CONCLUSIONS

The Ge-H stretching vibration in the IR spectra of 1-hydrogermatranes varies under the influence of the solvent and the temperature as a result of the presence of the transannular Ge \leftarrow N bond. The change in the length of this bond with variation in the polarity of the solvent and the temperature of the solutions is smaller in germatranes than for the Si \leftarrow N bond in the isostructural silatranes.

LITERATURE CITED

- M. G. Voronkov, E. I. Brodskaya, P. Reich, S. G. Shevchenko, V. P. Baryshok, and Yu. L. Frolov, J. Organometal. Chem., <u>164</u>, 35 (1979).
- 2. E. I. Brodskaya, M. G. Voronkov, D. D. Toryashinova, V. P. Baryshok, and
- S. V. Basenko, Seventh International Symposium on Organosilicon Chemistry, Japan (1984), p. 246.
- 3. A. N. Egorochkin and S. Ya. Khorshev, Usp. Khim., <u>49</u>, 1687 (1980).
- 4. L. O. Atovmyan, Ya. Ya. Bleidelis, A. A. Kemme, and R. P. Shibaeva, Zh. Strukt. Khim., 11, 318 (1970).
- V. A. Pestunovich, B. Z. Shterenberg, S. N. Tandura, V. P. Baryshok, M. G. Voronkov, N. V. Alekseev, N. Yu. Khromova, and T. K. Gar, Izv. Akad. Nauk SSSR. Ser. Khim., 2179 (1980).
- 6. E. E. Liepin'sh, A. F. Lapsinya, G. I. Zelchan, and Ya. E. Lukevits, Izv. Akad. Nauk Latv. SSR. Ser. Khim., 371 (1980).
- T. K. Gar, N. Yu. Khromova, S. N. Tandura, V. N. Bochkareva, A. E. Chernyshev, and V. F. Mironov, Zh. Obshch. Khim., <u>52</u>, 2579 (1982).
- 8. M. G. Voronkov and V. M. D'yakov, Silatranes [in Russian], Nauka, Novosibirsk (1978).
- 9. A. N. Egorochkin, S. Ya. Khorshev, N. S. Ostasheva, E. I. Sevastyanova, J. Stage, P. Riviere, and J. Barrau, J. Organomet. Chem., <u>105</u>, 311 (1976).
- 10. H. Poulet and J. P. Mathieu, Vibrational Spectra and Symmetry of Crystals [Russian translation], Mir, Moscow (1973), p. 323.
- A. Z. Gadzhiev, S. A. Kirillov, V. I. Martovitskii, and N. S. Yangieva, Zh. Prikl. Spektrosk., 29, 101 (1978).
- 12. A. Z. Gadzhiev and S. A. Kirillov, Zh. Prikl. Spektrosk., 21, 929 (1974).

STERIC STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLES. COMMUNICATION

37.* 2-PHENOXY-5,6-BENZ-1,3,2-DIOXAPHOSPHEPINES WITH TETRACOORDINATED

PHOSPHORUS ATOM

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The 2-dialkylamino-1,3,2-dioxaphosphepines (DOP) studied up to the present time are conformationally nonhomogeneous and exist in a conformational equilibrium between the twist form (T) and a chair form with an equatorial disposition of the NR₂ group (e-Ch), irrespective of the type of coordination of the phosphorus P^{III} [2, 3] or P^{IV} atom [1]. Data obtained from 2-phenoxy-1,3,2-DOP with P^{III} [4] and P^{IV} [5] were criticized in [1, 2] because of the absence of a complete analogy in the ³JPOCH values for six- and seven-membered rings, since the values of the valence angles at the heteroatom were very different. This is shown by the X-ray diffraction studies on 5,6-benz-1,3,2-DOP and the corresponding 1,3,2-dioxa-phosphorinanes carried out in [6]. In the present work, results are given for a conforma-

*For Communication 36, see [1].

