THREE-DIMENSIONAL STRUCTURE OF 5-PHENYL-5-SELENO-1,3,5-DIOXA- AND 5-PHENYL-5-SELENO-1,3,5-DIAZAPHOSPHORINANES

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Study of the equilibrium of the stereoisomers and conformers of 5-phenyl-1,3,5-dioxaphosphorinanes and their oxides and sulfides has shown that as the coordination number of the P atom increases, it shifts toward the form with axial orientation of the phenyl at P [1, 2]. A similar conclusion was reached for 5-phenyl-1,3,5-diazaphosphorinanes and their oxides and sulfides [3]. Such a direction of shift is contrary to what has been observed for 1-phenylphosphorinan-4-one and its oxides, sulfides, and selenides [4, 5], and can be explained by gauche interactions of the dipoles along the P−C bond [3] or by bond-orbital interactions [6]. It therefore became of interest to determine the three-dimensional structure of 5-phenyl-5-seleno-1,3,5-dioxa- and diazaphosphorinanes.

The stereoisomers of 5-phenyl-5-seleno-2,4,6-trimethyl-1,3,5-dioxaphosphorinane with mp 162°C (I) and 86°C (II) were obtained similarly to the stereoisomers of 5-thio-2,4,6-trimethyl-1,3,5-dioxaphosphorinane [7], from a mixture of the stereoisomers of 5-phenyl-2,4,6-trimethyl-1,3,5-dioxaphosphorinane and selenium. In the $^{31}P-\{^1H\}$ NMR spectrum, I and II had signals with chemical shifts (CS) of 24 and 18 ppm, and in the PMR spectrum they had SSCC of $^2J_{PH}$ = −13 and −7 Hz, respectively. From a comparison of these values with those given in [7] for the stereoisomers of 5-phenyl-5-thio-2,4,6-trimethyl-1,3,5-dioxaphosphorinane (27 and 24 ppm, 13.4 and 6.8 Hz, respectively, for $P = S_a$ and $P = S_e$), I and II were assigned to the axial (a) and equatorial (e) orientations, respectively, of the $P = Se$ bond. Compound I goes over to II completely when heated in the presence of p-toluenesulfonic acid. This confirms the conclusion reached previously concerning the increased stability of the form with the axial phenyl at P as the P coordination number increases:

(I) ⇌ (II)
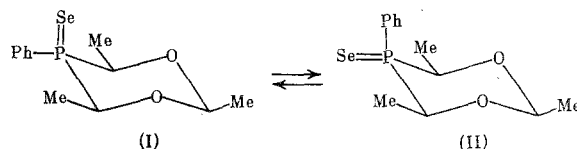
When the stereoisomers of 5-phenyl-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane [8] react with selenium, only one stereoisomer was separated in pure form, mp 131°C, CS in ^{31}P NMR spectrum 42 ppm. The PMR spectrum of III is shown in Fig. 1. From comparison with the PMR spectra of the stereoisomers of 5-phenyl-5-oxo- and 5-phenyl-5-thio-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane [8], it can be concluded that III is in the twist conformation. The stability of this form is due to the unfavorable interactions of the P−C bond in the chair conformation with the axial isopropyl group.

The isopropyl CH$_3$ signals of III were assigned by comparison with the PMR spectra of the stereoisomers of 5-phenyl-5-oxo- and 5-phenyl-5-thio-2,4,6-triiosopropyl-1,3,5-dioxaphosphorinane [8, 9]. The signals with 0.55 and 0.83 ppm CS and $^3J_{HH}$ = 6.8 Hz belong to the isopropyl at C^2. The methyls of the isopropyl group with $^3J_{HH}$ = 7 Hz at C^4 and C^6 are also mutually nonequivalent. If we allow for the nonequivalence of the methyls of the isopropyl group at C^2 and the analogy with other isopropyl-substituted 5-phenyl-1,3,5-dioxaphosphorinanes, it can be assumed that the CH$_3$ groups at C^4 and C^6 are nonequivalent to an isopropyl group. The CH$_3$ groups are anisochronic due to the diastereoisomerism caused by the asymmetry of the P atom [10], although a contribution from steric factors is also possible.
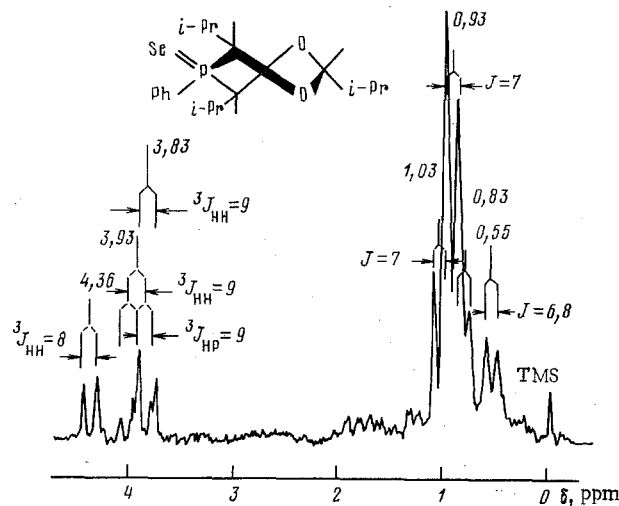
Fig. 1. PMR Spectrum of III in C_6H_6.

