THREE-DIMENSIONAL STRUCTURE OF

PHOSPHORUS-CONTAINING HETEROCYCLES

I. DIPOLE MOMENTS, KERR CONSTANTS, AND STRUCTURES OF SOME

2-CHLORO-1,3,2-DIOXAPHOSPHORINANES

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The dipole moments and molar Kerr constants of 2-chloro-5,5-dimethyl-2-chloro-, and 4-methyl-2-chloro-1,3,2-dioxaphosphorinanes were determined. It was found that a chair conformation with an equatorial P−Cl bond is realized in all cases.

A large number of papers devoted to the investigation of the three-dimensional structures of six-membered heterocycles containing a phosphorus atom in the ring, particularly 1,3,2-dioxaphosphorinane derivatives, have recently appeared. The most accurate data on the geometry of the rings were obtained for 2-oxa-1,3,2-dioxaphosphorinanes by means of x-ray diffraction analysis [1,2]. 1,3,2-Dioxaphosphorinane rings containing a tricoordinated phosphorus atom have received much less study. They were first obtained by the condensation of 1,3-glycols with phosphorus trichloride [3,4]. We have also studied compounds of this type (I-III) by means of dipole-moment (DM) methods.
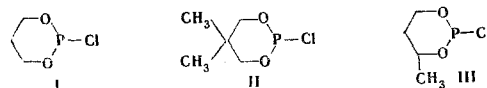
A number of investigators have attempted to study the three-dimensional structure of this type of compound by PMR spectroscopy [5-8]. Analysis of the chemical shifts and spin−spin coupling constants, as well as an investigation of the temperature dependence of the PMR spectra [5,6], demonstrate that the compounds exist as a single conformer. However, the difference in the $\mathfrak{J}_{AX}$ and $\mathfrak{J}_{BX}$ values (a system of the AA'BB'MX type is considered) is evidence in favor of the chair conformation, since the dihedral $POCH_A$ and $POCH_B$ angles that affect this interaction will differ greatly in the chair conformation, whereas these angles are approximately equal in the rigid boat form [5-7].

However, the authors could not rigorously prove the geometry of the P−Cl (or P−OCH$_3$) bond. In [7] it is concluded that this bond is in the axial position on the basis of the fact that anomeric effects induce greater preference for the axial position in the corresponding substituted 1,3-dioxanes. The same conclusion is drawn in [8]. It is substantiated by the fact that the adducts of phosphite with BH$_3$ have the chair structure with an axial P−OCH$_3$ bond. However, the drawing of such an analogy seems unjustified to us, since, first of all, the phosphorus atom changes its valence to become tetracoordinated, and, second, the steric requirements of the BH$_3$ group are far greater than the steric requirements of the ether oxygen. Gagnaire and co-workers [5,6], however, concluded that the 1,3,2-dioxaphosphorinane ring exists in the rigid chair conformation with an equatorial P−Cl bond as a consequence of the fact that strong 1,3-diaxial interactions are present in the axial conformer.

TABLE 1. Dipole Moments (DM) and Kerr Constants of 2-Chloro-1,3,2-dioxaphosphorinanes

| Con-formation	Calc. DM, D*	Calculated mK·10^{12}		
		I	II	III
A	2,94	−101	−71,6	a-CH$_3$ − 118 e-CH$_3$ − 105
B	3,37	144	199	a-CH$_3$ + 118 e-CH$_3$ + 121
C	2,68	− 56,3	− 51,9	a-CH$_3$ − 79,6 e-CH$_3$ − 51,9
Experimental values I II III 3,47 3,66 3,60		164	215	121

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* The calculated DM of I-III do not differ from one another, since the DM of the CH$_3$ group is equal to the DM of the C−H bond.

Thus it can be assumed that it can be absolutely definitively proved by means of the PMR spectra that the 1,3,2-dioxaphosphorinane ring does not have the flexible boat conformation. We therefore confront two problems — the determination of the three-dimensional structure of the ring and the elucidation of the position occupied by the P−Cl bond.

For this, we synthesized I-III and measured their DM and molar Kerr constants at 25°C in cyclohexane (Table 1). The following molecular geometry was assumed [1,2] in calculating the DM and Kerr constants: C−C 1.54 Å, C−O 1.44 Å, P−O 1.63 Å, P−Cl 2.084 Å, CCC 112°, COP 118°, and OPO and OPCl 99°.

