Electronic Properties and Transitions States involved in the Pyrrole Oligomerization

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ABSTRACT

The electrochemical pyrrole polymerization mechanism at initial stages is theoretically studied, through sequential monomer units coupling to obtain 2 to 9 oligomer formation. The transitions states, involved in the initial stages, give the sequential growing of oligomers and the electronic properties dependence. The relevance of these oligomers lies on their solubility in water as well as on the influence in uniformity of the final polymer film. The dependence of the growing chain and electronic properties has been studied by the Polarizable Continuum Method (PCM) and then water solvent effect is taking into account.

Keywords: pyrrole, transitions states, oligomerization, solvent effect, DFT study.

1 INTRODUCTION

The technological impact of polymer materials with conducting properties has been the aim of many academic and industrial studies to gain a better understanding of the phenomena involved in the synthesis and characterization of such materials. This is the case of polypyrrole, which is a polymer widely employed in industry [1], not only due to its inherent properties that make it amply usable in batteries, heavy duty capacitors, conductive textiles and fabrics, mechanical actuators, electrochemical sensors [2,3], but also due to its oxidative capability and water solubility. Furthermore, polypyrrole is commercially available and industrially produced [1, 4, 5]. The literature that has reported reaction mechanisms consider that such steps as electron transfer, proton transfer and direct pyrrole radicals formation may be involved during polymerization depending on the synthesis method used [4]. In the case of pyrrole electrochemical polymerization, it is assumed that the latter mechanism is the most likely reaction pathway. Additionally, the use of this method has shown that some operating variables like the nature of the electrolyte [6], the sort of solvent [7], the temperature [8] and pH [9] influence the process by promoting or controlling the interaction among the reaction intermediates.

The reaction mechanism involved during electrochemical polymerization appears to entail some difficulties [10-13]. The main one is related to the determination of the different reaction stages and polymerization's rate controlling step [12,13]. Apart from the poor solubility of certain pyrrole oligomers, there is the non-crystalline nature of the product that makes structure characterization and analysis of physical properties a difficult issue./ In this regard, quantum-chemical calculations provide additional information to elucidate the structure and stability of the species involved in the reaction mechanisms

2 METHODOLOGY

Calculations have been performed with *Gaussian03* [14] using the hybrid B3LYP functional [15] using the hybrid B3LYP (for singlet state) and UB3LYP (for triplet and doublet states) functional, with 6-311+(d, p) basis set in vacuo and with the Polarizable Continuum Method (PCM) [16] accounting for the solvent (water) effect.Geometry optimization calculations have been carried out for all the complexes involved (reactants, intermediates and products) and the frequencies were computed by using analytical second derivatives to check that the stationary points of the involved systems were corresponding to a minimum in the Potential Energy Surface (PES)./ For transitions state (TS) an initial guess was given and then the TS was relaxed in the direction of the reaction coordinate to verify that it connected the reactants and the product, by using IRC formalism implemented in Gaussian program. Frequency analyses were carried out to make sure first order saddle point for TS.

3 DISCUSSION AND RESULTS

To study the reaction mechanism of pyrrole dimmer it has made a scan of the dihedral angle N-C-C-N (ϕ) as it is shows in the Figure 1. The dimer formed displays different conformations around the Potential Energy Surface (PES) when torsion of the dihedral angle, -N-C-C-N- (ϕ) is carried out, vide Figure 1. The profile of the PES is rather similar to early reported by Yurtsever et at. [17]; where different levels of theory were compared. The relative dihedral angle rotation freedom may produce two more stable conformations which correspond to the nitrogens lying in a semi-trans (namely, trans-) and semi-cis conformation (namely,

cis-), the dihedral angle ϕ is about 28.5 and 44.9 degrees, respectively; and they are denoted as the trans-Prod1, and cis-Prod2 in Figure 1c. This result agrees with reported in [17]./ The notation cis- or trans- in this work is not a properly cis- trans- isomerization but we use this notation for the sake of simplicity and clarity.

