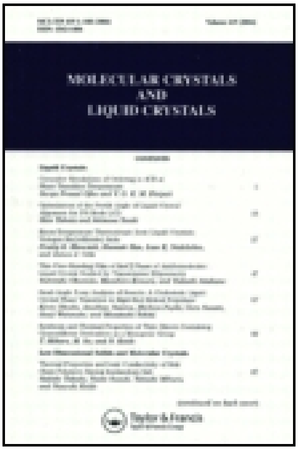

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XIII. Phosphorus Macrocycles-Theoretical Study

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XIII. PHOSPHORUS MACROCYCLES–THEORETICAL STUDY

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A theoretical study of silacalix[n]phosphinine, $n = 3,4$ at semiempirical level RHF approximation was performed. Molecular conformation, obtained as local minimum from semiempirical calculation, bond distances and bond angles are in good agreement with X-ray experimental geometry. The values of total energies showed silacalix[4]phosphinine more stable but heats of formation emphasized silacalix[3]phosphinine more stable thermodynamically. Complexation abilities were appreciated by assignment of n and π^* levels of silacalix[n]phosphinine. Result an improvement of σ-donating properties and good π-acceptor character was kept.

INTRODUCTION

In the last years supramolecular chemistry, a domain that opens new perspectives regarding fundamental studies and potential applications has known an increasing development [1,2]. Much interest is focused on supramolecular devices [3] operating with electrons, photons, ions or presenting specific chemical reactivity with applications in detections, medical and biological energy transfer processes such as: optical and electronic devices, ion carriers, ion channels, catalysis, photosynthesis mimics [1].

Macrocyclic nanosized structures received a special attention due their interesting structure and their great ability to form "host-guest" complexes with large applications in ionophore synthesis, catalysis, sensor devices [1–7]. A series of natural products that play an extremely important role in biochemical processes e.g. chlorophyll, hemoglobin, vitamin B12, consist in complexes of macrocyclic ligands.

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It was developed new approaches to synthesize heteroelement (N, S, Si) bridged calixarenes that showed special properties [7–9]. Silicon bridged macrocycles act as receptors for membrane transport of metal ions having good solubility in nonpolar organic solvents [8]. Analogous macrocycles with heteroaromatic constituents such as pyridine, triazyne, pirroles, furans, thiophenes, indoles were synthesized and described [7–10].

In view of obtaining binding sites with strong π-acceptor abilities and to balance σ-donating and π-accepting properties N Avarvari *et al.* succeeded to synthesize silacalix[n]phospinine and begun to investigate their coordinating properties [11–13]. The synthetic methods are based on $[4+2]$ Diels-Alder cycloaddition-cycloreversion reaction of 1,3,2-diazaphosphinine with sila-alkynes [11–13]. Phosphinine showed very interesting coordinating properties, a moderate σ-donor character with the lone pair of phosphorus situated at $-10\,\mathrm{eV}$ and a low lying LUMO at $-0.7\,\mathrm{eV}$ with higher coefficient at phosphorus atom confer increased π-acceptor character [14–15].

C. Elsenbroich *et al.* [16–18] obtained a number of stable homoleptic η^1 complexes of phosphabnezene, also a series of π complexes and $8e^-$ donor complexes of phosphinine are known [19–21]. Bisphosphinine displayed a good σ-donor and π-acceptor character stabilizing highly reduced transition metal centers [22–24]. A number of sp^2 hibridized phosphorus macrocyclic complexes were synthesized and characterized: silacalix[3]phosphinine $W(CO)_3$, silacalix[4]phosphinine Rh, Ir, Au, [13]. A kind of "CO- like" behavior of silacalix[4]phosphinine gold° complexe was emphasized by electrochemical studies [25].

In the present paper a theoretical study of silacalix[n]phosphinine, where $n = 3,4$ at semiempirical level was performed. Molecular geometries and conformations of phosphinine macrocycles resulted from semiempirical calculation were compared withexperimental data.

