CONFORMATIONAL ANALYSIS OF PHOSPHORUS POLYMERS WITH FLAME RETARDANT PROPERTY

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ABSTRACT

The phosphorous, halogen and nitrogen-containing polymers have excellent thermal stability and good flame retardant properties. In this paper the monomer structure of 4-(1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-yl)phenyl diphenyl phosphate was simulated by molecular mechanics calculations using the MMFF94s force field included in the Omega software. The conformations thus obtained were further minimized by the semiempirical RM1 method included in the MOPAC 2009 software The Omega conformation of minimum energy was energy optimized by the Hartree-Fock Self-Consistend Field (RHF) method, in order to obtain a stable structure. Structural compound features which characterize the most stable energetically conformations obtained by molecular mechanics and quantum chemical methods were compared with experimental data, yielding a unified structure.

INTRODUCTION

Phosphorus-containing polymers have been found in the last years to be technically interesting as engineering plastics, especially the phosphoric polyesters (polyphosphonates and polyphosphates) because of their excellent mechanical, electrical and flame resistance properties and also because of their analogy with the nucleic acids [1]. Also, the phosphorous, halogen and nitrogen-containing polymers are the most widely used, as commercial fire-retardant polymers [2].

Multilinear quantitative structure-property relationships models for glass transition temperature of a series of polyphosphates and polyphosphonates were reported [3] using molecular mechanics and AM1 calculated descriptors for polymer dimers. R^2 of 0.88 was obtained for 10 samples with the Sterimol B1 parameter and torsion angle C1, associated with packing preferences and the polymer backbone flexibility, respectively.

It was found that a similar polymer structure derived from 4-[1,1,1,3,3,3-hexafluoro-2-(4-hydroxyphenyl)propan-2-yl]phenyl phenyl phosphonate has the limiting oxygen index of 33 (%), being considered to have flame retardant property.

In the literature X-ray experimental data of the similar triphenyl phosphate structure is reported [4]. Structural backbone features of this compound are compared to the studied compound.

In this paper the monomer structure of the polymer derived from 4-[1,1,1,3,3,3-hexafluoro-2-(4-hydroxyphenyl)propan-2-yl]phenyl phenyl phosphonate (Fig. 1) was simulated by conformational analysis using molecular mechanics and quantum chemical methods, in vacuum. The conformations of minimum energy thus obtained were analyzed in order to elucidate the most stable structure.
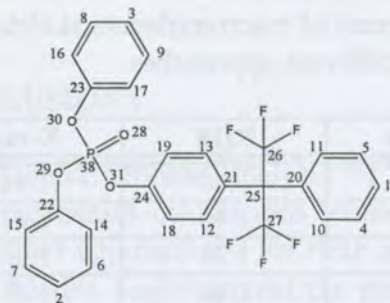
Fig. 1. Structure of the 4-(1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-yl)phenyl diphenyl phosphate

METHODS

Structure simulation by OMEGA software

The molecular monomer structure of the diphenyl phosphate polymer derived from the 4-[1,1,1,3,3,3-hexafluoro-2-(4-hydroxyphenyl)propan-2-yl]phenyl phenyl phosphonate was modelled by the conformational search ability of the Omega v.2.3.2 (OMEGA (version 2.3.2), OpenEye Science Software, 3600 Cerrillos Road, Suite 1107, Santa Fe, USA, 2008) program. SMILES notation was used as program input. The force field used was the 94s variant of the MMFF (Merck Molecular force field) [5] with coulomb interactions and the attractive part of the van der Waals interactions. For the generation of conformers, following parameters were used: a maximum of 200 conformers per compound, an energy cutoff of 10 kcal/mol relative to global minimum identified from the search and a RMSD fit value 0.6 Å was used to avoid redundant conformers.

Structure simulation by MOPAC

Structures of minimum energy obtained by molecular mechanics calculations were further minimized by quantum chemical calculations. Taking into account the big number of flexible bonds present in the compound skeleton, around which the rotation is quasi free, the semiempirical RM1 method [6] included in the MOPAC 2009 software (MOPAC 2009, James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, http://OpenMOPAC.net (2008)). was employed, with SCF convergence of 10^{-10}, RMS gradient value of 0.01 kcal/Å·mol as criterion to choose an optimized conformation and the EF and PRECISE keywords.

