

THREE-DIMENSIONAL STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLES

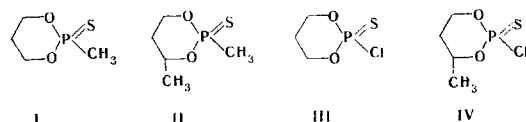
II.* DIPOLE MOMENTS AND KERR CONSTANTS OF SOME 2-THIONO-1,3,2-DIOXAPHOSPHORINANES

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The three-dimensional structure of a number of 2-thiono-1,3,2-dioxaphosphorinanes was studied by means of dipole moments, the Kerr effect, and theoretical conformational analysis with P^{31} NMR data. 2,4-Dimethyl- and 2-chloro-2-thiono-1,3,2-dioxaphosphorinanes have the chair conformation with an equatorial thionophosphoryl group; the 2-methyl derivative exist as an equilibrium mixture of the axial and equatorial conformers with predominance of the former. The participation of the boat form in the conformational equilibrium was established for 2-chloro-4-methyl derivative.

In a continuation of our studies of the three-dimensional structures of phosphorus-containing heterocycles, we have studied the structures of several 2-thiono-1,3,2-dioxaphosphorinanes (I-IV) by means of dipole moments (DM) and the Kerr effect.



The structure of the 1,3,2-dioxaphosphorinane ring, which contains a tetracoordinated phosphorus atom, was previously investigated in quite some detail by means of x-ray diffraction [2, 3] and PMR spectra [4-6]. The study was primarily devoted to the 2-oxo derivatives, for which a preference for the chair conformation with an equatorial phosphoryl group was demonstrated. A similar conclusion was also drawn for a small number of thionophosphoryl derivatives [6, 7]. Recently [8, 9], it was found that it was possible to separate the geometrical isomers of 2-hydroxy-4-methyl-2-thiono-1,3,2-dioxaphosphorinane and to determine their configurations by means of NMR spectroscopy [8, 9]. However, the ring conformations were not considered in this paper. It therefore seemed of interest to examine in greater detail the structure of 1,3,2-dioxaphosphorinanes with a thionophosphoryl group.

Since the NMR spectra unambiguously attest that 1,3,2-dioxaphosphorinane molecules exist in solution in symmetrical conformations and that the most stable form is the chair form for all of the investigated compounds in the absence of additional effects, chair conformations with equatorial (A) and axial (B) positions of the thionophosphoryl group were considered for I-IV. The experimental and calculated DM and molar Kerr constants are presented in Table 1.

* See [1] for communication I.

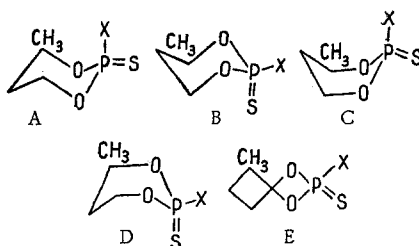
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TABLE 1. Dipole Moments and Kerr Constants for the Investigated Compounds

Compound	Parameter	Conformation				Exptl. data
		A, <i>a</i> -CH ₃	A, <i>e</i> -CH ₃	B, <i>a</i> -CH ₃	B, <i>e</i> -CH ₃	
I	μ, D		5,89		3,92	3,90
	$mK \cdot 10^{12}$		1287		204	436
II	μ, D		5,89		3,92	5,37
	$mK \cdot 10^{12}$	1273	1168	243	202	1175
III	μ, D		5,46		4,22	5,30
	$mK \cdot 10^{12}$		714		-110	1356
IV	μ, D		5,46		4,22	5,54
	$mK \cdot 10^{12}$	622	643	-149	-115	1195

The calculations were carried out for the following bond lengths and valence angles [2]: C-C 1.54 Å, C-O 1.44 Å, P-O 1.57 Å, C-C-C 111°, C-O-P 118°, O-P-O 106°, and O=P-O 114°. Two sets of bond moments were used [10]. The first, disregarding the DM of the unshared electron pair of the phosphorus atom, was as follows: P=S 2.62 D, P-CH₃ 1.28 D, P-Cl 0.56 D, and O-P 0.43 D. The second, taking into account an unshared-pair dipole moment of 1.35 D, calculated by the SCF method [10], was as follows: P=S 3.97 D, P-CH₃ 9.45 D, P-Cl 1.53 D, and P-O 0.54 D. It is easy to demonstrate that the use of one or another set does not affect the results of the calculations, since, in the first, the DM of the unshared pair is included implicitly in the DM of the bonds.