COMPUTATIONAL DETAILS

Geometries of phosphinine macrocycles were optimized using force field MM+ and semiempirical methods PM3 and MNDO/d from Hyperchem 5.11. programme. MNDO/d was taken into consideration as it was quoted in a previous paper it has to be included d orbitals of phosphorus to compute λ^3-heterobenzenes with phosphorus [26]. In order to obtain a better geometry we proceeded first to optimize the molecular with PM3 method, and reoptimized with MNDO/d method and again with PM3 method. It was obtained distinct conformers that correspond of local minimum. All computations have been carried out with RHF approximation for the F operator, the method with accelerate convergence was used with a convergence limit of 10^{-5} SCF. The molecules were considered in vacuum and the optimization algorithm Polak-Ribiere with a conjugate gradient RMS 0.001 kcal/molÅ was used.

RESULTS AND DISCUSSIONS

All conformations of phosphorus macrocycles obtained by semiempirical calculations are in reasonable agreement with X-ray data. Three geometry derived from: PM3 method-1, PM3-MNDO/d-2, and PM3-MNDO/d-PM3-3 combined methods were obtained.

Silacalix[3]phosphinine

Partial cone structure determined by X-ray diffraction with two phosphorus atoms pointed out above the plane of silicon atoms and the other pointed down to this plane of are reproduced by all semiempirical calculation as energetic minimum. PM3-MNDO/d-PM3 combined methods gave the best separation C-P, shorter than experimental averages by 0.014–1.016 Å, C-Si bond distances calculated with PM3-MNDO/d differ by only 0.016–0.02 Å from real distances. Bond length discrepancies lead to bond angles at phosphorus calculated with PM3 method that are lower than experimental values by 3.4–3.8° representing the best estimation in comparison with experimental average 105.8–106.1°. Si−C−P bond angles as resulted by PM3-MNDO/d calculation are lower by 0.9–1.2°, also good values gave PM3-MNDO/d-PM3 greater by 1.1° and lower by 0.5°. A better

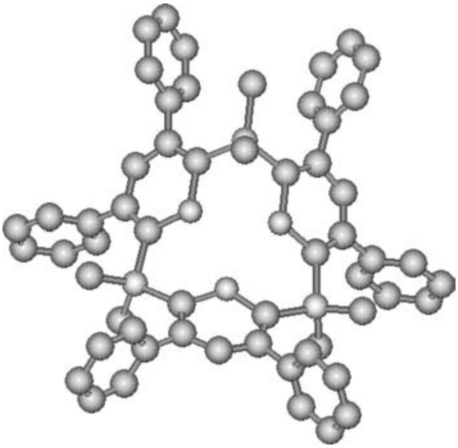


FIGURE 1 Molecular conformation of silacalix[3]phosphinine.

TABLE 1 Geometry of Silacalix[3]phosphinine

Geometry	P-C (Å)		C-Si (Å)		C-P-C		C-Si-C		Si-C-P	
X-ray	1.738	1.751	1.908	1.914	105.8	106.9	104.9	105.8	111.2	114.1
1	1.708	1.732	1.843	1.852	102.4	103.1	103.2	107.6	109.1	113.6
2	1.712	1.715	1.892	1.894	110.5	110.8	103.9	107.8	110.3	112.9
3	1.724	1.735	1.848	1.857	102.1	102.6	108.7	109.1	112.3	113.6

description of C-Si-C bond angle average is given by PM3-MNDO/d that are less by 1° and greater by 2° than real values while the results obtained by PM3 method differ by less 1.7° or 1.8° greater than experimental values.

Silacalix[4]phosphinine

Geometric parameters and molecular conformation are in agreement with bond distances, bond angles and opened-out partial cone shape with two phosphinine units situated in the plane of silicon atoms and the other two in parallel planes that are perpendicular to the first with phosphorus lone pairs displayed antiparallel as resulted from X-ray measurements.