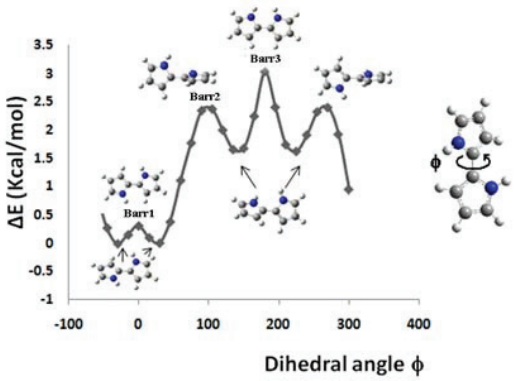


Figure 1. Graphical representation of the PES for the dihedral angle torsion, -N-C-C-N- (ϕ) showed on the right side of the picture. This graph displays the energy associated to the different model structural conformations. Level of theory B3LYP/6311+(d,p).

From the PES, vide Figure 1; the maximums in the profile correspond to perpendicular and planar conformations contrary to semi-empirical and smaller bases set than 4-31 are used [17], in which cases those conformations resulted as minima in the PES [11,17, 18], therefore a caution has to be taken when those levels of calculations are used. Then for the 6311+(d,p) where taken only the minimal conformations. The analysis of the differences among the structural changes along the PES, in Figure 1, shows that trans- and cis- conformations are minimums as the frequency calculation showed only positive values and also they are situated at minimum positions within the PES, being trans- more stable than cis- phase by 2.33 Kcal mol^{-1}. According to the picture, reaching the cis- conformation from trans- conformation requires a large energy supply of 2.37 Kcal mol^{-1} (Barr2), Barrier 1 (Barr1) indicates the amount of energy to the rocking mode between trans—trans passing by the planar conformation and is about 0.11 Kcal mol^{-1}; barrier 3 (Barr3) is about 1 Kcal mol^{-1} and indicates the amount of energy to the rocking mode but now between cis—cis conformation passing by the planar conformation. Based on the computed results, the energy barrier for converting the cis- into trans- structural conformation is not so high, and then both phases can be exit when the polymer is growing, although to reach cis- to trans- required less energy than the vice-verse.

It has been reported two mainly mechanisms to dimmer formation, where when the reaction mechanism in which the pyrrole radical cation, formed by imposing a potential to the electrode surface, reacts directly with a neutral molecule [19], vide Figure 2, or the chemical process goes through the reaction of two radical cations ($Py^{\bullet+}$) [20], vide Figure 3, in which case, both yielding the same products, namely, cis-prod and trans-prod. The latter system has two associated stages a single state in which the electrons could be coupled, and triplet state in which the electrons remain uncoupled, for triplet states UB3LYP/631+(d,p) level of theory was used. Now, for the first mechanism, the charge and mass balance of the overall process is similar to the one previously discussed, but the chemical process differs by the sequential steps and the intermediate species involved, see Figure 2 and 3. Since in this mechanism there are only one electron and one positive charge, then a doublet state is associated to the intermediate formed/ and for this study also UB3LYP/631+(d,p) level of theory was used.

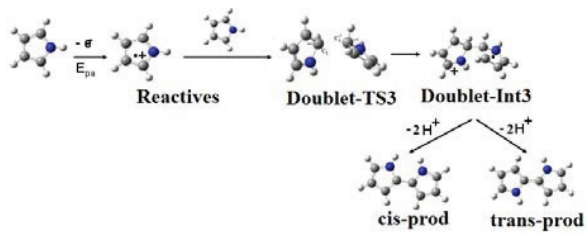


Figure 2. Reaction mechanism for one radical cation with a neutral molecule.

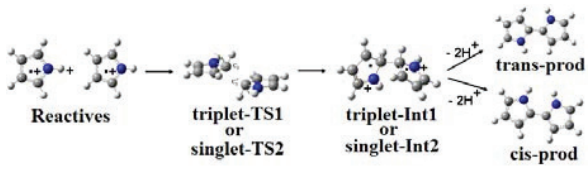


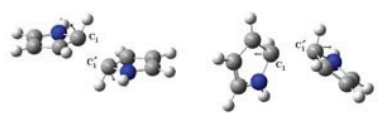
Figure 3. Reaction mechanism of two radical cations.

Then in the Table 1 shows the energy values obtained for both mechanism and also it is taking into account the solvent water effect. So, the non-interacting system for each mechanism followed was considered as a reference.

