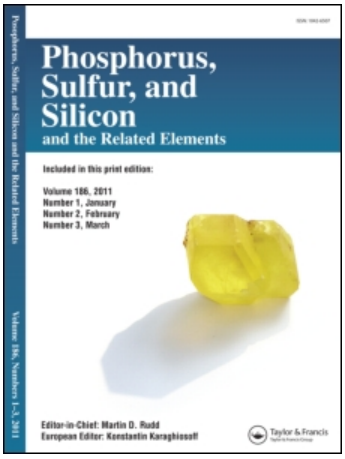


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Conformational Analysis of 1,4-Heterophosphinanes

Yana A. Vereshchagina[ab]; Aisylu A. Gazizova[a]; Denis V. Chachkov[a]; Eleonora A. Ishmaeva[b]; Mikhail G. Voronkov[c]

[a] Kazan State Technological University, Kazan, Russia [b] Kazan State University, Kazan, Russia [c] A. E. Favorsky Irkutsk Institute of Chemistry SB of RAS, Irkutsk, Russia

To cite this Article Vereshchagina, Yana A. , Gazizova, Aisylu A. , Chachkov, Denis V. , Ishmaeva, Eleonora A. and Voronkov, Mikhail G.(2008) 'Conformational Analysis of 1,4-Heterophosphinanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 2, 452 — 455

To link to this Article: DOI: 10.1080/10426500701761177

URL: http://dx.doi.org/10.1080/10426500701761177

Phosphorus, Sulfur, and Silicon, 183:452–455, 2008

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701761177

Taylor & Francis
Taylor & Francis Group

Conformational Analysis of 1,4-Heterophosphinanes

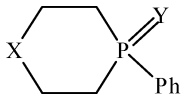
Yana A. Vereshchagina,[1,2] Aisylu A. Gazizova,[1] Denis V. Chachkov,[1] Eleonora A. Ishmaeva,[2] and Mikhail G. Voronkov[3]

[1]Kazan State Technological University, Kazan, Russia
[2]Kazan State University, Kazan, Russia
[3]A. E. Favorsky Irkutsk Institute of Chemistry SB of RAS, Irkutsk, Russia

Structure of 1,4-heterophosphinanes in solution was studied by the methods of dipole moments, Kerr effect, molecular mechanics, and density functional theory calculations. It was determined that chair conformation with an equatorial orientation of the exocyclic phenyl substituent is preferred for 1,4-heterophosphinanes independent of the second heteroatom in six-membered phosphorus heterocycle (oxygen, sulfur or silicon), and the coordination state of the phosphorus atom (σ^3P or σ^4P).

Keywords Conformational analysis; dipole moments; heterophosphinanes; quantum chemical calculations

Spatial structure of a number of six-membered phosphorus-containing heterocycles was studied in detail by the methods of X-ray, vibrational and NMR spectroscopy, Kerr effect, and dipole moments. Information about the structure of phosphacyclohexane analogs containing heteroatom in first position of the cycle is still scarce.[1–3] We carried out conformational analysis of 4-substituted 1,4-heterophosphinanes **1–3** (Scheme 1) using the methods of dipole moments, Kerr effect, molecular mechanics, and quantum chemical calculations (DFT B3LYP/6-31G*).



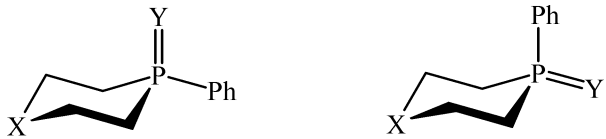
1 X = S, Y = Se
2 X = $SiMe_2$, Y = Se
3 X = $SiMe_2$, Y = lone pair of electrons (LPE)

SCHEME 1

Address correspondence to Yana A. Vereshchagina, Kazan State Technological University, K. Marx St., 68, Kazan, 420015, Russia. E-mail: yavereshchagina@yahoo.com

Previously, it has been determined that the oxygen analogue of these compounds, namely 4-phenyl-4-oxo-1,4-oxaphosphinane, has the *chair* form with equatorial orientation of the exocyclic phenyl substituent and axial orientation of the P=O group in solution.[3] We have studied how different heteroatoms in the cycle influence the structure of heterophosphinanes.

