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The Kerr Effect and the Structure of Organophosphorus Compounds

R.P.Arshinova

The results of research on the steric and electronic structures of organophosphorus compounds with the aid of the Kerr effect and the combined employment of the Kerr effect and other physical methods (dipole moments, depolarisation of Rayleigh light scattering, spectroscopic methods) are surveyed. The additive refractions, polarities and polarisabilities of phosphorus bonds are analysed and data are presented on the conformational analysis of acyclic phosphorus-containing molecules and four-, five-, and six-membered phosphorus-containing heterocycles.
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I. INTRODUCTION

The distribution of electron density in the molecule (polarity) and the ability of the electron clouds to shift under the influence of an electric field (polarisability) are fundamental properties of matter, which in many respects determine its structure and reactivity. There are only a few experimental methods for the direct investigation of the electrical and electro-optical characteristics of molecules. Among these, the dipole moment method (DM), which yields information about the polarity of molecules, occupies an important place. The less widely used methods of double refraction in an electric field (the Kerr effect) and of the depolarisation of Rayleigh light scattering are the only ones available for the study of polarisability.

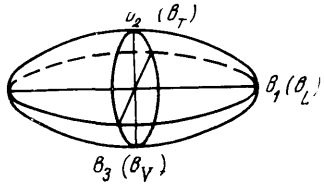
The polarisability α is defined as the dipole moment μ_{ind} induced by a unit electric field: $\alpha = \mu_{ind}/E$. For an isotropic species, the resultant vector of the induced moment is parallel to the applied field vector **E**. The polarisabilities of anisotropic species parallel and at right angles to the vector **E** are not equal ($\alpha_{\parallel} \neq \alpha_{\perp}$) and the induced dipole forms an angle with the vector **E**.

The anisotropic nature of a substance leads to the phenomenon of double refraction following the application of an electric field, i.e. at a given wavelength λ the refractive index n assumes different values in the directions parallel and at right angles to the applied field and we have $\Delta n = n_{\parallel} - n_{\perp} = B\lambda E^2$, where B is the Kerr constant, determined by the properties of the substance itself. The molar Kerr constant ${}_mK$, which is defined as the difference between the molecular refractions R for light polarised parallel and at right angles to **E**, is used in chemistry: ${}_mK = (R_{\parallel} - R_{\perp})/E^2$. For mixtures, ${}_mK$ is additive, so that the Kerr constant for a mixture of n isomers is

$$ {}_mK_{exp} = \sum_{i=1}^{n} {}_mK_i N_i $$

where N_i are the mole fractions of the isomers in the mixture and $\sum N_i = 1$.

In a theoretical treatment, the polarisabilities in different directions are described with the aid of the ellipsoid of polarisability



with three principal axes b_1, b_2, and b_3 for a molecule or b_L, b_T and b_V for an individual bond, where b_L is the longitudinal polarisability and b_T and b_V are the transverse and vertical polarisabilities respectively (the letter b denotes optical polarisability, i.e. the electron shift in the electromagnetic field of the light wave). It is assumed that b_L has the same direction as the bond. For axially symmetrical bonds, $b_L \neq b_T = b_V$.

In the general case, polarisability must be regarded as a function of the orientation of the species relative to the direction of the polarising field **E**. In a cartesian coordinate system, each component of the induced moment (m_x, m_y, and m_z) is a function of three components of **E** (E_x, E_y, and E_z). In terms of matrix notation, one can write $\mu_{ind} = \Phi E$, where Φ is the polarisability tensor:

$$ (\Phi) = \begin{vmatrix} b_{xx} & b_{xy} & b_{xz} \\ b_{yx} & b_{yy} & b_{yz} \\ b_{zx} & b_{zy} & b_{zz} \end{vmatrix} . $$

The components of this tensor are the induced moments arising in the direction of the i axis when the field acts along the j axis. The polarisability tensor is a symmetrical tensor of the second rank. The invariants of the tensor are its trace and anisotropy, equal to the difference between the principal axes of the polarisability ellipsoid: $\gamma = b_L - b_T$. The trace of the tensor b determines the molecular refraction of the substance. The components of the molecular polarisability tensor are closely related to the following three experimentally determined characteristics of the molecule:

1) The refraction R_∞ extrapolated to the infinite wavelength:

$$P_E = R_\infty = \frac{4\pi N}{9}(b_{xx} + b_{yy} + b_{zz}), \quad (2)$$

where P_E is the electronic polarisation. The polarisability determined from molecular refraction is the average optical polarisability:

$$\bar{b} = (b_1 + b_2 + b_3)/3 . \quad (3)$$

2) The coefficient of the depolarisation of the scattered light ${}_2\delta^2_\infty$:

$${}_2\delta^2_\infty = \frac{(b_{xx} - b_{yy})^2 + (b_{xx} - b_{zz})^2 + (b_{yy} - b_{zz})^2 + 6(b^2_{xy} + b^2_{xz} + b^2_{yz})}{(b_{xx} + b_{yy} + b_{zz})^2} . \quad (4)$$

3) The molar Kerr constant of the substance containing anisotropic (K_1) and dipole (K_2) components:

$${}_mK = K_1 + K_2 , \quad (5)$$

$$K_1 = \frac{2\pi N}{9kT} \cdot \frac{P_D}{45P_E}[(b_{xx} - b_{yy})^2 + (b_{xx} - b_{zz})^2 + (b_{yy} - b_{zz})^2 + 6(b^2_{xy} + b^2_{xz} + b^2_{yz})] , \quad (6)$$

$$K_2 = \frac{2\pi N}{9kT} \cdot \frac{1}{45kT}[m_x^2(2b_{xx} - b_{yy} - b_{zz}) + m_y^2(2b_{yy} - b_{xx} - b_{zz}) + m_z^2(2b_{zz} - b_{xx} - b_{yy}) + 6(m_x m_y b_{xy} + m_x m_z b_{xz} + m_y m_z b_{yz})] , \quad (7)$$

where P_D is the deformation polarisation.

Eqn. (7) includes the components of the dipole moment along the coordinate axes, so that the magnitude and direction of the molecular dipole moment must be known in order to find ${}_mK$.

The majority of studies carried out previously involved the measurement of the Kerr effect and the refraction [1,2]. Investigation of the depolarisation of Rayleigh light scattering gives rise to new possibilities both for applied structural research and in the study of detailed intramolecular interactions and electron redistributions [3].

This review is devoted to the principal results and possibilities which are available to investigators of organophosphorus compounds using the Kerr effect method in conjunction with Rayleigh light scattering data in many instances. Much attention has also been devoted to the methodological aspect of the application of the dipole moment method, since dipole moments in many respects determine the validity of the calculation of ${}_mK$.

II. THE KERR CONSTANTS OF PHOSPHORUS COMPOUNDS. THE ADDITIVE POLARITIES AND POLARISABILITIES OF PHOSPHORUS BONDS

1. The Kerr Constants of Phosphorus Compounds

The major advances achieved in the application of electro-optical methods to the study of the steric and electronic structures of organic compounds belonging to a wide variety of glasses (see the relevant reviews [1-3]) gave rise to the hope that these methods will be useful in the investigation of organophosphorus componnds, which are characterised by a wide variety of intramolecular electronic interactions: involving the lone electron pair (LEP), the multiple bond of phosphorus, etc.

