Structure of the Polymer Obtained from Bisphenol-A and Cl 2 P(O)CH 3

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STRUCTURE OF THE POLYMER OBTAINED FROM BISPHENOL-A AND Cl$_2$P(O)CH$_3$

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Using the step-by-step build-up approach, the possible conformations of compound PhOP(O)(Me)OPh(Me)$_2$Ph were constructed and geometrically optimized. Among the obtained structures 32 conformations belonging to low, comparable energy levels were used to construct the most stable dimers and tetramers of the title polymer. The results allowed us to estimate the geometrical structure of the polymer.

Keywords: Bisphenol-A; conformational analysis; Me-phosphonates; polymer; polymer structure

INTRODUCTION

Polyphosphonates built up from bisphenol A and different phosphonic dichlorides are useful flame-retardant engineering plastics with a partially crystalline structure. The degrees of order and some other properties, such as glass transition temperatures, strongly depend on the chemical constitution and geometrical structure of the polymer. Here we tentatively analyze the geometrical structure of the $-[OP(O)(CH_3)OC_6H_4C(CH_3)_2C_6H_4]_n-$ polymer, based solely on intramolecular factors.

CONFORMATIONAL ANALYSIS AND CONCLUSIONS

A tentative 3-D structure for **1** was established by conformational analysis of compound **2**. The phenyl ring I from **2** mimics the presence of the corresponding structural unit in the monomer (n-1).

In the conformational search the "build-up" approach[1] was used: joining together smaller fragments in known low energy structures obtained previously generates the structure of the complex molecule. All the calculations are performed using the HyperChem 5 package with the following parameters: AM1 Hamiltonian, SCF convergence 10^{-5}, Polak Ribiere geometry optimization algorithm, gradient at convergence 10^{-2}.

The conformational search begins with the analysis of two compounds: (i), MeP(O)(OMe)OPh; (ii), PhC(Me)$_2$Ph. For (i), based on our previous experience,[2] the OMe group is constrained in the *sp* position related to the P=O bond, and rotations around the P—O(Ph) and O—C(Ph) bonds are allowed. For (ii), rotation angles around the two (Me)C—C(Ph) bonds are the variable parameters. Energy maps were constructed depending on the rotation angles. Figure 1 illustrates the
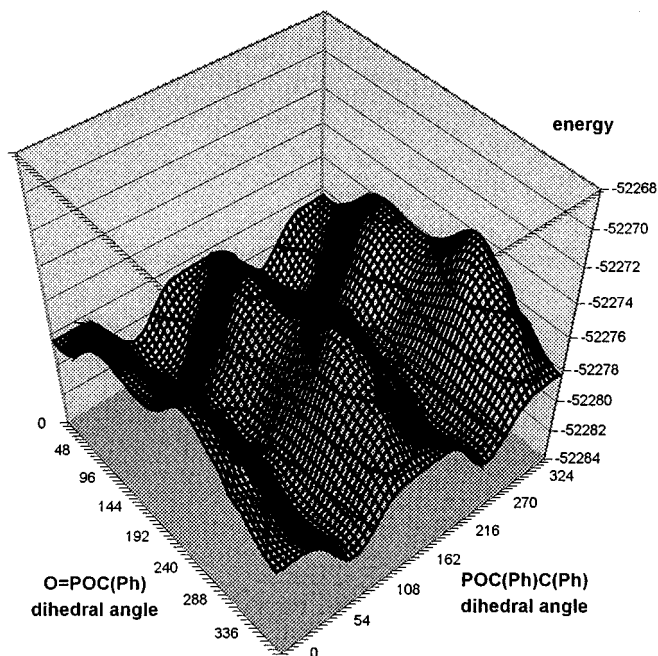

FIGURE 1 The 3D map of the energy of MeP(O)(OMe)OPh function of the two allowed rotation angle.

case of (i). Searching the maps for (i), respectively (ii) three, and respectively two independent conformations were identified. Using the corresponding dihedral angles obtained for compound (i), all the possible conformations were constructed and geometrically optimized for (iii), MeP(O)(OPh)OPh. In this step 8 conformers were obtained, 4 being mirror images of the other 4. Based on the results obtained for (ii) and (iii), the possible conformations for compound **2** were built up and geometrically optimized.

