

## ELECTRONIC AND STERIC STRUCTURE OF "QUASI-VERDAZYLS."

### I. PHOSPHAVERDAZYL AND ITS LEUCO BASE

A. M. Nesterenko, O. M. Polumbrik,  
and L. N. Markovskii

UDC 547.887+539.193

By the PNDO method in an spd basis, with complete optimization of geometry, the electronic and steric structure has been calculated for different conformers of a model phosphaverdazyl and its leuco base. The results are consistent with the interpretation given previously for the ESR spectra of phosphaverdazyls. Features of electronic structure are judged in terms of their influence on the physicochemical properties and reactivity of phosphatetrazines.

Stable organic radicals containing Period III elements have come under the close scrutiny of research workers in recent years [1-3], since studies of their physicochemical properties can yield valuable information on the structure and on the specific features of transmission of electronic effects in compounds containing a sulfur or phosphorus atom. A study of a number of the recently obtained, comparatively stable phosphahydrazidinyls (phosphaverdazyls) [4, 5] has confirmed the hypothesis of possible thermodynamic stability of highly polar (quasi-verdazyl) radicals [6].

Certain information on the electronic and steric structure of the verdazyls and their derivatives has been obtained in quantum-chemical studies [7, 8], but no information whatever is available on the structure of "quasi-verdazyls" as a whole, nor on phosphaverdazyls in particular.

We have calculated the electronic and steric structure of 3-methyl-3-oxo-1,2,3,4-tetrahydro-1,2,4,5-tetraaza-3-phosphorine (PVH) and 3-methyl-3-oxo-1,2,3,4-tetrahydro-1,2,4,5-tetraaza-3-phosphorin-1-yl (PV $\cdot$ ), compounds that are the simplest models of phosphaverdazyls. The calculations were performed in the PNDO approximation, using a program with which the 3d orbitals of the P atom could be included in the basis set [9]; the corresponding Slater-Condon spectral parameters, calculated by Hintze, were taken from [10]. All of the other parameters were selected in accordance with the values commonly taken in the CNDO/2 and PNDO methods [11]. The geometry was optimized by means of a program using the gradient method of finding the extremum [12].

Here we must note that even though the PNDO method in the spd basis that we used is not strictly invariant with respect to rotations of the coordinate system, the differences in values of the total energy of the compounds due to rotations of the Cartesian system of coordinates are very small, and the differences in the steric structure of the molecules are of no practical significance.

---

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR. Translated from Zhurnal Strukturnoi Khimii, Vol. 25, No. 2, pp. 45-50, March-April, 1984. Original article submitted April 6, 1982.

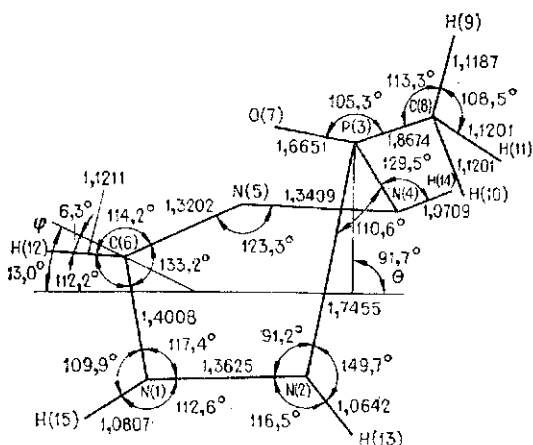


Fig. 1

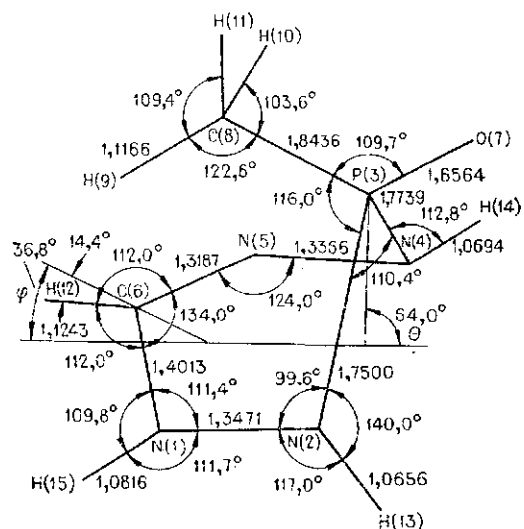


Fig. 2

Fig. 1. Steric structure of R-conformer (boat) of 3-methyl-3-oxo-1,2,3,4-tetrahydro-1,2,4,5-tetraaza-3-phosphorine.