Table 1 lists the phosphorus compounds investigated with the aid of the Kerr effect up to 1977 [4-32] (the numbering of the compounds in Table 1 is used henceforth in the text and in the other Tables). The first studies in this field, starting from 1961, were carried out by Le Fevre and coworkers [4,7,11,17,20,23,32] for twenty identically substituted compounds of three- and four-coordinated phosphorus. Certain difficulties, which will be noted below, limited further structural research.

Research involving the determination of the Kerr constants and of the degrees of depolarisation of Rayleigh light scattering in organophosphorus compounds was begun in Kazan in 1970 under the general supervision of Academician B. A. Arbuzov.

Table 1. The experimental Kerr constants for phosphorus compounds.

No. of compound	Compound	Solvent*	μ, D	$10^{12}{}_mK$**	Refs.
	Acyclic compounds				
I	PCl_3	b	0.89	−10.9	4
II	$OPCl_3$	b	2.42	−73.8	4
	ditto	c.t.	2.47	−46	5
III	$SPCl_3$	c.t	1.37	65	5
IV	CH_3OPCl_2 ***	c	1.97	30	6
V	$(CH_3O)_3P$	b	1.81	38	7
VI	$(C_2H_5O)_3P$	b	1.80	−4.4	7
VII	$(iso\text{-}C_3H_7O)_3P$	b	1.82	−47	7
VIII	$(n\text{-}C_{10}H_{21}O)_3P$	b	1.75	−153	7
IX	$(C_6H_5O)_3P$	b	1.51	−52	7
	ditto	c	1.63	32.5	8
X	$(CH_3O)_3PO$	b	3.18	−88	7
XI	$(C_6H_5O)_3PO$	b	3.12	−135	7
XII	$(n\text{-}C_3H_7O)_3PO$	b	3.18	−184	7
XIII	$(iso\text{-}C_3H_7O)_3PO$	b	2.84	−128	7
XIV	$(C_5H_{10}O)_3PO$	b	3.14	−207	7
XV	$(t\text{-}C_4H_9O)_3PO$	c.t.	2.33	63	9
XVI	$(C_6H_5O)_3PO$	b	2.89	−133	7
XVII	$(CH_3O)_3P$	c.t.	2.71	138	10
XVIII	$(CH_3)_3P$	d	1.19	−10.1	11
XIX	$(CH_3)_3PO$	d	4.39	−39.5	11
	ditto	b	4.29	387	11
XX	$(CH_3)_3PS$	d	4.87	634	11
	ditto	b	4.73	1.1	11
XXI	$(ClCH_2)_3PO$	c.t.	2.34	−55	12
XXII	$(ClCH_2)(CH_3)_2PO$	c.t.	2.96	44	13
XXIII	$(ClCH_2)_2(CH_3)PO$	c.t.	2.57	33.6	14
XXIV	$(BrCH_2)_2(CH_3)PO$	c.t.	3.70	74	15
XXV	$(BrCH_2)_3PO$	c.t.	3.61	−128	15
XXVI	$CH_3P(O)Cl_2$	c.t.	3.35	−102	5
XXVII	$CH_3ClCHP(O)Cl_2$	c.t.	2.97	−68	16
XXVIII	$CH_3P(S)Cl_2$	c.t.	2.92	−13	5
XXIX	$CCl_3P(S)Cl_2$	c.t.	1.83	−66	5
XXX	$(C_6H_5)_3P$	b	1.50	−100	17
XXXI	$(C_6H_5)P(CH_3)_2$	c	1.20	1**	18
XXXII	$(p\text{-}CH_3C_6H_4)P(CH_3)_2$	c	1.40	5±2**	19
XXXIII	$(p\text{-}CNC_6H_4)P(CH_3)_2$	d	4.40	132**	18
XXXIV	$(C_6H_5)P(t\text{-}C_4H_9)_2$	c	1.50	2**	18
XXXV	$(p\text{-}CH_3C_6H_4)P(t\text{-}C_4H_9)_2$	c	2.12	10±3**	19
XXXVI	$(C_6H_5)_3PO$	b	4.49	−828	20
	ditto	c.t.	4.44	−590	21
XXXVII	$(p\text{-}ClC_6H_4)_3PO$	c.t.	3.14	−579	21
XXXVIII	$(m\text{-}ClC_6H_4)_3PO$	c.t.	4.78	−453	21
XXXIX	$(p\text{-}CH_3C_6H_4)_3PO$	c.t.	5.02	−1159	21
XL	$(m\text{-}CH_3C_6H_4)_3PO$	c.t.	4.57	−556	21
XLI	$(C_6H_5)_2P(O)CCl_3$	c.t.	3.81	240	22
XLII	$(p\text{-}CH_3C_6H_4)_2P(O)CCl_3$	c.t	4.75	−1	22
XLIII	$(p\text{-}ClC_6H_4)_2P(O)CCl_3$	c.t	2.82	100	22
XLIV	$(p\text{-}CH_3C_6H_4)P(O)(CH_3)_2$	c.t	4.30	30**	18
XLV	$(p\text{-}ClC_6H_4)P(O)(CH_3)_2$	d	4.60	24.9**	18
XLVI	$(p\text{-}CH_3C_6H_4)P(O)(t\text{-}C_4H_9)_2$	c.t	4.85	44.4**	18
XLVII	$(C_6H_5)_3PS$	b	4.79	−446	20
XLVIII	phosphonitrile chloride trimer	b	0.14	2.1	23
	1,3-Thiaphosphetans				
XLIX	3-chloro-3-thiono-	c.t	2.18	205	24
L	3-methoxy-3-oxo-	c.t	2.76	−44	25
LI	3-methoxy-3-thiono	c.t	2.68	6.8	25
	1,3,2-Dioxaphospholanes				
LII	2-chloro-***	c	3.12	85.5	26
LIII	2-chloro-4-methyl-	c	3.47	102.8	26
LIV	DL-2-chloro-4,5-dimethyl-	c	3.84	84.9	26
LV	*meso*-2-chloro-4,5-dimethyl-	c	3.63	−61.1	26
LVI	2-chloro-4,4,5,6-tetramethyl-	c	3.38	−53.8	26
LVII	2-chloro-2-oxo-	c.t	4.72	313	126
LVIII	2-chloro-4-methyl-2-oxo-	c.t	5.30	437	126
LIX	DL-2-chloro-4,5-dimethyl-2-oxo-	c.t	5.50	405	126
LX	*meso*-2-chloro-4,5-dimethyl-2-oxo-	c.t	5.49	334	126
LXI	2-chloro-4,4,5,5-tetramethyl-2-oxo-	c.t	5.89	602	126
LXII	2-chloro-2-thiono-	c.t	4.57	479	126
LXIII	2-chloro-4-methyl-2-thiono-	c.t	4.83	968	126
LXIV	DL-2-chloro-4,5-dimethyl-2-thiono-	c.t	5.45	675	126
LXV	*meso*-2-chloro-4,5-dimethyl-2-thiono-	c.t	5.38	676	126
LXVI	2-chloro-4,4,5,5-tetramethyl-2-thiono-	c.t	5.56	886	126
LXVII	*o*-phenylene phenyl phosphite	c	2.05	−35.5	8
LXVIII	*oop*-tri-t-butylphenyl *o*-phenylene phosphite	c	2.00	157	8

Table 1. (cont'd.)

