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# The σ-Donating and π-Accepting Properties of *ortho*-$Si(CH_3)_3$ Phosphinine Macrocycles

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ABSTRACT: *A theoretical investigation of both the* ortho-*$Si(CH_3)_3$ phosphinine and some silacalix[*n*]phosphinines was performed. The optimized geometries agree well with those reported from X-ray analysis and other structural studies. The silacalix[*n*]phosphinine macrocyle is very flexible because of the C—Si—C bridges. This, in turn, makes possible the formation of strained configurations in solid packed structures. In the silacalix[3]phosphinine, a P—P bonding interaction that is presumably responsible for its structural and electronic features seems to exist. The molecular orbital calculations corroborate that both the π-accepting properties and the σ-donating capacities of the phosphinine unit may be enhanced by* ortho-*$Si(CH_3)_3$ substitution. These features satisfy the proposal of the synthesizers as regards the production of macrocyclic phosphorus compounds, with good π-accepting properties and strong σ-donating capacities, which are sufficiently flexible as to encapsulate metals with coordination spheres of different geometries.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:160–169, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10118

## *INTRODUCTION*

Phosphorus compounds have attracted much attention over the past few years because of their practical applications in catalysis, in the photodecomposition of water, and in photovoltaic cells as well as in synthetic phosphorus chemistry and coordination chemistry [1–6]. Among the organic phosphorus compounds, the phosphorus macrocycles (and particularly phosphinine and its derivatives) have been extensively studied [1–8]. More recently, the synthesis of the silacalix[*n*]phosphinines, a novel class of macrocycle phosphinines that represent the first $sp^2$-based phosphorus macrocycles was reported [9]. Additionally, metal complexes of the silacalix[*n*]phosphinines have been synthesized and studied both experimentally and theoretically [10].

The interest in phosphinine and its derivatives is based on the fact that the unique properties of $sp^2$-hybridized phosphorus atom (poor σ-donating but good π-accepting abilities) can be here fully expressed [11]. Thus this specific property can be exploited in catalysis [2] and for the stabilization of highly reduced transition-metal species [10]. Nevertheless, in some cases it would be desirable to have phosphinine derivatives in which the σ-donating properties were improved. The enhancement of both the electron σ-donating and π-accepting abilities of phosphinine would be achieved by adequate peripheral substitution. The group $Si(CH_3)_3$ in ortho-position has been used for this purpose [7,12].

At the same time, some chemists are interested in the synthesis of phosphorus macrocyclic structures that have flexible cavities with strong π-acceptor

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bonding sites. These compounds, because of their flexibility, can be used to encapsulate metals with coordination spheres of different sizes and geometries [7,9,10]. One paradigmatic example of these compounds are the silacalix[*n*]phosphinines mentioned above [9,10].

In the present paper, a theoretical study about (i) the influence of the *ortho*-Si(CH$_3$)$_3$ substitution on the electronic properties of phosphinine and (ii) the molecular electronic structure of the silacalix[*n*]phosphinines is performed. Our interest deals with the molecular and electronic properties of macrocycles, particularly of pyrrole macrocycles (porphyrins, phthalocyanines, and subphthalocyanines) [13]. The study of phosphorus macrocycles gives us the possibility of extending our experience to another class of macrocycle compounds bearing in mind that the replacement of nitrogen by phosphorus atoms in aromatic structures causes dramatic changes in the resulting electronic properties [7]. The calixphyrins, whose synthesis was reported very recently [14], constitute the structural bridge between these two classes of compounds.

## *COMPUTATIONAL DETAILS*

In order to study the effect of the *ortho*-Si(CH$_3$)$_3$ substitution on the molecular electronic structure of the phosphinine, the following systems were calculated: (i) phosphinine (**1**), (ii) the *ortho*-Si(CH$_3$)$_3$ phosphinine derivative (**2**), and (iii) some silacalix[*n*]phosphinines, which are macrocyclic compounds with Si(CH$_3$)$_3$ bridge groups binding the phosphinine units and/or the five-membered heterocycles. The compounds labeled **3, 4, 15**, and **16** in the paper [9] are the silacalix[*n*]phosphinines used for our calculations. In the present work they are designed as compounds **3, 4, 5**, and **6**, respectively.

We have adopted the following notation: (h) designs the phosphinine rings located in the plane of the silicon atoms, i.e. the *quite*-horizontal phosphinine rings, whereas (v) identifies the perpendicular phosphinine (either thiophene or furan) rings. The carbon atoms of the five-membered rings are conventionally named α or β, depending on their position with respect to the heteroatom (S or O). The carbon atoms of the phosphinine units are named *o*, *m*, or *p* according to their position with respect to the phosphorus atom.

In the case of compound **4** two structural situations were considered: the vertical (v) phosphinine units (whose phosphorus atoms are indistinctively named in this work as P1 and P3 or P(v)) are either in the same direction (structure **4A**) or in opposite directions (structure **4B**). This approach was selected in order to test the hypothesis of Avarvari et al. [9] which assumes that the second configuration minimizes the interactions of the unpaired electrons of the phosphorus atoms with the lone pairs of the other two P atoms.

