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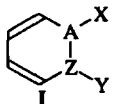
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## Quantum-Chemical Investigation of Electronic and Spatial Structure of 1,2-Dihydro 1,2-Azaphosphorines and their Analogs

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As part of our studies of 1,2-dihydro 1,2-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 substituents at the hetero atoms are at different sides of the cycle, a



bridge	Bond length, Å					substituent at phosphorus being axial. The P atom is pyramidal, N atom is planar.
	C-C	(A)C=C	C=C(Z)	A-B	P-Cl	
-CH <sub>2</sub> -CH <sub>2</sub> -	1.475	1.324	1.324	1.533	-	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 <sub>2</sub> groups in 1,3-cyclo hexadiene, it becoming especially evident for azaphosphorines. Torsion angles around cycle bonds are essentially
-CH <sub>2</sub> -NH-	1.466	1.325	1.330	1.455	-	
-PH-CH <sub>2</sub> -	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	-	
-PCI-CH <sub>2</sub> -	1.469	1.330	1.325	1.850	2.102	
-PCI-NH-	1.448	1.337	1.335	1.695	2.379	
-PCI-NMe-	1.445	1.337	1.336	1.698	2.155	

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** (-PCI-NMe-) and chemical shifts (δ) of these atoms in <sup>13</sup>C NMR spectra of 1-*tert*buthyl 2-chloro 1,2-dihydro 1,2-azaphosphorine **I** (-PCI-NBu<sup>t</sup>-): q = 75.86 + 138.5q; r = 0.969, s<sub>0</sub> = 3.13.

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