No. of compound	Compound	Solvent*	μ, D	$10^{12}{}_mK$**	Refs.
	1,3,2-Dioxaphosphorinanes				
LXIX	2-chloro-	c	3.47	164	6,27
LXX	2-chloro-5,5-dimethyl***	c	3.66	215	6,27
	ditto	d	3.21	198	6,27
LXXI	2-chloro-4-methyl-	c	3.60	121	27
LXXII	3,9-dichloro-2,4,8,10-tetraoxa-3,9-spiro[5,5]undecane	d	2.36	—69	6
LXXIII	2-chloro-5,5-dichloromethyl	c	2.76	21.4	127
LXXIV	2-chloro-5,5-dibromomethyl	c	2.31	—23.2	127
LXXV	2-chloro-2-oxo-	c.t	5.89	556	29
LXXVI	2-chloro-2-thiono-	c.t	5.50	1355	30
LXXVII	2-chloro-4-methyl-2-thiono-	c.t	5.54	1195	30
LXXVIII	2-methyl-2-oxo-	c.t	4.24	63	29
LXXIX	2-oxo-2-triphenylmethyl	c.t	4.38	534	29
LXXX	*cis*-2,4-dimethyl-2-oxo-	c.t	6.36	346	128
LXXXI	2-methyl-2-thiono-	c.t	3.90	4.36	30
LXXXII	2,4-dimethyl-2-thiono-	c.t	5.37	1175	30
LXXXIII	*cis*-2-methoxy-4-methyl-	c	2.87	12.5	31
LXXXIV	*trans*-2-methoxy-4-methyl-	c	3.40	39.3	34
LXXXV	*cis*-2-methoxy-4-methyl-2-oxo-	c.t	6.07	344	31
LXXXVI	*trans*-2-methoxy-4-methyl-2-oxo-	c.t	4.46	165	31
LXXXVII	*cis*-2-methoxy-4-methyl-2-thiono-	c.t	5.51	929	31
LXXXVIII	*trans*-2-methoxy-4-methyl-2-thiono-	c.t	3.93	298	31
LXXXIX	2-phenoxy-	c	2.75	—83	129
XC	2-(*p*-bromophenoxy)-	c	3.82	470	129
XCI	2-(*p*-nitrophenoxy)-	c	6.32	3257	129
XCII ***	2-(*oop*-tri-t-butylphenoxy)-	c	2.82	—88	129
XCIII	2-(*o*-nitrophenoxy)-	c	5.44	63	129
XCIV	*cis*-2-hydro-4-methyl-2-oxo-	c.t	5.77	541	130
XCV	*trans*-2-hydro-4-methyl-2-oxo-	c.t	4.19	160	130
XCVI	2-hydro-5,5-dimethyl-2-oxo	c.t	4.72	274	130
XCVII	2-hydro-5,5-bis(chloromethyl)-2-oxo-	c.t	4.55	142	127
XCVIII	2-hydro-5,5-bis(bromomethyl)-2-oxo	c.t	4.51	28	127
XCIX	5,5-dimethyl-2-phenyl-	c	3.31	—298	—
C	$CH_3C(CH_2O)_3P$	d	4.15	368	32
CI	$CH_3C(CH_2O)_3PO$	d	7.10	1519	32
CII	$CH_3C(CH_2O)_3PS$	d	6.77	2637	32
	1,3,2-Dithiophosphorinanes				
CIII	2-chloro-	c	3.18	78	—
CIV	2-phenyl-	c	3.42	—344	—
CV	2-methyl-2-thiono-	c.t	4.22	639	—
CVI	2-methoxy-2-oxo-1,2-oxaphosphorinane	c.t	4.46	314	128

*Solvents: d = dioxan; b = benzene; c.t. = carbon tetrachloride; c = cyclohexane.

**Here and henceforth in the text the constants ${}_mK$ are understood to be multiplied by 10^{-12}. The exceptions are compounds (XXXI)–(XXXV) and (XLIV)–(XLVI) for which the values of ${}_mK$ were determined to within 10^{-11}.

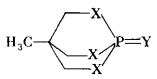
***The degrees of depolarisation of Rayleigh light scattering $2\delta^2_{\infty} \times 10^3$ were determined for these compounds and the following values were obtained: 8.3 for (IV); 11.4 for (LII); 17.4 for (LXX); 3.4 for (XCII); 4.6 for (CIII).

2. The Additive Computational Scheme for Phosphorus Compounds

The theoretical treatment of the electrical and electro-optical properties of molecules is based on the hypothesis that they are additive. A characteristic dipole moment vector and polarisability tensor can be ascribed to each chemical bond or group of atoms. This is usually done on the basis of experimental data for a limited number of molecules, called the model compounds. The bond parameters obtained in this way make it possible to calculate the physical constants of a large set of molecules. The additive values of the bond parameters are effective and express not only the properties of the bonds themselves but also the influence on the latter of neighbouring substituents in the model compounds. The mutual influence may change on passing to systems with another environment; in this case, the deviations from additivity serve as a measure of the intramolecular interaction.

The validity of the valence-optical additive scheme can be regarded as firmly established to a zeroth approximation [33]. This scheme can be extended not only to the dipole moments and the anisotropic bond polarisabilities but also to the derivatives of these quantities with respect to changes in bond length, serving thus as the basis of the modern theory of intensities in infrared and Raman spectra, which is in good agreement with experiment [33].

The simplest identically substituted molecules, known *a priori* not to exhibit conformational isomerism, are chosen for phosphorus derivatives as model compounds. These substances are of the type PX_3 and $Y{=}PX_3$, in which the threefold symmetry axis coincides with the direction of the resultant dipole moment of the P–X and P=Y bonds and with the direction of the longitudinal b_1 axis of the molecular polarisability ellipsoid. For non-regular groups P–X–R, where X = O, S, NR, etc., the model compounds used [32,34] are rigidly fixed bicyclic systems of the type



Y = LEP, O, S,

where internal rotation is impossible. The corresponding additive parameters of the phosphorus bonds may be calculated from the experimental dipole moments and Kerr constants ${}_mK$ by a vector or tensor expansion with the subtraction of certain parameters of the carbon bonds. As mentioned above, refraction data are also necessary in order to find the axes of the polarisability ellipsoids.

The numerical values of the phosphorus bond refractions have been analysed most fully by Tolkmith [35]. On the basis of extensive experimental data (for 500 phosphorus compounds), he concluded that the refraction of the given bond depends both on the environment of the phosphorus atom itself and on the nature of the substituent in the P–X–R chain. The phosphorus bond refractions most frequently employed are listed in Table 2.

