SPATIAL STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLES.23. 2-PHENOXY-1,3,2-DIOXAPHOSPHORINANES WITH FOUR-

COORDINATE PHOSPHORUS

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In the example of 2-phenoxy-1,3,2-dioxaphosphorinanes (2-phenoxy-1,3,2-DOP) it has been shown [1] that the introduction of trivalent phosphorus next to a Ph-O group favors the realization of an orthogonal conformation, in which the π orbitals of the benzene ring are noncoplanar to the p pair of electrons of the sp²-hybridized O atom. The difference between the types of electronic interactions of three- and four-coordinate phosphorus (P^{III} and P^{IV}) makes the conformational study of the corresponding analogs with P^{IV}, i.e., derivatives of 2-phenoxy-2-oxo(thiono)-1,3,2-DOP, interesting. In addition, such an investigation makes it possible to reveal the features of the conformational behavior of systems with P^{III} and P^{IV}.

The structure of compounds I-III was determined in the crystalline state [2-4].



Compounds I-III have a chair conformation with a gauche (g) axial (a) orientation of the OPh group. The dihedral angle φ , which characterizes the relative positions of the P=Y multiple bond and the O-Ph bond and is measured from the trans orientation (t), is 124° in I [2] and 134.3° in II [3]. The plane of the benzene ring in II forms the angle $L\omega = 84.2°$ with the plane of the P-O-C (phenyl) bond [3], i.e., a noncoplanar orientation of the π orbitals is observed, precisely as in 2-phenoxy-1,3,2-DOP. In solutions 1,3,2-DOP derivatives with PIV display a tendency for the equilibrium existence of two chair forms. According to the PMR spectra, such an equilibrium does not exist for I or its dimethyl analog [5, 6]. Up to a 10% admixture of the second conformer was found in II in [7]. Dipole moment measurements indicate that the predominant conformation of I is a chair with a t, α -OPh group [8]. However, such a structure should be destabilized by the strong 1,3-diaxial interaction. The conformation of I predicted by quantum-mechanical calculations according to the CNDO/2 method [9] is consistent with that found in the crystal phase, but the calculated dipole moment of such a structure differs significantly from the experimental dipole moment (6.82 [9] and 5.71 D [8], respectively). 4-Methyl- and 4,6-dimethyl-1,3,2-DOP were studied in [5, 10]. The contradictory nature of the data obtained by different physical methods for 2-phenoxy-2-oxo(thiono)-1,3,2-DOP has made it necessary to carry out more exact and systematic investigations of their spatial structure.

We carried out the synthesis and study of the structure of a number of phenoxy derivatives of 1,3,2-DOP and their p-bromo analogs:



The methods of vibrational spectroscopy were used to determine the conformational homogeneity (the configurational homogeneity of VII was established by an analysis of the PMR spectra),

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and measurement of the dipole moment and the Kerr effect were used for identification of the conformations, as in [1].

EXPERIMENTAL

The IR spectra (400-4000 cm^{-1}) were measured on a UR-20 spectrometer, and the Raman spectra were measured on a Coderg PHO spectrometer according to a method similar to that in [11]. The dipole moments and the Kerr constants of the compounds were determined in CC14 solutions [with the exception of the trivalent derivative 2-phenoxy-4-methyl-1,3,2-DOP (VIII), which was measured in cyclohexane] at 25°C. The coefficients in the theoretical equations are given in Table 1.

2-Phenoxy-2-oxo-1,3,2-DOP (I) and 2-p-bromophenoxy-2-oxo-1,3,2-DOP (IV) were obtained by oxidizing the corresponding phosphites [1] with NO₂ in CH_2Cl_2 at -40 to -50°C. After the removal of the solvent in a vacuum, the solid residue was recrystallized twice from CCL4. with activated charcoal. The products were white powders with mp 69-70°C (I) (compare [5]) and 58-59°C (IV) (the yield was 49%). Found: (IV) C 37.20; H 3.65; P 10.89%. Calculated for C₉H₁₀O₄PBr: C 36.89; H 3.44; P 10.57%. δ³¹P 16 ppm.

2-Phenoxy-2-thiono-1,3,2-DOP (V), 2-p-bromophenoxy-2-thiono-1,3,2-DOP (VI), and 2-phenoxy-2-thiono-4-methyl-1,3,2-DOP (VII) were obtained by adding sulfur to the corresponding phosphites with boiling in dioxane for 3-4 h. Product V, which was purified with the aid of column chromatography on Silica Gel KSK (the eluent was 1:3 petroleum ether: benzene), has mp 44-45°C (yellowish crystals, the yield was 42%). Found: C 47.03; H 4.84; P 13.49%. Calculated for $C_{9H_{11}O_{3}SP$: C 46.96; H 4.78; P 13.47%. $\delta^{31}P$ -55 ppm. Compound VI was obtained in the form of a white powder with mp 100-101°C (twofold recrystallization from CCl4), and the yield was 50%. Found: C 35.27; H 3.25; P 9.91%. Calculated for C₉H₁₀O₃SPBr: C 34.97; H 3.26; P 10.02%. δ³¹P-56 ppm.