It is easy to show that the magnitude of the moment of the unshared electron pair (UEP) has no effect on the result of the calculation of the DM of compounds of this type via a vector additive scheme, since this moment is included in implicit form in the dipole moment of the bonds calculated from the experimental DM of symmetrical compounds. Thus, if it is assumed that the UEP of the phosphorus atom has zero polarity, the DM of the P−Cl bond calculated from the experimental DM of phosphorus trichloride [9] is +0.56 D, while the DM of the P−O bond found from the DM of 4-phospha-3,5,8-trioxabicyclo[2.2.2]octane [9] is −0.43 D. The use of a UEP moment of 1.35 D, as we have found from calculations via the self-consistent field method [10], leads to P−Cl and P−O bond moments of 1.53 and 0.54 D, respectively. In accordance with the existing theoretical concepts, these values seem more reliable. However, this is of no significance in the calculation of the molecular DM via an additive scheme. The calculation of the DM of the possible structures of the studied compounds on the basis of both sets of bond moments gives identical results.

A chair conformation with an axial P−Cl bond (A), a chair conformation with an equatorial P−Cl bond (B), and a skew form (C) were examined. It is apparent from the data in Table 1 that all of the calculated DM values for the chair conformation are close to the experimental values, but they are in best agreement with the DM of the chair form with an equatorial P−Cl bond (DM$_{cal}$ 3.37 D, DM$_{ex}$ ~3.4-3.6 D).

A   B   C
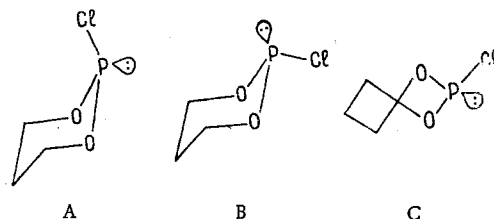
In order to definitely convince ourselves that I-III have the same structure, we calculated their Kerr constants from Eqs. (35) and (36) in [11], during which the polarizability ellipsoids of the structures were considered to be the tensor additive sum of the bonded ellipsoids. Because of their isotropic character, C−H bonds were not taken into account in the calculations. The following bond polarizabilities were used: C−C p$_L$ = 0.98 Å^3, p$_T$ = 0.27 Å^3; C−O p$_L$ = 0.89 Å^3, p$_T$ = 0.46 Å^3; P−O p$_L$ = 0.86 Å^3, p$_T$ = 1.45 Å^3 [11, 12]. The anisotropy of the P−Cl bond (p$_L$ = 5.12 Å^3, p$_T$ = 2.46 Å^3) was calculated from the experimental molar

TABLE 2. Experimentally Determined Parameters of Dioxaphosphor-
inanes

Comp.	$\alpha\varepsilon_0$	$-\beta$	γ	δ	DM, D	$mK\cdot10^{12}$
I	8,070	0,722	0,027	94,559	3,47	164
II	7,433	0,557	0,041	100,835	3,66	215
III	7,945	0,605	0,064	53,722	3,60	121

Kerr constant of phosphorus trichloride [13]. It should be noted that when this sort of approach is used, the anisotropy of the polarizability of the UEP enters in implicit form into the polarizabilities of the P—O and P—Cl bonds, and variation in its magnitude does not change the finite value of the molar Kerr constant.

A comparison of the experimental and calculated Kerr constants (Table 1) leads us to the absolutely unambiguous conclusion that I-III have the chair form with an equatorial P—Cl bond, since the calculated Kerr constants, like the experimental constants, prove to be positive only for this conformation. The close correspondence between the calculated and experimental constants, however, is evidence for a rigid ring form.

In contrast to the first two compounds, III can exist as geometrical cis and trans isomers. The following geometry of the substituents in the chair form is possible for the trans isomer: equatorial P—Cl, axial CH_3, axial P—Cl, and equatorial CH_3. The geometry possible for the cis isomer is: equatorial P—Cl, equatorial CH_3, axial P—Cl, and axial CH_3. The Kerr-effect-method does not provide us with an answer as to which isomer we have investigated.