The phosphinine **1** and its derivative **2** were calculated (including full geometry optimization) using DFT methods. The functional used in the DFT calculations was the B3LYP [15], which has been extensively employed in other theoretical investigations of macrocyclic compounds [13] including the phosphorus ones [8,10,12]. The selected basis set was 6-31G$^{**}$. In order to minimize the computational effort, the silacalix[*n*]phosphinines were firstly optimized at semiempirical level and secondly, single point ab initio and DFT calculations were performed over the optimized semiempirical geometries.

The semiempirical calculations were carried out using the MOPAC package, version 6.0 [16] with the PM3 Hamiltonian [17]. The geometrical optimization was carried out with an "eigenvector following" (EF) procedure [18]. The optimization threshold for the value of the gradient norm was fixed at 0.01 kcal mol$^{-1}$ (Å or radians) whereas the maximum step size allowed during the optimization procedure was 0.02 (Å or radians). In ab initio and DFT single-point calculations of the silacalix[*n*]phosphinines the selected basis set was 6-31G$^{**}$. The ab initio and DFT studies were supported by the Gaussian 98 program [19].

## *RESULTS AND DISCUSSION*

### *Molecular Geometries*

The phosphinine ring is planar in the fully optimized geometries of **1** and **2** and retains its planarity in the silacalix[*n*]phosphinines. The results obtained for **1** are in complete agreement with those obtained by other authors experimentally and theoretically at similar computational levels [8]. Taking into account (i) that **1** and **2** have been extensively studied by other authors [8] and (ii) the excellent agreement of our results with those reported by them, no special comments are devoted here to their structural data. The optimized geometries of the macrocycles **4, 5**, and **6** reproduce the cone-shaped structures observed in X-ray studies [9], whereas the compound **3** is flatter than any other of its family. This fact is also in correspondence with experimental reports [9].

Figures 1–4 show the molecular representations of the optimized geometries for the studied compounds. When the complexity of the structures recommended it, we included different views of each molecule. In Tables 1 and 2 some of the geometrical parameters of the studied silacalix[*n*]phosphinines

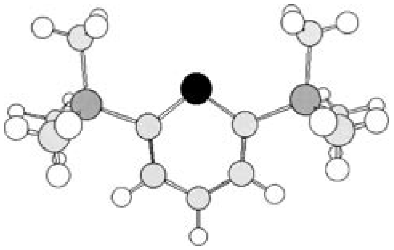


**FIGURE 1** Molecular representation of the optimized geometry for the 2,6-bis(trimethylsilyl)phosphinine (**2**). White: hydrogen, light grey: carbon, dark grey: silicon, and black: phosphorus.

are summarized. These tables present the mean values of geometrical parameters.

The geometry optimization shows that, in the phosphinine ring, the chemical bonds are elongated with the *ortho*-Si$(CH_3)_3$ substitution, whereas the bond angle C—P—C is opened. Tables 1 and 2 indicate that the geometry of the phosphinine ring is not significantly altered when involved in the macrocycle constitution. This indicates that only those geometrical parameters related with the silacalix[*n*]phosphinine macrocyclic configuration, such as the C—Si bond length and the C—Si—C bond angle, for example, change from one compound to another.

From Tables 1 and 2 it can be concluded that the optimized geometries agree with those obtained experimentally [9] for the silacalix[*n*]phosphinines. The relative deviations of the calculated geometrical parameters with respect to experimental ones lie in the intervals 0.2–2.9 and 0.1–7.8% for bond distances and angles, respectively. The major deviation of the calculated values is observed for the bridge angles C—Si—C. The calculated values are 4.1–7.4° greater than those determined experimentally. This may indicate that the molecules of the studied compounds in solid phase are constrained because of crystal packing effects.

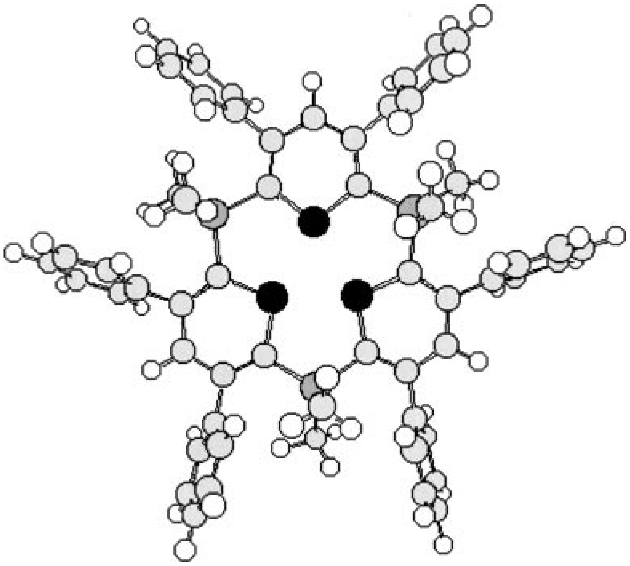


**FIGURE 2** Molecular overview of the optimized geometry for the silacalix[3]phosphinine (**3**). White: hydrogen, light grey: carbon, dark grey: silicon, and black: phosphorus.