TABLE 1. PMR Spectral Parameters of IV-VII in Solution, and Content of Forms with Pha at P Atom in (A)

Compound	δ, ppm				J, Hz					(A), %	Solvent
	H_A	H_B	H_C	H_D	PH_A	PH_B	H_AH_B	PH_D	H_CH_D		
(IV)	4,77	4,12	5,29	4,67	−10,4	0,4	−15	4	−12	43	CH₃CN
	4,45	3,95	5,01	4,01	−10,1	0,6	−15	4	−13	48	C₆H₆
	4,41	3,90	5,08	4,52	−9,0	0,5	−14	4	−12	67	CCl₄
(V)	4,77	4,12	5,29	4,67	−10,4	0,4	−15	4	−12	43	CH₃CN
	4,46	4,03	5,05	4,11	−10,4	0,7	−15	4	−12	43	C₆H₈
	4,33	3,88	5,04	4,34	−9,6	0,6	−14	5	−12	57	CCl₄
(VI)	4,79	4,12	5,18	4,68	−9,7	0,3	−14	4	−12	55	CH₃CN
	4,23	3,89	4,63	3,81	−9,6	0,6	−14	4	−12	57	C₆H₆
	4,43	3,95	5,19	4,45	−9,6	0,6	−15	5	−12	57	CCl₄
(VII)	2,89	2,24			−10,0	3,0	−13			50	C₆H₈
	3,69	3,21			−9,5	1,5	−14			56	CCl₄

The N,N-disubstituted 5-phenyl-5-seleno-1,3,5-diazaphosphorinanes were obtained by the addition of selenium to the N,N-disubstituted 5-phenyl-1,3,5-diazaphosphorinanes [3]. The three-dimensional structures were studied by PMR spectroscopy and dipole moments (DM):
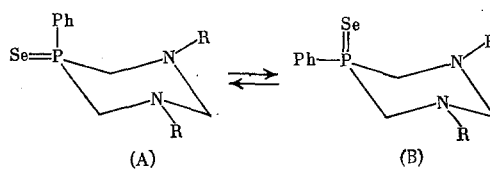
R = Ph (IV), $C_6H_4CH_3$-p (V), C_6H_4Br-p (VI), CH_2Ph (VII).

The PMR parameters of IV-VII are given in Table 1. The spectra of the methylene protons of the ring correspond to a $(AB)_2CDX$ system, where A and B are the axial and equatorial protons at the carbon atoms at the 4 and 6 positions; C and D are the axial and equatorial protons at the carbon atom in the 2 position, and X is the phosphorus nucleus. The high nonequivalence values of the CS of the methylene protons at one and the same carbon indicate that the rings under consideration have predominantly the chair formation [11]. According to the W rule, the protons at C^2 that interact with P with SSCC $^4J_{PH}$ = 4.5 Hz are equatorial (D), while those that do not interact are axial (C). Protons A and B were assigned on the basis of a comparison of the spectra of IV-VII with those of N,N-disubstituted 5-phenyl-5-thio-1,3,5-diazaphosphorinanes [3]. To proton B were assigned the signals lying in a higher field, and split from the P atom with a lower SSCC, than for proton A. The absolute values of $^2J_{PH_B}$ are smaller than those for the thio analogs [3], and have positive signs.

