2. A calculation of the frequencies and modes of the normal vibrations of 2-seleno-2-chloro-1,3,2-dioxaphosphorinane has been made.

3. The studied molecules under the experimental conditions were conformationally uniform.

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CONFORMATIONAL EQUILIBRIUM OF N,N-DISUBSTITUTED 5-PHENYL-1,3,5-DIAZAPHOSPHORINANES AND THEIR DERIVATIVES

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A comparison of the conformational free energies of the NCH_3 groups in 1-methylpiperidine [1], 1,3-dimethyl-1,3-diazane [2], 1-methyl-1,3-oxazane [3], and 1,3,5-trimethyl-1,3,5-triazane [4] shows that an interaction occurs between the heteroatoms of the ring in 1,3-position in the case of axial orientation (*a*) of the unshared electron pairs (UEP), which, it is assumed, possess an electrostatic nature and which is caused by a repulsion of the dipoles of UEP [5]. The study of the conformational equilibrium of N,N-disubstituted 5-phenyl-1,3,5-diazaphosphorinanes (I)-(IV) and their derivatives (V)-(XII) allows us to assess this interaction with the participation of the P atom. In the case of P(IV) we have the polar P=O(S) bond instead of UEP.

The three conformers (A), (B), and (C) can exist in the equilibrium of (I)-(XII):

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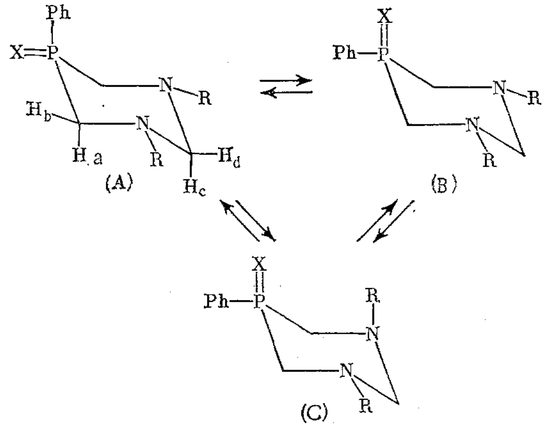


X = UEP, R = Ph(I), $C_6H_4CH_3$-*p*(II), C_6H_4Br-*p*(III), CH_2Ph(IV); X = O, R = Ph(V), $C_6H_4CH_3$-*p*(VI), C_6H_4Br-*p*(VII), CH_2Ph(VIII); X = S, R = Ph(IX), $C_6H_4CH_3$-*p*(X), C_6H_4Br-*p*(XI), CH_2Ph(XII).

The equilibrium has been studied before by the dipole moment method (DM) and NMR; it was assumed that a conformer with axial orientation of the substituent at the N atom was absent from the mixture [6, 7]. This assumption was made on the basis of the values of the geminal SSCC of protons of the CH_2 group between the N atoms. In the case of benzyl and aryl at the N atom, the SSCC are close to the SSCC of the models with the minimum and maximum electron densities at N in the axial position, respectively [8]. Due to the small difference between the SSCC of the models, such an assessment can only be qualitative and does not exclude the presence of significant amounts of the conformer with axial orientation of the substituent at N in the equilibrium mixture. In the present work the equation which relates the square of the experimental DM with the squares of DM and the molar fractions of forms (A), (B), (C) was

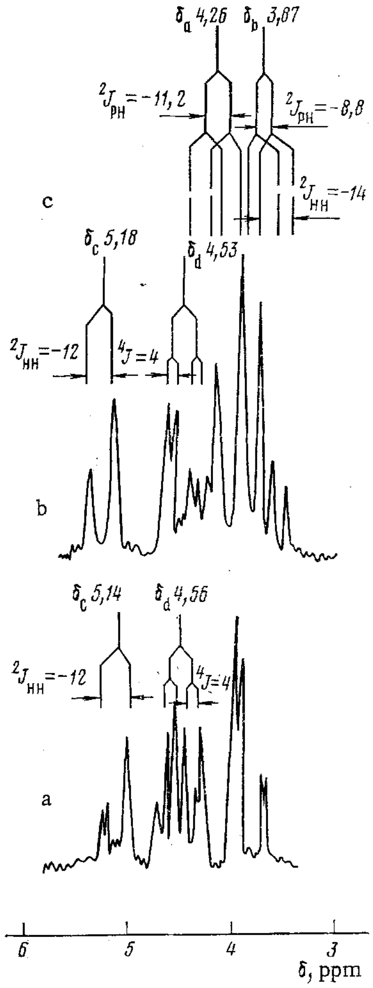
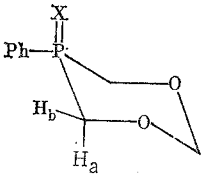


