity, however, is small. For example, a twist angle of 20° between the monomer units would cost only 0.1 eV. Thus, INDO predicts a rigid, coplanar configuration for the dimer radical cation, but allows for small deviations from planarity, without affecting its reactivity severely (Figure 6).

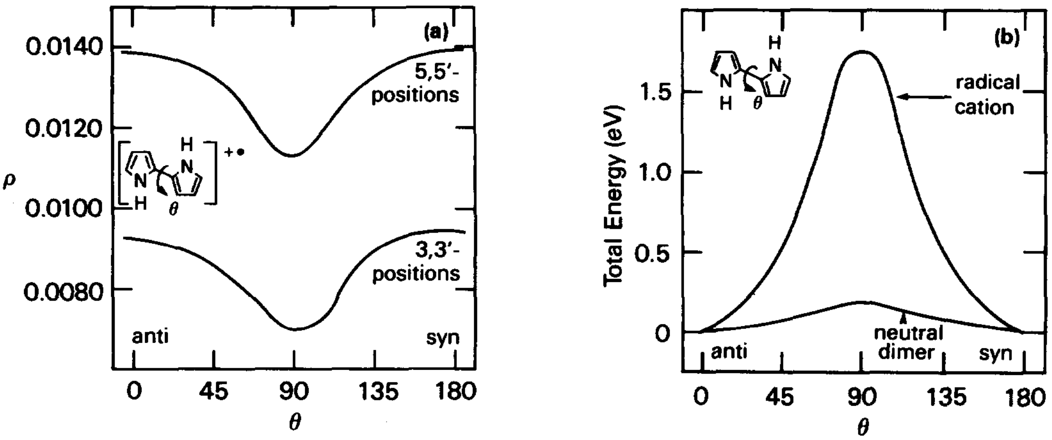


Figure 6. (a) The dependence of the spin density distribution in 2,2'-bipyrrole on the relative twist angle of the two monomer units. (b) INDO and CNDO torsional energy diagram of the 2,2'-bipyrrole radical cation and neutral dimer, respectively.

For the neutral dimer [6], CNDO calculations of the torsional potential portrays a barrier height of $\Delta E_{90}=0.18$ eV (Figure 6). Such a barrier height would, at ordinary temperatures, allow rapid rotation due to molecular collisions. However, Galasso *et al.*[17] have previously calculated *via* an extended Huckel molecular orbital calculation, a barrier height of ca. 0.40 eV, suggesting that the pyrrole dimer is a rigid molecule. These workers also calculated the barrier height of the related 2,2'-bifuran, which also exhibited a barrier height of approximately $\Delta E_{90}=0.35$ eV, leading to similar conclusions. More recent MIM calculations by Abu-Eittah *et al.*[18] support such a torsional energy for 2,2'-bifuran. Thus, by analogy, it appears that the CNDO method used here for 2,2'-bipyrrole underestimates the barrier height, at least when compared to the other methods.

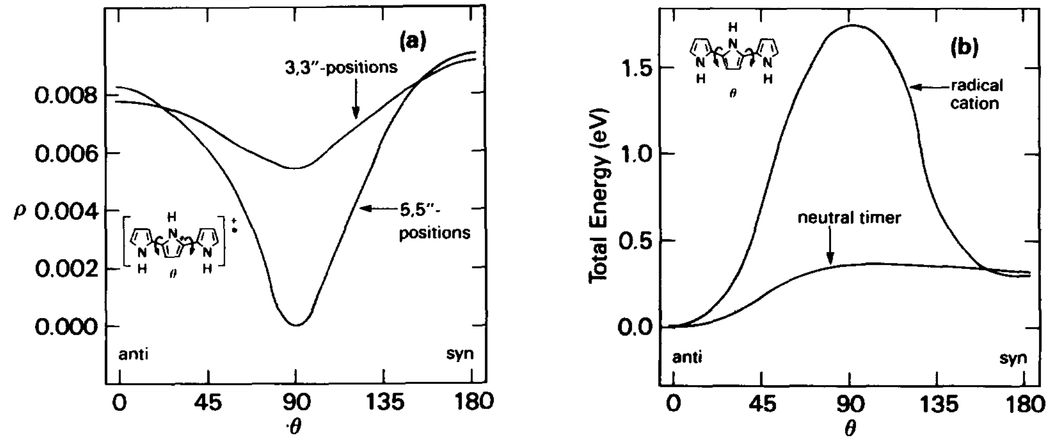


Figure 7. (a) The dependence of the spin density distribution in 2,2':5',2''-terpyrrole on the relative twist angle of the central pyrrole monomer unit. (b) INDO and CNDO torsional potential diagram of the 2,2':5',2''-terpyrrole radical cation and neutral trimer, respectively.

The reactivity of the 2,2':5',2''-terpyrrole radical cation [13], unlike that of the dimer radical cation, is severely dependent on the twist angle of the pyrrole rings (Figure 7) . Thus, while the 3,3''- and the 5,5''-positions have the highest spin density when the pyrrole units are coplanar, twisting the central ring by 90° reduces the spin density at the 3,3''-positions by approximately 30%, and the 5,5''-positions have virtually no spin density at this conformation. However, a torsional barrier of $\Delta E_{90}=1.7$ eV predicted by the INDO calculations prevents free rotation of the central ring. As with the dimer, small deviations from planarity (Figure 7) do not greatly alter the spin density distribution, *i.e.*, the reactivity of [13]. Our INDO calculations predict a minimum value at $\theta=0°$, which corresponds to the anti configuration. The anti form is lower energy by 0.30 eV than the syn form.

For the neutral trimer [12], CNDO calculations of the torsional energy predict a minimum at $\theta=0°$, and a barrier height of $\Delta E_{90}=0.38$ eV. The anti form is more stable than the syn form by 0.34 eV, and the barrier height of 0.38 eV is substantial at ordinary temperatures (Figure 7). Thus, the neutral trimer can be expected to be rigid and in the coplanar, anticonfiguration.[14]

To summarize, the INDO calculations predict that during electropolymerization, as the oligomeric units increase in chain length, the α-positions no longer remain the exclusively reactive sites. Also, INDO/CNDO calculations reveal that the reactivity of the pyrrole dimer and trimer radical cations are not greatly affected by small deviations from planarity. However, the steep barrier heights suggest that the monomer units in the polymer should strongly prefer to be coplanar.

CONCLUSIONS

The studies outlined here reveal that the reactivity patterns of oligomeric radical cations differ from those of the corresponding monomers, not only quantitatively, but also qualitatively. Thus, oligomeric $R^{\dot{+}}$ are predicted to be more stable, with reactive sites that can be chemically inequivalent to those of the monomers. This suggests that as the polymerization of aromatic molecules procedes, non-regular linkages can form in increasing fashion. For the case of polypyrrole, this means that whereas initially the oxidative coupling of the pyrrole nuclei will predominantly result in α,α-linkages, increasing chain length of the growing oligomer will render linkages to the β-positions of the pyrrole units competitive. This should result in a non-regular linkage pattern, and any attempt to bias analytical studies with the simple-minded view that polypyrrole is exclusively α,α'-linked could be quite frustrating, if not grossly misleading.

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