TABLE 2. Calculated and Experimental Dipole Moments of A and B Conformers, and Equilibrium Content of A in IV-VII

Compound	μ_{exp}, D	$m_{P=Se}=3,73$ D			$m_{P=Se}=4,0$ D		
		μ_A	μ_B	(A), %	μ_A	μ_B	(A), %
(IV)	4,06	2,70	5,49	60	2,96	5,75	68
(V)	4,54	3,06	5,51	46	3,32	5,77	57
(VI)	3,06	1,13	5,80	75	1,37	6,01	78
(VII)	5,32	4,34	5,79	36	4,59	6,06	54

In order to determine the equilibria of the conformers of IV-VII with the axial and equatorial orientations of the phenyl at the P atom from the spectra, I and II were used as model compounds. The $^2J_{PH}$ SSCC are quite stable to the effect of substituents at the C and P atoms on the P—C bond, and such an approach has proved to be correct for the N,N-disubstituted 5-phenyl-1,3,5-diazaphorphorinanes and their oxides and sulfides [3]. The SSCC of I and II were determined in benzene, acetonitrile, and CCl_4, and no solvent effect was found. The content of the forms with axial phenyl at the P atom in the conformational equilibria of IV-VII in the solutions is given in Table 1.

The dipole moments of IV-VII were measured in benzene at 25°C. They are: IV, 4.06 D (coefficients of calculating equations $\alpha = 4.9144$, $\gamma = 0.4373$); V, 4.54 D ($\alpha = 5.5202$, $\gamma = 0.2847$); VI, 3.06 D ($\alpha = 2.2011$, $\gamma = 0.3582$); VII, 5.32 D ($\alpha = 7.4633$, $\gamma = 0.2586$). In calculating the DM of the chair conformations with axial and equatorial orientations of the P = Se bond, we used the geometrical parameters and the bond polarities given in [12]. The moment of the seleno—phosphoryl bond has recently been estimated in [13], and is evidence for significant fluctuations of bond polarity depending on the nature of the substituent at the P atom. For the compounds that we considered, DM of the seleno—phosphoryl group can be taken as equal to that calculated from $Ph_3P = Se$ [13], $m_{P=Se} = 3.73$ D, or from trialkylphosphine selenide [13], $m_{P=Se} = 4.0$ D. Both values were used to calculate the polarity of conformers A and B (Table 2). The increase in the polarity of the seleno—phosphoryl bond causes some equalization in the population of the IV-VI conformers. This agrees with the Exner principle concerning the iso-conformational capability of compounds with phenyl or p-substituted phenyl substituents [14]. Therefore, the values in the last column of Table 2 are more reliable.

The data of Table 2 establish the predominance, in the IV-VI equilibria, of the conformer with the axial phenyl at the P atom; its population density is about 70%. For VII, equal participation of both conformers in the equilibrium is apparently typical. Like Table 1, Table 2 confirms the conclusion that the stability of the conformer with the axial phenyl at P increases as one goes from 5-phenyl-1,3,5-diazaphosphorinanes (3-17% by SSCC, 30% by DM) to their derivatives [3]. The difference between the results obtained by the two methods is of the sort noticed earlier for the oxides and sulfides [3]. The difference can be due to the necessity, in the DM method, for calculating conformations that differ in substituent orientation at the N atom. PMR spectroscopy gives the content of the forms that differ in orientation of the phenyl at P.

The direction of the equilibrium shift in going from 5-phenyl-2,4,6-trimethyl-1,3,5-dioxaphosphorinane (84% of the form with Ph_a at P) to its selenide (100%) and from 5-phenyl-1,3,5-diazaphosphorinanes (3-17%) to their selenides (43-57%) is opposite to that in going from 1-phenylphosphorinan-4-one (28%) to its selenide (4%). Probably the equilibrium position for the 5-phenyl-1,3,5-dioxa- and 5-phenyl-1,3,5-diazaphosphorinanes is determined by the same factors as for the oxides and sulfides [3].

EXPERIMENTAL

PMR spectra were recorded on a Varian T-60 apparatus (60 MHz, 34.5°C, TMS internal standard). ^{31}P NMR spectra were recorded on a KGU-4 NMR spectrometer (10.2 MHz) with noise isolator for protons at 25.2 MHz.

5-Phenyl-5-seleno-2,4,6-trimethyl-1,3,5-dioxaphosphorinane (I). To a solution of 1.5 g of 5-phenyl-2,4,6-trimethyl-1,3,5-dioxaphosphorinane [7] in 5 ml of C_6H_6 in an Ar atmosphere was added an excess of powdered Se. The mixture was heated for 30 min at 90°C, the solvent was removed, and the residue was crystallized from CH_3OH. Yield 0.6 g (30%), mp 162°C, δ ^{31}P 24 ppm (CH_3OH). Found: C 47.43; H 5.58; P 10.00%. $C_{12}H_{17}O_2PSe$. Calculated: C 47.52; H 5.61; P 10.23%.