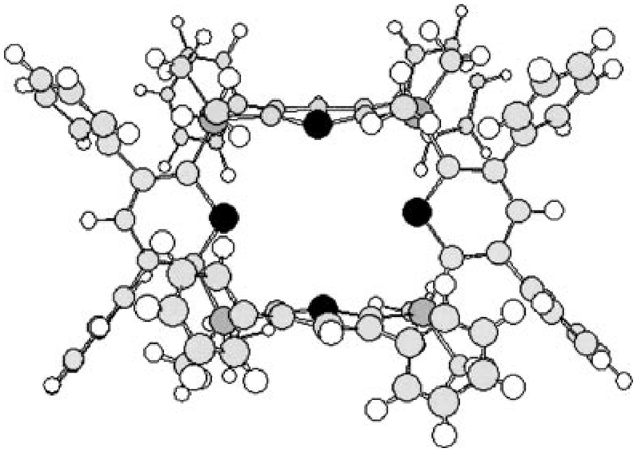


**FIGURE 3** Molecular representation of the optimized geometry for the silacalix[4]phosphinine (**4B**). White: hydrogen, light grey: carbon, dark grey: silicon, and black: phosphorus.

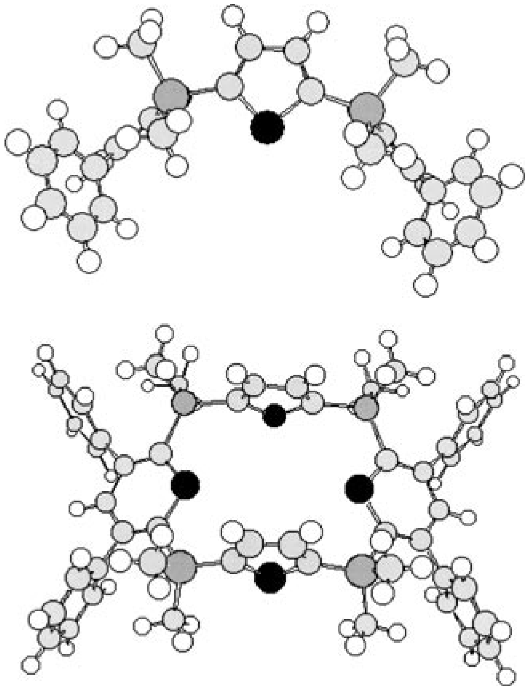


**FIGURE 4** An overview of the molecular point of the *z*-axis (top) and the *xy* plane (bottom) for the optimized geometries of the thiophene-silacalix[4]phosphinine (**5**) and the furan-silacalix[4]phosphinine (**6**). White: hydrogen, light grey: carbon, dark grey: silicon, and black: phosphorus.

**TABLE 1** Calculated and Experimental [7] Values of Some Selected Geometrical Parameters Both for **3** and **4**

| | *Compound* **3** | | *Compound* **4** | | |
|---|---|---|---|---|---|
| | *Calc.* | *Exp.* | *Calc.* **4A** | *Calc.* **4B** | *Exp.* |
| Bond distances (Å) | | | | | |
| P–C$_o$ | 1.735 | 1.744 | 1.698 | 1.698 | 1.740 |
| C$_o$–C$_m$ | 1.380 | – | 1.382 | 1.382 | – |
| C$_m$–C$_p$ | 1.398 | – | 1.400 | 1.400 | – |
| C$_o$–Si | 1.853 | 1.910 | 1.869 | 1.870 | 1.892 |
| Mean dev. | 0.03 | | 0.03 | 0.03 | |
| RMS | $1.7 \times 10^{-3}$ | | $1.3 \times 10^{-3}$ | $1.2 \times 10^{-3}$ | |
| Rel. dev. | 0.1–3.1% | | 0.1–2.7% | 0.3–2.9% | |
| Bond angles (°) | | | | | |
| C$_o$–Si–C$_o$ | 110.8 | 105.0 | 115.1 | 113.9 | 108.6 |
| C$_o$–P–C$_o$ | 102.3 | 106.3 | 107.0 | 106.8 | 105.8 |
| Si–C$_o$–P | 114.3 | 113.2 | 113.6 | 114.1 | 114.3 |
| Si–C$_o$–C$_m$ | 121.7 | 120.9 | 125.0 | 124.6 | – |
| Mean dev. | 3.0 | | 3.5 | 2.7 | |
| RMS | 14.1 | | 20.7 | 13.7 | |
| Rel. dev. | 0.1–4.9% | | 0.2–8.6% | 7.8% | |
| Mean interatomic distances (Å) | | | | | |
| $d_n$ | – | – | 6.266 | 8.541 | – |
| $d_h$ | – | – | 13.849 | 13.937 | |
| $d_v$ | – | – | 6.046 | 10.622 | – |

Relative and mean deviations of the calculated values with respect to the experimental ones; root mean squares (RMS) of the comparison between experimental and calculated data; neighboring ($d_n$), horizontal ($d_h$), and vertical ($d_v$) mean interatomic distances between phosphinine units in compounds **4A** and **4B**.