Crystallized VII was washed with ether, mp 71-72°C (the yield was 50%) [5]. Found: C 49.50; H 5.16; P 13.02%. Calculated for C₁₀H₁₃O₃SP: C 49.18; H 5.32; P 12.7%. δ ³¹P-54 ppm.

Compound VIII was synthesized by reacting 2-C1-4-methyl-1,3,2-DOP with phenol in ether in the presence of triethylamine with cooling of the reaction mixture by crushed ice with salt, bp 123°C (4 mm Hg), np²⁵ 1.5210, d4²⁵ 1.1606 (according to [12]: bp 132-133°C (7 mm Hg), np²⁰ 1.5145). The analysis of the PMR spectra of VIII points out the presence of a 10% admixture of a second stereoisomer with a cis arrangement of the Ph=0 and $4-CH_3$ groups. Compound VII is a pure stereoisomer.

DISCUSSION

The problem of determining the conformational homogeneity of compounds I and IV-VII was solved by comparing and analyzing the spectra of the liquids (solutions) and crystals over a maximally wide spectral range. Following the crystallization of I, IV, and VII all the bands observed in the spectra of the liquids in the 400-4000-cm⁻¹ region are maintained in the spectra of the crystals, and there are only changes in the relative intensities, as well as frequency shifts of some of the bands (some of the spectra are shown in Figs. la and lb). The crystallization of V and VI is accompanied by similar changes in the spectra, and, in addition, the bands at 638 (V) and 650 cm^{-1} (VI) in the IR spectra and the line at 649 cm^{-1} in the Raman spectrum (VI) are obliterated. On the basis of these data it may be concluded

TABLE	1.	Coefficients	in	the	Theoretical	Equations
for 1	and	IV-VIII				
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Com- pound	α	β	Ŷ	δ	μ, D	$m^{K \cdot 10^{12}}$	
(I) (IV) (V) (VI) (VII) (VII)	$29,38 \\ 21,56 \\ 21,25 \\ 19,38 \\ 23,54 \\ 3,08$	$\begin{array}{c} 0,7336\\ 0,0619\\ 0,0497\\ 0,2172\\ -0,9954\\ 0,3868\end{array}$	0,2524 0,2632 0,2961 0,4350 0,0520 0,2761	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	5,68 5,77 4,99 5,50 5,41 2,64	$-80 \\ -174 \\ 137 \\ 127 \\ 181 \\ 246$	



Fig. 1. Infrared spectra of I (a), IV (b), V (c), and VI (d) in the liquid (1) and crystalline (2, 3) states. The frequencies discussed in the text are designated by asterisks.



Fig. 2. Exner graph for I and V and for their p-bromo derivatives IV and VI: 1) experimental point for I and IV; 2) for V and VI.

that in the liquid and solutions the thiophosphoryl derivatives V and VI exist in the form of mixtures of at least two conformers. The bands at 638 and 667 (V) and at 650 and 681 cm⁻¹ (VI) may be assigned to the $v_{P=S}$ vibrations of two different conformers. This assignment is supported by a comparison of the spectra of V and VI with the spectra of I and IV (Figs. 1a-1d), the analogous bands being absent in the spectra of I and IV.

The investigation carried out does not provide any basis to assume the existence of several conformers in the liquid and in solutions of I and IV. The $v_{P=0}$ bands in the spectra of liquid and crystalline I and IV have complicated contours, which may be attributed to the superposition of other vibrations. When IV is crystallized by cooling a liquid film, just as in the case of 2-p-bromophenoxy-1,3,2-DOP [1], two crystalline modifications with significantly different IR spectra are obtained (see Fig. 1b). The series of vibrations differs by 10-12 cm⁻¹, and the corresponding bands are single, do not have multiplet Davydov splitting, and can all be assigned to different vibrations. These differences can apparently be attributed to the formation of crystalline modifications of IV with different conformations. The stabilization of the less favorable among them is due to the gain in the crystallattice energy [13].