5-Phenyl-5-seleno-2,4,6-trimethyl-1,3,5-dioxaphosphorinane (II). A solution of 0.2 g of I in 10 ml of C_6H_6 was boiled for 6 h with a catalytic amount of p-toluenesulfonic acid. The extent of isomerization was followed by the ^{31}P NMR spectrum. The solvent was removed in vacuum. The yield of II was about 100%, mp 86°C, δ ^{31}P 18 ppm (C_6H_6). Found: C 47.43; H 5.60; P 10.12%. $C_{12}H_{17}O_2PSe$. Calculated: C 47.52; H 5.61; P 10.23%.

5-Phenyl-5-seleno-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (III). To a solution of 2 g of 5-phenyl-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane [8] in 5 ml of C_6H_6 in an Ar atmosphere was added an excess of powdered Se. The mixture was heated for 30 min at 80°C, the solvent was removed, and the residue was chromatographed on a silica gel column with 20 : 1 petroleum ether : diethyl ether. A mixture of stereoisomers with ^{31}P δ of 33 and 14 ppm was separated in the first fractions, and a stereoisomer with ^{31}P δ of 42 ppm in the last fractions. The yield of the single isomer was 0.3 g (12%), mp 131°C. Found: C 55.86; H 7.65; P 7.79%. $C_{18}H_{29}O_2PSe$. Calculated: C 55.81; H 7.49; P 8.01%.

1,3,5-Triphenyl-5-seleno-1,3,5-diazaphosphorinane (IV). Onto 1.15 g (3.5 mmole) of 1,3,5-triphenyl-1,3,5-diazaphosphorinane [3] in 10 ml of CH_3CN was sprinkled an excess of Se. The mixture was heated to boiling and left over night. The excess Se was removed, the solvent was evaporated off, and the residue was crystallized from CH_3CN. The yield of IV was 0.85 g (60%), mp 108-110°C, ^{31}P δ 6 ppm (CH_3CN). Found: C 61.80; H 5.08; P 7.42%. $C_{21}H_{21}PN_2Se$. Calculated: C 61.31; H 5.11; P 7.54%.

5-Phenyl-5-seleno-1,3-di-p-tolyl-1,3,5-diazaphosphorinane (V). To 1.45 g (4 mmoles) of 5-phenyl-1,3-di-p-tolyl-1,3,5-diazaphorphorinane [3] in 10 ml of CH_3CN was added an excess of Se. The mixture was heated to boiling and left over night. The excess selenium was removed, the solvent was evaporated off, and the precipitated crystals were filtered off. The yield of V was 1.22 g (69%), mp 106-107°C, ^{31}P δ 6 ppm (CH_3CN). Found: C 63.59; H 5.68; P 7.42%. $C_{23}H_{25}PN_2Se$. Calculated: C 62.89; H 5.69; P 7.06%.

5-Phenyl-5-seleno-1,3,5-di-p-bromophenyl-1,3,5-diazaphosphorinane (VI). Compound VI was obtained similarly to V from 5-phenyl-1,3-di-p-bromophenyl-1,3,5-diazaphosphorinane [3]. Yield of VI 81%, mp 125-127°C, ^{31}P δ 6 ppm (C_5H_5N). Found: C 44.95; H 3.29; P 5.30%. $C_{21}H_{19}PN_2SeBr_2$. Calculated: C 44.28; H 3.34; P 5.45%.

5-Phenyl-5-seleno-1,3-dibenzyl-1,3,5-diazaphosphorinane (VII). Compound VII was obtained similarly to V from 5-phenyl-1,3-dibenzyl-1,3,5-diazaphosphorinane [3]. Yield of VII 68%, mp 109-110°C, ^{31}P δ 3 ppm (CH_3CN). Found: C 61.91; H 5.69; P 6.88%. $C_{23}H_{25}PN_2Se$. Calculated: C 62.87; H 5.69; P 6.88%.

CONCLUSIONS

1. Substituted 5-phenyl-5-seleno-1,3,5-dioxaphosphorinanes exist as stereoisomers that differ in the orientation of substituents at the P and C atoms. In the case of 5-phenyl-5-seleno-2,4,6-trimethyl-1,3,5-dioxaphosphorinane, the thermodynamically stable stereoisomer is the one in the chain conformation with an axial phenyl at the phosphorus atom.

2. 5-Phenyl-5-seleno-1,3,5-diazaphosphorinanes are mixtures of conformers that differ in the orientation of the phenyl at the phosphorus atom.

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