Originally, we studied the conformational composition of **1–3** by the molecular mechanics method using Dashevsky-Plyamovaty's force field.[4] The analysis of obtained results shows the energetical preference of *chair* conformations for all investigated compounds. Previously, the same conclusion was drawn for the oxygen analogue of the studied phosphinanes.[3]



chair$_e$ *chair*$_a$

SCHEME 2

Subsequent identification of the forms in the conformational equilibrium was performed by the method of dipole moments. We determined the experimental dipole moments for **1–3** in dioxane solution using the second Debye method, and calculated the dipole moments for *chair* conformations using the vector-additive scheme (Table I). The comparison of the experimental dipole moments with the calculated values shows that **1-3** have a *chair*$_e$ conformation with the preferred equatorial orientation of the Ph substituent.

In contrast to the dipole moment, the Kerr constant is sensitive to a rotation of the benzene ring about the P−C$_{ar}$ bond. Therefore, we determined the experimental Kerr constant of phosphinane **2** in dioxane solution, and calculated the Kerr constants for two possible orientations of a phenyl group: in the first form, the Ph group and the P=Se bond have parallel arrangement, and in the second form, they are perpendicular. The analysis of the experimental and calculated Kerr constants for **2** led to a conclusion about the preferred *chair* conformation of the six-membered cycle with the parallel orientation of the phenyl ring and the selenophosphoryl group.

The relative energies and the theoretical polarities of the possible conformers of examined compounds were calculated using DFT B3LYP/6-31G* method (Table II). The conformers with axial orientation of the P–Se bond (**1**, **2**) or the LPE at the phosphorus atom (**3**) and

TABLE I Experimental and Calculated Dipole Moments of Heterophosphinanes 1–3

Compound	μ_{calc}, D		μ_{expt}, D (dioxane)
	Chair$_a$	Chair$_e$	
1	4.07	4.31	4.39
2	4.71	5.13	5.30
3	0.96	1.87	1.82

equatorial orientation of the phenyl substituent have the global energy minima. Note that the experimental data are in a good agreement with the theoretical results for **1–3**.

Thus, the study of spatial structure of 1,4-heterophosphinane systems, carried out using the complex of supplementing each other physical methods as well as theoretical calculations, showed that the preferred conformation of 1,4-thia- and silaphosphinanes with σ^4P is the *chair* form with axial orientation of the P=Y bond and equatorial orientation of the Ph group. In solution, conformational behavior of 1,4-heterophosphinanes with σ^4P is analogous to that of the phosphinanes systems. The introduction of the second heteroatom (oxygen, sulfur, or silicon) to the fourth position of heterocycle does not affect the preferred axial orientation of the P=Y bond and equatorial orientation of the phenyl group, the latter is also kept in tri-valence derivative.

TABLE II Data of B3LYP/6-31* Calculations and μ_{expt} of 1–3

Conformer		ΔE, kcal·mol^{-1}	μ_{theor}, D	μ_{expt}, D
Chair$_a$	$\mathbf{1}^a_{\parallel}$	4.90	4.72	4.39
	$\mathbf{1}^b_{\perp}$	5.12	4.66	
Chair$_e$	$\mathbf{1}_{\parallel}$	0	4.37	
	$\mathbf{1}_{\perp}$	is not achieved		
Chair$_a$	**2**||	4.53	5.61	5.30
	2⊥	5.17	5.85	
Chair$_e$	**2**||	0	4.69	
	2⊥	is not achieved		
Chair$_a$	**3**||	3.50	1.54	1.82
	3⊥	0.90	1.61	
Chair$_e$	**3**||	0	1.32	
	3⊥	0.46	1.40	

[a]The P=Se bond and the Ph ring are parallel; and
[b]the P=Se bond and the Ph ring are perpendicular.

REFERENCES

[1] B. M. Gatenhouse and B. K. Miskin, *Acta Crystallogr.*, **30,** 2212 (1974).
[2] A. N. Chekhlov, N. A. Bondarenko, M. V. Raitarskaya, N. V. Rudomino, E. N. Tsvetkov, and I. V. Martynov, *Izv. AN SSSR. Ser. Khim.*, 2625 (1988).
[3] F. Kh. Karataeva, I. K. Kushnikovskaya, I. I. Patsanovsky, and E. A. Ishmaeva, *Zh. Obshch. Khim.*, **61,** 2562 (1991).
[4] A. Kh. Plyamovaty, V. G. Dashevsky, and M. I. Kabachnik, *Dokl. AN SSSR*, **234**, 1100 (1977).