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Quantumchemical Investigation of Unsaturated Sixmembered Heterocycles: I. Steric and Electronic Structures of 1,2-dihydro-1,2-azaphosphorin

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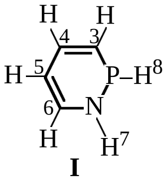
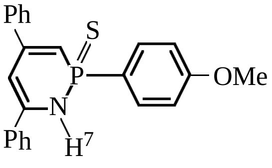
Abstract—By quantumchemical calculations of 1,2-dihydro-1,2-azaphosphorin by semiempirical and *ab initio* calculations we discovered that in gas phase it has twist form with planar nitrogen and pyramidal phosphorus atoms, the latter with a pseudoaxial substituent. The N–H and P–H bonds occupy anticlinal positions.

Earlier we [1–4] and French investigators [5] prepared 1,2-disubstituted 1,2,3,5- and 1,2,4,6-tetrasubstituted 1,2-dihydro-1,2-azaphosphorins with tetracoordinated phosphorus atom, the derivatives of compound **I**.



I

These compound can be considered as *syn-peri*-planar (*s-cis*) 1,3-butadienes, closed by the diatomic P–N bridge into a sixmembered ring. An interesting problem is the mutual influence in such compounds of conjugated diene system and the dihetero-bridge. However, up to now there is no data on steric and electronic structure of such antiaromatic $(8\pi,n)$ heterocycles. No systematic data was found concerning similar heterocyclic systems (1,2-diheterynes) with other hetero-bridges. There are only X-ray structural data for 2-*p*-methoxyphenyl-4,6-diphenyl-1,2-dihydro-2-thio-1,2-azaphosphorin (**II**) with tetracoordinated phosphorus atom [6, 7].



II

For elucidation of electronic and steric structure of nonsubstituted 1,2-dihydro-1,2-azaphosphorin (**I**) we performed corresponding quantumchemical calculations. The *ab initio* calculation of this simple enough molecule can be performed with a wide basic set, and one can follow to the influence of the complexity of used basis on the results of the calculation, to compare results of nonempirical and semiempirical calculations and to find the optimal basis for the calculation of more complex molecules. Preliminary results of our calculations for compound **I**, its analogs with other heterobridges, and related compounds were published earlier [8, 9].

All the calculations were performed with complete geometry optimization using GAMESS [10] program package. The semiempiric calculations were conducted in MNDO and AM1 approximations. For the *ab initio* calculations we applied STO 3G, 3-21G, and 6–31G bases as well as 3-21G(d) including *d* functions on phosphorus, 6-31G(d) and 6-31G(2d), with *d* functions on C, N and P, and 3-21G(d,p), 6–31G(d,p) and 6-311G(d,p), which, besides, included *p* functions on H atoms. For the more precise description of lone electron pairs, we applied the bases 6-31++G and 6-31++G(d) with inclusion of diffuse *s* functions on hydrogen atoms and *s* and *p* functions on the other atoms. The *z* matrix was taken in correspondence with recommendations given in the GAMESS manual [10] for sixmembered ring (all six bond lengths including the closing one and three alternating pairs of bond and dihedral angles were predefined) It is noteworthy that traditional consecutive definition of *z* matrix did not lead to errors. For the stationary points we calculated second derivative matrix confirming their nature as the potential energy minima. The Fig. 1 was drawn using a PLATON 98 [11] routine.

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Table 1. Energy (a.u.) and bond lengths (Å) in compounds **I** and **II**.

Method	–*E*	N–P	P–C^3	C^3=C^4	C^4–C^5	C^5=C^6	C^6–N
Compound **I**							
AM1	34.118	1.621	1.678	1.339	1.439	1.366	1.365
MNDO	35.283	1.666	1.718	1.352	1.454	1.366	1.388
STO 3G	543.723	1.778	1.862	1.316	1.479	1.323	1.420
3-21G	547.211	1.758	1.857	1.327	1.459	1.335	1.378
3-21G(d)	547.324	1.707	1.812	1.331	1.460	1.333	1.390
3-21G(d,p)	547.359	1.708	1.812	1.332	1.461	1.334	1.392
6-31G	549.969	1.782	1.860	1.334	1.456	1.342	1.375
6-31++G	549.979	1.780	1.859	1.337	1.457	1.345	1.374
6-31G(d)	550.096	1.718	1.820	1.332	1.460	1.336	1.376
6-31G(2d)	550.101	1.712	1.818	1.329	1.459	1.332	1.374
6-31++G(d)	550.106	1.720	1.820	1.335	1.460	1.339	1.375
6-31G(d,p)	550.110	1.717	1.820	1.332	1.460	1.335	1.376
6-311G(d,p)	550.173	1.712	1.820	1.331	1.461	1.335	1.376
Compound **II**							
X-ray structural analysis [6, 7]	–	1.687	1.745	1.339	1.440	1.355	1.377

Tables 1–7 show the results of the performed calculations. The pyramidality of nitrogen and phosphorus atoms ($\Sigma\alpha$) is estimated from the sums of bond angles at the atoms, the ring planarity (*pl*) is given by average deviation of torsion angles of six endocyclic bonds from the value for the cisoid arrangement. Tables 1, 3–5 contain for comparison the experimental geometric parameters measured for compound **II**.