Fig. 1. NMR spectra of methylene protons of the ring: a) (IX) in CH_3CN; b) (V) in $CHCl_3$; c) theoretical spectrum of (V) (J, Hz).

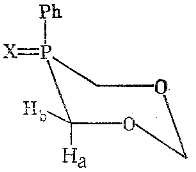
used to calculate the maximum and minimum molar fractions of form (A), while varying the molar fractions of forms (B) and (C) from zero to a value with a physical sense (the sum of the molar fractions of all forms is equal to unity). The minimum corresponded to the equilibrium (A) ⇄ (B), the maximum to the equilibrium (A) ⇄ (C). Exceptions (III), where the minimum corresponded to the equilibrium of three forms, (IV), where the sum of their molar fractions was obtained due to equal values of DM for forms (A) and (C), and (VIII) and (XII), where the relationship of minimum and maximum is opposite. The molar fraction of the form (A) in the equilibrium of three forms was obtained from the SSCC of $^2J_{PH_a}$ and $^2J_{PH_e}$. Comparison of the results obtained by the two methods gave information about the equilibrium composition.

The values of DM of (I)-(XII) and the parameters of the NMR spectra of (I)-(IV) were taken from [6, 7]. The parameters of the spectra of (V)-(XII) are given in Table 1. The spectra are typical for the spin system $(AB)_2CDX$ (Fig. 1). Separation of the protons H_a and H_b and determination of the molar fraction of form (A) was achieved by comparison of the spectra of (I)-(XII) with the spectra of the conformers of 5-phenyl-1,3,5-dioxaphosphorinanes and their derivatives.

The average values of $^2J_{PH_a}$ and $^2J_{PH_e}$ of conformers of 5-phenyl-1,3,5-dioxaphosphorinanes and their derivatives are given in [9]. The $^2J_{PH_a}$ values of conformers with Ph_a and Ph_e were taken as being equal to the corresponding SSCC of stereoisomers of 5-phenyl-2,4,6-trimethyl-1,3,5-dioxaphosphorinanes and their derivatives, differing in the orientation of Ph at the P atom [10, 11]. Substitution of these values in the equations relating the average $^2J_{PH}$ with the $^2J_{PH}$ of the conformers and their molar fractions in two solvents gave the $^2J_{PH_b}$ values of the conformers. The $^2J_{PH}$ of phosphorinanes are not strongly dependent on the substituents on the P and C atoms and remain constant even when the oxygen atom at the C atom is replaced by N [12-14]. This should also be the case with the oxides and sulfides of phorsphorinanes. The conformers of 5-phenyl-1,3,5-dioxaphosphorinanes and their derivatives were therefore taken as models for the corresponding conformers of (I)-(XII). Tests confirmed that the solvent had no effect on the SSCC of the stereoisomers of 5-phenyl-1,3,5-dioxaphosphorinanes and their derivatives.