The high polarity of I, IV, and VII (see Table 1) is additional evidence of their conformational homogeneity. The fact that the dipole moment of V is lower than the dipole moment of geometrically pure VII (4.99 and 5.41 D, respectively), which exists in the form of a single conformer, is evidence of an appreciable admixture of a less polar isomer. In order



Fig. 3. Polarized IR spectra of crystalline I (a', a") and V (b', b"). Here a' and a" (b' and b") are the spectra with two mutually perpendicular polarizations of the radiation. The asterisks denote the frequencies discussed in the text.

to identify the conformers we calculated the dipole moments of I and IV-VII on the basis of the polarity parameters found from the dipole moment of 2-phenoxy-1,3,2-DOP [1] and the geometry of the ring [2, 3]. Taking into account some indefiniteness associated with the value of the polarity of the P=Y multiple bond [14], which should apparently be close to $m_{P=Y}$ in the corresponding phosphates, we carried out the calculations with $m_{P=Y} = 3.0$ D.

The subsequent analysis of the polarity of the conformations found yielded evidence of a higher dipole moment (by ~ 0.2 to 0.5 D). Figure 2 presents an Exners graph [15] for compounds I and IV-VI. The points corresponding to the squares of the experimental dipole moments of phosphoryl derivatives I and IV lie in the region of the g, α orientation of the PhO group. The positions of the points on the graph indicate that the angle φ in I and IV is less than 134° (it has been evaluated as 124° by x-ray diffraction analysis [2]) and that the dipole moment of the P=0 group is greater than 3.0 D. In the thiophosphoryl analogs the points corresponding to the experimental values are in the region between the two alternative chair conformations with a g, α and a g,e orientation of the PhO group, indicating that there is an equilibrium (according to the data from the PMR and IR spectra) between these two forms. The g, α conformer is dominant.

A comparative analysis of the IR spectra of crystals of I and V makes it possible to reveal the identical nature of their conformations from the dichroism of the bands in the polarized IR spectra of the crystals [16]. In the case of I (Fig. 3a), the most suitable bands for the analysis are the $\nu_{P=0}$ bands at 1300 and 1010 cm⁻¹, which are assigned to a vibration of the phenyl ring of type A₁, and in the case of V, they are the $\nu_{P=S}$ bands at 670 and 1010 cm⁻¹. On the basis of the assignment of the vibrations it may be assumed that the transition moments $\partial \bar{\mu}/\partial Q_i$ are directed along the P=Y and O-C (phenyl) bonds. In the g conformation the directions of the $\partial \bar{\mu}/\partial Q_i$ of the bands singled out have an angle equal to 60°; therefore, we should expect a significant difference between the values of $\alpha_{max}(\nu_{P=Y})$ and $\alpha_{max}(\nu_{O=C})$.

The experimentally observed values are α_{max} (1300) = α_{max} (1010) + 90° in I (see Fig. 3a) and α_{max} (670) = α_{max} (1010) + 90° in V (Fig. 3b); therefore, both compounds have a g conformation in the crystalline state.

The conclusions drawn for compounds I and V are in agreement with [2-7] and reflect the significant differences in the conformational behavior of 2-phenoxyl-1,3,2-DOP with PIII



Fig. 4. Dependence of the calculated Kerr constants of I, IV, and VII on the angle of rotation of the plane of the benzene ring ω .

and P^{IV} . In the former case, a cis, a structure is stabilized, and in the latter case, a g, a structure is stabilized. They are apparently due to the different types of curves for the potential energy of the rotation around the P^{III} —0 and P^{IV} —0 bonds.

The orientation of the plane of the benzene ring was established with the aid of the Kerr effect for the conformations found above for I, IV, and VII, which exist in one form. The calculation was carried out on the basis of the polarizability ellipsoids of the bonds, which were determined in [1]. According to [14], the values $b_L = 2.19$ and $b_T = 1.37$ Å³ and the values $b_L = 6.72$ and $b_T = 3.46$ Å³ were assumed for the phosphoryl and thiophosphoryl group, respectively.

The calculated values of the Kerr constants are presented in graphic form as a function of the angle ω in Fig. 4. In each case, two solutions were obtained: for I $\omega_1 = 84^\circ$, $\omega_2 = 150^\circ$; for IV $\omega_1 = 50^\circ$, $\omega_2 = 156^\circ$; for VII $\omega_1 = 72^\circ$, $\omega_2 = 160^\circ$. The first of them, ω_1 , for I and VII is close to the value determined by x-ray diffraction analysis for V. Taking into account that the analysis carried out above of the IR and Raman spectra of compounds I, IV, and VII does not point out any changes in the spatial structure upon the transition from the crystalline state to solutions, we prefer the first set of solutions. It fits the noncoplanar orientation of the orbitals of the benzene ring and the pair of p electrons of the sp²-hybridized oxygen atom in I and VII. The p-bromo derivative (IV) has a somewhat more compact structure.