**TABLE 2** Calculated and Experimental [7] Values of Some Selected Geometrical Parameters Both for **5** and **6**

| | *Compound* **5** | | *Compound* **6** | |
|---|---|---|---|---|
| | *Calc.* | *Exp.* | *Calc.* | *Exp.* |
| Bond distances (Å) | | | | |
| X–C$_\alpha$ | 1.721 | 1.725 | 1.379 | 1.383 |
| C$_\alpha$–C$_\beta$ | 1.366 | – | 1.379 | – |
| C$_\beta$–C$_\beta$ | 1.437 | – | 1.431 | – |
| P–C$_o$ | 1.695 | 1.740 | 1.695 | 1.740 |
| C$_o$–C$_m$ | 1.381 | – | 1.382 | – |
| C$_m$–C$_p$ | 1.400 | – | 1.400 | – |
| C$_\alpha$–Si | 1.834 | 1.867 | 1.855 | 1.867 |
| C$_o$–Si | 1.892 | 1.891 | 1.860 | 1.891 |
| Mean dev. | 0.02 | | 0.02 | |
| RMS | $7.8 \times 10^{-4}$ | | $7.8 \times 10^{-4}$ | |
| Rel. dev. | 0.1–2.7% | | 0.2–2.6% | |
| Bond angles (°) | | | | |
| C$_\alpha$–Si–C$_o$ | 114.4 | 107.0 | 114.7 | 110.6 |
| C$_\alpha$–X–C$_\alpha$ | 92.4 | 94.2 | 108.0 | 108.0 |
| C$_o$–P–C$_o$ | 106.7 | 105.9 | 107.0 | 105.9 |
| Si–C$_\alpha$–X | 122.5 | 120.5 | 120.7 | 118.5 |
| Si–C$_o$–P | 114.8 | 114.4 | 115.2 | 114.4 |
| Si–C$_\alpha$–C$_\beta$ | 126.3 | – | 130.1 | – |
| Si–C$_o$–C$_m$ | 123.4 | – | 123.5 | – |
| X–C$_\alpha$–C$_\beta$ | 111.2 | – | 109.1 | – |
| Mean dev. | 2.8 | | 1.9 | |
| RMS | 15.3 | | 6.0 | |
| Rel. dev. | 0.3–6.9% | | 0.4–3.8% | |

Statistical treatment of the data included the same parameters of Table 1.

Compound **3** is quasi-planar with two phosphinine rings located close to the plane of the silicon atoms, whereas the third one is a little more deviated from this plane. The phosphinine units are slightly distorted and twisted with respect to the axis that contains the phosphorus atom. For macrocycle **4** (in the two structures considered) two opposing phosphinine subunits (P2 and P4) lie almost in the plane defined by the four silicon atoms, whereas the two other subunits (P1 and P3) are located in two parallel planes that are perpendicular to the first one. The calculated compound **4B** has the opened-out partial cone conformation observed by Avarvari et al. [9] in the solid state using X-ray diffraction.

It is interesting to note that molecules **4A** and **4B** are very similar from the geometrical point of view (see Table 1), but differ in their stabilities, as the calculated heat of formations 285.1 and 259.9 kcal $\mathrm{mol}^{-1}$, respectively, indicate. The structure **4B** is more stable than the structure **4A**. According to Avarvari et al. [9] the structure **4B** minimizes the interactions between the electron lone pairs that belong to phosphorus atoms. Indeed, in the parallel structure **4A** the phosphorus atoms that occupy the vertices of a regular quadrilateral are 4.090 Å long, whereas in the antiparallel structure **4B** the edges of the quadrilateral are 0.050 Å longer than in structure **4A**. Another contributing factor to the stability of the structure **4B** is related to the minimization of steric repulsion among the peripheral benzene rings. As shown in Table 1, the phenyl groups in the structure **4B** are maximally separated with respect to the molecular arrangement **4A** and, correspondingly, the van der Waals repulsive interactions must be minimized. According to our calculations, the distance between the opposing atoms P1 and P3 is longer than the nonbonding distance P2-P4, offering an alternative picture to that one obtained by Avarvari et al. using X-ray diffraction [9].

Compounds **5** and **6** exhibit cone-shape centrosymmetric structures with the two phosphinine rings lying on similar planes, whereas the five-membered rings are perpendicularly located with respect to the former. The PM3 calculations reproduce very well the C—X bond distances and the C—X—C bond angles determined experimentally (see Table 2), but yield an inverse quantitative relationship of the calculated cavity sizes for **5** and **6**. Avarvari et al. found that the cavity size of the sulfur derivative **5** is clearly smaller than that of its oxygen counterpart **6**. The corresponding calculated magnitudes were 34.5 and 31.9 Å$^2$ for **5** and **6**, respectively. This result, together with that previously mentioned regarding the cavity size in compound **4** (see above), reinforced the hypothesis about the existence of structural constraints for the molecular crystals of these compounds.