Now it has been discussed the case of the radical cation-radical cation interaction, [($Py^{\bullet+}$) + ($Py^{\bullet+}$)]. Table 1 shows the ΔE for the different intermediate systems involved and their degree of stabilization, *in vacuo*. The ΔE for the singlet and triplet states were calculated from the difference in energy between products and reagents, i. e., [($^{\bullet+}Py$—$Py^{\bullet+}$)] – [($Py^{\bullet+}$) + ($Py^{\bullet+}$)], vide Table 1, in which for the singlet state yielded 31.9 kcal mol^{-1} for cis-int1 intermediate and 32.4 kcal mol^{-1} for trans-int1 intermediate over the reactants energy. Of course, to reach these intermediates a Transition State (TS) are involved for each one. The structure obtained for the TS is shown in the Figure 4(a), for the $^{\bullet+}Py$—$Py^{\bullet+}$ approaching. The calculated activation energy for Singlet-TS2 corresponds to 71.57 Kcal $mol^{-1,}$ for trans- and 56.88 Kcal mol^{-1} for cis- conformations. Analysing its corresponding Singlet-TS2 geometry, the arrows in the Figure 3 indicate the displacements associated to the imaginary frequency. The C_1-C_1' distance in both

involved transitions states, one to trans- one to cis-conformations is 2.20 Å, same as that reported by Lacroix et al. [21] and their activation energy value by [21] is about 74.5 Kcal mol^{-1} at AM1//AM1 and 60.5 Kcal mol^{-1} at B3LYP//AM1 levels of theory in gas-phase; but it is not specified for which specific state.

For the triplet state only one intermediate Cis-int1 was stabilized, Trans-int1 was not stabilized, a repulsion effect for trans- isomer was observed. Then, the energy obtained for the Triplet-TS1 in cis- conformation is 120.71 kcal mol^{-1} and the energy stabilization to reach Triplet-Int1 (cis-conformation) is about 26.71 kcal mol^{-1}, with activation energy of 94.0 kcal mol^{-1}. All the differences energy values for the associated intermediates are higher than for the non-interacting system, which means that high activation energy is required, thus, this interaction might not be favored at vacuo conditions. That is not the case for the pyrrole radical cation interacting with a neutral molecule as can be seen in the Table 1, where only one associated transition state was obtained and it corresponds to cis-conformation. The Doublet-TS3 looks like the Cis conformation obtained the two radicals cations interactions. Nevertheless this doublet-TS3 yielding the cis- trans- conformation intermediates and now a stabilization of 12.0 and 20.0 kcal mol^{-1} with respect to the non-interacting system is obtained for cis and trans, respectively.



(a) **(b)**

Figure 4. Transitions states geometries, for the pyrrole-pyrrole interaction. (a) to trans conformation and (b) to cis conformation. The pictures displays the Schematical displacements associated to the imaginary frequencies of the corresponding TS. The C_1-C_1' distance in the TS is 2.20 Å. Level of theory B3LYP/6311+(d,p).

When water in taking into account as a solvent, by PCM, it is showed meaningful changes, as can be compared in the Table 1. The activations barriers diminish enormously does not matter which mechanism is about, but also, the profile in inverted and now the radical cation interactions results stabilized more than radical cation-neutral molecule by about 30 kcal mol^{-1}. It has to be noted that both cis-, trans- conformations are stabilized in the same proportion which means lower selectivity by water presence, as they have also similar energy activation (Singlet-TS2) also. The triplet state again is not stabilized. For the radical cation interacting with a neutral molecule seems more selective to trans- conformation, compare Doublet-TS3 with Doublet-Int3 in the last column of the Table. This obtained result gives an insight of the mechanism profile and some preferences that could be governed in a reaction oligomerization, which certainly gives the final properties of the product.

Systems	*In vacuo*		With solvent effect (water)	
Non-interacting	$(Py^{\bullet+})$ + $(Py^{\bullet+})$	$(Py^{\bullet+})$ + Py(N)	$(Py^{\bullet+})$ + $(Py^{\bullet+})$	$(Py^{\bullet+})$ + Py(N)
Reference system	0.00	0.00	0.00	0.00
Interacting	$(^{\bullet+}Py—Py^{\bullet+})$	$(Py^{\bullet+})$—Py(N)	$(^{\bullet+}Py—Py^{\bullet+})$	$(Py^{\bullet+})$—Py(N)
Triplet-**TS1**	120.71 (Cis) ----- (Trans)	----	59.17 (Cis) ------- (Trans)	----
Triplet-**Int1**	94.0 (Cis) ----- (Trans)	----	26.0 (Cis) ----- (Trans)	----
Singlet-**TS2**	56.88 (Cis) 71.57 (Trans)	----	9.79 (Cis) 11.03 (Trans)	----
Singlet-**Int2**	31.9 (Cis) 32.4 (Trans)	----	-35.7 (Cis) -37.4 (Trans)	----
Doublet-**TS3**	----	14.18 (Cis) ----- (Trans)	----	2.67 (Cis) 25.8 (Trans)
Doublet-**Int3**		-12.0 (Cis) -20.0 (trans)		1.0 (Cis) -6.0 (trans)