Fig. 2. Steric structure of S-conformer (boat) of 3-methyl-3-oxo-1,2,3,4-tetrahydro-1,2,4,5-tetraaza-3-phosphorine.

TABLE 1. Electronic Structure of Model Phosphaverdazyls and Leucophosphaverdazyls

Property of conformations	PVH (R)	PVH (S)	PV (R)	PV (S)
$E_{tot}$ , eV	-2402,3683	-2402,2646	-2379,8351	-2379,9307
$E_{HOMO}$ , eV	-9,673	-9,515	-9,749	-9,588
$E_{LUMO}$ , eV	0,462	0,688	0,613	0,343
$\mu$ , D	4,095	6,630	3,699	4,826
Charge on atom N(1)	-0,034	-0,059	-0,082	-0,116
Charge on atom N(2)	-0,159	-0,138	-0,105	-0,081
Charge on atom P(3)	0,279	0,266	0,291	0,285
Charge on atom N(4)	-0,142	-0,107	-0,105	-0,081
Charge on atom N(5)	-0,076	-0,106	-0,082	-0,116
Charge on atom C(6)	0,234	0,242	0,214	0,225
Charge on atom O(7)	-0,340	-0,371	-0,315	-0,371
Charge on atom H(12)	-0,025	-0,040	-0,027	-0,035
Charge on atom H(13)	0,095	0,106	0,106	0,109
Charge on atom H(15)	0,061	0,051	—	—
Wyberg indexes of bond				
N(1)—N(2)	0,960	0,984	1,071	1,074
P(3)—N(2)	1,208	1,225	1,091	1,118
N(4)—P(3)	1,066	1,103	1,091	1,118
N(4)—N(5)	1,008	1,019	1,071	1,074
N(5)—C(6)	1,619	1,638	1,270	1,275
C(6)—N(1)	1,025	1,038	1,270	1,275
P(3)—O(7)	1,887	1,958	1,767	1,959
N(1)—H(15)	0,928	0,928	—	—
Energy of bond N(1)—N(2), eV	-28,25	-28,24	-30,90	-31,04
Energy of bond P(3)—N(2)	-24,00	-24,23	-21,99	-22,51
Energy of bond N(4)—N(5)	-29,00	-29,40	-30,90	-31,04
Energy of bond N(5)—C(6)	-39,15	-39,58	-34,22	-34,33
Energy of bond N(1)—C(6)	-30,28	-30,43	-34,22	-34,33
Energy of bond C(6)—H(12)	-20,34	-20,23	-20,26	-20,22
Energy of bond P(3)—O(7)	-30,08	-31,74	-28,78	-31,85
Energy of bond N(1)—H(15)	-19,36	-19,28	—	—
Energy of bond H(15)—O(7)	-0,93	-0,06	—	—

Since there are two possible modes of locating the  $P(O)CH_3$  group relative to the plane of the heteroring, the total number of conformers for these phosphaverdazyls will be twice that in the case of triphenylverdazyl. Since it was previously shown [8] that the most stable conformation of the tetrazine heteroring is the boat configuration, all calculations were performed for this conformation only. The data obtained on the steric structure of the leucophosphaverdazyls in conformations R and S are shown in Figs. 1 and 2, respectively.

A comparison of the bond lengths and angles of the model leucoverdazyl [8] and leucophosphaverdazyls leads us to the following conclusions: a) With relatively small changes in the bond angles in the fragment N(5)-C(6)-N(1), the corresponding bonds N(5)-C(6) and C(6)-N(1) in the leucophosphaverdazyl are approximately 0.02 Å longer, which indicates a substantial weakening of conjugation in the heteroring; b) there is an appreciable increase in the noncoplanarity of the four nitrogen atoms of the heteroring; in the leucophosphaverdazyls the increases are  $6.5^\circ$  and  $8.6^\circ$  for the conformers R and S, respectively; here, the boat is substantially "deepened," since the angles  $\varphi$  and  $\theta$  are considerably increased.

