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Conformational Analysis of 1-Sila-4-phospha-2,5-cyclohexadienes

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Abstract—Conformational analysis of 1-sila-4-phospha-2,5-cyclohexadienes was performed using the methods of dipole moments and quantum-chemicall calculations (DFT B3LYP/6-31G*). Irrespective of the degree of coordination of the phosphorus atom (3 or 4) the unsaturated six-membered heterocycles adopt the conformation of a flattened *boat* with the exocyclic phenyl group oriented perpendicular to the double bonds of the heterocycle. This conformation rules out the possibility of intramolecular transannular interaction between the phosphorus and silicon atoms.

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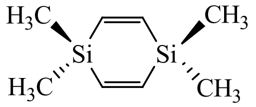
Published data on the conformations of compounds having two planar fragments in the ring are rare. It was stated in review [1] that for the derivatives of 1,4-cyclohexadiene the only possibility for variation of conformation of the planar six-membered ring is its bending so that the cycle adopts the *boat* conformation.

Investigation of the structure of 1,4-cyclohexadiene by the methods of vibrational and rotational spectroscopy, gas electron diffraction, and NMR spectroscopy led to the conclusion on the planar structure of the molecule [2], the potential well being very shallow, the effective angle equal to 167°. Nevertheless, in some works some nonplanarity of the six-membered ring was suggested [3], although calculations showed predominance of the planar structure [2].

As to the phosphorus analogs of 1,4-cyclohexadiene, only few data are available. Only the structure of 1-R-2,6-di-*tert*-butyl-4-phenyl-4-oxo-1-aza-4-phospha-2,5-cyclohexadienes (R = H, *t*-Bu) is known [3]. XRD study of these compounds showed that the six-membered heterocycles in their molecules are planar. For the silicon-containing cyclohexadienes, a distorted *chair*-like conformation was found in the sterically overloaded 1,1,4,4-tetraphenyl-1,4-disila-2,5-cyclohexadiene as determined by XRD analysis [4]. Bokii and Struchkov attributed the formation of this structures to the steric hindrances between the bulky substituents. Several examples of XRD study are known for organophosphorus compounds with two multiple bonds C=N and C=C, for example, the rings with the C=N and P=N bonds [5], and also six-membered rings [6]. In the case of 3,5-diene [5] the six-membered heterocycle has the conformation of a strongly flattened *boat*, in 2,4-diene [6] the molecular fragment containing multiple bonds is also strongly flattened, which allowed to Chekhlov a suggestion on the delocalization of the π-electron density.

Therefore, it is of obvious interest to investigate the structure and polarity of 1,4-silaphospha-2,5-cyclohexadienes containing in the six-membered ring both the phosphorus and silicon atoms. Additional interest in these compounds is due to the fact that the presence of a donor (three-coordinate phosphorus atom) and acceptor ($SiMe_2$ group) centers in one molecule may result in an intramolecular transannular interaction P→Si.

In the present paper we report on the conformational analysis of 1,1-dimethyl-1-sila-4-phenyl-4-phospha-2,5-cyclohexadiene (**I**) and 1,1-dimethyl-1-sila-4-seleno-4-phenyl-4-phospha-2,5-cyclohexadiene (**II**) by the methods of dipole moments and quantum chemistry (DFT B3LYP/6-31G*). The planar and *boat* conformations with the equatorial (B_e) and axial (B_a) exocyclic substituent at the phosphorus atom have been analyzed. As a reference compound, the six-membered heterocycle with two silicon atoms and two C=C bonds, namely, 1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**III**) was chosen.



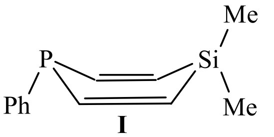
III

According to quantum-chemical calculations the ring in disilacyclohexadiene **III** is ideally planar, the methyl groups are perpendicular to the plane of the ring, the theoretical dipole moment is equal to zero.

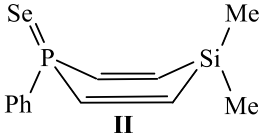
Below, the dipole moments of silaphosphacyclohexadienes **I, II** are given obtained experimentally, calculated using the additive vector scheme, and by quantum-chemical procedures.