One of the most outstanding structural characteristic of the silacalix[*n*]phosphinines is the flexibility of the C—Si—C bridge. The size of the cavity and the stability of the macrocycle depend directly on the C—Si—C bond angle. For compounds **4A** and **4B** a systematic study on the variation of the structural and energetic parameters with the value of the C—Si—C bond angle was carried out. These results are shown in Fig. 5.

The P—P interatomic distances (for both pairs of opposite phosphorus atoms), and consequently the cavity size, increase with the increasing of the C—Si—C bond angle. On the other hand, the stability of the compounds has a minimum for a cavity size of 33–34 Å$^2$ (110–115° for C—Si—C bond angle). This means that C—Si—C bond angles, smaller or bigger than those in the equilibrium, are responsible for a significant strain in the macrocycle. The P—P(v,h) vs. C—Si—C bond angle curves are not parallel. Therefore, a change in the order of the P—P(v) and P—P(h) interatomic distances can be expected, i.e., a C—Si—C bond angle exists for which the P1—P3 distance becomes longer than the P2—P4 distance such as the X-ray experiment reported. However, this change is only obtained for C—Si—C bond angles that are greater than 120°, for which the macrocycle is remarkably unstable. Current results also indicate that the particular geometries obtained by X-ray studies by Avarvari et al. do not correspond to an energy minimum, but rather result from packing forces in the crystal as those authors observed in Ref. [9].

The flexibility of the silacalix[*n*]phosphinines macrocycle has been proved experimentally by the formation of Rh(0) complexes of phosphinine-containing macrocycles [10] in which the distance between the opposite P atoms was reduced up to ca. 4.54 Å and the metal presence in the center of the macrocycle cavity produced an appreciable effect on its geometry but preserved the macrocycle entity.

The C—Si bond distances as well as the C—Si—C and C—P—C bond angles of the 4-membered macrocycles (compounds **4, 5**, and **6**) are larger than in the 3-membered macrocycle (compound **3**): the C—Si bond length is ~1.87 Å for compounds **4, 5**, and **6** and 0.02 Å shorter in compound **3**. The C—Si—C and C—P—C bond angles are ca. 5° larger for **4, 5**, and **6** than these angles are in **3**. This fact can be understood as an enlargement of the structure in the 4-membered macrocycles which gives rise to a shortening (~0.02 Å) of the P—C bond distances (see Tables 1 and 2).