We should particularly note the unusually small values of the calculated bond angles at the N(4) and N(2) atoms — the corresponding bond angles are only slightly greater than  $90^\circ$ . Such an unexpected conformation of the heteroring of the leucophosphaverdazyls proved to be the most stable, possibly because of overestimation, in the standard parametrization methods PNDO and CNDO/2, of the two-center components of the total energy [11]. However, in spite of the probable overestimation of the "bending" of the heteroring upon replacement of the  $CH_2$  group in the leucoverdazyl by the phosphoryl group, we can be reasonably sure that, on the whole, a real trend has been observed in the changes in steric structure, since upon cyclization of substituted phosphorus-containing azines, the chemical shift of the  $^{31}P$  atom drops off appreciably [13]; quantum-chemical calculations indicate that a decrease in the bond angle at the nitrogen atoms leads to deshielding of the neighboring phosphorus atom [14].

A comparison of the features of steric structure of the R and S conformers enables us to conclude that when the conformation is changed, the principal changes take place in the fragment bonded directly to the H(15) atom. The most probable reason for this is apparently the changes in strength of the O-H hydrogen bond. Here we must note that the H(15) atom of the leucophosphaverdazyl is located considerably higher above the plane of the heteroring than in the leucoverdazyls. Here, its nonvalence interactions, both with the O atom and with the P atom or the methyl group, are relatively small. For the R conformer, the data from the calculation indicate the presence of a hydrogen bond N(1)-H(15)-O(7), the energy of which is  $-0.93$  eV.\*

In Table 1 we present data on the electronic structure of these conformers, from which we can draw the following conclusions: a) The most thermodynamically favorable is conformation R (apparently because of the presence of the above-mentioned intramolecular hydrogen bond); b) in comparison with the leucoverdazyl, the tendency of the leucophosphaverdazyl to manifest donor properties is somewhat lower; conversely, the acceptor properties are substantially reinforced. Here there is also an increase in the dipole moment of the molecule, particularly for the less thermodynamically stable conformer S. The Wyberg indexes of the bonds of the heteroring of the leucophosphaverdazyl are somewhat smaller. The appreciable weakening of all bonds in the heteroring also enables us to conclude that there is a relative decrease in thermodynamic stability of the leucophosphaverdazyls in comparison with the leucoverdazyls.

In spite of the fact that the thermochemical strength of the N-H(15) bond, determined as the difference between the total energies of the reaction products and the initial substances in their equilibrium states, is 18.4 kJ/mole greater in the leucophosphaverdazyl than in the leucoverdazyl, the "adiabatic" strength of the first bond is substantially smaller; this fact can probably be explained by the presence of the hydrogen bond in the leucophosphaverdazyls.

The increase in the thermochemical strength of the N-H(15) bond, apparently, may also be manifested in the higher stability of the leucophosphaverdazyl with respect to dehydrating agents, and also in reactions of deprotonation. However, it should be kept in view that abstraction of a proton from the leucophosphaverdazyl by strong Lewis bases may be facilitated substantially by possible complexation of the metal ions with the phosphoryl group, since in this case, a rather stable five-membered ring can be formed:

\*The interaction is obviously the reason for the strong broadening of the band for vibrations of the N-H bond in the IR spectra of leucophosphaverdazyls [5].