X	H_a	H_b
UEP	−7	20
O	−16	−8,2
S	−13,4	−5,3



X	H_a	H_b
UEP	22	7
O	0	−6,2
S	−6,8	0

The minimum and maximum contents of form (A), calculated from DM and corresponding to the equilibria (A) ⇄ (B) and (A) ⇄ (C), and the contents calculated from SSCC for (I)-(XII) are shown in Table 2. It can be seen that the calculations based on $^2J_{PH_a}$ and $^2J_{PH_b}$ lead to similar results. This confirms the correctness of the assumptions on which the selection of the model was based. The deviations can be ascribed to a smaller interval of changes of SSCC $^2J_{PH_b}$ and to distortion of the conformation of form (C). Except for (III) and (IV), the molar fractions of form (A) calculated from SSCC lie in all cases outside the limits of the minimum and maximum values calculated from DM. This indicates that (I)-(II), (V)-(VII), and (IX)-(XI) have an equilibrium of forms (A) and (B), while (VIII) and (XII) have an equilibrium of forms (A) and (C), and (III) and (IV) an equilibrium of all three forms. Since DM gives for (IV) the sum of the molar fractions of forms (A) and (C) and NMR determines the molar fraction of form (A), the difference gives the molar fraction of form (C) and demonstrates the high concentration of this form at equilibrium. The fact that the values calculated from SSCC are somewhat lower than the values obtained from DM is probably due to a systematic error of the methods, related to the models, and to the influence of the solvents.

X-Ray diffraction analysis data obtained on (IV) confirm the stability of form (C) in the above systems. The coordinates of the non-hydrogen atoms are given in Table 3; their individual thermal parameters and the coordinates of the hydrogen atoms can be obtained from the authors. The bond lengths are given in Table 4 and the geometry of the molecule is shown in Fig. 2. The atoms $C^1N^1N^2C^3$ of the central ring $PN_2C_3(A)$ form a planar fragment with a precision of 0.05 Å. The conformation of the ring A is a chair, in which the planes C^1PC^3 form the angles 52.9 and 58.3°, respectively, with the plane $C^1N^1N^2C^3$. The atoms N^1 and N^2 come

TABLE 1. Parameters of NMR Spectra of Compounds (V)-(XII) in Solution

Compound	Solvent	δ, ppm				J, Hz				
		H_a	H_b	H_c	H_d	PH_a	PH_b	H_aH_b	PH_d	H_cH_d
(V)	$CHCl_3$	4,26	3,87	5,18	4,53	−11,2	−8,8	−14	3	−12
(VI)	$CHCl_3$	4,20	3,81	5,08	4,48	−10,2	−7,8	−14	3	−12
(VII)	$CHCl_3$	4,20	3,89	5,05	4,61	−10,4	−6,6	−14	2	−12
(VIII)	CCl_4	3,99	3,24	3,77	3,43	−11,1	−6,3	−14		−10
(IX)	CH_3CN	4,60	3,95	5,14	4,56	−9,6	−2,2	−14	4	−12
(X)	CH_3CN	4,53	3,88	5,06	4,60	−10,0	−2,4	−14	4	−12
(XI)	CH_3CN	4,59	3,97	5,04	4,58	−9,3	−1,8	−14	4	−12
(XII)	CCl_4	3,58	3,06			−10,4	−3,8	−14		

TABLE 2. Mole Fraction of Form (A) at Equilibrium for Compounds (I)-(XII), Calculated from DM (N_{min} and N_{max}) and from SSCC $^2J_{PH_a}$ and $^2J_{PH_b}$ (N_1 and N_2)

Compound	N_{min}	N_{max}	N_1	N_2	Compound	N_{min}	N_{max}	N_1	Compound	N_{min}	N_{max}	N_1	N_2
(I)	24	61	14	15	(V)	54	63	30	(IX)	71	80	58	58
(II)	34	57	17	31	(VI)	56	70	36	(X)	71	77	52	55
(III)	0	61	9	27	(VII)	48	75	35	(XI)	73	86	62	66
(IV)	39		3	0	(VIII)	78	51	31	(XII)	72	39	45	28

Note. The DM for (I)-(IV) were determined in C_6H_6; for (V)-(XII) in CCl_4. The NMR spectra of (I)-(IV) were obtained in C_6H_6 and $CHCl_3$, of (V)-(VII) in $CHCl_3$, of (IX)-(XI) in CH_3CN, and of (VIII) and (XII) in CCl_4.