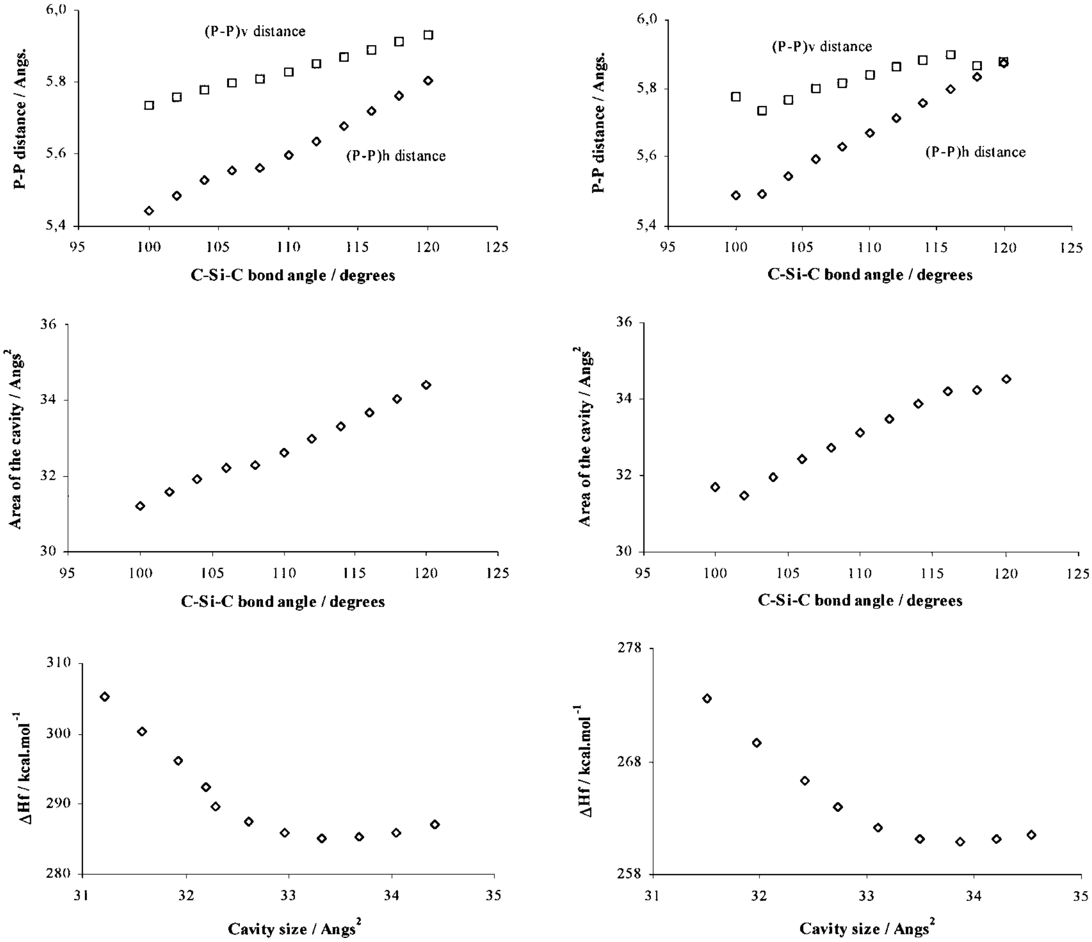


**FIGURE 5** Influence of the C–Si–C bond angle flexibility on the geometric and energetic aspects of **4A** (left) and **4B** (right). Variation of the P1-P3(v) and P2-P4(h) distances (top) and the dimension of the cavity (middle) with the bond angle. Variation of the stability (bottom) of the macrocycle with the dimension of the cavity.

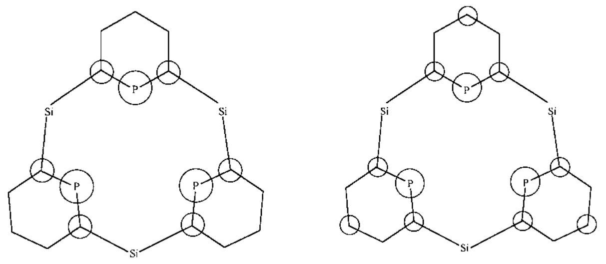
The macrocycle cavity of compound **3** is significantly smaller than those of the 4-membered macrocycles. In compound **3** the internal cavity is delimited by three phosphorus atoms which occupy the vertices of an isosceles triangle with a base of 2.55 Å and sides of 2.50 Å. Under these conditions a P—P interaction can be expected (see section "The P—P Interaction in the Silacalix[3]phosphinine"). This hypothesis is supported by the finding of Cataldo et al. [12] of P—P bond formation by successive one-electron reduction of two-phosphinine-containing macrocycles whose P—P distances (calculated at B3LYP/6-31G* and 6-31+G* levels) lie in the interval 2.368–2.763 Å, which is of the same order as that of the nonbonding P—P distances calculated in the present work for compound **3**.

## *Molecular Orbitals*

Table 3 and Fig. 6 summarize the molecular orbital calculations for the studied compounds. Table 3 shows both the orbital energies and the character for

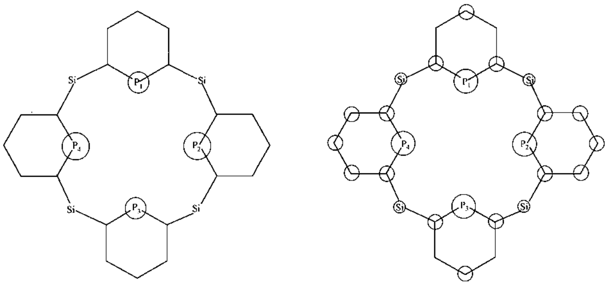
**TABLE 3** Energies (in eV) and Character of Both the HOMOs and LUMOs of the Studied Compounds **1–6**

| | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| L+1 | −0.555 (π) | −0.610 (π) | −1.021 (π) | −1.179 (π) | −1.122 (π) | −1.133 (π) |
| L | −1.345 (π) | −1.405 (π) | −2.117 (π) | −1.242 (π) | −1.149 (π) | −1.204 (π) |
| H | −6.659 (π) | −6.449 (π) | −4.886 (σ) | −6.093 (σ) | −5.815 (σ) | −5.498 (σ) |
| H − 1 | −7.258 (π) | −6.902 (σ) | −5.080 (σ) | −6.220 (π) | −6.045 (σ) | −5.682 (σ) |
| H − 2 | −7.298 (σ) | −6.924 (π) | −5.918 (π) | −6.269 (σ + π) | −6.250 (σ) | −6.331 (σ + π) |



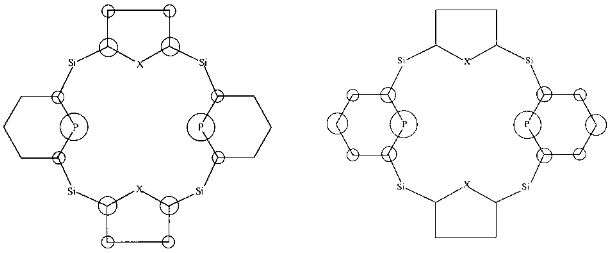
e orbital

$a_1$ orbital



$a_1$ orbital

$a_1$ orbital



$b_2$ orbital

$b_2$ orbital for compound 5
$a_1$ orbital for compound 6

**FIGURE 6** Total atomic contributions both to the HOMO (left) and to the LUMO (right) for **3** (top), **4** (middle), and **5, 6** (bottom).

the highest occupied (HOMOs) and the lowest unoccupied (LUMOs) molecular orbitals.