Table 1. Energy difference values, in kcal mol^{-1},for intermediate systems and transitions states (TS) involved in the reaction mechanism for the two processes, in vacuo and with solvent effect. Non-interacting system is taking as a reference state. Calculated values are at B3LYP/6311+G(d,p) level of theory. Vide Figures 2 and 3 for identified the involved systems.

Chain lenght	Eg, eV		
	In vacuo	Solvent effect	Experimental (23)
1	5.55	5.95	5.96
2	4.82	4.79	4.37
3	4.17	4.20	3.61
4	3.87	3.91	3.48
5	3.63	3.67	2.82
6	4.07	4.10	2.77
7	3.43	3.46	2.45
8	3.37	3.40	2.28
9	3.34	3.37	2.10

Table 2. $|E_{HOMO}-E_{LUMO}|$ (E_g) energy difference for the different oligomers, calculated in vacuo and with water as solvent effect. Comparison of the PCM calculated energy gap (Eg) for Py and the sequential formed oligomers until 9 units at in vacuo and with water (solvent) effect. Applied level of theory: B3LYP/6-311+(d,p). Eg= $|E_{HOMO}-E_{LUMO}|$, Chain lenght=number of coupled Py units (oligomers)

When the oligomer increases, some of the electronic properties changes as the $|E_{HOMO}-E_{LUMO}|$ (E_g) energy difference. In the Table 2, the growing of Py-oligomer is presented and depicted schematically in Figure 3. The comparison involves experimental literature reported values. It can be observed that for the initial monomer

and until the 4 units Py-oligomer, the trend in theoretical calculated E_g for both at in vacuo and with water conditions decreases, in line with the experimental energy values, vide Table 2. However, from the 5 units Py-oligomer on there is a more pronounced difference between these E_g´s being more notorious for the 6 units Py oligomer where the theoretical energy suddenly increases to start lowering again for the further Py-oligomer. Within these calculations, the properties of water such as dipolar momentum and conductivity were accounted for, but no strong contribution to the calculated E_g is observed as compared to vacuo conditions, vide Figure 5.

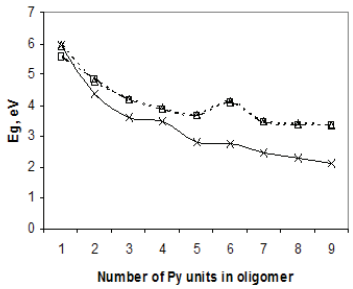


Figure 5. Calculated energy Eg, at in vacuo conditions (□) and in the presence of water (Δ) and that experimental literature reported (X) (17), as a function of the chain length of the Py-oligomer. Level of theory: B3LYP/6-311+(d,p). $Eg = | E_{HOMO} - E_{LUMO} |$.

4 CONCLUSION

The mechanism involving one neutral and one radical cation interaction yields better stabilization in vacuo than when the water is presented, contrary to the two radicals cations interaction, where water presence stabilized the transitions states and intermediates. The obtained results showed that when water is taking into account, by PCM, the reaction mechanism stabilized the transitions states involved along the reaction and gives low selectivity to the products, as cis- trans- conformation have similar stabilization.

The electronic properties of the pyrrole molecule and its consecutive oligomers until a 9 units Py-oligomer were calculated finding proper fit to those experimental reported values. The stabilization of E_g for all the molecules decreases as the oligomer chain length increases which is ascribed to the distribution through the HOMO-LUMO of the stepwise products. No apparent energy contribution from water, used as solvent, on the formed stepwise Py-oligomer is obtained. This indicates that water does not affect the final oligomer properties, but it contributes to Py activation energies by enhancing the polarization of the reactant molecule as compared to vacuo conditions in line with experimental reported results.

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