TABLE 3. Coordinates of the Non-Hydrogen Atoms ($\cdot 10^4$) and Their Anisotropic Temperature Factors

Atom	X	Y	Z	Atom	X	Y	Z
P	9117(1)	3581	6789(1)	C^{11}	6733(4)	3563(18)	5403(6)
N^1	7319(3)	5684(11)	5771(4)	C^{12}	6177(4)	3024(12)	6144(5)
N^2	8353(3)	5266(11)	4666(4)	C^{13}	5497(4)	4634(14)	6220(6)
C^1	8124(4)	5430(14)	6893(5)	C^{14}	4950(5)	4130(16)	6854(7)
C^2	7625(4)	6666(13)	4922(5)	C^{15}	5062(6)	2054(19)	7442(7)
C^3	9275(4)	5301(15)	5653(5)	C^{16}	5730(7)	482(18)	7377(7)
C^4	8453(5)	6166(15)	3617(5)	C^{17}	6275(6)	935(16)	6728(7)
C^5	7601(4)	5470(14)	2539(5)	C^{18}	10122(4)	4486(13)	8105(5)
C^6	7118(4)	3381(18)	2447(6)	C^{19}	10362(5)	2881(14)	8987(7)
C^7	6353(5)	2838(15)	1407(7)	C^{20}	11111(6)	3433(27)	10039(6)
C^8	6104(6)	4370(20)	503(7)	C^{21}	11615(5)	5428(22)	10178(6)
C^9	6562(6)	6414(19)	593(7)	C^{22}	11375(5)	7003(18)	9314(7)
C^{10}	7321(5)	6987(15)	1617(6)	C^{23}	10627(6)	6523(16)	8269(6)

TABLE 4. Main Bond Lengths, Å

Bond	Length	Bond	Length
$P-C^1$	1,867(7)	N^2-C^2	1,480(9)
$P-C^3$	1,823(7)	N^2-C^3	1,464(8)
$P-C^{18}$	1,839(7)	N^2-C^4	1,474(8)
N^1-C^1	1,475(8)	C^4-C^5	1,521(9)
N^1-C^2	1,424(9)	$C^{11}-C^{12}$	1,491(9)
N^1-C^{11}	1,47(1)		

out from the planes of the three atoms linked to each of them by 0.47 Å (N^1) and 0.38 Å (N^2). The atoms C^4 and C^{18} occupy equatorial positions and their deviations from the mean-square plane A are equal to 0.07 and 0.93 Å. The atom C^{11} is axial, its deviation from the above plane is equal to 1.66 Å. The P atom deviates from the plane $C^1C^3C^{18}$ by 0.86 Å. The geometry of the substituents is the usual one. The benzene rings B, C, and D are planar within the limits 0.003, 0.006, and 0.001 Å, respectively. The ring D forms with the mean-square plane of the ring A the angle 74.6°C. Consequently, (IV) in the crystalline state exists in the chair conformation with axial orientation of the benzyl group on one of the N atoms.

The appearance of a conformer with an axial substituent at the N atom in the equilibrium of (III) and (IV) indicates an interaction of the heteroatoms in the case of axial orientation of UEP in the 1,3,5-diazaphosphorinane system. However, the P(III) atom does not participate in this interaction. The values of the conformational free energies of the substituents at the N atom in (IV) are similar to those in 1,3-dimethyl-1,3-diazane [2] and are equal to -0.34 and -0.4 kcal/mole. In 1,3,5-trimethyl-1,3,5-triazane, where all three heteroatoms take part in the interaction, the equilibrium is shifted towards the formation of the conformer with axial orientation of CH_3 on one of the N atoms [4]. A further confirmation of the fact that only the N atoms in the 1,3,5-diazaphosphorinanes interact in the case of axial orientation of UEP, is the absence of only an insignificant content of the conformer with an axial substituent at the N atom in the equilibrium (I)-(III), where the electron density is shifted from the N atom to the phenyl ring. The conformer content with Ph_a at the P atom in the equilibrium of 5-phenyl-1,3,5-dioxaphosphorinane (86% [9]), 1-phenylphosphorinane (40% [15]), (I)-(III), and (IV) correlates with the steric requirements of the fragment in β-position to the P atom ($O < CH_2 < NAr < NBz$).

The P(IV) atom participates in the interaction with the N atoms in the case of axial orientation of the P=O bond [8] and the UEP of N. This manifests itself in the shift of the equilibrium towards the conformer with Ph_a at the P atom when (I)-(IV) are converted to their oxides and sulfides. The direction of the shift is opposite to that observed in the conversion of 1-phenyl-phosphorinan-4-one to its oxide and sulfide [16]; it is analogous to the shift observed for 5-phenyl-1,3,5-dioxaphosphorinane and its derivatives [9], and is in accordance with the electrostatic character of the interaction of the ring heteroatoms in the 1,3 position in the case of axial orientation of UEP.