The Kerr constants of the various structures were calculated from Eqs. (35) and (36) in [11] for the following bond polarizabilities: C-C $b_L = 0.98 \text{ \AA}^3$, $b_T = 0.27 \text{ \AA}^3$; C-O $b_L = 0.89 \text{ \AA}^3$, $b_T = 0.46 \text{ \AA}^3$; the C-H bonds were considered to be isotropic and were disregarded [11]. The axes of the polarizability ellipsoids of the bonds of the tetracoordinated phosphorus atom were equated with the differences in the ellipsoids of the bonds of tricoordinated phosphorus [10] and the unshared electron pair, during which the latter was taken as isotropic with $\alpha = 2.1 \text{ \AA}^3$ [12]. They are as follows: P-O $b_L = 0.15 \text{ \AA}^3$, $b_T = 0.74 \text{ \AA}^3$; P-Cl $b_L = 4.41 \text{ \AA}^3$, $b_T = 1.75 \text{ \AA}^3$; P=S $b_L = 6.72 \text{ \AA}^3$, $b_T = 3.46 \text{ \AA}^3$; P-C $b_L = 1.57 \text{ \AA}^3$, $b_T = 0.08 \text{ \AA}^3$.

A comparison of the experimental dipole moments with one another demonstrates that, while the polarities of chloro derivatives III and IV are close, the DM of I and II differ markedly, which indicates a difference in their conformations. The DM and Kerr constants found for II and IV are closest to the values calculated for form A; for I, on the other hand, the DM corresponds to an axial position of the P=S bond. The IR spectroscopic data indicate the presence of a conformational equilibrium [13], while methylated derivative II exists only with an equatorial orientation of the thionophosphoryl group. Stabilization of one of the conformers is possible if the methyl group in II occupies an energetically favorable equatorial position. In fact, the Kerr constant determined for this compound is in excellent agreement with the value calculated precisely for an equatorial methyl group (the *cis* configuration with respect to the P=S bond). The good convergence confirms the applicability of the additive scheme of the polarizabilities to dioxaphosphorinanes with P=S and P-C bonds (I, II) and is evidence for the reliability of the constants calculated for the conformers of I. The experimental value corresponds to 0.8 mole fraction of form B, which is in agreement with the spectroscopic data [13]. However, the DM does not exceed the calculated value for form B. This may be a consequence of the inadequacy of the simple additive scheme. It should be noted that the P ³¹ NMR chemical shifts in I ($\delta = -97$ ppm in CCl₄ relative to 85% H₃PO₄ as the external standard) and II ($\delta = -89$ ppm) differ: the nucleus of the phosphorus atom is more shielded when the thionophosphoryl group is in the equatorial position. An attempt was made to estimate the change in the electronic structure of the phosphorus bonds as the ring conformation changes. In doing so, it was assumed that the transition between forms A and B has the greatest effect on the polarity of the P-O bonds, since conjugation of the unshared electron pairs of the oxygen atoms with the 3d orbitals of phosphorus can be realized in one of these forms. For phosphoryl compounds, this sort of interaction is maximal for a *trans* orientation of the C-O and P=O

TABLE 2. Steric Interactions in Dioxaphosphorinanes

Conformation	Type of interaction	E, kcal/mole
A	C—H...Cl—P	-0,14
	C—H...CH ₃ —P	-0,04
	C—CH ₃ ...Cl—P	3,84
	C—CH ₃ ...H—C	1,15
B	C—H...S=P	-0,14
C	C—H...Cl—P	1,57

TABLE 3. Kerr Constants of the Possible Structures of IV

Conformation of 4-CH ₃	Ring conformation	Orientation of 4-CH ₃	$m^k \cdot 10^{12}$
trans relative to P=S	A	a	1341
	B	e	111
	C	e	1253
	E	e	366
cis relative to P=S	A	e	1294
	B	a	74
	C	a	1267
	E	a	235

TABLE 4. Dipole Moments and Kerr Constants of the Investigated Compounds

Compound	αe_0	$-\beta$	γ	δ	μ, D	$m^k \cdot 10^{12}$
I	19,874	0,303	0,420	390,281	3,90	436
II	34,103	0,335	0,380	957,440	5,37	1175
III	32,000	0,245	0,360	1061,860	5,30	1356
IV	32,401	0,222	0,360	867,863	5,54	1195

bonds [14]. However, a comparison of the P^{31} NMR and Cl^{35} NQR data and the dissociation constants of the acids [15] attests to the presence of $p_{\pi}-d_{\pi}$ conjugation only in the phosphoryl group. This is evidence in favor of the fact that the thionophosphoryl bond should change only slightly on passing from form A to B; the same can be assumed for the P—C bond. A knowledge of the position of the IA \rightleftharpoons IB equilibrium and the DM of conformer A (the experimental value for II, which is satisfactorily described by the additive scheme) makes it possible to calculate the polarity of form B as 3.43 D. The effective DM of the P—O bond is then 0.10 D instead of 0.43 D. Thus an interaction moment of ~ 0.3 D, which corresponds to a change in the chemical shift of P^{31} of 8 ppm, occurs in the chair conformation with an axial phosphoryl group.

