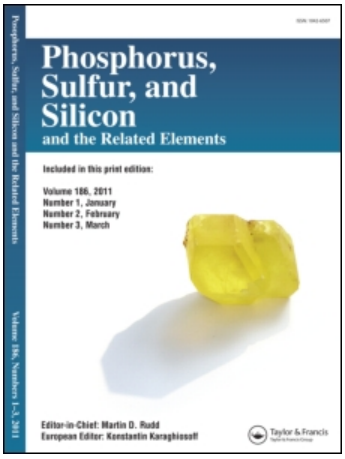

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Quantum-Chemical Investigation of Electronic and Spatial Structure of 1,2-Dihydro 1,2-Azaphosphorines and their Analogs

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To cite this Article Levina, Elina Ya. , Zverev, Vladislav V. and Kibardin, Alexander M.(1999) 'Quantum-Chemical Investigation of Electronic and Spatial Structure of 1,2-Dihydro 1,2-Azaphosphorines and their Analogs', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 177
To link to this Article: DOI: 10.1080/10426509908053569
URL: http://dx.doi.org/10.1080/10426509908053569

Phosphorus, Sulfur and Silicon, 1999, Vol. 147, pp. 177-177
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Quantum-Chemical Investigation of Electronic and Spatial Structure of 1,2-Dihydro 1,2-Azaphosphorines and their Analogs

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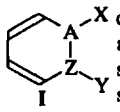
As part of our studies of 1,2-dihydro1,2-azaphosphorines [1, 2], we have carried out *ab initio* investigation of the set of model six membered (hetero)cycles **1** and defined the influence of the bridge A–Z on the their parameters (3-21G* and 6-31G*, GAMESS, full optimization of geometry). In all structures studied only one twist conformer is realized. In PN structures substitutients at the hetero atoms are at different sides of the cycle, a substitutient at phosphorus being axial. The P atom is pyramidal, N atom is planar.



I

Bond length, Å					
bridge	C-C	(A)C=C	C=C(Z)	A-B	P–Cl
$-CH_2-CH_2-$	1.475	1.324	1.324	1.533	–
$-CH_2-NH-$	1.466	1.325	1.330	1.455	–
$-PH-CH_2-$	1.472	1.328	1.325	1.858	–
-PH-NH-	1.460	1.332	1.336	1.718	–
-PH-NMe-	1.454	1.334	1.343	1.787	–
-NH-NH-	1.467	1.324	1.324	1.406	–
$-PCl-CH_2-$	1.469	1.330	1.325	1.850	2.102
-PCl-NH-	1.448	1.337	1.335	1.695	2.379
-PCl-NMe-	1.445	1.337	1.336	1.698	2.155

There is a tendency of shortening of a single C–C bond and lengthening of double C=C bonds induced by substitution a heteroatom for one or two CH_2 groups in 1,3-cyclo hexadiene, it becoming especially evident for azaphosphorines. Torsion angles around cycle bonds are essentially different; the maximum being an angle around A–Z bond (about 34° for P(H)–C and P(H)-N, about 25° for P(Cl)–N). A torsion angle around C–C bond in the diene system (10–17°) is dependent mainly on a bridge length. Values of C–C=C–A and C–C=C–Z dihedral angles are less than 6.5°. So, introduction of hetero atoms, as well as of Cl atom, planarises **I**, the effect of Cl being more in PN systems than in PC ones.

There is a good linear correlation of values of Lowdin charges (q) on cycle carbon atoms in model structure **I** (-PCl-NMe-) and chemical shifts (δ) of these atoms in ^{13}C NMR spectra of 1-*tert*buthyl 2-chloro 1,2-dihydro 1,2-azaphosphorine **I** (-PCl-NBu^t-): $q = 75.86 + 138.5q$; $r = 0.969$, $s_0 = 3.13$.

References

[1] Ya. A. Levina, A.N. Pudovik, Sh.K Latypov, R.Z. Musin, A.M. Kibardin, Izv. Akad. Nauk SSSR, Ser. Khim. (Russ. Chem. Bull.), **1989**, 490.

[2] Ya. A. Levina, A.N. Pudovik, A.M. Kibardin, Zh. Obshch. Khim.(J. Gen. Chem.), **60**, 759, (1990).