Table 2. The refractions of the phosphorus bonds for the D line of Na. [35]

Bond	R_D	Bond	R_D	Bond	R_D
P^{III} LEP	5.4	P—NC_2	1.3	P—Cl	6.95
P—OH, P—OP	1.45	P—N=C	1.9	P—Br	10.2
P—OC, P—OSi	1.35	P—C_{sp^3}	1.85	P—Si	3.4
P—SH	6.25	P—C_{arom}	2.75	P—P	3.5
P—SC, P—SSi	5.65	P—C≡N	2.55	P=O	4.15
P—SP	5.3	P—CCl_3	2.7	P=S	11.9
P—SeP	7.3	P—C=O	2.05	P=Se	15.6
P—NH_2	1.7	P—H	2.2	P=N	5.8
P—NHC, P—NP	1.5	P—F	1.5		

It follows from the above that the creation of an additive computational scheme is based on a comparison of data for compounds of three- and four-coordinated phosphorus. The former (PX_3) serve as a basis for the determination of the P–X bond parameters. The P=Y bond parameters are determined as the vector or tensor differences between the corresponding experimental values for PX_3 and YPX_3. A weak aspect of such calculation is the hypothesis that the parameters of the P^{III}–X and P^{IV}–X bonds remain unchanged. Evidently, in most cases the inaccuracy of the result should be compensated implicitly by a distortion

of the values for P=Y. However, the difference is caused not only by the different states of hybridisation of the central atom, but also by the uncertainty of the contribution of the phosphorus(III) LEP to the required parameters in the initial PX_3 molecules.

3. The Influence of the Dipole Moment of the Lone Electron Pair on the Results of Calculations

The problem of the degree of displacement of the centre of gravity of the LEP electron cloud relative to the positively charged atomic nucleus ($\bar{x}$), which determines the LEP dipole moment ($m_{LEP} = 2e\bar{x}$) is widely discussed in the literature. However, the direct experimental determination of $\bar{x}$ is extremely difficult. The proposed methods [36,37] are laborious and not very reliable, since the experimental error is close to the postulated displacement of the charge. For a phosphorus atom with a valence angle of 93.4°, analysis of the intensities of the absorption bands in infrared spectra [36] yielded 0.2 D. Comparison of the experimental dipole moments of triarylphosphines and the valence angles led the authors [38] to the conclusion that the maximum phosphorus(III) LEP dipole moment is 2.93 D. Smaller values follow from quantum-mechanical calculations: 1.35 D [27] (valence angle 100°) and 1.15 D in phosphine. [39]

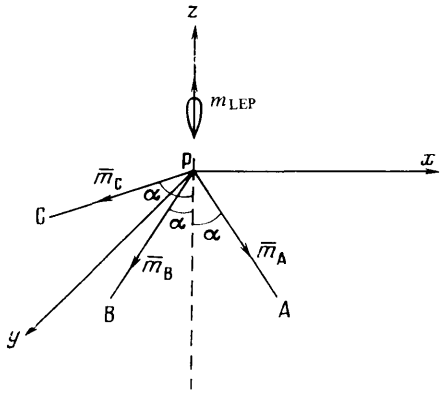


Figure 1. The configuration of the P(ABC) molecule in the cartesian coordinate system.

According to Mauret and Fayet [40], the dipole moment of trialkylphosphines (1.6 D) is equal to m_{LEP} as a consequence of the similarity of the electronegativities of the carbon and phosphorus atoms. The unknown parameter may be determined on the basis of the vector additive scheme for the dipole moments of several compounds, specifying m_{LEP} as an independent vector together with the bond dipole moments, as has been done in a number of studies [41-43]; $m_{LEP} = 0.92$ D [41] and $m_{LEP} = 1.49$ D [43] was obtained. Calculations of this kind are sensitive to the chosen angular parameters. When the latter are equal, the relation between the molecular and the required dipole moments is in most cases linear, deviations from linearity being caused not only by the contribution of the LEP moment but also by non-additivity factors, appearing as a result of the mutual influence of the atoms and the differences between the valence angles. In such cases, a small (in absolute magnitude) change in the non-additivity factor can ultimately lead to a wide variation in the parameters being determined. This in fact explains the fairly large difference (approximately 0.6 D) between the values found by Matrosov et al. [41] and Chernokal'skii et al. [43]

Thus the problems of the absolute value of the LEP moment of the phosphorus atom can be regarded as still open. However, in the light of the problems solved with the aid of the dipole moments and Kerr effect methods, it is important to determine the influence of the dipole moment of the lone electron pair m_{LEP} on the magnitude and direction of the resultant dipole moment. We shall consider this problem for non-identically substituted molecules of the type P(ABC), since in the case of molecules with symmetrical substitution m_{LEP} enters implicitly into the bond moments of the given atom obtained by the vector resolution of the experimental dipole moments of model compounds. Three symetrically substituted compounds PA_3, PB_3, and PC_3 with the molecular dipole moments μA, μB, and μC serve as the model compounds for the determination of the P–A, P–B, and P–C bond moments designated by m_A, m_B, and m_C. Each bond moment m_i, where i = A, B, or C, is calculated as follows:

$$m_i = \frac{\mu_i - m_{LEP}}{3\cos\alpha}, \qquad (8)$$

where α is the angle formed by the bond with the three-fold symmetry axis (Fig. 1).

The dipole moment μ of the compound P(ABC) is then expressed by the following sum:

$$\mu^2 = [m_{LEP} + \cos\alpha\,(m_A + m_B + m_C)]_z^2 + \left[m_A \sin\alpha - \right.$$
$$\left. - \frac{1}{2}(m_B + m_C)\sin\alpha\right]_x^2 + [2(m_B - m_C)\sin\alpha]_y^2 . \qquad (9)$$

The substitution in this expression of the bond moments determined for symmetrical compounds by Eqn. (8) (for identical angles) leads to the final expression

$$\mu^2 = \left[\frac{(\mu_A + \mu_B + \mu_C)}{3}\right]_z^2 + \left[\frac{(2\mu_A + \mu_B + \mu_C)}{6}\tan\alpha\right]_x^2 +$$
$$+ \left[\frac{2(\mu_B - \mu_C)}{3}\tan\alpha\right]_y^2, \qquad (10)$$

in which m_{LEP} cancels out fully.

Eqn. (10) shows that, for the determination of the magnitude and direction of the resultant molecular moments of asymmetrically substituted compounds, in most cases [with the exception of substances of the type $PH_n(CH_3)_{3-n}$ with n = 1–3, where the valence angles at the phosphorus atom are appreciably less than 100°C] there is no need for the introduction of the vector of the LEP moment as an independent parameter. Since the compounds considered [PA_3, PB_3, PC_3, and P(ABC)] can differ by their intramolecular interactions, the contributions of the interaction moment, called above the non-additivity factor, must be introduced into Eqns. (9) and (10).

4. The Dipole Moments of Phosphorus Bonds

The disposition of the bonds at the phosphorus atoms may be regarded as nearly tetrahedral, if the fourth bond is represented by the lone electron pair.