PM3-MNDO/d optimization gave the best P−C bond distance lower by only 0.018° and 0.030 Å, C−Si bond distances lower by 0.004 Å or greater by 0.009 Å than real separation. Bond angles at phosphorus as resulted

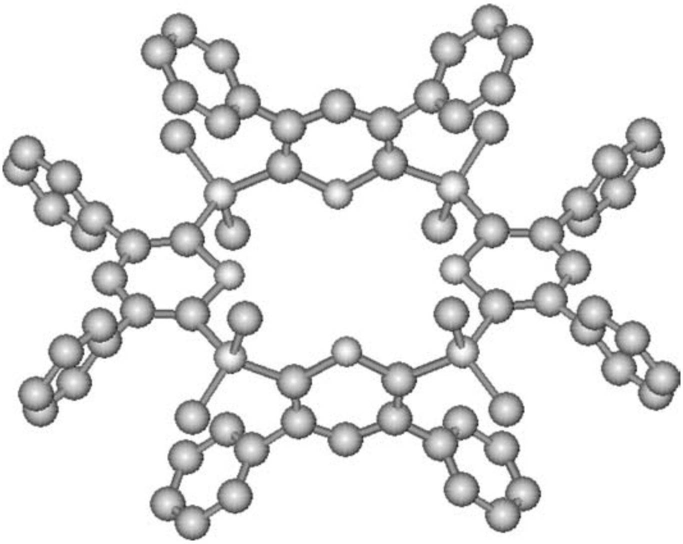


FIGURE 2 Molecular conformation of silacalix[4]phosphine.

TABLE 2 Geometry of Silacalix[4]phosphinine

Geometry	P-C (Å)		C-Si (Å)		C-P-C		C-Si-C		Si-C-P	
X-ray	1.734	1.747	1.883	1.900	105.0	106.3	108.0	109.4	112.5	115.6
1	1.693	1.704	1.860	1.875	106.5	107.4	112.3	115.3	109.7	115.3
2	1.716	1.717	1.887	1.891	110.7	111.0	110.8	111.0	112.4	113.4
3	1.697	1.698	1.866	1.868	106.3	107.4	114.0	114.1	112.7	114.1

from PM3-MNDO/d-PM3 optimization differ by only 1.1–1.5° from real average, while P—C—Si bond angles obtained by PM3-MNDO/d-PM3 method are greater by only 0.2° or lower by 1.5° than real values representing the best calculated values. For C—Si—C bond angles PM3-MNDO/d structural results not exceed experimental values more than 1.6–2.8°. A better description of cavity size is derived from PM3-MNDO/d geometry, distance from the two phosphorus atoms oriented antiparellel 5.645 Å (5.650 Å experimental) larger than the distance from the other two phosphorus atoms that rely approximatively in the plane of the silicon atoms 6.122 Å (5.788 Å experimental). PM3 and PM3-MNDO/d-PM3 gave 6.020 Å −5.829 Å and 5.855 Å −5.751 Å respectively.

Thermodynamic Stability

The calculated heats of formation and total energy of phosphinine macrocycles are given in Table 3.

It is apparent from data displayed in Table 3 that silacalix[4] phosphinine is more stable having the lowest total energy, but the values of heat of formation showed silacalix[3] phosphinine relatively the most stable thermodynamically; all methods are consistent with these observations. The values of total energies and heats of formation obtained by PM3 differ from these obtained by MNDO/d that emphasized the influence of d orbital upon these properties.

TABLE 3 Total Energy and Heats of Formation of Phosphinine Macrocycles

No.	Geometry	Total energy(Kcal/mol)	ΔH_f (Kcal/mol)
1	Silacalix[3]phosphinine-PM3	−187169.333	215.589
2	Silacalix[3]phosphinine-PM3-MNDO/d	−199958.950	140.147
3	Silacalix[3]phosphinine-PM3-MNDO/d-PM3	−187170.991	213.930
4	Silacalix[4]phosphinine-PM3	−249553.908	292.655
5	Silacalix[4]phosphinine-PM3-MNDO/d	−266612.388	186.408
6	Silacalix[4]phosphinine-PM3-MNDO/d-PM3	−249553.256	293.306

HOMO-3 n-Type orbital of silacalix[3]phosphinine -8.462eV.

