

Theoretical Study of the Configuration of Pyrrole Oligomers.

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It is common knowledge that polypyrrole is formed in the polymerization reaction of charged oligopyrroles in strong interaction with counter anions, thus, experimental and theoretical study of oligomers gives also insight into the synthesis process of polypyrrole.

In the present work semi-empirical quantum chemical calculations with AM1 [1] and PM3 [2] parameterizations from the Mopac package were applied for the study of *syn* and *anti*-conformations (Fig. 1) of charged and uncharged pyrrole oligomers with and without counter-anions.

In many cases, only the uncharged and all *anti* conformation pyrrole oligomers (and polymer chains) are considered significant for the (theoretical) description of polypyrrole. The critical influence of (positive) charge as well as the charge-compensating presence of the anions is often overlooked. Calculations [3] have indicated that the all-*anti* is indeed the most energetically favorable conformation of uncharged as well as charged pyrrole oligomers.

However, the situation is changed if counter-ions and the effect of the polar medium are also taken into account. The calculated dipole moments and the stabilizing effect of anions for pyrrole oligomer cations in *syn* conformation are much higher than that of the respective *anti* conformers. This suggests that the oligomer cations formed during the synthesis process of polypyrrole in the polar medium and in the presence of anions may take the *syn* conformation.

The corresponding structure of the polymer chain built up of *syn* oligomers would be the helical coil (Fig. 2.). These types of helical configurations resulting in rod-like formations have been obtained experimentally [4]. The size of the stepping between the rings in the coil depends strongly on the charge on the coil as well as on the choice of the counter anions compensating the charge.

Depending on the anions and the level of doping of the oligomers the second anion may change the structure of the oligomer completely. In case of helical coils and high doping levels the anions inside the coil cannot get too close to each other as their negative charges have strong repulsion. An alternative configuration could be something in between the all-*syn* and the all-*anti* conformations. In this configuration the anions are placed reasonably far apart for minimal repulsion and still have strong interaction with the oligomer. In addition, the oligomer is planar, thus, enabling the positive charge to be well delocalized.

This kind of chains can be packed quite tightly together, resulting in higher crystallinity and poor mobility of anions.

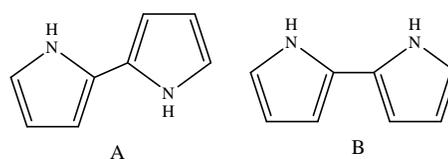


Fig. 1. Pyrrole dimers in A) *anti*; B) *syn* conformation.

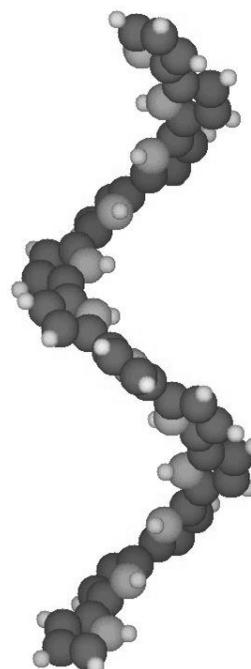


Fig. 2. AM1 optimized helical coil of a neutral 12-unit pyrrole oligomer in all-*syn* conformation.

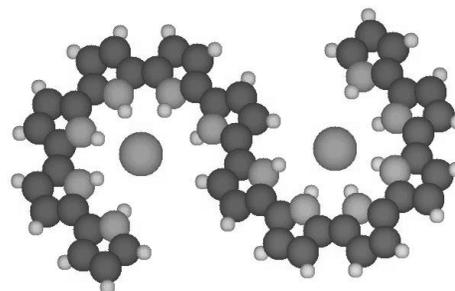


Fig. 3. AM1 optimized 12-unit pyrrole oligomer tetra-cation (Py)₁₂⁺⁴ with two anions in the "S-configuration".

References.

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