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Com- pound	Solvent	т., к	δ H ₄	δ _{H4′}	Δδ	<i>− ^{∎J}</i> H₄H _⊈ ′	°J _{PH4}	${}^{s\!J}_{\mathrm{PH}_{4'}}$	Σ v $_{ m PH}^{*}$
(I)	Acetone	183 303	5,57	5,13	0,63 0,44	13,6	5,0 9,5	27,0 22,2	32,0 31,7
	CCl4	263 263 303 393	5,18	5,06	$0,29 \\ 0,22 \\ 0,12 \\ -0,04$	14,0	12,0 14,0 15,5 17,0	19,7 18,2 16,7 15,7	31,7 32,6 33,2 32,7
(II)	Acetone	193 303 373	5,58	5,39 1	0,62 0,19 0,02	13,3	11,0 16,5 17,8	23,7 19,0 18,0	34,7 35,5 35,8
(III)	Acetone CCl ₄	213 313 300	5,53 5,46	5,40 5,10	0,44 0,13 0,36	13,4 13,9	14,5 18,7 15,2	20,7 18,1 23,6	35,2 36,8 38,8

TABLE 1. Parameters of Methylene Protons in ¹H NMR Spectra o1 2-Phenoxy-1,3,2-dioxaphosphepines (I)-(III)

*Possible limits of change in the value of $^{3}J\mathrm{PH}_{a}$ are 0.5-3 Hz.

tional analysis of 2-phenoxy-2-oxo-5,6-benz-1,3,2-DOP (I) and its thio- and selenophosphoryl derivatives (II) and (III) by ¹H NMR spectroscopy, dipole moments (DM), and Kerr effect methods:



Y = O(I), S(II), Se(III).

Only for the phosphepine fragment can three possible conformations - Ch, T (C_2 symmetry), and a distorted twist-boat - be proposed:



In the Ch and TB forms, the exocyclic substituents at the P atom occupy an axial (a) or equatorial (e) position. Besides the above-enumerated conformational parameters, the Kerr effect and DM methods make it possible to draw conclusions for this type of systems with X = OPh on the character of the internal rotation with respect to the exocyclic P-O bond and the O-C_{Sp}²(Ph) bond. In the first case, a stabilization is possible with an anti (A)-, gauche (G)- and syn (S)-disposition of the phenyl group in relation to the P=Y bond [7, 8], and in the second case, the conformation is determined by the dihedral angle ω between the plane of the benzene ring and a plane formed by the P-OC_{Sp}²(Ph) bonds (a position where these places coincide corresponds to a zero value of the angle) [7, 8].

The data on the conformational homogeneity (or nonhomogeneity) of the compounds obtained from the analysis of the temperature changes in the ¹H NMR spectra. The most informative for the structural assignments are the vicinal spin-spin coupling constants (SSCC) ³JPOCH. Treatment of the temperature dependences of these constants for compounds (I-III) is difficult because of the possibility of the appearance of flexible forms (T and TB) at equilibrium and the absence of model SSCC [1, 2]. The poor solubility of the compounds at low temperatures and the low barrier for the transition between the forms made it impossible to obtain spectral parameters for the "frozen" conformers. In these cases, the method described in [9] for the determination of a constant of an a-CH \neq e-Ch type of equilibrium (K) from the SSCC values averaged over a wide range of temperatures is useful. Thus, the deviation of the ln K vs. 1/T graph from the linear dependence is a reliable criterion for the presence of flexible forms in the conformational equilibrium. Table 1 shows the spectral parameters of methylene protons of compounds (I)-(III). For the oxide (I), the



Fig. 1. Dependence of logarithm of contant of $a-CH \neq e-Ch$ equilibrium on reciprocal temperature: 1) for oxide (I) in acetone; 2) for (I) in CCl₄; 3) for sulfide (III) in acetone.