Mathematically this is analogous to the tetrahedral orientation of bonds at a carbon atom; consequently the

vector of the LEP moment is analogous to the vector of the C–H bond dipole moment, which serves as a basis for the determination of the dipole moments of all the remaining bonds of organic compounds. It follows from Eqn. (10) that the absolute value of m_{LEP} has no influence on the results of calculations, but is closely related to the intermediate values of m_i, i.e. to the bond moments. This fact can explain the existence of several sets of bond moments differing by the initial data. The principal requirement for a correct calculation of dipole moments is therefore a unique set of initial parameters. For phosphorus compounds, the number of such systems of parameters is increased owing to the different absolute values of m_{LEP} adopted by different investigators.

Table 3. The dipole moments of phosphorus bonds.

Bond	Bond dipole moments, D
P — O	— 0.48[48]; — 0.6[10]; — 0.75[49]; 0[6,50]*; 0.54 (1.35)[27]; 1.1 (0.91)[42]
P — S	— 0.85[1] [S_2P (S) C]**; —0.25[52] [S_2P (S) C]**; — 0.58[52] [S_2P (S) Cl]**; — 0.8; 0 (0.92)[42]
P — F	0.72[24]; 1.4 (0.91)[42]; —0.56[50]; 1.02[53]
P — Cl	0.66[54]; 0.56[27]; 0.81[53]; 1.53 (1.35)[27]; 1.2 (0.9)[42]; —0.42[49]
P — Br	0.36[53]; 1.1 (0.9)[42]
P — I	0.0[53]; 0.7 (0.9)[42]
P — H	—0.36[29]; 0.1 (0.9)[42]; 0.371 (0.2)[55]; 1.0 [O_2P (O) H][56]; —0.36 [O_2P (O) H]; — 0.13—0.67[36]
P — Se	1.24[57]
P — N	0.31[58]; —1.4 and — 2.10 (P—Cl)[58]***; ~ 0 (P—NMe_2)[58]; —0.8 (P=S)[58]***; 0.03[59]; 0.4 (1.35)[60]; 0.8 (P)^{IV}[60]; —0.8; —1.8; — 1.4 (PNCO)[61]
P—C_{sp^3}	—0.58[24]; —0.39 (Et_3P)[54]; —0.6[62]; — 0.1 (0.9)[42]; — 0.94[50]; 0.690 (0.2)[55]; — 1.11[49]
P—$C^{***}_{sp^2}$ (olefin)	—0.7 (0.9)[42]; — 0.75[50]; — 0.9[62] and — 0.82[63] [(C=C) O_2PO]
P — C_{sp^2} (phenyl)	—0.39[65]; 0.4 (0.9)[42]; — 0.16 ($Me_2PC_6H_5$Me-*p*)[19]; —0.57 [(t-C_4H_9)$_2$PC_6H_4Me-*p*][19]
P — C_{sp}	1.3 (0.9)[42]; ~ 0.5 [(C ≡ C) O_2PO][62]
P= N	0.6[50]; 2.27[66]
P = O****	4.1[42] и 3.13[5] [Cl_3PO]; 3.0 [R_2N_3PO][5]; 4.1 and 3.40[5] [Me_3PO]; 2.95 [Ph_3PO][5,20]; 2.95[20,34]; 2.90[67]; 3.9 (0.9)[42] [O_3PO]; 3.40 [C_2P (O) Cl][24]
P= S*****	2.62[24]; 3.97 (1.35)[30]; 3.2[53]; 3.6 (0.9)[42] [O_3PS]; 2.03[5]; 3.2 (0.9)[42]; 3.88[5]; 4.6 (0.9)[42] [C_3PS]; 3.3[20,34] [Ph_3PS]; 3.26 [C_2 (O) PS][24]; 3.15[24] and 2.63[5] [C_2ClPS]; 2.91 [C_2FPS]

*Despite the identical values of m_{P-O}, the calculations in Refs. 6 and 50 were based on different initial data: m_{C-O} = 1.12 D, found from the dipole moments of tetrahydropyran and 1,3-dioxan (m_{H-C} = 0.28 D and m_{LEP} = 0) was used in Ref. 6, while m_{P-O} was calculated from the dipole moment of the bicyclic phosphite (C); in Ref. 50, the moment m_{Alk-O} = 0.87 D was determined from the measured dipole moments of dialkyl esters after eliminating the contribution of the rotational vibrations of the molecule to the polarisation, while m_{P-O} was calculated on the basis of a compound whose bonds are fixed in space—triethyl phosphite, for which the *cis*, *cis*, *cis*-conformation was adopted, but was not subsequently confirmed by an electron diffraction study of trimethyl phosphite [70].

**In the calculation of m_{P-S} and m_{P-N} in Refs. 52 and 58, the P=S bond moment was treated as a constant value equal to 2.62 D.

***The interaction moments in different conjugated systems were calculated in Refs. 48 and 63–65.

****The high sensitivity of $m_{P=O}$ to the electronegativities of the substituents was demonstrated in Refs. 50, 60, and 68: $m_{P-O} = 4.80 - 0.353\,\Sigma X$, where X is the Thomas–Chattenden "shift constant".

*****According to Refs. 60 and 69, $m_{P=S} = 9.75 - 0.924\,\Sigma X$.

One of the first studies on the analysis of the dipole moments of organophosphorus compounds was performed in Kazan by Arbuzov and Rakov [44]. The bond dipole moments were examined most fully and systematically for the first time by Arbuzov and Shavsha [45–47]. It is nowadays postulated that the bond moments depend to a large extent on the environment at the phosphorus atom. Table 3 presents some of the bond dipole moments most widely used in calculations. If $m_{LEP} \neq 0$ and if the bond moments have been determined from the dipole moments of compounds asymmetrically substituted relative to the phosphorus atom, then Table 3 indicates in brackets, after the dipole moment, the value of m_{LEP} adopted by the authors and the intermediate environment at the phosphorus atom. The dipole moments calculated taking into account m_{LEP} appear to be more reliable in the light of the existing theoretical ideas. However, as shown above, in the additive calculation of dipole moments this is not important and identical results are obtained.

It follows from the data in Table 3 that the phosphorus bond dipole moments are extremely sensitive to the environment and in the analysis of the dipole moments of phosphorus compounds it is therefore desirable to examine the entire set of bonds. The method of isoelectric maps [6], whereby it is possible to find simultaneously bond and structural parameters, is extremely promising in this respect. It is described in detail in Section IV for 1,3,2-dioxaphosphorinane derivatives as an example.

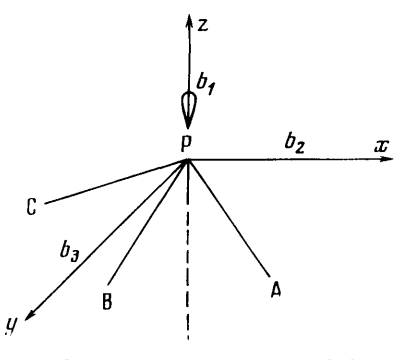


Figure 2. The directions of the axes of the polarisability ellipsoid of the P(ABC) molecule.