Structure simulation by Gaussian

Gaussian 03W (Gaussian 03, Gaussian, Inc., Wallingford CT, 2004.) was used to model the structure of the 4-(1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-yl)phenyl diphenyl phosphate. The Hartree-Fock Self-Consistend Field (RHF) method was employed, with 3-21G basis set for geometry optimization and frequency calculation.

RESULTS AND DISCUSSION

148 conformers were found by Omega software for the 4-(1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-yl)phenyl diphenyl phosphate structure. Ten flexible angles were used in the conformational search. All these conformations were further minimized by the RM1 approach. Two conformers of very close energy were obtained by the RM1 method (see Table 1). The most stable energetically Omega conformer was, also, used in RHF minimizations.

Table 1. Bond lengths (in Å) and torsion angles (in degrees) of macromolecule skeleton of minimum energy conformer obtained by different approaches

Bond length	RM1	MMFF94s	RHF	X-ray
C23-O30	1.36	1.37	1.40	1.46
C22-O29	1.36	1.37	1.40	1.42
C24-O31	1.35	1.36	1.39	1.36
Average	1.36	1.37	1.40	1.41
O30-P38	1.59	1.62	1.61	1.61
O29-P38	1.59	1.62	1.61	1.65
O31-P38	1.61	1.62	1.62	1.62
Average	1.60	1.62	1.61	1.63
Torsion angles				
C16-C23-O30-P38	95.34 (+ac)* -87.42 (-sc)**	-0.01 (sp)	26.68 (sp)	
C14-C22-O29-P38	-87.42 (-sc)* -90.6 (-ac)**	0.01 (sp)	25.29 (sp)	
C18-C24-O31-P38	7.93 (sp)* 8.06 (sp)**	-179.99 (ap)	-160.17 (ap)	
C23-O30-P38-O28	118.61 (+ac)* 171.0 (ap)**	-59.99 (-sc)	-38.96 (-sc)	
C22-O29-P38-O28	171.3 (ap)* 118.66 (+ac)**	-60.00 (-sc)	-37.79 (-sc)	
C24-O31-P38-O28	28.19 (sp)* 28.10 (sp)**	-60.00 (-sc)	-32.53 (-sc)	
C12-C21-C25-C20	-44.26 (-sc)* -44.24 (-sc)**	-59.99 (-sc)	-45.36 (-sc)	
C10-C20-C25-C21	-45.74 (-sc)* -45.71 (-sc)**	-60.00 (-sc)	-45.99 (-sc)	

*conformer obtained by the RM1 method, having the heat of formation of -441.624 kcal/mol
**conformer obtained by the RM1 method, having the heat of formation of -441.6239 kcal/mol

Following general structural features were derived from the inspection of the 4-(1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-yl)phenyl diphenyl phosphate minimized energy structure: a) The bond lengths around the phosphorus atom are closer to experimental X-ray data in case of Gaussian software conformer; b) Similar arrangements of the backbone torsion angles of conformers obtained by the MMFF94s force field and by the RHF method were observed. Eclipsed and trans arrangements of the Car-Car-O-P torsion angles were noticed in case of MMFF94s and RHF conformations. Closer arrangements (anticlinal and eclipsed) to the same X-ray torsion angle were observed in RM1 conformer; c) Gauche arrangement of the Car-O-P=O torsion angle could be found in the MMFF94s and RHF conformers. Eclipsed and gauche arrangements of the same torsion angle were observed in X-ray structure. The corresponding torsion angle of the RM1 structures have eclipsed and trans arrangements; d) Gauche arrangement of the Car-Car-C-Car torsion angles (between the phenyl rings) was observed.

Conformations having the torsion angles around the P-O bonds in the ± gauche, ± eclipsed, or trans forms are considered to be acceptable, in accordance to X-ray experimental data of some organo-phosphorus compounds. Thus, this condition was fulfilled by all minimum energy conformers derived by all methods.

CONCLUSIONS

- Conformational analysis of a diphenyl phosphate was performed by molecular mechanics calculations employing the MMFF94s force field, by the semiempirical RM1 approach and the RHF method in order to obtain a consistent molecular structure.
- Torsion angles around the phosphorus atom had arrangements in agreement to X-ray data
- The conformer obtained by the RHF approach was closer to the experimental structure.
- This information is useful for further modelling of polymer flame retardancy property.

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