EXPERIMENTAL

The PMR spectra were obtained on a Varian T-60 spectrometer at 34.5°C on 10% solutions; the solvent signal was used as the reference.

The crystals of (IV) were monoclinic, at 20°C $a = 14.888(3)$, $b = 5.7622(1)$, $c = 12.557(2)$, Å, $\beta = 112.064(9)°$, $Z = 2$, spatial group $P2_1$. Lattice parameters and intensities of 1520 images from $F^2 \leqslant 5\sigma$ were measured on an automatic four-circle Hilger-Watts diffractometer (λCu K_α, graphite monochromator, $\theta/2\theta$ scanning, $\theta \leqslant 66°$). The structure was interpreted by the direct method, using the MULTAN program. The non-hydrogen atoms were defined first in the isotropic, then in an anisotropic approximation. The H atoms of the benzene rings and of

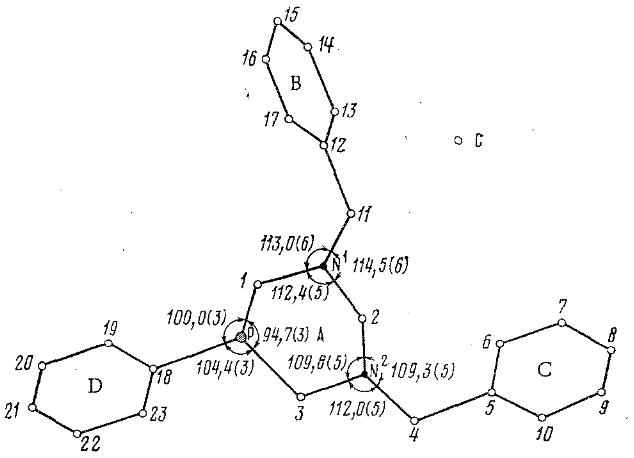


Fig. 2. Geometry of molecule (IV), main bond lengths and valence angles, derived from x-ray diffraction data.

the CH_2 groups were introduced into the calculated positions and defined isotropically with a fixed $B_{iso} = 6$ Å. The values of $R = 0.073$, of $R_W = 0.084$. All calculations were made on an Eclipse 8/200 minicomputer, using the EXTL programs.

Compounds (I)-(IV) and (IX)-(XII) were prepared using the procedures given in [6, 7].

5-Phenyl-5-oxo-1,3-diphenyl-1,3,5-diazaphosphorinane (V). A 0.065-g (0.0054 mole) sample of PhN_3 in 3 ml CH_3CN was added to 0.18 g (0.0054 mole) (I) in 5 ml CH_3CN. Evolution of gaseous products and of heat was observed. The mixture was brought to a boil and evaporated from an open beaker at 40-50°C. The residue was crystallized from CH_3CN. Yield of (V) 0.11 g (60%), mp 147-148°C, $\delta^{31}P = 16$ ppm (CH_3CN) (see [7]).

5-Phenyl-5-oxo-1,3-di-p-tolyl-1,3,5-diazaphosphorinane (VI). Compound (VI) was obtained from (II) in the same way as (V); yield 52%, mp 180-182°C, $\delta^{31}P = 16$ ppm (DMSO) (see [7]).

5-Phenyl-5-oxo-1,3-di-p-bromophenyl-1,3,5-diazaphosphorinane (VII). Compound (VII) was prepared from (III) in the same way as (V); yield 80%, mp 196-197°C, $\delta^{31}P = 16$ ppm (DMSO) (see [7]).

5-Phenyl-5-oxo-1,3-dibenzyl-1,3,5-diazaphosphorinane (VIII). Compound (VIII) was prepared from (IV) in the same way as (V); yield 72%, mp 157-158°C, $\delta^{31}P = 16$ ppm (DMSO) (see [7]).

CONCLUSIONS

In the conformational equilibrium of N,N-disubstituted 5-phenyl-1,3,5-diazaphosphorinanes and their oxides and sulfides forms can exist with an axial substituent on one of the heteroatoms, as well as a form with all equatorial substituents at the P and N atoms.

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