The data in Table 1 shows that both semimpirical and *ab initio* calculations result in qualitatively similar descriptions of the structure of azaphosphorin **I**. Use of ten nonempirical bases from 3-21G to 6-311G(d,p) including 6-31++G and 6-31++G(d), give little different results, at least in comparison with the results obtained by whole array of the used methods. However, the *ab initio* calculations with simple non-valence-split basis set STO 3G differ from the calculations with above mentioned ten nonempirical sets like semiempirical calculations, that is, is not preferred. Therefore in further discussion the terms "*ab initio*" and "nonempirical calculations" assumes application of ten basic sets from 3-21G to 6-311G(d,p), while STO 3G is excluded.

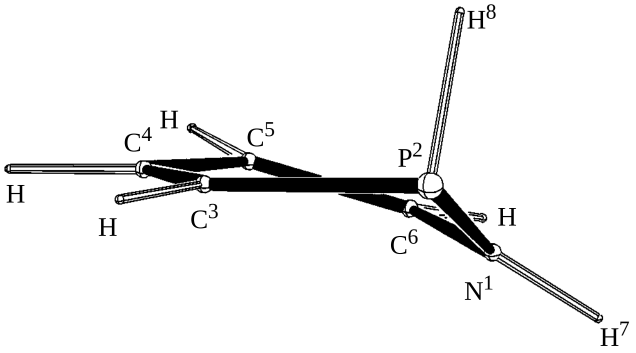

Fig. 1. Molecular structure of azaphosphorin **I**.

Naturally, splitting of basic set of core electrons affects the total energy value much more than extension of the basic set by inclusion of hydrogen *d* and/or *p* functions: in the series 3-21G–3-21G(d)–3-21G(d,p) and 6-31G–6-31G(d)–6-31G(2d)–6-31G(d,p) the energy falls down much slower than in going from 3-21 series to 6-31. Therewith, the energy calculated with 3-21G(d,p) basis , turns to be higher than those with 6-31G with no *d* functions. In both the series, effect of *d* functions on the decrease of calculated energy is higher that adding of *p* functions. Ever less effect occurs at splitting of *d* functions in 6-31G(2d) and extra splitting of the function of valence electrons in 6-311G(d,p) method. Introduction of diffuse *s* and *p* orbitals [6-31++G and 6-31++G(d) methods] also weakly affects value of the total energy of the molecule. These observations are in correspondence with commonly occurred at comparison of calculations for simple organic molecules with different basic sets [12] and hence 1,2-azaphosphorin (**I**) is not anomalous. Finally, it is noteworthy the trend to shortening of P–C and P–N bonds, increasing of bond angles at P and N atoms and increasing of torsion angles with these atoms at the extension of basic sets. Splitting of basic functions also affects the same torsion angles.

Table 2. Bond orders in compound **I**

Method	N–P	P–C^3	C^3=C^4	C^4–C^5	C^5=C^6	C^6–N
STO 3G	0.916	0.962	1.900	1.059	1.818	1.055
3-21G	0.707	0.857	1.759	1.066	1.700	0.946
3-21G(d)	0.853	0.926	1.784	1.060	1.721	0.940
3-21G(d,p)	0.855	0.925	1.789	1.065	1.722	0.945
6-31G	0.658	0.914	1.780	1.092	1.772	0.887
6-31++G	0.288	0.731	1.973	1.234	2.124	0.783
6-31G(d)	0.857	0.968	1.858	1.093	1.803	1.008
6-31G(2d)	0.962	1.023	1.870	1.114	1.795	1.107
6-31++G(d)	0.581	0.964	2.084	1.196	2.213	0.943
6-31G(d,p)	0.854	0.854	1.849	1.090	1.793	1.002
6-311G(d,p)	0.864	0.971	1.830	1.052	1.790	1.003

