POLYCARBONITRILE: AN EVALUATION USING ELECTRONIC STRUCTURE METHODS TO ANALYZE THEIR RESPECTIVE ELECTRONIC AND STRUCTURAL STABILITY

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Abstract

This work presents an investigation of the structural stability of polycarbonitrile with different monomeric units to confirm the pertinence of not using a cis-trans geometry, but an intermediate structure. Thermochemical and non-linear optic properties are calculated and compared to different conformations at the density functional level of theory.

Key words: Polycarbonitrile, Electronic structure, Structural stability

Introduction

The fact that polyacetylene (PA) is isoelectronic with polycarbonitrile (PCN) has induced many theoretical studies to investigate PCN using a fully trans structure.¹ Del Nero, Laks and Custodio analyzing conformers in totally trans, cis-transoidal, and trans-cisoidal structures using semi-empirical, Hartree-Fock, MP2 and density functional theory (DFT) methods suggested that there was a possible planarity deviation to reach the global minimum of the energy surface.^{2,3} Therefore, theoretical data for PCN from the literature may present significant deviations if this non-planarity is not taken into account.

The objective of this work is to show that the use of fully trans molecular geometry for PCN can generate significant errors in the interpretation of the results, such as polarizability and hyperpolarizability, because these properties are intrinsically related to the spatial arrangement of the atoms in the molecule.

Methods

Different structures in the ground state were analyzed at the DFT level of theory using the following functionals: B3LYP, CAM-B3LYP, and M06-2X with aug-cc-pVDZ and aug-cc-pTDZ basis functions. These functionals are recognized for their accuracy, frequent use and the last two include dispersion correction. From these calculations, extrapolation formulas for complete basis set were estimated. The calculations were performed with the Gaussian 09 program.

Results and Discussion

The rotational barrier of the central C-N single bond of PCN was carried out to determine the most stable structure of the polymer. This analysis was done with 4, 8, and 12 monomeric units and some results are summarized in Fig.1. Non-linear optical properties, such as anisotropy of polarizability and hyperpolarizability, were calculated for each dihedral angle, and some results are summarized in Table 1.

Figure 1. Energy profile for PCN at the DFT CAM-B3LYP level.

Table 1. Non-linear optical properties calculated at the DFT B3LYP level of theory for PCN 8.

	Trans	Cis	Global minimum
Polarizability (a.u)	144.21	97.900	90.661
Hyperpolarizability (a.u)	1341.2	487.31	382.61

Conclusions

From the analysis of the rotational energies, the more stable structure of PCN presents a significant deviation of the planarity. The properties calculated from different conformational structures changed drastically. The most significant changes were observed for hyperpolarizability.

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¹ Springborg M. A comparison between polyacetylene and polycarbonitrile. Zeitschrift für Naturforschung A. 1993 Feb 1;48(1-2):159-64.

² Del Nero J, Laks B, Custodio R. Polycarbonitrile: A semiempirical, ab initio and density functional study of molecular stability. Synthetic metals. 1997 Mar 15;85(1-3):1127-8.

³ de Moraes G, Custodio R. Polycarbonitrile: A DFT investigation of structural stability.