Like the polarities, the P^{31} NMR frequencies for III and IV are equal (-60 ppm). Chloro derivative III exists in a single conformation [13], which, according to the dipole moment, is a chair with an equatorial P=S bond. However, the Kerr constant calculated for this structure is considerably lower than the experimental value, although it is the closest one to it. The reason for this may be the strong interaction of the readily polarizable P—Cl and P=S bonds. This is taken into account by the introduction of the effective anisotropy of the polarizability of the P—Cl bond, calculated from the experimental data for III. It can be used in the calculation of the anisotropy of the polarizability of the conformers of compounds of this type. Thus the spectroscopic data for IV indicate the equilibrium of three three-dimensional forms, in which the two of equal polarity predominate [13]. The magnitude of the dipole moment (Table 1) indicates a predominantly equatorial orientation of the thionophosphoryl group. It is substantially preferable, since III exists exclusively in this conformation. The appearance of a complex conformational equilibrium when a methyl group is introduced into the 4 position may be due only to its unfavorable axial orientation in A. It can be concluded that the C—CH₃ bond in IV is in the trans position relative to P=S. The relative stability of chair B (with an equatorial methyl group but an unfavorable axial orientation of the thionophosphoryl group) and boat C (with equatorial C—CH₃ and P=S bonds) is completely understandable; the less polar IV form can also be represented as the twist conformation (E), in which the energy of orientation of the P—O bonds is less than that in B. A boat with an axial thionophosphoryl group (D) is not stabilized by any factors.

The qualitative examination is confirmed by the calculation of the energies of three-dimensional forms of IV with respect to a structure of the III type. The energies of the steric interactions [16] are presented in Table 2.

The presence of an axial methyl group destabilizes form A considerably (~4.8 kcal/mole). The energy in boat C is made up of an interaction of the C-H . . . Cl-P type and two barriers to orientation of the C-O bonds (3.8 kcal/mole). The energy of twist from E is a little less. The values calculated for the conformers of IV (excluding boat D) using the effective anisotropy of the P-Cl bond are presented in Table 3.

Considerably better convergence with the experimental results ($1195 \cdot 10^{-12}$), as compared with the values presented in Table 1, is achieved. The assignment of the configuration of the methyl group on the basis of the Kerr constants cannot be confirmed, but the least polar of the three forms participating in the equilibrium can be identified. The amount of it present is ~20%. The anisotropy of the polarizability of the two conformers that are undoubtedly present in the mixture (A and C) is so close that variations in their relative amounts do not affect the Kerr constant of the mixture. The experimental value corresponds to the presence of ~20% of the chair form with an axial thionophosphoryl group (form B).

Thus the relative stabilities of the conformers in thionophosphoryl compounds with P-C (I, II) and P-Cl (III, IV) bonds differ. In the absence of additional factors, i.e., for unsubstituted derivatives I and III, the axial orientation of the P=S bond is more stable in the first case, and the equatorial orientation is realized exclusively in the second. In order to ascertain the reasons for this phenomenon, the energies of steric interactions between the substituents attached to phosphorus and the axial hydrogen atoms were compared (Table 2). The steric requirements are in the order $\text{CH}_3 > \text{S}=\text{Cl}$, but the differences in the energies are extremely small. An examination of the dipole-dipole interactions, as in [10], leads to two sets of energy parameters corresponding to the two sets of bond dipole moments indicated above. In both cases, conformations with equatorial thionophosphoryl groups are more favorable for chloro derivatives III and IV. (The difference in energy is ~0.5 kcal/mole.) A still larger value (0.9 kcal/mole) is obtained for I and II when the DM of the unshared pair is taken into account. The calculations demonstrate that it is impossible to explain the effect of substituents attached to the phosphorus atom on the ring conformation on the basis of classical concepts. Analysis of the P^{31} NMR chemical shifts and the bond DM demonstrates that there are also quantum-chemical interactions. An examination of them will be carried out in one of our subsequent studies.

EXPERIMENTAL

Compounds I and II were obtained by the reaction of $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ with 1,3-trimethyleneglycol and 1,3-butyleneglycol in hot benzene in the presence of triethylamine [17]. The previously unreported 2,4-dimethyl-2-thiono-1,3,2-dioxaphosphorinane (II) had bp 88-90° (0.5 mm), d_4^{20} 1.2495, and n_D^{20} 1.5210. Found: P 18.6; S 18.0%; MR_D 40.44. $\text{C}_5\text{H}_{11}\text{O}_2\text{PS}$. Calculated: P 18.5; S 19.0%; MR_D 40.92. Compounds III and IV were synthesized from PSCl_3 and the appropriate 1,3-glycols by the method in [18]. The DM and molar Kerr constants were determined from CCl_4 solutions by the method in [19]. The coefficients of the equations used in the calculations are presented in Table 4.

The P^{31} NMR spectra were obtained with a YaMR-KGU-4 spectrometer with an adapter for recording P^{31} spectra by É. I. Gol'dfarb, to whom the authors are sincerely grateful.

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