5. The Anisotropy of the Polarisability of Phosphorus Bonds

In the calculation of the additive parameters of the polarisability ellipsoids of phosphorus bonds, the problem of the allowance for the LEP contribution remains obscure, as for dipole moments. We shall place a symmetrically substituted molecule PA_3, PB_3, or PC_3 in a cartesian coordinate system, as shown in Fig. 2 for the P(ABC) molecule. Denoting the molecular anisotropy of polarisability by $\Gamma_i = b_1 - b_2$, it is possible to calculate the anisotropy of the polarisability of the ith bond:

$$\gamma_i = \frac{\Gamma_i - \gamma_{LEP}}{4.5\cos^2\alpha - 1}. \qquad (11)$$

The differences between the diagonal elements and the non-diagonal components of the molecular polarisability

tensor matrix of the P(ABC) molecule, which are necessary for the calculation of ${}_{m}K$, can be calculated in conformity with Eqns. (6) and (7):

$$\begin{aligned}
b_{xx} - b_{yy} &= -\gamma_A(1-\cos^2\alpha) - \sum_{i=B,C} 0.5\gamma_i(1-\cos^2\alpha);\\
b_{xx} - b_{zz} &= \gamma_A(1-2\cos^2\alpha) + \sum_{i=B,C} \gamma_i(0.25-1.25\cos^2\alpha) - \text{LEP};\\
b_{yy} - b_{zz} &= -\gamma_A\cos^2\alpha + \sum_{i=B,C} \gamma_i(0.75-1.75\cos^2\alpha) - \text{LEP};\\
b_{xy} &= \sum_{i=B,C} (\mp\gamma_i \sin^2\alpha\cdot\cos 60^\circ\cdot\sin 60^\circ);\\
b_{xz} &= -\gamma_A\cos\alpha\cdot\sin\alpha + \sum_{i=B,C} (\gamma_i\cos\alpha\cdot\sin\alpha\cdot\cos 60^\circ);\\
b_{yz} &= \sum_{i=B,C} (\mp\gamma_i\cos\alpha\cdot\sin\alpha\cdot\cos 60^\circ).
\end{aligned} \qquad (12)$$

Table 4. The parameters of the polarisability ellipsoids of bonds and groups of atoms in phosphorus compounds.

Group of atoms or bond	b_1 or b_L	b_2 or $b_T = b_V$	Compound	Refs.
O_3P	4.13	3.50	C	32
$P^{III} - O$	0.86	1.45	C	1
$P^{III} - O$	1.09	1.34	LXXXIV	129
$P^{III} - O$	2.28	0.74	IV	6
$P^{III} - O$	2.52	0.62	XCIX	**
$P^{III} - O$	2.54	0.61	LII	6
$P^{III} - O$	3.05	0.35	LXX	6
$P^{III} - O$	3.32	0.21	XCII	129
$P^{III} - O$ (Ph)	2.82	0.47	XCII	129
O_3PO	4.19	2.75	CI	32
O_3PS	8.69	4.92	CII	32
$P^{IV} - O$	0.15	0.74	CI	32
$P^{III} - C_{sp^3}$	2.28	0.79	XVIII	11
$P^{IV} - C_{sp^3}$	1.57	0.08	XIX	11
$P^{III} - C_{sp^2}$ (aryl)	1.20	1.50*	—	1
$P^{III} - C_{sp^2}$ (aryl)	3.28	0.79	—	**
$P^{IV} - H$	0.1	1.2	XCIV, XCV	130
$P^{III} - S$	3.24	2.59	CIII	**
$P^{III} - Cl$	5.12	2.46	I	4
$P^{III} - Cl$	4.55	2.75	IV	6
$P^{III} - Cl$	3.60	3.23	LII	6
$P^{III} - Cl$	2.46	3.79	CIII	**
$P^{III} - Cl$	2.21	3.91	LXX	6
$P^{IV} - Cl$	4.75	1.63	XXVIII	5
$P^{IV} - Cl$	4.14	1.75	II	4
$P^{IV} - Cl$	1.76	3.07	LXXVI	30
P = O	2.0	1.50	XIX	11
P = O	2.08	1.43	LXXV	5
P = O	2.19	1.38	CI, XCIV	32
P = O	2.54	1.02	II	5
P = S	6.72	3.46	CII	32
P = S	7.0	3.90	XX	11
P = S	7.47	3.08	XXVIII, XXIX	5
P = S	7.88	2.72	III	5

*Calculated from the molecular refraction and the empirical equation relating b_L and the bond length[1].
**Calculated by the author of the review.
***See Section III.

Substitution of γ_i from Eqn. (11) in Eqn. (12) leads to expressions where the contribution of the LEP vanishes after appropriate mathematical operations, and only the experimental quantities Γ_A, Γ_B, and Γ_C remain, i.e. there is no need to take into account in an explicit form the LEP polarisability ellipsoid. Taking into account the absolute value of the LEP polarisability $b = 6.3$ Å^3 found by Tolkmith[35], it is possible to calculate the required parameters of the four-coordinated phosphorus bonds: they are equated to the differences between the axes of the polarisability ellipsoids of the bonds and the isotropic lone pair of the tervalent atom. Table 4 presents the parameters of the polarisability ellipsoid of bonds and groups of atoms obtained in this way.

We may note the wide variation of the bond polarisability parameters, particularly on passing from symmetrically substituted to asymmetrically substituted compounds. This invalidates the usually employed method of calculation for such systems (see above) and requires a non-trivial approach. For this reason, compounds of three- and four-coordinated phosphorus will be henceforth considered separately.

6. The Solvent Effect

In the practical application of the values quoted in Table 1, particular attention must be paid to the possible interaction of the given compounds with the solvent. Thus Le Fevre's attempt to use the parameters found for the polarisability ellipsoids of the phosphite and phosphate groups in the analysis of the structures of the trialkyl phosphites (V)–(VIII) and the trialkyl phosphates (X) to (XVI) was unsuccessful[7]. It was subsequently observed that the experimental values of ${}_{m}K$ in benzene differ considerably from those determined in other solvents [see the data for compounds (IX), (XIX), (XX), and (XXVI) in Table 1]. This can be explained by the formation of complexes by phosphorus compounds with benzene[11], so that the conclusions reached by Le Fevre and coworkers[7,17,20] are incorrect. The use of the bond polarisability ellipsoids found for compounds (I), (II), (XXX), (XXVI), and (XLVII), whose ${}_{m}K$ values were determined in benzene, also requires particular caution.

III. THE STERIC AND ELECTRONIC EFFECTS IN PHOSPHORUS(III) COMPOUNDS

The use of the Kerr effect in conformational analysis and in the study of intramolecular electronic effects requires the knowledge of the polarisability ellipsoids of bonds or groups of atoms. Comparison of the experimental constants ${}_{m}K$ and the values calculated for various rotational isomers permits conclusions about the steric structure, while comparison of the true values and those obtained on the basis of the additive resolution of the polarisability ellipsoids gives rise to the possibility of analysing the electron redistribution in the molecules being compared. The dipole moments and the constants ${}_{m}K$ are calculated from the bond lengths and valence angles (see the relevant reviews for phosphorus compounds[74-76]) by the method of Corey and Sneen[77].