LUMO+2π*-Type orbital of silacalix[3]phosphinine -0.403eV.

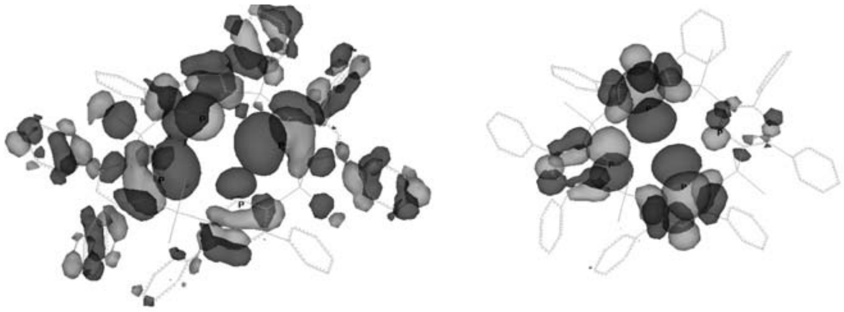
FIGURE 3 Molecular orbitals of silacalix[3]phosphinine.

Coordinating Properties

In view to find out more information about electronic structure and complexation abilities of silacalix[n]phosphinines we investigated molecular orbital structure. In order to obtain more accurate ascription of molecular orbital type we plotted graphic molecular orbital (Figs. 3, 4).

Silacalix[3]phosphinine

The highest occupied OM and the next two occupied levels are π type at -7.522 eV followed by n-levels that correspond to different combination of lone pairs of phosphorus atoms rely between -9.051 eV and -8.462 eV,



HOMO-7n-Type orbital of silacalix[4]phosphinine -9.080eV.

LUMO+2π*-Type orbital of silacalix[4]phosphinine, -0.484eV.

FIGURE 4 Molecular orbitals of silacalix[4]phosphinine.

higher than –10.0 eV of phosphinine that suggest an improved σ-donor capacity. Participation coefficients of p_z atomic orbital of the phosphorus atoms 1,2 and 3 from phosphinine units are dominant in molecular orbitals LUMO, LUMO + 1 and LUMO + 2 of silacalix[3]phosphinine. The lowest unoccupied π^* orbital rely at -0.868 eV with a large localization at phosphorus $c_{P1z} = 0.396$, $c_{P2z} = 0.681$, $c_{P3z} = 0.382$ (Fig. 3). X-ray structure of Silacalix[3]phosphinine· $W(CO)_3$ complex showed three phosphorus atoms interacted with metal fragment [13].

Silacalix[4]phosphinine

The combination of the lone pairs of phosphorus atoms rely after four double occupied π levels between -9.139 eV and -8.873 eV(HOMO-8.404 eV), that emphasized as in the case of silacalix[3]phosphinine a better σ-donor ability. Pz atomic orbital participation of the phosphorus atoms 1 and 3 from phosphinine units are dominant in molecular orbitals LUMO, LUMO + 1, LUMO + 2 and LUMO + 3 of silacalix[4]phosphinine. A good π-acceptor capacity derived from π^* LUMO at -0.508 eV localized essentially at two phosphorus atoms $c_{P1z} = 0.130$, $c_{P3z} = 0.450$ was obtained(Fig. 4). X-ray diffraction study of silacalix[4]phosphinine· Gold complexe showed only two phosphorus atoms interacted with gold, the other two having a weak interaction.

CONCLUSIONS

All molecular modeling at semiempirical level PM3 and MNDO/d gave conformations and geometries that are in good agreement with experiment. The best optimization for the silacalix[n]phosphinines was achieved by PM3-MNDO/d combined method. The problem of relative stability of macrocycles isn't too clear however the published papers reported macrocycles having very good air stability unlike phosphinine.The differences between various properties calculate with PM3 and MNDO/d methods demonstrate the influence of d orbitals upon these properties. σ-Donating abilities were improved with respect to phosphinine and π-acceptor capacity was kept.

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