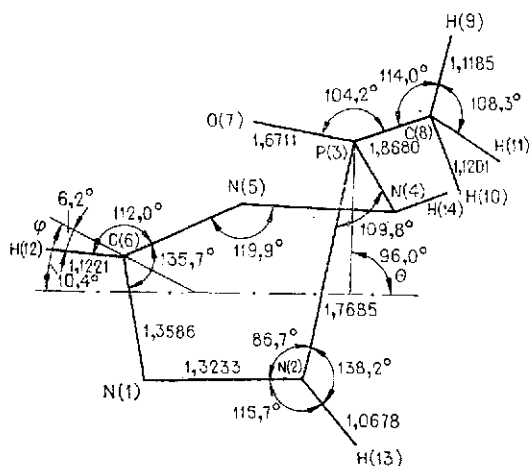


Fig. 3

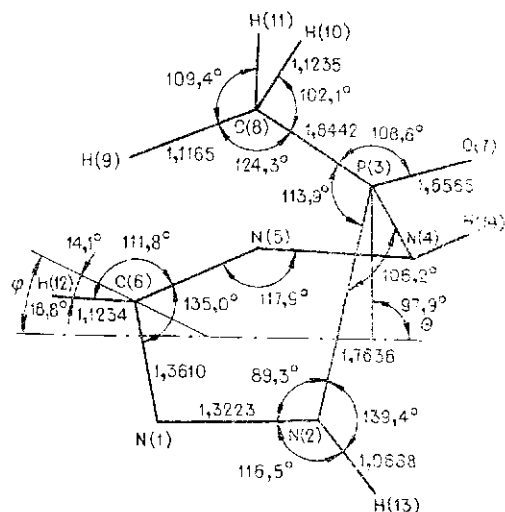
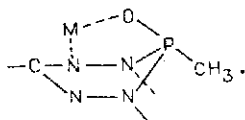


Fig. 4

Fig. 3. Steric structure of R-conformer (boat) of 3-methyl-3-oxo-1,2,3,4-tetrahydro-1,2,4,5-tetraaza-3-phosphorin-1-yl.

Fig. 4. Steric structure of S-conformer (boat) of 3-methyl-3-oxo-1,2,3,4-tetrahydro-1,2,4,5-tetraaza-3-phosphorin-1-yl.



In Figs. 3 and 4 we present data on the steric structure of the radicals of the phosphaverdazyl. (The designations of the conformations correspond to those used previously.) A comparison of these data with the corresponding structural parameters of the verdazyl radical [7] leads to the conclusion that there is a somewhat greater similarity in their structure than in the structures of the leuco derivatives. It is interesting to note that when the change is made from the leuco derivatives to the corresponding radicals, the magnitude of the angle  $\theta$  decreases appreciably, and the fragment N(1)N(2)P(3)N(4)N(5) becomes more nearly planar. In both the leucophosphaverdazyl and the phosphaverdazyl, the magnitude of the bond angle at the carbon atom in the heteroring is considerably greater than the corresponding angle in the verdazyls, which is close to the value of  $120^\circ$  that is characteristic for atoms in  $sp^2$  hybridization. In all of the compounds that were studied, the P atom has a very nearly tetrahedral environment. The same as for the verdazyls, the formation of the radical from the leuco derivative, for the compounds we have studied, is accompanied by a decrease in the N-N bond length, indicating an increase in conjugation in the heteroring.

In Table 1 we listed the data obtained on the electronic structure of the phosphaverdazyls that we have studied. The most thermodynamically favorable in this case, in contrast to the leucophosphaverdazyls, is the S conformer. This is apparently related to the absence, in this radical, of an intramolecular hydrogen bond, which in the leucophosphaverdazyls tends to stabilize the R conformer. For both compounds, the heat of the inversion transition is quite small, approximately 9 kJ/mole. The dipole moments of the phosphaverdazyls are appreciably higher than for the verdazyl; the ionization potential changes relatively little. However, there is an appreciable increase in the electron affinity and hence in the tendency to form anions. Here, the formal charges on the N(1) and N(5) atoms are somewhat smaller than in the verdazyl radical. We can assume that the phosphaverdazyls will be weaker electron donors than the verdazyls. The increase in the formal charge on the C(6) atom, the same as the increase in the polarity of the molecule as a whole, should evidently lead to an increase in the rates of reaction of phosphaverdazyls in interactions that include the formation of cyclic intermediate states in the first stages [6]. We must also note that the certain decrease in the Wyberg bond indexes of the majority of the bonds in the heteroring of the phosphaverdazyl in comparison with the corresponding verdazyl, the same as the decrease in strength of these bonds, in-

TABLE 2. Comparison of Calculated and Experimental Data on Distribution of Spin Density in Phosphaverdazyls