The data in Table 1 show that the values of ${}_{m}K$ for 2-X-1,3,2-dioxaphosphorinane molecules have been most fully investigated. These compounds have been used traditionally in the Kazan School of Chemistry. As early as the beginning of the 1950s, A. E. Arbuzov and coworkers developed methods for the synthesis of various saturated phosphorus-containing heterocycles[71-73] and began the first studies of their physical and chemical properties.

It is noteworthy that phosphorus(III) compounds are characterised by a wide variety of effects due to the mutual influence of atoms; this is shown particularly by the wide scale of changes in the chemical shifts due to the phosphorus atomic nucleus in $^{31}P^{III}$ NMR (from −230 to +450 p.p.m.) compared with four- (from −130 to +115 p.p.m.) and five-coordinated phosphorus (from −30 to +100 p.p.m.)

The problem therefore arises of the validity of employing the usual additive parameters for the calculation, since incorrect results may be obtained when no account is taken of the high sensitivity of the electrical and electro-optical bond characteristics to electronic interactions.

This hypothesis was confirmed in a study of the structure of one of the simplest 1,3,2-dioxaphosphorinanes – 2-chloro-1,3,2-dioxaphosphorinane (LXIX), which exists solely as the chair conformer. The calculation of dipole moment and the constant $_mK$ for compound (LXIX) from the parameters found from the corresponding values for symmetrically substituted derivatives leads to the conclusion that the P–Cl bond is equatorial[27]:



$\mu_A = 2.94$ D; $_mK = -101$ $\mu_e = 3.37$ D; $_mK = 144$

$\mu_{exp.} = 3.47$ D; $_mK_{exp.} = 164$

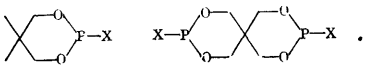
This conclusion conflicted with electron diffraction data[78] and the analysis of ^{1}H NMR spectra[79–82] and chemical reactions[82], but agreed with the calculation of the band contours in vibrational spectra[83]. It may be that the inaccuracies of the additive phosphorus bond parameters led to erroneous results in the application of the dipole moment and Kerr effect methods.

The ideal solution to the problem of the selection of the additive parameters for solving conformational problems was one in which both bond and structural parameters are determined simultaneously. Bearing in mind that the exact calculation of $_mK$ is impossible without knowledge of the exact values of the dipole moments, we shall consider initially how correct are the bond dipole moments employed.

1. The Nature of the Electron Density Distribution in 2-X-1,3,2-Dioxaphosphorinanes

The simultaneous determination of the phosphorus bond dipole moments (m_{P-O} and m_{P-X}) and of the orientation (axial or equatorial) of the exocyclic substituent X, i.e. three unknown parameters, is possible by extending the range of compounds investigated which are known *a priori* to have identical structures (the so called isoconformational compounds) but different directions of the molecular dipole moment.

It is useful to compare 2-X-1,3,2-dioxaphosphorinanes with their 5-spiro-analogues, which have been indeed shown to have identical structures by the study of steric interactions[84] and by the analysis of ^{1}H NMR spectra[85]:



The symmetry of spiro-compounds is such that the dipole moments of the ring P–O bonds have little effect on the final results as a consequence of the mutual cancellation of the m_{P-O} values. The dipole moment of compound (LXIX), calculated with the usual parameters for the equatorial conformation (3.37 D), is closer to the experimental value (3.47 D) than the moment for the axial conformation (2.94 D), whereas there is no doubt that the P–Cl bond in the spiro-analogue (LXXII) has the axial orientation [$\mu_{aa} = 2.01$; $\mu_{ee} = 3.53$; $\mu_{exp} = 2.10$ D (Arbuzov et al.[6])].

A method for the simultaneous determination of the structure and phosphorus bond dipole moments has been proposed[6] on the basis of data for the two types of compounds considered. The bond polarities m_{P-O} and m_{P-X} were treated as the unknown quantities. Vector summation of the bond dipole moments makes it possible to express the experimental dipole moments of the compounds as functions of the unknown quantities m_{P-O} and m_{P-X} for the axial and equatorial conformations. Each of the three equations described a three-dimensional surface in the space defined by the coordinates m_{P-O}, m_{P-X}, and the resultant moment μ. Their intersection by the μ^2_{exp} plane yields constant-property lines whose projections on to the m_{P-O} and m_{P-X} planes are illustrated graphically in Fig. 3 (for X = Cl). The method may be referred to as the method of isoelectric maps. An analytical solution of the systems of equations is also possible, but the graphical procedure is simpler and clearer. The solution, consisting of a compatible set of bond moments for both types of compounds, are given by the points of intersection of the straight lines representing μ^2_{exp} for compound (LXXII) with the curves corresponding to μ^2_{exp} for compound (LXIX). The requirement that the values obtained are physically significant, i.e. that the parameters thus found do not differ greatly from the values obtained for the dipole moments of symmetrically substituted compounds, serves as a criterion of the validity of the particular solution. Fig. 3 shows that, for the equatorial conformation of the P–Cl bond, the phosphorus bond moments satisfying simultaneously the experimental dipole moments have improbable values; for the axial orientation of the chlorine atom, the unique solution $m_{P-O} = -0.72$ D and $m_{P-Cl} = 0.92$ D [6] is acceptable. The higher polarity of P–Cl bond in 2-chloro-1,3,2-dioxaphosphorinane compared with PCl_3 is consistent with the lower ^{35}Cl NQR frequency and the greater length of the P–Cl bond[86].

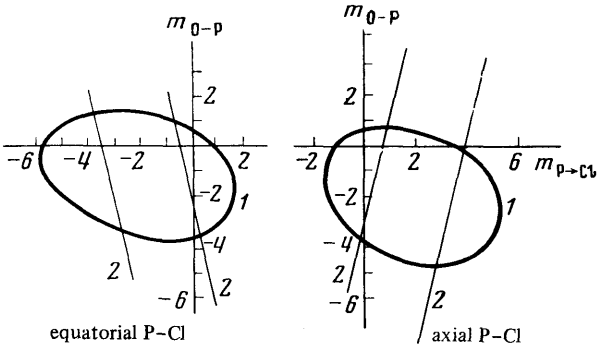


Figure 3. Dependence of the squares of the dipole moments of compounds (LXX) (curve *1*) and (LXXII) (curve *2*) on the dipole moments of the P–O ($m_{O \to P}$) and P–Cl ($m_{P \to Cl}$) bonds.