TABLE 2. Thermodynamic Parameters of Conformational Equilibrium e-Ch ⇄ a-Ch in 2-Phenoxy-1,3,2-dioxaphosphepines (I)-(III)

Compound	Solvent	−∆H, kJ/mole	∆S, J/ mole•deg	Т., К	n _{a-K}
(I) (II) (III)	Acetone CCl ₄ Acetone	$-3,3\pm1,7$ $-3,0\pm1,7$ $-2,3\pm1,7$	$-10,0\pm1,7$ 7,1±1,7 6,9±1,7	253 298 298 298	$\begin{matrix} 0,75\pm0,03\\0,52\pm0,03\\0,41\pm0,03\\0,47\pm0,03\end{matrix}$

sum of vincinal SSCC remains unchanged over a wide range of temperatures, and therefore there is no need to introduce corrections for the difference in the observed ³JPH. For sulfide (II) and selenide (III) this sum depends directly on the temperature, but the effect cannot be related to the presence of the T form at equilibrium: in the case of a rapid $T \neq T^*$ pseudorotation, the values of the constants of the averaged T-form are approximately equal, because for the phosphates the ³JPOCH values are independent of the orientation of the exocyclic substituents at the P atom, but are determined only by the dihedral POCH angle [10]. As a result, the contribution to the two observed ³JPOCH introduced by the T-form remains practically constant with a change in temperature. On the whole, the temperature dependence of the sum of SSCC is probably determined by the difference of ${}^{3}Jtrans$ in the two Ch-forms, caused by the difference in the dihedral angles around the P-O bonds [11, 12]. An extrapolation into the low temperatures made it possible to determine the ³JPH_a + JPH_e sum for sulfide (II) as 34.0 Hz, and for the selenide (III) 34.8 Hz. In Table 2 thermodynamic parameters ΔH and ΔS of the conformational equilibrium a-Ch \neq e-Ch are given . These were obtained by the treatment of the dependence of the difference of the observed SSCC for (I) in CCl₄ and of the corrected dependence for (II) and (III). The graph depicting the change in the equilibrium constant as the function of the reciprocal temperature is given in Fig. 1, which shows the dependence for oxide (I) in a more polar medium - acetone. It is seen that this dependence is not linear, which is explained by the appearance at equilibrium of the more polar T-form, while the predominant form in the three-component equilibrium a-Ch $\stackrel{?}{\downarrow}$ T $\stackrel{?}{\downarrow}$ e-Ch is the form a-Ch with the largest DM. This conclusion is based on the change in the ratio of the Ch-conformers with the change in the dielectric constant of the medium. In contrast to oxide (I), for sulfide (II) and selenide (III) changing of the solution from acetone to the nonpolar CCl_{4} leads to an increase in the difference between the two SSCC ${}^{3}JPOCH$. This indicates a shift of the conformational equilibrium in CCl₄ in the direction of the less polar form, which is the e-Ch-form (Table 3). Thus, the temperature changes in the vicinal SSCC ${}^{3}JPOCH$ in the ${}^{1}H$ NMR spectra of compounds (I) in CCl₄ and of (II) and (III) in acetone are described by a two-component equilibrium of the two Ch-form.

Examination of experimental DM of the compounds also points to a difference in the conformational behavior of oxide (I) with μ = 4.85 D and that of sulfide and selenide. The DM's of the latter compounds are similar and equal 3.82 and 3.83 D, respectively. and the

TABLE 3. Dipole Moments (μ , D) and Kerr Constants ($mK \cdot 10^{12}$, esu, at $\omega = 90^{\circ}$) for 2-Phenoxy-1,3,2-dioxaphosphephines (I)-(III)