Table 3. Bond angles (deg) in compounds **I** and **II**

Method	NPC^3	PC^3C^4	$C^3C^4C^5$	$C^4C^5C^6$	C^5C^6N	C^6NP	H^7NP	H^7NC^6	H^8PN	H^8PC^3
					Compound **I**					
AM1	106.4	122.2	122.8	121.1	124.4	122.7	117.6	119.3	102.3	98.7
MNDO	103.0	123.9	122.4	122.8	121.9	125.9	115.2	116.9	100.2	98.3
STO 3G	100.7	122.3	124.5	123.1	126.1	122.0	114.1	113.0	96.9	96.9
3-21G	97.5	120.5	124.8	121.8	123.9	122.8	119.0	118.2	98.7	98.1
3-21G(d)	98.2	120.9	123.9	121.4	122.8	122.9	119.4	117.7	99.8	97.7
3-21G(d,p)	98.2	121.0	123.9	121.4	122.8	122.9	119.4	117.7	99.9	99.7
6-31G	97.0	121.0	124.8	122.0	123.8	123.1	118.2	118.7	98.2	98.6
6-31++G	96.9	121.1	124.7	122.0	123.7	123.4	118.4	118.2	97.6	98.2
6-31G(d)	97.7	120.8	124.1	121.2	123.0	123.2	118.9	117.8	99.9	98.1
6-31(2d)	97.4	120.9	124.0	121.1	122.9	123.1	118.1	117.8	100.2	97.8
6-31++(d)	97.4	120.9	123.9	121.2	122.9	123.1	118.8	117.6	99.4	97.9
6-31G(d,p)	97.7	120.8	124.1	121.2	123.1	123.1	118.2	118.7	98.2	98.6
6-311G(d,p)	97.7	120.8	124.0	121.2	123.0	123.2	119.0	117.5	100.0	98.0
					Compound **II**					
X-ray structural analysis [6, 7]	99.4	124.9	121.6	123.8	121.0	126.1	113.2	119.5	–	–

The bond lengths in azaphosphorin **I** listed in Table 1 quite correspond to the expected for PN [13] fragment and 1,3-diene system both in open chains and rings [14]. Judging from the bond length and bond order (Table 2) we conclude that the P–N bonds has no attributes indicating its multiplicity. Moreover, use of diffuse orbitals results in abnormal low bond orders for this bond. The C^3=C^4 bond occupying α-position to phosphorus atom is slightly shorter than the C^5=C^6 bond in α-position to nitrogen. This trend can be traced in calculations with all the methods, therewith nonempirical calculations show less difference. The bond orders for these two bonds (Table 2) agree with the noted trend in their lengths (Table 1). This all probably points to greater ability of nitrogen lone pair to *n*–π interaction with the conjugated system as compared with the phosphorus lone pair, as it was shown in [15, 16]. Bond angles in this molecule (Table 3) also fall to the range expected for such structural fragments [13, 14].

The torsion angles characteristic of the turn around ring bonds (Table 4) differ considerably, the twisting at P–N bond is maximal. According to the *ab initio* calculations it achieves up to 35°. Twisting of the double bonds around the intermediate C–C bond under the conditions of a rigid cyclic system is much less than in *s-cis*-1,3-butadiene (~40° [17]). According to calculations in the extended bases, it lies near 16.5°–16.8°, closely to that determined for 1,3-cyclo-

Table 4. Torsion angles (deg) in compounds **I** and **II**

Method	NPC^3C^4	$PC^3C^4C^5$	$C^3C^4C^5C^5$	$C^4C^5C^6N$	C^5C^6NP	C^6NPC^3	H^7NPC^3	$H^7NC^6C^5$	$H^8PC^3C^4$	H^8PNC^6	H^7NPH^8
	Compound **I**										
AM1	357.6	358.6	3.9	358.3	357.3	4.4	191.9	169.7	103.3	261.3	88.8
MNDO	359.4	359.2	2.9	356.6	1.8	0.1	196.6	165.0	102.0	259.0	95.5
STO 3G	350.0	2.7	7.8	352.0	357.5	9.9	228.5	139.4	88.4	271.5	130.0
3-21G	337.2	3.6	16.1	352.0	340.3	30.9	211.9	159.4	77.1	291.5	112.5
3-21G(d)	336.0	3.2	16.5	353.3	337.4	33.7	214.2	157.0	77.1	294.5	115.0
3-21G(d,p)	336.1	3.1	16.5	353.2	337.5	33.6	214.3	156.9	77.3	294.3	115.0
6-31G	337.7	3.7	15.6	352.5	340.5	30.2	209.9	160.9	77.2	290.5	110.1
6-31++G	337.8	3.6	15.8	352.3	340.7	30.2	209.5	161.4	76.7	290.9	110.2
6-31G(d)	336.3	2.9	16.6	353.5	336.9	34.0	209.2	161.6	77.5	294.3	109.5
6-31(2d)	336.1	2.3	16.7	354.9	334.5	35.6	203.5	166.6	77.5	296.3	104.2
6-31++(d)	335.6	3.1	16.8	353.7	335.9	35.1	207.3	163.6	76.3	295.7	108.0
6-31G(d,p)	336.3	2.9	16.6	353.6	336.8	34.0	209.2	161.6	77.5	294.3	109.4
6-311G(d,p)	336.0	2.8	16.8	353.7	336.2	34.7	208.5	162.3	77.3	295.1	108.9
	Compound **II**										
X-ray structural analysis [7]	345.6	4.7	3.7	357.6	342.6	20.9	171.7	184.2	–	–	–