Figure 6 gives the atomic contributions to the frontier molecular orbitals. In these representations the diameter of the circles is proportional to the values of $C_i$. $C_i$ is defined as $C_i = \sum |c_i|$, where $c_i$ are the coefficients of the atomic orbitals in the molecular orbital linear combination. For all the silacalix[$n$]phosphinines the mean plane of the molecule is located on the $xy$ plane, the $x$-axis being oriented in the direction of P4-P2. The $z$-axis coincides with the corresponding symmetry axis for each compound.

For phosphinine and its *ortho*-$Si(CH_3)_3$ derivative, because of their planarity, the $\sigma$- or $\pi$-character of the molecular orbitals can be established without doubt. However, for silacalix[$n$]phosphinines (and specially in the case of the compounds **4, 5**, and **6**) the $\sigma$- or $\pi$-character of the molecular orbitals is not so easily determined. Some of them result from the contribution of atomic orbitals of different spatial distributions. Nonetheless, it is possible to recognize a prevailing character.

Table 3 demonstrates that *ortho*-$Si(CH_3)_3$ substitution simultaneously improves the $\sigma$-donating and $\pi$-accepting properties of the phosphinine, compound **3** having both the HOMO and the LUMO energies among the studied series. The latter is presumably related with the P—P interaction mentioned in the previous section (see section "The P—P Interaction in the Silacalix[3]phosphinine").

The near-frontier molecular orbital profiles vary from one silacalix[$n$]phosphinine to another, but Fig. 6 shows that the main contribution to those orbitals correspond to the phosphorus atoms of the phosphinine units and other atoms of the cavity. This means that the chemically more-active atoms are located precisely around the macrocycle cavity. This result confirms the proposal of Avarvari et al. [9] for creating flexible phosphorus cavities to encapsulate metals of different sizes using chemical mechanisms.

In compounds **3** and **4**, the HOMOs are mainly located over specific regions of the molecule, whereas the LUMOs are more extended over the whole molecule. That is, LUMOs are more collective than HOMOs. One difference can be established between compounds **3** and **4**: in the former, the contributions of all phosphinine units are very similar because of their quite-planar spatial distributions, but in the latter one the contributions of the horizontal and perpendicular phosphinine units are remarkably different. In compound **3**, as expected from its tendency to planarity, the HOMOs and LUMOs have pure $\sigma$- and $\pi$-characters, respectively (Table 3), but in compound **4** the picture is more complicated. The HOMO-1 in compound **4** does not contain contributions of the perpendicular phosphinine groups and its $\pi$-character results from the contributions of the $p_z$ atomic orbitals. That is, it can be rationalized as two interacting phosphinine HOMOs (the phosphinine rings being frontally located in the same plane). The electron repulsive interaction between both phosphinine rings explains the destabilization (0.439 eV) of the HOMO-1 in compound **4** with respect to the HOMO of the phosphinine. On the other hand, compound **4** needs to combine the $p_x$ contributions of the horizontal phosphorus with the $p_y$ contributions of the vertical ones to yield an HOMO that involves the four phosphorus atoms of the macrocycle cavity. Compound **4** has the major atomic contributions to LUMOs on the planar part of the molecule having $\pi$-character. Finally, compounds **3** and **4** show a significant contribution of the silicon atoms to their $\pi$-accepting properties.

The profiles of the frontier orbitals of compounds **5** and **6** preserve some of the characteristics revealed for compound **4**. However, the idea of a reactive cavity is less evident because O and S atoms do not make any contribution to the more active molecular orbitals. Additionally, the carbon atoms of the thiophen(furan) rings contribute to their $\sigma$-donating properties but do not contribute to the $\pi$-accepting ones. Some distinctive features observed in the electronic structure of Rh(0) complexes with compounds **4** and **5** [10] are in correspondence with the details revealed by our calculations. While the ligand orbitals largely participate in the SOMO of the Rh(0) **4** complex including the four phosphorus atoms, in the Rh(0) **5** complex the unpaired electron is mainly delocalized on the rhodium and two phosphorus atoms, the spin density being very small on each sulfur atom.

### *The P—P Interaction in the Silacalix[3]phosphinine*

In order to confirm the existence of a P—P bonding interaction in compound **3**, two different dimeric structures with variable P—P distances were calculated (Fig. 7): (i) A simple diphosphinine system (Fig. 7a) with linear configuration and (ii) the macrocyclic dimer **1a** in Ref. [12] (Fig. 7b). The calculations were performed at B3LYP/6-31G** level.

The geometry of the macrocyclic dimer was optimized for different frozen P—P nonbonding distances. It was observed that the macrocyclic dimer finds an energy minimum for 2.5–3.0 Å which agrees with the P—P nonbonding distance observed in **3**. As shown in Fig. 8 the HOMO energies of the dimers increase with the decreasing of the P—P distance. For both the simple-linear and the macrocyclic dimers the values obtained fit in the interval of 2.5–3.0 Å, so that they are almost identical. The energies for the frontier orbitals for the interval of 2.5–3.0 Å are similar to those values found in compound **3**. Therefore, the $\sigma$-character of the HOMO and the $\pi$-character of the LUMO observed in compound **3** is reproduced in the model dimers.