	Experi- ment		4,85	-355	3,82	259	3,83	395
	TB *	ß	4,35 454	$^{3,98}_{-277}$	4,03 819	3,67 98	3,92	209,57
		G"	$^{4,96}_{1062}$	-284	$^{4,65}_{1420}$	$^{4,32}_{118}$	4,54 1413	$^{4,22}_{239}$
		હં	4,76 887	4,40 75	4,44 1294	4,09 481	4,33	3,98 604
		¥	$^{6,15}_{2022}$	-138	5,83 2608	5,50	2799	5,39 709
	ц	S	4,01	271	3,70	604	3,59	702
		Ŀ	4,47	372	4,16	748	4,05	861
		A	5,88	1199	5,57	1776	5,45	1961
	Ch E	α	5,42 66	3,22 742	5,08 -1141	3,00 657	$\frac{4}{96}$	2,93 613
		Ŀ	-1670	$^{3,66}_{794}$	5,43 -680	$^{3,43}_{723}$	5,31 - 361	3,35 680
		A	7,08 2147	5,02 774	6,76 1077	4,75 816	6,64 1511	4,66 819
	Param- eter		$\overset{h}{\overset{H}{\operatorname{M}}}$	$\overset{\mathfrak{h}}{\mu}_{K}$	$^{\mu}_{K}$	$\overset{\mu}{}_{m}K$	μ_{M}	μ_{K}
	Position of P-OPh		a	ಲ	a .	v	B	۵
	Com-	punod	(I)		(11)		(III)	,

 $\frac{x_0^4}{x_0^4}$ gauche form at the side of the 0^1 atom, G'' - at the side of the 0^3 atom.



Fig. 2. Graphical dependence of the square of the DM vs. Kerr constant for 2-phenoxy-2-oxo-1,3,2-dioxaphosphepine (I).

1 D increase in the polarity of the first compound cannot be explained by the small difference in the values of m(P = Y), with Y = 0, S, Se, in phenyl phosphates [8]; this shows that in the phosphoryl derivative (I) the more polar form predominates. Additional information was obtained by comparison of the experimental and calculated values of DM and Kerr constants. The calculation was carried out using the polarity and polarizability parameters of the P bonds obtained for the corresponding 2-phenoxy-1,3,2-dioxaphosphorinanes with PIV [7, 8]. The geometry of the cyclic fragment was taken into account in accordance with the x-ray diffraction data for 5,6-benz-1,3,2-DOP [6]. In the Ch-conformation, from the a- to the e-structure [11, 13, 14]; in the a-form, the intracyclic POC angles are 2-3° larger than in e-Ch, in the G-conformation the OPO(Ph) angles acquire values of 106 and 100° for a-Ch, and 103, 100° for e-Ch whereby the higher value corresponds to the syn-disposition of the O-P-O-C(Ph) bond. The graphical dependences of the square of the DM vs. the Kerr constant give the most descriptive representation of the compounds, and these are shown in Figs. 2-4, respectively, for each of the compounds studied. Some of the values obtained (the Kerr constants are given for the angle $\omega = 90^{\circ}$) are also given in Table 3, which includes additional data for the TB form. Figures 2-4 clearly show that both DM and Kerr constants change within wide limits. This makes it possible to make unequivocal choice from among the forms studied. In all cases the position of the experimental point corresponds to either T (or TB)-form or to the equilibrium of the Ch-forms. This agrees with the above analysis of the temperature dependence of the ¹H NMR spectra. This position of the point and also the examination of the tabulated data show that the syn- or gauche-conformer of the e-Ch form must take part in the equilibrium. Considering that contrary to the a-orientation of the phenoxyl group, at the e-orientation there are no steric restrictions for the realization of the antiorientation, we can conclude that in the a-Ch conformation this may be the same syn or the gauche form. Such an in pairs examination of the position of the experimental points on the graphs shows that the a-Ch $\stackrel{>}{\downarrow}$ e-Ch equilibrium with a gauche oriented phenoxyl group, whose benzene ring plane is approximately orthogonal to the plane of the P-O-C_{SD}² bonds ($\omega \sim 90^\circ$), corresponds best with the experimental data. In the case of the sulfide (II) and selenide (III), the equilibrium is shifted in the direction of the e-conformer by \sim 75%, while in the oxide, the values obtained correspond to approximately equal contents of the Ch-forms.