Table 5. Planarity (deg) of compounds **I** and **II**

Method	Σα at the nitrogen atom	Σα at the phosphorus atom	*pl*
	Compound **I**		
AM1	350.4	307.4	2.7
MNDO	358.0	301.5	1.5
STO 3G	349.1	294.5	6.9
3-21G	360.0	294.3	16.9
3-21G(d)	360.0	297.5	17.8
3-21G(d,p)	360.0	295.8	17.7
6-31G	360.0	293.8	16.5
6-31++G	360.0	292.7	16.5
6-31G(d)	359.8	297.5	17.8
6-31G(2d)	359.0	295.4	18.2
6-31++G(d)	359.5	294.7	18.3
6-31G(d,p)	359.9	294.5	17.8
6-311G(d,p)	359.7	297.5	18.1
	Compound **II**		
X-ray structural analysis [6, 7]	358.8	–	10.6

hexadiene by electronography and microwave spectroscopy (17–18.5°) [17, 18]. Deviations of the bonds between heteroatoms and C_{sp^2} atoms from the corresponding C=C–C planes are small, *ab initio* gives 2°–4° for phosphorus and –5° to –8° for nitrogen.

Consideration of endocyclic torsion angles (Table 4) and whole planarity index (*pl*) (Table 5) shows that both semiempirical methods and STO 3G overestimate total planarity of the ring as compared with *ab initio* calculations.

From all the calculations follows that azaphosphorin **I** exists in *twist* conformation with nonplanar (nonempirical and MNDO) or almost planar (AM1 and STO 3G) nitrogen atom and pyramidal phosphorus atom possessing a pseudoaxial substituent. The substituents at heteroatoms have *anti-clynal* arrangement at different sides of the conventional ring plane (*trans*). The four atoms, P, C^3, C^4 and C^5 falls almost in a plane, whereas N and C^6 deviate from the plane, hence the *twist* conformation of the molecule can be described approximately as an *envelope* with cut off nonplanar corner of the flap (Fig. 1).

To the end of consideration of azaphosphorin **I** geometry we can resuming that most of calculated geometric parameters of this compound little differ from those determined by X-ray crystallography for 2-thia-1,2-dihydro-1,2-azaphosphorin (**II**) [6, 7] (Table 1, 3–5). Moreover, the latter in some cases fall to the range of values calculated for **I** despite the fact that compound **II** differs from **I** by the presence of substituents at the double bond and phosphorus atom, by the phosphorus coordination number, by the existence of big enough sulfur atom at phosphorus, and by phase state (a crystal). Restricting ourselves to

Table 6. Atomic charges (a.u.) and dipole moments of compound **I**

Method	Atomic charge								μ, D
	N	P	C^3	C^4	C^5	C^6	H^7	H^8	
AM1	–0.493	0.659	–0.453	–0.051	–0.297	0.027	–0.167	0.233	1.54
MNDO	–0.475	0.540	–0.328	–0.039	–0.221	0.140	–0.152	0.188	1.34
STO 3G	–0.421	0.220	–0.155	–0.048	–0.113	0.057	–0.003	0.187	1.27
3-21G	–1.066	0.887	–0.735	–0.132	–0.382	0.184	0.359	–0.070	1.52
3-21G(d)	–0.957	0.684	–0.580	–0.181	–0.363	0.148	–0.049	0.354	1.72
3-21G(d,p)	–0.856	0.723	–0.495	–0.100	–0.274	0.234	0.254	–0.090	1.68
6-31G	–1.104	0.813	–0.640	–0.044	–0.315	0.217	–0.071	0.375	1.37
6-31++G	–0.964	0.612	–0.632	–0.084	–0.220	–0.098	0.025	0.471	1.30
6-31G(d)	–0.905	0.571	–0.501	–0.095	–0.307	–0.125	–0.675	0.391	1.59
6-31(2d)	–0.864	–0.503	–0.663	–0.004	–0.317	–0.027	–0.017	0.473	1.53
6-31++G(d)	–0.707	0.292	–0.366	–0.117	–0.265	0.014	0.018	0.372	1.63
6-31G(d,p)	–0.829	0.614	–0.451	–0.045	–0.253	0.175	–0.108	0.313	1.58
6-311G(d,p)	–0.730	0.634	–0.452	0.008	–0.274	–0.225	–0.104	0.258	1.55

