THE STABILITY OF SOME CHEMICAL SYSTEMS ESTABLISHED BY AM1 SEMIEMPIRICAL METHOD

by
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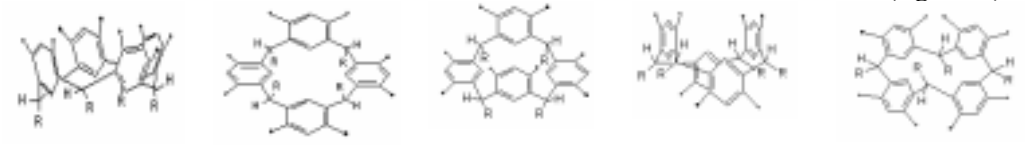
Abstract: In this paper are presented the results obtained by some mathematical calculations over isomer structures of four chemical systems relied on calix[4]resorcinarenes functionalized with organic-phosphorus groups. By AM1 semiempirical method were calculated the heats of formation for all possible isomers, the most stable isomer for those four chemical systems been distinguished.
Keywords: AM1 semiempirical method; calix[4]resorcinarenes.

INTRODUCTION

With the rapidly development of calix[4]resorcinarenes[1] chemistry in the last years, it started, even too little, as these chemical systems to be theoretical studied by some mathematical calculations. Calix[4]resorcinarenes can adopt five possible conformation[2]: "cone"; "1,2-alternate"; "1,3-alternate"; "chair" and "boat" (**figure 1**).



"cone" "chair" "boat" "1,3-aternate" "1,2-alternate"

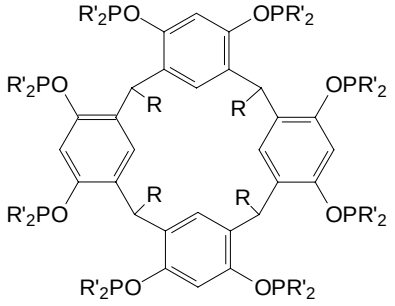
Figure 1. All five possible conformations of calix[4]resorcinarenes

Everyone of these five possible conformations of calix[4]resorcinarenes can have six possible conformations, given by the equatorial or axial position of R radical from the methylene bridge. So every conformation has the following configurations: "*aaaa*" (all four R groups from the methylene bridge are in axial position); "*aaae*" (three groups are axial and one equatorial); "*aaee*" (two neighboring groups are axial and two are equatorial); "*aeae*" (two not neighboring groups are axial and the others two are equatorial); "*aeee*" (one groups is axial and the others three are equatorial); "*eeee*" (all four R groups from the methylene bridge are in equatorial position). The calix[4]resorcinarenes chemistry is very important because of their properties to be complexation agents used as extractants of some anions[3], cations[4] and neutral molecules[5] from residual waters. These complexation properties of calix[4]resorcinarenes can be improved by their functionalization with organic-phosphorus groups[6,7]. These chemical systems are obtained by the

calix[4]resorcinarenes treatment with organic-phosphorus chlorides, the reaction taking place in triethylamine[8].

RESULTS AND DISCUSSION

It was realized an computational study by AM1 semiempirical method[9] of isomers structures of four calix[4]resorcinarenes functionalized with organic-phosphorus groups. The chemical systems based on calix[4]resorcinarenes functionalized with organic-phosphorus groups were studied by AM1 semiempirical method, but the conformational and configurational structures were realized and optimized by Hyper Chem programmer. Because of the sterical hindrances appeared once with the bulky organic-phosphorus groups substitution at the calix[4]resorcinarenes, the "cone" conformation with all its six configurations couldn't be realized, so the heats of formation were calculated only for others four conformations, together with the adequate configurations. In **scheme 1** are presented all four studied chemical systems.



1. R= CH_3, R'= CH_3,

2. R= CH_3, R'= C_2H_5

3. R= C_3H_7, R'=CH_3,

4. R= C_3H_7, R'= C_2H_5.

Scheme 1.

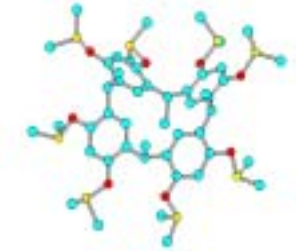
In **table 1** are presented the heats of formation of all conformations and configurations.

Table 1. The heats of formations of all four calix[4]resorcinarenes functionalized with organic-phosphorus groups.