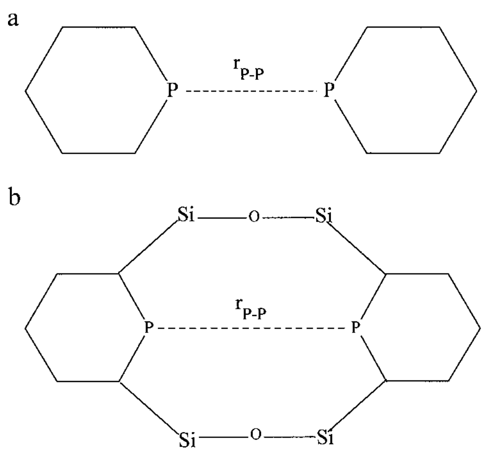


**FIGURE 7** Model structures calculated for studying the P—P interaction in the silacalix[3]phosphinine **3**.

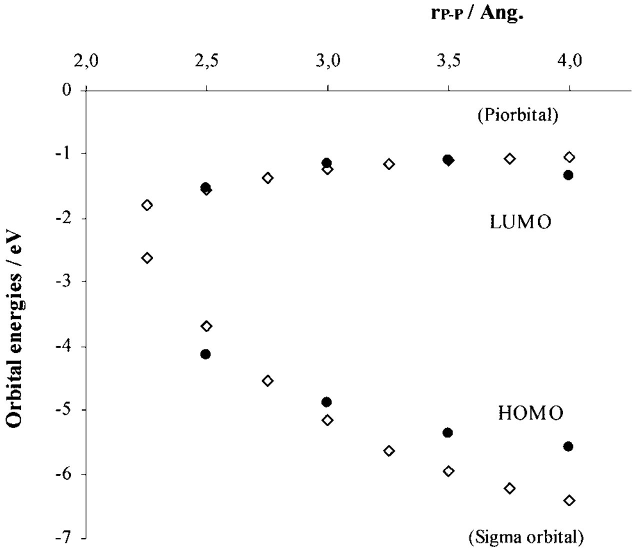


**FIGURE 8** Energies (in eV) of the frontier orbitals for the dimeric structures calculated in the present work. Open diamonds correspond to linear dimers (see Fig. 7a). Solid circles correspond to the macrocyclic dimers (see Fig. 7b).

The proposed P—P bonding interaction in compound **3** would explain the quasi-planar geometry observed by X-ray studies and obtained in geometry optimization calculations. Presumably, compound **3** tends to planarity in order to maximize the overlapping of the electronic clouds of the P atoms. This process, which occurs because of the flexibility of the C—Si—C bridges, minimizes the energy of the system.

This idea can be understood when the structure of the silacalix[3]phosphinine and the structure of the subphthalocyanine (SubPc) are compared [13a]. The SubPc is the analogue of **3** in the family of pyrrole-aza macrocycles. In this family—unlike that in silacalix[*n*]phosphinines—the 4-membered macrocycles (the phthalocyanines) are, as a rule, planar, whereas the 3-membered ones (the SubPcs) exhibit pyramidal configuration. This is mainly because of the repulsive interactions among the three isoindole units bonded by the *meso*-nitrogen atoms [13a]. On the other hand, in compound **3** the arising P—P attractive interaction could overtake the repulsion among the phosphinine units. In the SubPcs, the attraction among the pyrrole nitrogens—equivalent to the P—P interaction in **3**—does not exist.

## CONCLUDING REMARKS

The present calculations confirm that *ortho*-Si$(CH_3)_3$ substitution in phosphinine improves its σ-donating and π-accepting properties. Moreover, results also show that macrocycle arrangements structured by phosphinine (thiophene/furane) units linked by C—Si—C bridges have flexible cavities with strong π-acceptor bonding sites which are adequate to encapsulate metals.

Quantum chemical geometry optimizations at a semiempirical level adequately reproduce the cone-shape structure as well as the X-ray geometry for a family of silacalix[*n*]phosphinines. The major discrepancy between experimental and theoretical data was obtained for C—Si—C bond angles, since the calculated values are 4.1–7.4° bigger than those obtained experimentally.

The C—Si—C joint provides a remarkable flexibility to the silacalix[*n*]phosphinines. Thus, the C—Si—C bond angle values may vary within a wide interval preserving the macrocycle conformation but producing appreciable variations on the stability of the compounds and monotonous variations in the cavity size.

The calculations only reproduce the relative dimensions of the macrocycle cavity for unstable structures observed experimentally. The comparison of the structural information obtained by experimental X-ray and by computational procedures reveals that the particular geometries previously obtained by X-ray diffraction do not correspond to an energy minimum, but result from packing forces in the crystal.

The calculations show that the main contributions to HOMOs and LUMOs correspond, as a rule, to the atoms that belong to the macrocycle cavity. This fact confirms the proposal of some chemists for obtaining structurally flexible and chemically active cavities to house metals of different sizes and geometric environments.

In silacalix[3]phosphinine macrocycles, the P atoms interact chemically, thus determining an exceptional decreasing of the HOMO–LUMO *gap* with respect to the 4-membered macrocycles. This suggests that P—P interaction in this class of compounds strongly modifies the electronic structure of the phosphinine ring.

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