At the end of this step 64 conformations were found: $16 + 16$ mirror images belonging to low, comparable energy levels (a gap of 0.38 kcal/mole), and $16 + 16$ belonging to two groups with higher energy (with about 1.1, respectively 2.1 kcal/mole). In Table I some structural characteristics are presented for the first 16 conformations of **2**.

The first 32 conformations of **2** were used to construct the most stable dimers of **1**, by the superposition of the phenyl rings I and III for the consecutive monomers. 1015 sterically allowed structures were processed. Generally the conformation of the individual monomer units remained conserved in the optimization process. The most stable O=POC(Ph) torsion angles around each P atom are those that belong to the $sp - sc$ structures, as compared to the $sc - sc$ pairs. Energetically

TABLE I[a] Structural and Energetic Characteristics of the Most Stable Conformations of Compound **2**

	P	PI	PII	Ph	Ph	ΔH_{form} (kcal/mole)	μ (D)
1	$+ac$	$+sp$	$-sc$	$+sc$	$+sc$	-111.596 (-111.594)	1.975 (1.969)
10	$+ac$	$+sp$	$-sc$	$+ac$	$+ac$	-111.346 (-111.344)	2.108 (2.103)
8	$+ac$	$+sp$	$-sc$	$-ac$	$-ac$	-111.472 (-111.470)	2.009 (2.039)
5	$+ac$	$+sp$	$-sc$	$-sc$	$-sc$	-111.495 (-111.497)	1.860 (1.886)
3	$-ap$	$-sc$	$+sp$	$+sc$	$+sc$	-111.524 (-111.525)	2.049 (2.069)
6	$-ap$	$-sc$	$+sp$	$+ac$	$+ac$	-111.483 (-111.491)	2.097 (2.111)
4	$-ap$	$-sc$	$+sp$	$-ac$	$-ac$	-111.520 (-111.515)	1.895 (1.888)
2	$-ap$	$-sc$	$+sp$	$-sc$	$-sc$	-111.532 (-111.533)	1.850 (1.857)
16	$-ap$	$+sc$	$+sc$	$+sc$	$+sc$	-111.207 (-111.210)	2.929 (3.063)
7	$-ap$	$+sc$	$+sc$	$-ac$	$-ac$	-111.471 (-111.476)	2.785 (2.902)
9	$-ap$	$+sc$	$+sc$	$+sc$	$+sc$	-111.399 (-111.399)	2.777 (2.780)
13	$-ap$	$+sc$	$+sc$	$-sc$	$-sc$	-111.310 (-111.311)	2.950 (2.967)
15	$-sc$	$+sc$	$+sc$	$+sc$	$+sc$	-111.218 (-111.220)	2.751 (2.843)
11	$-sc$	$+sc$	$+sc$	$+ac$	$+ac$	-111.317 (-111.318)	2.615 (2.699)
12	$-sc$	$+sc$	$+sc$	$-ac$	$-ac$	-111.316 (-111.310)	2.547 (2.575)
14	$-sc$	$+sc$	$+sc$	$-sc$	$-sc$	-111.306 (-111.307)	2.660 (2.719)

[a]P, C(Me)POC(PhI) angle; PI, O=POC(PhI); PII, O=POC(PhII); Ph, C(PhII)C(PhII)CC(PhIII) and, respectively, C(PhIII)C(PhIII)CC(PhII); ΔH_{form}, heat of formation; μ, dipole moment; the values for the mirror image compounds are given in brackets, as resulted from the calculations.

the most stable dimers are combinations of two different monomers, except that formed by the monomer 3. However the 3-3 dimer has about 0.6 kcal/mole higher energy than the most stable mixed dimer (3–6, with calculated heat of formation $\Delta H_{form} = -247.172$ kcal/mole).

For the energetically most stable 25 dimers, we have tried to build up and optimize the corresponding tetramers, but only 14 of these allow the construction without considerable steric hindrance.

A certain sterical disability to adopt energetically stable ordered structures by regular repetition of some low energy monomer or dimer units is found out. This would represent the origin of the partially crystalline structure of the polymer.

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