Properties of conformations	R	S	Experimental data
HFS constant on atom, mT			
N(1)	0,83	0,80	0,64
N(2)	0,72	0,53	0,46
H(12)	0,54	0,54	0,105
H(13)	-0,22	-0,38	—
<sup>13</sup> C(6)	-1,64	-1,64	—
<sup>13</sup> C(8)	0,66	-0,08	—
<sup>31</sup> P(3)	—	—	~0,48
Spin density on 3s orbital of P(3) atom	0,144	-0,003	—
Spin density on atom			
N(1)	0,515	0,524	—
N(2)	0,195	0,189	—
P(3)	0,230	-0,050	—
C(6)	-0,363	-0,374	—
O(7)	-0,343	0,200	—

dicating a decrease in thermodynamic stability when the methylene group is replaced by phosphoryl, enables us to conclude that the phosphaverdazyls are lower in stability than the verdazyls. The lower kinetic stability of the phosphaverdazyls in comparison with the verdazyl radicals can be explained by their greater polarity, and also by the considerable transfer of spin density to the phosphoryl group (Table 2).

The hyperfine interaction constants, calculated in the conventional manner for the PNDO method, are listed in Table 2. In contrast to the verdazyl radical, in the phosphaverdazyls the splittings on the N atoms differ appreciably in magnitude. The magnitudes of the s-spin density on the P atom lead us to the conclusion that there is a very strong influence of conformational transitions in the phosphaverdazyls on the HFS constants. A comparison of the values obtained for the hyperfine splitting constants on the nuclei with the experimentally determined values for 1,2,3,4-tetrahydro-2,4-dimethyl-3-oxo-3-phenyl-1,2,4,5-tetraazaphosphorin-1-yl and 1,2,3,4-tetrahydro-2,4-dimethyl-3-oxo-3,6-diphenyl-1,2,4,5-tetraazaphosphorin-1-yl [4, 5] indicates the suitability of this model approach, as well as agreement with the assignment of HFS constants on N nuclei that was made in [5] by means of ESR and double electron-nuclear magnetic resonance (ENDOR). The only substantial difference is in the overstated value of  $a^H$  for the H(12) atom. The experimental value  $a^H = 0.1$  mT can apparently be explained by changes in  $a^H$  with rapid boat-chair conformational transitions in the phosphaverdazyls [7].

#### LITERATURE CITED

1. Ya. A. Levin and E. I. Vorkunova, Homolytic Chemistry of Phosphorus [in Russian], Nauka, Moscow (1978), p. 318.
2. M. J. S. Gynane, A. Hudson, M. Lappert, et al., J. Chem. Soc., Dalton Trans., 12, 2428 (1980).
3. L. N. Markovskii, V. S. Talanov, O. M. Polumbrik, and Yu. G. Shermolovich, Zh. Org. Khim., 17, 2640 (1981).
4. P. P. Kornuta, V. N. Bobkov, O. M. Polumbrik, and L. N. Markovskii, Zh. Obshch. Khim., 48, 697 (1978).
5. F. A. Neugebauer and H. Fischer, Z. Naturforsch. B, 35, 250 (1980).
6. O. M. Polumbrik, A. M. Nesterenko, and L. N. Markovskii, Dokl. Akad. Nauk SSSR, 240, 640 (1978).
7. O. M. Polumbrik, A. M. Nesterenko, and L. N. Markovskii, Zh. Strukt. Khim., 20, 571 (1979).
8. A. M. Nesterenko, O. M. Polumbrik, and L. N. Markovskii, Zh. Strukt. Khim., 22, No. 4, 3 (1981).
9. A. M. Nesterenko and V. G. Maslov, Zh. Strukt. Khim., 20, 949 (1979).
10. J. J. Kaufman and R. Predney, Int. J. Quantum Chem., Symp., 6, 231 (1972).
11. J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York (1970), p. 231.

12. A. M. Nesterenko and V. G. Maslov, Summaries of Papers from 5th All-Union Conference "Utilization of Computers in Molecular Spectroscopy and Chemical Research" [in Russian], Novosibirsk, September 9-12, 1980, published Novosibirsk (1980), p. 154.
13. J. P. Majoral, M. Revel, R. Kraemer, et al., J. Heterocycl. Chem., 14, 749 (1977).
14. A. S. Tarasevich and A. M. Nesterenko, Teor. Éksp. Khim., 17, 750 (1981).