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Chemical Physics Letters 406 (2005) 504–508
CHEMICAL PHYSICS LETTERS
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Conformational properties of poly (vinyl Fluoride) based upon ab initio electronic structure calculations

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Received 15 December 2004; in final form 4 March 2005
Available online 31 March 2005

Abstract

The geometries and conformational energies of model segments of poly (vinyl fluoride) (PVF) are obtained from quantum chemistry calculations and used to determine the statistical weight parameters in a rotational isomeric state (RIS) model. The interaction energies show that the electrostatic interaction is important in the molecules containing high electronegative atoms. The calculated characteristic ratio is in agreement with available theoretical values by means of molecular mechanics (MM).

1. Introduction

In past several decades, the RIS method has became a popular tool to analyze the physical properties of polymers [1,2]. However, it is important to obtain the statistical weight parameters in RIS theory. The conformational energies are used to determine the rotational interaction energies, by means of which statistical weight parameters can be obtained. This method of determining the statistical weight parameters requests the accuracy of conformational energies. It is popular to calculate conformational energies and geometry properties by MM method. But the MM calculations do not explicitly treat the electrons in a molecular system [3]. Instead, the calculation is based upon the interactions among nuclei. Therefore, the MM method can not accurately describe the molecule systems where the electronic effects are predominant. Moreover, the force field achieved good results only for a limited class of molecules. No force field can be generally used for all molecular systems. In recent years, electronic structure theory has been developed quickly. In order to better quantify the conformational energies, several groups have successfully employed ab initio electronic structure (quantum chemistry) calculations on the model segments of polymers. Quantum chemistry calculation bases upon the interactions among electrons rather than nuclei. So it can describe molecular systems where the electronic effects are predominant and be applicable for all kinds of molecules. Smith et al. have performed quantum chemistry calculations for many polymer systems and achieved good results on the conformational energies [4–7].

Carballeira et al. [8] have analyzed the conformational characteristics of PVF and poly (vinyl bromide) (PVB) by modeling dimers and trimers using MM method. The results provide the geometry and total conformational energy data required for the parametrization of the RIS model for PVF and PVB. In this work, we employ high level ab initio quantum chemistry calculation on 2,4-difluoropentane (DFP) and 2,4,6-trifluoroheptane (TFH) in an attempt to estimate the contribution of electronic effects to the conformational energy in PVF. The interaction energies determined are different from those from MM calculations. In this Letter, we first present the geometries and conformational energies of DFP and TFH obtained from quantum chemistry calculations, then describe the

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doi:10.1016/j.cplett.2005.03.046

parametrization of an RIS model, which is used in calculating the physical properties of PVF.

2. Quantum chemistry calculations

Geometries and conformational energies of model segments of PVF, i.e., DFP and TFH, are determined at MP2 level using a 6-311++g** basis set. Conformational geometries are determined by fully optimizing the original molecule geometries. Vibrational frequencies are calculated to verify the stationary points. All quantum chemistry calculations are performed with the quantum chemistry package GAUSSIAN 03. Fig. 1 shows the chain characteristics for DFP and TFH. We have designated those carbon atoms with F atom occurring in front of the plane as 'D' center, and those with F behind as 'L'. Tables 1 and 2 list energies and geometries of the most important conformers of DFP and TFH, respectively. The energies are given with respect to the lowest energy conformation of each model molecule. Other conformers having higher energies are not stationary.