Table 7. Energy of selected orbitals, eV

Method	HOMO-1	HOMO	LUMO	Δ(LUMO–HOMO)
AM1	–9.68	–7.85	0.41	8.26
MNDO	–10.83	–8.32	0.21	8.52
STO 3G	–8.91	–6.24	6.81	13.05
3-21G	–9.97	–7.74	3.48	11.22
3-21G(d)	–9.75	–7.85	3.41	11.26
3-21G(d,p)	–9.76	–7.84	3.39	11.23
6-31G	–10.03	7.67	3.23	10.90
6-31++G	–10.2	–7.81	1.07	8.88
6-31G(d)	–9.79	–7.77	3.35	11.12
6-31G(2d)	–9.76	–7.77	3.36	11.13
6-31++G(d)	–9.97	–7.92	1.06	8.98
6-31G(d,p)	–9.78	–7.77	3.34	11.11
6-311G(d,p)	–9.88	–7.91	3.04	10.95

comparison of nonempirical calculations, we can see clear tendency in the difference of certain parameters for phosphorus and nitrogen. In compound **I** the P–C bond by 0.07–0.16 Å, P–N by 0.02–0.10 Å longer, the H^7NP angle by 4.9–6.2° greater and $H^7NC^6C^5$ angle by 27.3° less than related parameters in **II**. Nevertheless, juding from both nonempirical calculations for **I** and X-ray data for **II** we resume that nitrogen atom has almost planar bond configuration: Σα 359–360° from calculations for **I** and 358.8° from X-ray data for a crystal of **II**.

Consideration of the Mulliken atomic charges (Table 6) shows that regardless the applied method the phosphorus atom possess partial positive charge, while the nitrogen has partial negative charge. Semiempirical methods give larger absolute value of charge on phosphorus, while *ab initio* calculations results in larger charge on the nitrogen. Correspondingly, carbon atom near phosphorus (C^3) always possess negative charge, which is almost in any calculation [except 6-31++G, 6-31++G(d) d 6-31G(2d)] is less in value compared to phosphorus. The carbon atom near nitrogen (C^6) has a small charge, and different methods can give different signs. Both the central carbon atoms C^4 and C^5 possess negative charges, that two-three-fold greater on the C^5. The 6-311G(d,p) calculation gave almost zero charge on C^4. Whole the azaphosphorin **I** molecule is moderately polarized, as follows from the calculated electric dipole moment value.

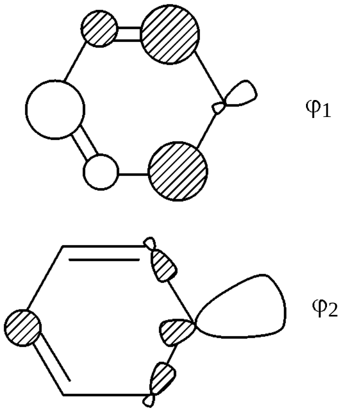

Fig. 2. General view of two upper occupied molecular orbitals in azaphosphorin **I**. $\varphi_1 = \pi^- - n_N - \lambda n_P$, $\varphi_2 = n_P - \lambda\sigma$.

Upper occupied orbital [HOMO (φ_1)] in 1,2-azaphosphorin (**I**) is an antibonding combination of π orbitals of two π bonds and the nitrogen lone pair, with insignificant contribution of the phosphorus lone pair. This orbital obviously controls electron-donor properties of the heterocycle. It is distant by significant energy interval from the next occupied orbital (φ_2) which is of σ-type predominantly. This orbital comprises mainly the phosphorus lone pair (Fig. 2). Orbital energies and energy gap between HOMO and the lowest unoccupied orbital (LUMO) are almost the same in all the used *ab initio* calculations, and only introducing of diffuse orbitals lowers LUMO energy and the gap becomes narrow (Table 7).

Comparative analysis of the calculations shows that regardless of the basis set the calculations give practically the same descriptions for structure of azaphosphorin **I**. Therefore extension of the basis set over 6-31G(d) seems unreasonable for phosphorin **I** and similar molecules as it consumes much computer time with no additional effect.

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