We shall compare the results obtained with the data for the six-membered 2-phenoxy-1,3,2-dioxaphosphorinanes with PIV. The most important is the relative stabilization of the seven-membered 1,3,2-DOP in the Ch-form with an e-orientation of the phosphoryl group; in the thio- and selenophosphoryl analogs, the equilibrium of the chair-like forms is shifted



Fig. 3. Graphical dependence of the square of the DM vs. Kerr constant for 2-phenoxy-2-thiono-1,3,2-dioxaphosphepine (II).

Fig. 4. Graphical dependence of the square of the DM vs. Kerr constant for 2-phenoxy-2-seleno-1,3,2-dioxaphos-phepine (III).

in the direction of the e-conformer. At the same time, the tendency to increase the proportion of the a-Ch form on transition from oxide to sulfide and selenide is retained [6-8, 11, 13, 14]. In all the cyclic compounds studied up to the present time, the conformation of the exocyclic fragment PIV(Y)-OPh remains unchanged: the phenyl group acquires a gauche conformation in relation to the P-Y bond both for the a-Ch and the e-Ch forms, while the plane of the benzene ring is orthogonal to the plane of the P-O-C_{SP}² bonds [7, 8, 15]. The orthogonal disposition excludes the possibility of p-m-conjugation between the p-unshared electron pair of the exocyclic oxygen atom and the benzene ring m-electron. The reason for this phenomenon occurring in the organophosphorus compounds (competition between the p-m- and $\pi-\sigma^*$ -conjugation) has been discussed in detail by one of the authors in [15].

The comparative analysis of the steric structure of the seven-membered 2-X-1,3,2-DOP compounds studied shows that in contrast to 2-dialkylamino derivatives, in 2-phenoxy-1,3,2-DOP a relative stabilization of the chair-like conformations is observed. The presence of the flexible form in the compounds studied was detected only in oxide (I) in a polar solvent.

EXPERIMENTAL

The ¹H NMR spectra were obtained on a Varian HA-100 D spectrometer on a 100 MHz frequency, equipped with a V-4341/V-6057 temperature regulating attachment. The DM and the Kerr constants were determined at 25°C in CCl₄. The coefficients of the calculated equations were equal to (I) α = 16.826, γ = 0.421, δ = -164.78; (II) α = 10.078; γ = 0.451, δ = 122.263; (III) α = 8.821, γ = 0.457, δ = 158.63.

<u>2-Phenoxy-5,6-benz-1,3,2-dioxaphosphepine (IV).</u> A mixture of 6.9 g (0.05 mole) of phthalyl alcohol, 15.5 g (0.05 mmole) of triphenyl phosphite, and 0.1 g of Na was stirred for 3 h at 115°C in a N₂ current. After the removal of phenol, the residue was distilled in vacuo, bp 153°C ($2 \cdot 10^{-2}$ mm Hg), yield 69%, δ^{-31} P 123 ppm.

<u>2-Phenoxy-2-oxo-5,6-benz-1,3,2-dioxaphosphepine (I).</u> A solution of 2.4 g (0.01 mole) of phosphite (IV) in 10 ml of CH_2Cl_2 was added dropwise to 1 g (0.01 mole) of N_2O_4 in 5 ml

of CH_2Cl_2 at -60°C. The solvent was evaporated, and the residue was recrystallized from a cyclohexane-benzene mixture (20:1), mp 91-92°C. Found: C 60.89; H 4.86; P 11.38%. $C_{14}H_{13}O_4P$. Calculated: C 60.87; H 4.74; P 11.21%; $\delta^{-31}P$ -7 ppm.