The trans state 't', gauche states 'g^+' and 'g^-' are defined in Fig. 2. The states g^+ and g^- are related to the state t by clockwise and counterclockwise rotation of 120°, respectively. Depending on the quantum chemistry calculated geometries, the torsion angles deviate generally from the standard values 180° (t), 60° (g^+) and −60° (g^-) by 5–15° in either directions in order to alleviate steric and electrostatic repulsions. It should be noted that the steric and electrostatic repulsions are between the atoms and groups separated by three bonds (first-order interaction), which

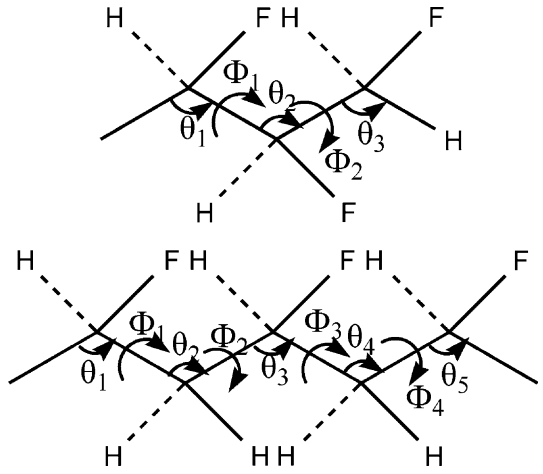

Fig. 1. Chain characteristics for DFP and TFH.

Table 1
Calculated geometries and total energies of 2,4-difluoropentane, angle in degree, energy in kcal/mol

Conformer	ϕ_1	ϕ_2	θ_1	θ_2	θ_3	Energy
LDtt	177.3	177.2	113.5	113.1	113.5	0.00
LDtg$^+$	172.1	74.6	115.5	114.9	113.0	1.60
LDg$^+$g$^+$	60.4	60.4	114.3	114.3	114.3	2.14
LDg$^-$g$^-$	−52.2	−52.2	116.5	118.3	116.5	2.60
LDg$^+$g$^-$	92.7	−56.1	116.7	115.3	114.9	3.53
LDtg$^-$	−176.1	−42.4	115.2	116.4	112.7	3.48
LLtg$^-$	−173.5	−60.4	114.5	113.9	113.3	1.00
LLtg$^+$	164.0	55.1	113.1	115.1	116.1	1.16
LLg$^+$g$^+$	66.3	50.0	115.2	116.4	115.3	2.26
LLtt	171.8	−169.6	112.8	115.5	112.9	3.26
LLg$^+$g$^-$	63.7	−96.3	114.7	113.8	115.7	3.27

Table 2
Calculated geometries and total energies of 2,4,6-trifluoroheptane, angle in degree, energy in kcal/mol

Conformer	ϕ_1	ϕ_2	ϕ_3	ϕ_4	θ_1	θ_2	θ_3	θ_4	θ_5	Energy
DLDtttt	−177.5	−178.2	−178.2	177.4	113.4	113.0	113.2	113.0	113.4	0.00
DLDttg$^+$g$^+$	−177.0	−178.1	62.7	58.1	114.3	114.3	114.3	112.8	113.4	1.54
DLDttg$^+$g$^-$	−174.9	−171.7	95.0	−55.2	116.4	114.4	114.3	112.9	113.6	2.76
LDDttg$^+$t	178.0	173.1	56.0	167.0	113.3	112.4	115.7	115.0	113.1	0.35
LDDtttg$^+$	177.8	176.1	173.3	60.4	114.4	113.6	113.1	112.6	113.4	0.56
LDDttg$^-$t	178.2	−177.3	−62.5	−173.3	113.2	112.9	114.3	114.1	113.2	1.19
LDDg$^+$g$^+$tg$^+$	59.8	60.4	170.8	59.7	114.2	114.1	113.9	113.5	114.3	2.65
LDDtg$^+$g$^-$t	167.0	62.6	−92.0	177.1	113.0	115.9	116.3	114.0	112.8	2.79
DDDtg$^+$tg$^+$	172.8	60.8	170.8	60.1	113.3	113.5	114.0	113.4	114.3	1.38
DDDg$^-$ttg$^+$	−60.4	−174.6	174.7	60.5	114.5	113.7	113.0	113.7	114.5	1.86
DDDtg$^+$g$^-$t	−175.1	95.6	−58.1	−174.8	112.9	113.8	114.9	114.7	113.3	3.19