The conclusion regarding the three-dimensional structure of I-III contradicts the results obtained for compounds of the tetracoordinated phosphorus atom in which the P = O bond already occupies the equatorial position. This sort of conformation can be determined by the effects of conjugation of the unshared pair of electrons of the endocyclic oxygen atoms and the orbitals of the phosphorus atom. As was demonstrated in [14], it is a maximum for a trans orientation of the C—O and P = O bonds, i.e., for an equatorial orientation of the latter. If it is assumed that, as a consequence of the considerably lower compression of the 3d orbitals in trivalent phosphorus derivatives, the effect of their overlap with the UEP of the ester oxygen atoms is insignificant, it should not have an appreciable effect on the relative conformational preference of the isomers. In this case, the latter is determined by the usual steric factors that stabilize the equatorial position of a bulky substituent. As for the energy of the dipole—dipole interaction, which is the reason for the so-called "anomeric effect," it also should stabilize the chair conformation with an equatorial P—Cl bond, since, according to [15], as a consequence of repulsion of the dipoles of the UEP, the latter tend to orient themselves in an antiparallel manner. This is achieved to a maximum degree when the UEP of phosphorus is axially oriented (structure B). As in [16], our theoretical calculations have actually demonstrated that due to the electrostatic interactions of the two dipoles of the C—O bonds with the moments of P—Cl and UEP, the preference for structure B is no less than 1.3 kcal/mole as compared with the axial P—Cl bond (A). Thus the indicated factors may explain the experimentally observed conformation of 2-chloro-1,3,2-dioxa-phosphorinanes.

EXPERIMENTAL

The 2-chloro-1,3,2-dioxaphosphorinanes were obtained by the method in [1,4] and had the following physical constants: I, bp 70-71° (17 mm) and n_D^{20} 1.4858; II, bp 71° (10 mm) and n_D^{20} 1.4768 (Found: P 18.1%. $C_5H_{10}ClO_2P$. Calculated: P 18.4%); III, bp 63° (12 mm) and n_D^{20} 1.4780. Literature data: I, bp 70-71° (17 mm) and n_D^{20} 1.4850 [4]; III, bp 65° (12 mm) and n_D^{20} 1.4765 [4].

The molar Kerr constants were determined in cyclohexane at 25° and were calculated from the equation [11]

$$mK = sK_1(1-\beta+\gamma+\delta-H\gamma-I\alpha\varepsilon_1),$$

where $H = 4n_{D_1}^2$ $(n_{D_1}^2 + 2)$, $I = 2/(\varepsilon_1 + 2)$, sK_1 is the specific Kerr constant of cyclohexane, $n_{D_1}^{25} = 1.4235$, $d_4^{25} = 0.7783$ [17], $\varepsilon_1 = 2.0199$ [18]; the Kerr constant of the pure solvent $(B\cdot10^{17})$ was found experimentally to be 0.057. Then, H = 2.013, I = 0.498, and $sK_1 = 1.420\cdot10^{-14}$. The coefficients of the computational equations are presented in Table 2.

LITERATURE CITED

1. H. J. Geise, Rec. Trav. Chim., **86**, 362 (1967).
2. T. A. Beineke, Chem. Comm., 860 (1966).
3. A. E. Arbuzov, V. M. Zoroastrova, and N. I. Rizpolozhenskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 208 (1948).
4. A. E. Arbuzov and V. M. Zoroastrova, Izv. Akad. Nauk SSSR, Ser. Khim., 779 (1952).
5. D. Gagnaire and J. B. Robert, Bull. Soc. Chim. France, 2240 (1967).
6. D. Gagnaire, J. B. Robert, and J. Verrier, Bull. Soc. Chim. France, 2392 (1968).
7. J. H. Hargis and W. G. Bentrude, Tet. Letters, 5365 (1968).
8. D. W. White, G. K. McEwen, and I. G. Verkade, Tet. Letters, 5369 (1968).
9. O. A. Osipov and V. I. Minkin, Handbook of Dipole Moments [in Russian], Moscow (1965).
10. R. D. Brown and B. A. W. Coller, Theor. Chim. Acta, **7**, 259 (1967).
11. R. I. W. Le Fevre, in: Advances in Physical Organic Chemistry, V. Gold (editor), Vol. 3, New York—London (1965).
12. R. I. Le Fevre, B. I. Orr, and G. L. D. Ritchie, J. Chem. Soc. B, 273 (1966).
13. N. Hacket and R. I. W. Le Fevre, J. Chem. Soc., 2612 (1961).
14. R. H. Collin, J. Am. Chem. Soc., **88**, 3281 (1961).
15. R. O. Hutchins, L. D. Kopp, and E. L. Eliel, J. Am. Chem. Soc., **90**, 7174 (1967).
16. L. K. Yuldasheva, R. P. Arshinova, and S. G. Vul'fson, Izv. Akad. Nauk SSSR, Ser. Khim., 555 (1969).
17. V. M. Tatevskii (editor), Physicochemical Properties of Individual Hydrocarbons [in Russian], Gostoptekhizdat (1960).
18. R. I. W. Le Fevre, Trans. Faraday Soc., **34**, 1127 (1938).