<u>2-Phenoxy-2-thiono-5,6-benz-1,3,2-dioxaphosphepine (II).</u> A mixture of 2.4 g (0.01 mole) of (IV) and 0.6 g (0.02 of sulfur in 30 ml of toluene was boiled for 3 h. After the removal of solvent, 10 ml of MeCN were added to the residue. Excess sulfur was filtered off, the filtrate was evaporated, and the residue was recrystallized from an ether-benzene mixture (10:1), mp 86-88°C. Found: C 57.61; H 4.31; P 10%. $C_{14}H_{13}O_2PS$. Calculated: C 57.53; H 4.48; P 10.60%. $\delta^{-31}P$ 64 ppm.

<u>2-Phenoxy-2-seleno-5,6-benz-1,3,2-dioxaphosphepine (III)</u>. A mixture of 2.4 g (0.01 mole) of (IV) and 1.6 g (0.02 mole) of selenium in 40 ml of dioxane was boiled for 3 h. The excess selenium was filtered off, the solvent was evaporated, and the residue was recrystallized from an ether-benzene mixture (1:1), mp 105-106°C. Found: P 9.20%. $C_{14}H_{13}O_3PSe$. Calculated: P 9.13%. δ ³¹P 70 ppm.

CONCLUSIONS

1. 2-Phenoxy-2-oxo(thiono, seleno)-5,6-benz-1,3,2-dioxaphosphepines in solutions of nonpolar solvents are characterized by an equilibrium of two chair-like forms, which in the case of the sulfide and selenide is shifted in the direction of a conformer with an equatorial orientation of the phenoxyl group; in the oxide, at equilibrium, the proportions of two conformers are approximately the same. In solutions of polar solvents, a three component equilibrium is observed for the oxide, in which the flexible forms as well as the chair-like forms are present.

2. In accordance with the dipole moments and Kerr effect data, in all conformations, the compounds studied are characterized by a gauche conformation of the phenyl group in relation to the P=O (P=S, P=Se) bond and by an orthogonal disposition of the benzene ring π -orbitals and the p-unshared electron pair on the exocyclic oxygen atom.

LITERATURE CITED

- 1. R. A. Kadyrov, R. P. Arshinova, V. V. Klochkov, A. V. Aganov, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 799 (1985).
- 2. B. A. Arbuzov, R. A. Kadyrov, V. V. Klochkov, R. P. Arshinova, and A. V. Aganov, Izv. Akad. Nauk SSSR, Ser. Khim., 588 (1982).
- 3. B. A. Arbuzov, A. V. Aganov, V. V. Klochkov, R. A. Kadyrov, and R. P. Arshinova, Izv. Akad. Nauk SSSR, Ser. Khim., 1195 (1982).
- 4. A. C. Guimaraes and J. B. Robert, Tetrahedron Lett., 473 (1976).
- 5. A. C. Guimaraes, J. B. Robert, C. Taieb, and J. Tabony, Org. Magn. Reson., <u>11</u>, 411 (1978).
- 6. A. Grand and J. B. Robert, Acta Crystallogr., <u>B34</u>, 199 (1978).
- 7. R. P. Arshinova, T. D. Sorokina, A. B. Remizov, G. E. Koroleva, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 2242 (1979).
- 8. R. P. Arshinova, R. A. Kadyrov, V. V. Klochkov, A. V. Aganov, R. Kh. Shakirov, R. R. Shagidullin, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 2512 (1984).
- 9. V. V. Klochkov, A. V. Aganov, Yu. Yu. Samitov, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 2638 (1983).
- 10. J. A. Mosbo, Org. Magn. Reson., <u>11</u>, 281 (1978).
- 11. P. Van Nuffel, A. T. H. Lenstra, and H. J. Gaise, Bull. Soc. Chim. Belg., <u>91</u>, 43 (1982).
- 12. D. Bouchu, Phosphorus Sulfur, <u>15</u>, 33 (1983).
- 13. R. O. Day, D. G. Gorenstein, and R. R. Holmes, Inorg. Chem., 22, 2192 (1983).
- 14. R. Grand and J. B. Robert, Acta Crystallogr., <u>B31</u>, 2502 (1975).
- 15. R. P. Arshinova, Usp. Khim., <u>53</u>, 595 (1984).