

POLYCARBONITRILE: A DFT INVESTIGATION OF STRUCTURAL STABILITY

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INTRODUCTION

The fact that polyacetylene (PA) $[C_2H_2]_\infty$ is isoelectronic with polycarbonitrile (PCN) $[CHNH]_\infty$ has caused many theoretical studies to investigate the later compound in diverse levels of theories, but using a fully trans structure [1], since this is the most stable structure for PA. More recent studies of the structural and thermodynamic stability using PCN in fully trans, cis-transoidal, and trans-cisoidal configurations have indicated that the cis-transoidal structure is more stable than a fully trans [2] showing that the use of the fully trans configuration of the PCN can generate errors, as for example the study polarizability and hyperpolarizability of this polymer [3].

In this work the structural stability of polyacetylene with different number of monomeric units was evaluated by substituting carbon atoms by nitrogen, but maintaining nitrogens always separated by at least one carbon atom.

METHODS

Different structures in the ground state was analyzed at the density functional theory (DFT) level with different functionals such as: B3LYP, CAM-B3LYP and M06-2X and aug-cc-pVDZ basic functions. Maximum and minimum points were also analyzed by using ab initio

calculations at the CCSD(T) and QCISD levels. All calculations were performed using the Gaussian09 program.

RESULTS AND DISCUSSION

A total of 34 isomers were analyzed by fixing the central dihedral angle of the structure every 5 degrees and optimizing all other geometric parameters. The conformational energy of pure PA is confirmed to be the fully trans planar as the most stable structure. The substitution of 2 alternating carbons by 2 nitrogens in trans configuration still shows to be the most stable. However, in these cases, a most stable conformation between the cis structure and the trans structure was observed presenting a stability of the order of $1.7 \text{ kcal mol}^{-1}$ relative to the trans configuration (see Fig.1 as example).

For tetramers, the structure of the PA in trans conformation has a difference between cis and trans of $3.4 \text{ kcal mol}^{-1}$. The rotational barrier for the cis-trans interconversion is of the order of $8.2 \text{ kcal mol}^{-1}$. The substitution of 2 carbons alternated by 2 nitrogens reduces this difference to $1.9 \text{ kcal mol}^{-1}$. The difference between the structures in of tetramers in which nitrogens are not alternating, the rotational barrier is of the order of $6.0 \text{ kcal mol}^{-1}$. The substitution of 3 alternate carbons leads to a more stable intermediary

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Simpósio Brasileiro de Química Teórica 2017

12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

conformation with an equilibrium dihedral angle of 40° and a difference of $1.3 \text{ kcal mol}^{-1}$ concerning trans configuration and $1.4 \text{ kcal mol}^{-1}$ for the cis configuration. The rotational barrier from trans to cis is of the order of $2.5 \text{ kcal mol}^{-1}$. Polymers with 3 carbon with no alternating nitrogen present the trans conformation as most stable by $6.8 \text{ kcal mol}^{-1}$ with respect to cis, while with 2 alternating nitrogens the difference is $6.1 \text{ kcal mol}^{-1}$.

The relative conformational energy curve of the polymer with the 4 alternating carbons replaced by nitrogen is shown in Figure 1. One of the most stable structures is shown in Figure 2.

CONCLUSIONS

Our results indicate that PCN or similar compounds are unlikely to be planar as suggested previously in an exploratory work [3]. The PA modifications replacing carbons by nitrogens and increasing the chain has produced non-planar stable structures with equilibrium dihedral angles between $\pm 40^\circ$ and $\pm 60^\circ$. These non-planar structures differ from those used in literature to study optical properties of PCN. Most likely, significant changes in the calculated optical and electronic properties of PCN will be observed with respect to the literature [4]. Calculations in this sense are in progress and will be presented in the meeting.

Key-words: Polycarbonitrile, Conformational analysis, Density functional theory, Electronic properties

Support: The authors would like to thank the financial support from: FAPESP –

CEPID, CNPq, FAEPEX– UNICAMP and CENAPAD-SP.

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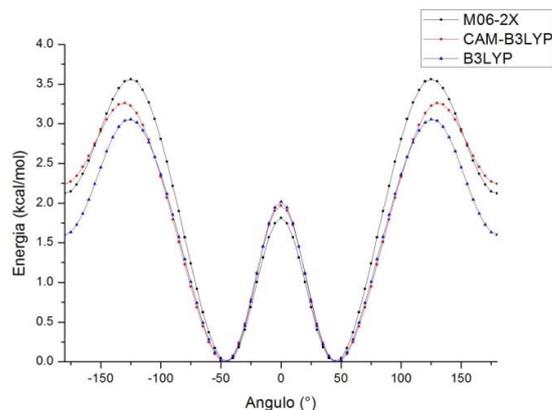


Figure 1. Relative conformational energy curve as a function of the dead center of the single central bond of the compound $\text{HN}=\text{CH}-\text{N}=\text{CH}-\text{N}=\text{CH}-\text{N}=\text{CH}_2$.

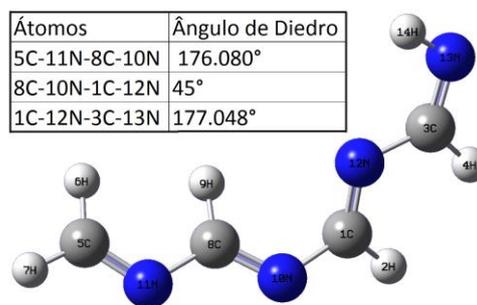


Figure 2. More stable conformation of the compound $\text{HN}=\text{CH}-\text{N}=\text{CH}-\text{N}=\text{CH}-\text{N}=\text{CH}_2$ and dihedral.