CONCLUSIONS

1. The change in the valence state of the phosphorus atom influences the orientation with respect to the P-O(Ph) bond in 2-phenoxy-2-oxo(thiono)-1,3,2-dioxaphosphorinanes.

2. An orthogonal conformation is realized in the O-Ph fragment of the compounds investigated, regardless of the hybridization of the phosphorus.

LITERATURE CITED

- 1. B. A. Arbuzov, R. P. Arshinova, T. D. Sorokina, A. B. Remizov, and G. E. Koroleva, Izv. Akad. Nauk SSSR, Ser. Khim., 1977, 2006.
- 2. H. J. Geise, Rec. Trav. Chim., 86, 362 (1967).
- 3. A. Grand and J. B. Robert, Acta Crystallogr., <u>B31</u>, 2523 (1975).

4. R. Wagner, W. Jensen, and W. Wadsworth, Cryst. Struct Commun., 2, 507 (1973).
5. J. P. Majoral and J. Navech, Bull. Soc. Chim. France, 1971, 95.
6. L. D. Hall and R. B. Malcolm, Can. J. Chem., <u>50</u>, 2092 (1972).
7. J. P. Dutasta, A. Grand, J. B. Robert, and M. Taieb, Tetrahedron Lett., <u>1974</u>, 2659.
8. M. Kainosho and T. Shimozava, Tetrahedron Lett., <u>1969</u>, 865.
9. K. Faegri, T. Gramstad, and K. Tjessem, J. Mol. Struct., <u>32</u>, 37 (1976).
10. J. P. Majoral and J. Navech, Bull. Soc. Chim. France, <u>1971</u>, 2609.
11. A. B. Remizov, Zh. Prikl. Spektrosk., <u>22</u>, 251 (1975).
12. É. E. Nifant'ev and I. V. Fursenko, Zh. Obshch. Khim., <u>38</u>, 1295 (1968).
13. A. I. Kitaigorodskii, Molecular Crystals [in Russian], Nauka (1971).
14. B. A. Arbuzov and R. P. Arshinova, Dokl. Akad. Nauk SSSR, <u>227</u>, 1371 (1976).
15. O. Exner and V. Jehlička, Collect. Czech. Chem. Commun., <u>30</u>, 639 (1965).
16. A. B. Remizov, Opt. Spektrosk., <u>39</u>, 204 (1975).

DIPOLE MOMENTS AND SPATIAL STRUCTURE OF ARYLDICHLOROARSINES

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The spatial structure of molecules of the phenylarsines and their analogs in solutions has scarcely been studied. The establishment of the angle of rotation of the plane of the aromatic ring might provide some information regarding the nature of the potential due to rotation around the C_{ar} -As bond. The triphenyl derivatives were investigated in [1, 2], where it was postulated that all three groups have the same orientation.

In the present work we used the method of dipole moments to study the p- and o-substituted aryldichloroarsines $X-C_6H_4AsCl_2$, where X = H (I), p-CH₃ (II), p-Cl (III), p-Br (IV), p-I (V), p-NO₂ (VI), o-CH₃ (VII), o-Cl (VIII), o-Br (IX), o-NO₂ (X), and o-CH₃O (XI).

EXPERIMENTAL

Compounds I-XI were obtained according to the method in [3] by reducing the corresponding arsonic acids with sulfur dioxide in hydrochloric acid solutions.

The experimental dipole moments were determined according to Debye's second method [4] at 298°K in $CC1_4$. The measurements of the dielectric constants and the indices of refraction of the solutions were carried out on an IDM instrument [5] and an IRF-23 refractometer. The results of the measurements are presented in Table 1.

DISCUSSION

The molecular dipole moments of I-VI do not depend on the internal rotation, while the moments of VII-XI are determined by the orientation of the plane of the phenyl ring relative to the AsCl₂ group. From the dipole moments of I-VI we can calculate the necessary additive

TABLE 1. Coefficients in Equations for Calculating Dipole Moments

Com- pound	α	Ŷ	p _{or} cm ³	μ, D	Com- pound	α	Ŷ	por [°] cm ³	μ, D
(I) (II) (III) (IV) (V) (V)	7,889 8,908 3,463 3,278 3,324 6,383	0,328 0,415 0,490 0,433 0,675 1,222	 177,88 212,39 80,33 90,15 96,64 144,48	2,94 3,21 1,97 2,09 2,16 2,65	(VII) (VIII) (IX) (X) (XI)	7,500 7,655 6,818 14,690 13,750	0,486 0,577 0,573 0,289 0,650	175,20 191,74 198,50 409,10 350,31	2,91 3,04 3,10 4,45 4,12

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