Comp. no.	**I**	**II**
μ_{theor}, D	1.32	5.21
μ_{calc}, D	1.97	5.30
μ_{exp}, D	2.05	5.76

Unlike compound **III**, the replacement of one of the silicon atoms in the ring by the phosphorous atom results in nonplanarity of the six-membered ring. For cyclohexadienes **I, II** quantum chemical calculations revealed only one energy minimum corresponding to a flattened *boat* conformation with the phenyl substituent perpendicular to the plane of the double bonds of the heterocycle. We failed to find local energy minima corresponding to planar or *chair*-like conformations. The optimized conformations of compounds **I, II** are given below.



I



II

From the results of calculations, the ring in molecule **I** has the conformation of a flattened *boat*, the *chair* conformer does not exist. The out-of-plane angle between the phosphorus atom and the plane of the double bonds C=C is 25°, for the silicon atom, 14°. The methyl groups and the plane of the phenyl ring are perpendicular to the ring plane (the plane of the double bonds C=C). The dipole moment is equal to 1.32 D.

The conformation of the ring in molecule **II** is also a flattened *boat*, the *chair* conformer does not exist either. The out-of-plane angle between the phosphorus atom and the plane of the double bonds C=C is 11°, for the silicon atom, 6°. The methyl groups, the plane of the phenyl ring, and the P=Se bond are perpendicular to the ring plane (the plane of the double bonds C=C). The dipole moment is equal to 5.21 D.

According to the obtained conformational result the theoretically possible transannular intramolecular electronic interaction P→Si in hexadiene **I** with the three-coordinate phosphorus atom cannot be realized because of the structure of the molecule. The P···Si distance is 3.528 (**I**) and 3.532 Å (**II**), which is somewhat less then the sum of the van der Waals radii (3.9 Å). According to calculations (B3LYP/6-31G*), the electron density between the P and Si atoms in molecule **I** is 0.036 *e*, which is about 10 times less than in a normal covalent bond (for comparison, the electron density in this molecule between the atoms PC= is 0.328 *e*). As follows from the presented data, the calculated dipole moments adequately describe the experimental data on the polarity of the studied silaphosphacyclohexadienes. Theoretical values of polarity are also close to the experiment although the difference is larger, probably, due to errors in the method of calculations B3LYP/6-31G*.

Therefore, 1-sila-4-phospha-2,5-cyclohexadienes in solution exist in the conformation of a flattened *boat* with the exocyclic phenyl group perpendicular to the plane of the double C=C bonds of the heterocycle.

For a hypothetical planar structure of cyclohexadiene **I** with the three-coordinate phosphorus atom the dipole moment calculated using the vector additive scheme is equal to 1.12 D, and for cyclohexadiene **II** to 3.61 D. Both values are substantially (by ~1 and >2 D) less than the experimental dipole moments of the studied compounds, so, this structure can be rejected from the consideration for both compounds.

The following dipole bond and group moments were used in the calculations: *m*($SiCH_3$) 1.48 D [7], *m*(PhP) 1.09 D [8], *m*(P=Se) 4.0 D [9], the group moment *m*(SiVin) 1.02 D [10].

EXPERIMENTAL

The studied compounds are hydrolytically unstable, therefore all physicochemical measurements of quantitative characteristics of their electric properties and refraction indices were performed in an argon atmosphere for a series of 4–6 solutions of the compounds in dioxane at 25±0.2°C. The solvent was purified directly prior to measurements using standard procedures described in [11]. For determination of experimental values of the dipole moments the second Debye method was used based on the measurement of the dielectric permeability of diluted solutions in nonpolar solvent [12]. The dielectric permeability of the solutions was measured on a IDM-2 instrument [13] in pulse regime. The error of measurements of dielectric permeability was ±0.5%.

Refraction indices of the solutions were measured on an IRF-23 refractometer (error ±0.00005) for the *D*-line of sodium.

Comp. no.	**I**	**II**
α	2.966	14.404
γ	0.502	0.379
P_{or}, cm^3	86.829	684.953
μ, D	2.05	5.76

Coefficients of the calculated equation and experimental dipole moments of the studied compounds are given above. The error in determination of the experimental dipole moments was ±0.05 D.

Quantum-chemical calculations of compounds **I–III** with full geometry optimization were performed with the Gaussian 03 program package [14]. The stationary points were identified as energy minima from the calculation of the second derivatives; in all cases the eigenvalues of the Hessian were positive. All calculations were performed in the Kazan Branch of Interdepartamental Supercomputer Center of the Russian Academy of Sciences.

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