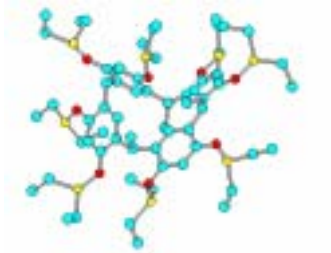
Conformation	**Configuration**	**Compound / The heat of formation (Kcal/mol)**			
		1.	**2.**	**3.**	**4.**
"1,2-alternate"	*"aaaa"*	**-380,91**	**-413,69**	-428,66	-449,07
	"aaae"	-377,06	-409,81	-420,37	-440,57
	"aaee"	-370,74	-407,85	-416,07	-433,07
	"aeae"	-368,04	-405,86	-415,30	-431,01
	"aeee"	-364,13	-404,01	-411,18	-427,27
	"eeee"	-361,81	-399,61	-401,85	-421,04
"1,3-alternate"	*"aaaa"*	-366,62	-410,02	-414,87	-449,62

Conformation	**Configuration**	**Compound / The heat of formation (Kcal/mol)**			
		1.	**2.**	**3.**	**4.**
	"aaae"	-369,32	-412,68	-415,65	-447,16
	"aaee"	-369,31	-414,01	-418,26	-443,52
	"aeae"	-370,15	-412,58	-412,74	-449,89
	"aeee"	-370,08	-413,62	-413,48	-450,19
	"eeee"	-370,48	-411,42	-416,24	-447,67
"chair"	*"aaaa"*	-376,63	-413,62	-426,11	-458,48
	"aaae"	-375,22	-410,20	-418,31	-446,30
	"aaee"	-370,74	-406,34	-406,29	-434,29
	"aeae"	-368,04	-406,25	-412,08	-441,54
	"aeee"	-364,13	-402,89	-404,43	-434,31
	"eeee"	-361,81	-399,52	-386,01	-426,16
"boat"	*"aaaa"*	-379,88	-413,50	-429,01	-456,43
	"aaae"	-372,52	-401,08	-423,22	-451,45
	"aaee"	-371,01	-396,89	-416,84	-446,03
	"aeae"	-371,64	-400,32	-413,94	-450,13
	"aeee"	-360,99	-396,53	-406,05	-439,62
	"eeee"	-357,85	-386,55	-402,52	-426,26

As follows down here are presented the optimized structures of all the most stabile conformations and configurations of all four chemical systems of the calix[4]resorcinarenes functionalised with organic-phosphorus groups:



1.



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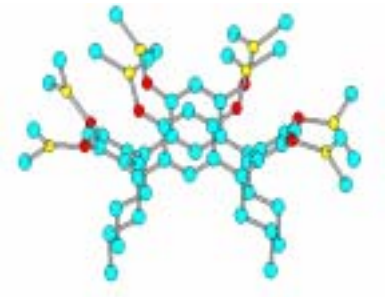

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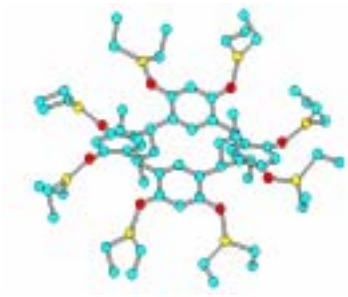

4.

As seen in **table 1**, the compounds **1** and **2**, derivatives of C-methyl-calix[4]resorcinarene both prefers the "*aaaa*" configuration (all Methyl groups in axial position) of "*1,2-alternate*" conformer. The compounds **3** and **4**, derivatives of C-propyl-calix[4]resorcinarenes it was observed that the derivative with eight $P(Me)_2$ groups (**3**), prefer the "*aaaa*" configuration of "*boat*" conformer, while the C-propyl-calix[4]resorcinarene functionalized with eight $P(Et)_2$ groups (**4**), prefer the "*aaaa*" configuration of "*chair*" conformer. This is possible because of the bigger volume of the ethyl groups comparatively with the methyl groups.

CONCLUSIONS

From the study realized over all four chemical systems of calix[4]resorcinarenes functionalized with organic-phosphorus groups it was seen that for all these systems the "*aaaa*" configuration, in which all for groups of methylene bridge are in axial position, is the most stabile, because of the weak interactions between these groups and the calix[4]resorcinarene macrocycle skeleton. These interactions are very present if the R groups from the methylene bridge are in equatorial position. The stability of one of conformers depends on volume of organic-phosphorus groups substituted at the calix[4]resorcinarenes. So the AM1 semiempirical method is very successful concerning the finding of an possible structure for an certain compound, which is usefully to the chemists to synthesize new intricate chemical systems and which are applied in different domains.

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