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POLYCARBONITRILE: A SEMIEMPIRICAL, *AB INITIO* AND DENSITY FUNCTIONAL STUDY OF MOLECULAR STABILITY

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Abstract

The theoretical literature data with respect to the electronic properties of this compound is quite scarce and makes use of the planar all-trans structure as the most stable for the calculations. In this work semiempirical (AM1 and PM3), *ab initio* (at the Hartree-Fock level) and density functional theory (using the correlation functional of Vosko, Wilk and Nussair) were used to analyse the conformational stability of the all-trans and all-cis dimers, trimers and tetramers of polycarbonitrile. The semiempirical and ab initio calculations at the Hartree-Fock level showed in general that the all-trans structure with respect to other conformers is the most unstable structure. The inclusion of electronic correlation energy through the MP2 calculations or the VWN functional method suggest that the trans structure is the most stable. The relative energies calculated at the correlated level presented differences around 2 kcal/mol among the different conformers. While the all-cis compounds presented a planar structure for any of the three methods, the all-trans polymer showed a strong deviation of planarity with a set of local minima in its energy surface. These results suggest that further calculations on the electronic properties of this polymer can be significantly different of those actually available in the literature.

key words: polycarbonitrile, semiempirical, *ab initio*, density functional method, conformational structure.

1. Introduction

Even though trans polycarbonitrile shows many similarities with trans polyacetylene, it is not clear that polycarbonitrile can be considered a synthetic metal [1]. The first theorical study done by karpfen [2], employing ab-initio crystal orbital calculations, predicted that the structure with alternating carbon-nitrogen bond distances is more stable than the equidistant one, in complete analogy to what occurs with polyacetylene. Brédas et al. [3], using the valence effective hamiltonian approach, folowed the geometry optimized by Karpfen to carried out band structure calculations of polycarbonitrile.

2. Methods

The molecular geometry of the dimer, trimer and tetramer of carbonitrile were fully optimized using semiempirical, *ab initio* and density functional methods.

The standard 3-21g and 6-31g basis sets were used for all *ab initio* calculations. A single polarization function was included in the 3-21g basis set for atoms other than hydrogen, 3-21g*. The calculations using the 6-31g basis set included polarization functions in all atoms, 6-31g**. The small size of the dimer allowed the inclusion of eletronic correlation by means of Møller-Plesset (MP) perturbation theory to second order [4].

The structure of the three molecules were also optimized through the density functional theory using the correlation functional of Vosko, Wilk and Nusair (VWN) [5] with DN** basis set.

3. Results and Discussion

The analisys of the conformational stability was carried out through the difference between the total energy of a conformer and the total energy of the trans specie ($\Delta E = E(\text{conformer}) - E(\text{trans})$). Table 1-3 shows the relatives energies of different conformers of the dimer calculated by the semiempirical, *ab initio* and density functional methods. A general overview indicates a similar tendency of the results obtained at the Hartree-Fock (HF) level of theory. The semiempirical (AM1 and PM3) and the Hartree-Fock *ab initio* (3-21g* and 6-31g**) calculations suggest that the trans-cis conformer is more stable than the trans one. The AM1 method provides a greater stability of the trans-cis structure than the PM3 and HF *ab initio* methods. However, the inclusion of electronic correlation effects through the VWN funcional or the MP2 *ab initio* method change the order of stability. Both methods suggests that the trans conformer is more stable than the trans-cis specie. While the MP2 calculations provides a small difference in energy favoring the trans specie, the VWN funcional shows a greater stability of the trans specie by ≈1kcal/mol. The better performance of the

methods including correlation energy in literature when compared with Hartree-Fock results and the agreement between VWN and MP2 suggest that these results are describing more realistically the conformational stability of the carbonitrile dimer than the Hartree-Fock results.

Considering the larger size of these molecules the correlation energy was analyzed only through the density functional calculations.

Table 1-4 shows the total and the relative energies of some of the trimer conformers. Once more the semiempirical and Hartree-Fock *ab initio* results indicate that the trans conformer is the most unstable specie. However, the inclusion of correlation energy energy through the VWN functional changes the order of conformational stability. The same conclusion can be observed with respect to the tetramer. Some interesting trends can be observed in Tables 1-5. The AM1 provides the largest relative energies for the dimer, trimer and tetramer when compared with any of the *ab initio* results. On the other hand there is a reasonable agreement between the PM3 relative energies and those calculated for the three molecules by the *ab initio* method with the 3-21g* basis set. The improvement in the basis set, from 3-21g* to 6-31g**, tends to increase the stability of the trans conformer although the trans conformer is still the most unstable structure. The inclusion of electronic correlation energy through the VWN functional change the order of stability suggesting that the trans structure is the most stable one. However, the relative stability is not very pronounced. The VWN results suggest a difference in energy around 2 kcal/mol supporting the greater stability of the structures. In other words, it is difficult to suggest from such small relative energies that the structure of the polymethineimine polymer is predominantly a trans structure. It is more reasonable to suggests that the polymeric structure is a combination of a sequence of different conformers.

4. Conclusion

The semiempirical and *ab initio* calculations at the Hartree-Fock level showed that the all-trans structure with respect to other conformers is the most unstable structure. The improvement in the basis set at the *ab initio* Hartree-Fock level tends to increase the stability of the trans conformer although the trans conformer is still the most unstable structure. The inclusion of electronic correlation energy through the MP2 calculations or the VWN functional method suggest that the trans structure is the most stable. The relative energies calculated at the correlated level presented differences around 2 kcal/mol among the different conformers. These small differences in the relative energies and the not so high rotational barrier among some conformers suggest that the polymeric structure is not constituted by a single conformer, but probably by a combination of different conformers.

Another interesting aspect observed with respect to the structure of the larger structures is that the all-cis compounds presented a planar structure for any of the three methods. However, the all-trans polymer showed a strong deviation of planarity with a set of local minima in its energy surface. Considering that some of the calculations on the electronic properties available in the literature were carried out with the all-trans planar structure, the nonplanarity of the trans structure suggests that significant changes in the available information should be expected.

5. References

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Table 1. Relatives energies for $C_2N_2H_4$, $C_3N_3H_5$ and $C_4N_4H_6$

Method	conformer	ΔE (trans=0)	ΔE (trans=0)	ΔE (trans=0)
AM1	TRANS	0	0	0
AM1	TRANS-CIS	-6.81	-14.536	-16.24
AM1	CIS-TRANS	--	-8.078	-22.678
PM3	TRANS	0	0	0
PM3	TRANS-CIS	-3.08	-6.735	-6.671
PM3	CIS-TRANS	--	-3.632	-10.655
FDT/VWN**	TRANS	0	0	0
FDT/VWN**	TRANS-CIS	1.682 E-3	4.513 E-3	-3.917 E-3
FDT/VWN**	CIS-TRANS	--	1.6184 E-3	3.578 E-3
3-21G*	TRANS	0	0	0
3-21G*	TRANS-CIS	-5.177 E-3	-1.23247 E-2	-1.32671 E-2
3-21G*	CIS-TRANS	--	-7.0034 E-3	-1.85108 E-2
6-31G**	TRANS	0	0	0
6-31G**	TRANS-CIS	-1.673 E-3	-7.5035 E-3	3.2215 E-3
6-31G**	CIS-TRANS	--	1.8773 E-3	-6.3705 E-3
MP2-6-31G**	TRANS	0	--	--
MP2-6-31G**	TRANS-CIS	2.694E-4	--	--