Of the eight possible solutions for X = NEt_2 (Fig. 4), only one is realistic—with $m_{P-O} = 0.65$ and $m_{P-N} = 1.37$ D; it corresponds to the equatorial position of the P–N bond[87]. In 2-phenyl-1,3,2-dioxaphosphorinanes (Fig. 5), two solutions are most probable: $m_{Ph-P} = -0.95$ and $m_{O-P} = 0.06$ D for the axially oriented phenyl group and

m_{Ph-P} = 0.96 and m_{O-P} = 0.43 D for its equatorial position. By resorting to the dipole moment of a third isoconformational compound, namely 5-methyl-5-nitro-2-phenyl-1,3,2-dioxaphosphorinane (μ_{exp} = 6.23 D),[88] a choice between these two possible solutions still cannot be made. Since comparison of the experimental dipole moments of triphenylphosphine and its tri-*p*-substituted derivatives shows that the moment of the Ph–P group is directed towards the benzene ring, we give preference to the first solution.

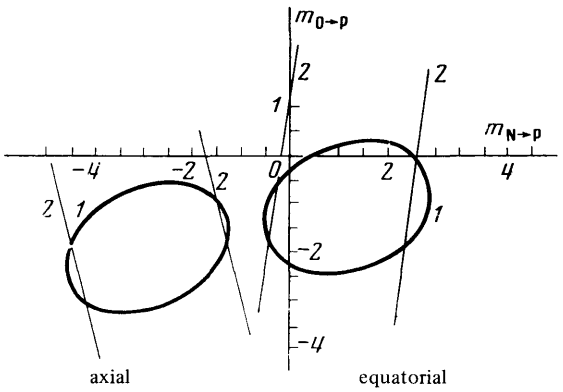


Figure 4. Dependence of the squares of the dipole moments of 2-diethylamino-1,3,2-dioxaphosphorinane (curve *1*) and its 5-spiro-analogue (curve *2*) on the dipole moments of the P–O ($m_{O\to P}$) and P–N ($m_{N\to P}$) bonds.

The symmetry of the substitution of phosphorus atoms in 2-alkoxy-1,3,2-dioxaphosphorinanes (X = O-Alk) eliminates the necessity for the determination of the P–O bond dipole moment and one can therefore assume that the calculation of the dipole moments of these compounds using m_{P-O} = 0,[6] found from the dipole moment of the bicyclic phosphite (C), is valid. Determination of the structure of compounds of this type is a more difficult problem, since, apart from the position of the exocyclic bond, it is necessary to determine the orientation of the P–O–Alk fragment relative to the phosphorus LEP (*cis*-, *trans*-, or *gauche*-, Fig. 6). Graphical comparison of the values of μ^2 for two isoconformational compounds—2-ethoxy-1,3,2-dioxaphosphorinane and the 5-spiro-analogue (Fig. 7*a*)—makes it possible to determine two unknown structural parameters: the axial position of the exocyclic P–O bond and the *gauche*-orientation of the ethoxy-group[84]. The application of an analogous method to 2-phenoxy-1,3,2-dioxaphosphorinanes (Fig. 7*b*)[84,129] on the assumption that the values of m_{P-O} for the ring and exocyclic bonds are equal leads to the conclusion that the phenoxy-group has the *cis*-orientation. However, in the compounds examined the environment at the phosphorus atom is not rigorously symmetrical, since the exocyclic P–O bond adjoins the benzene ring and not the alkyl group.

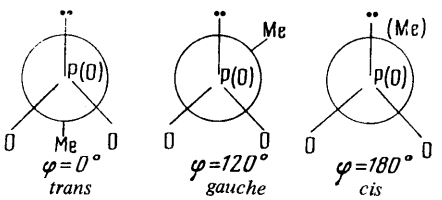


Figure 6. Internal rotation relative to the exocyclic P–O bond determined by the dihedral angle φ.

A change in the dipole moments of the P–O bonds should not lead to a sharp alteration of the principal structural conclusions—they can change only to give the *gauche*-conformation. If one disregards structural parameters, then there are only two unknown quantities—the dipole moments of the exocyclic and ring P–O bonds; it is therefore quite sufficient to examine two isoconformational compounds whose dipole moments are not linearly related: compound (LXXXIX) and its 5-spiro-analogue (μ_{exp} = 2.89 D). In setting up systems of equations for $m_{Ph-O(PIII)}$ corresponding to the *cis*- and *gauche*-forms, 1.10 D was used[8]. Simultaneous solution of each system of equations yielded the following parameters:

$m_{O-P(acyclic)}$ = 0.22 and $m_{O-P(cyclic)}$ = +0.8 D for the *cis*-form;

$m_{O-P(acyclic)}$ = −0.8 and $m_{O-P(cyclic)}$ = +0.42 D for the *gauche*-form.

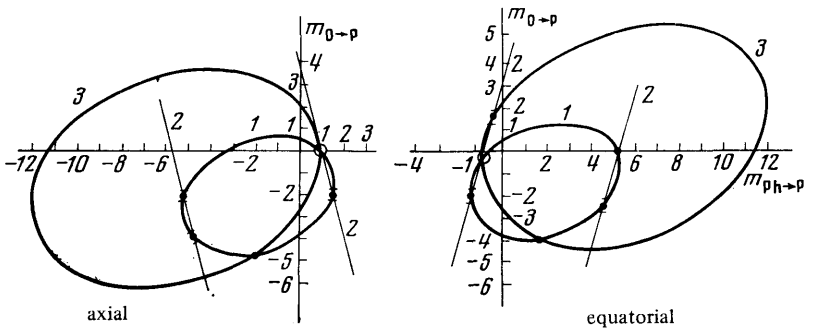


Figure 5. Dependence of the squares of the dipole moments of 2-phenyl-1,3,2-dioxaphosphorinane (curve *1*), its 5-spiro-analogue (curve *2*), and the 5-methyl-5-nitro-derivative (curve *3*) on the dipole moments of the P–O ($m_{O\to P}$) and Ph–P ($m_{Ph\to P}$) bonds.

A choice can be made between these two sets, i.e. the third structural parameter can be found, only when additional dipole moment data for other isoconformational compounds are resorted to: the *p*-bromo derivative of compound (XC) and the *p*-nitro-derivative of compound (XCI). The results of the calculations show that the agreement with experiment is reached only for the *cis*-form. The bond polarity data obtained made it possible to estimate the angle of rotation of the benzene ring in the *o*-substituted (*o*-bromo- and *o*-nitro-) derivatives. The experimental data ageee with the calculated results for the structure where the benzene ring is perpendicular to the plane of the $P-O-C_{aryl}$ bonds.

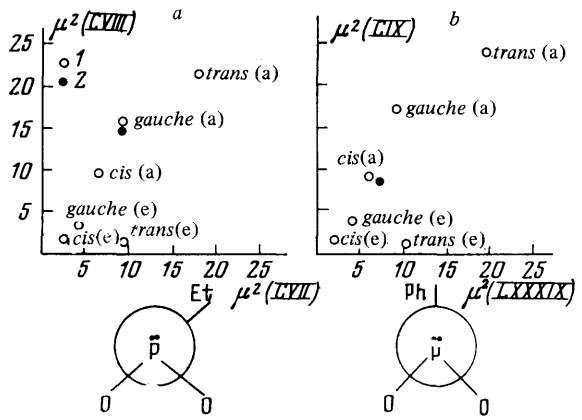


Figure 7. Graphical relations between the squares of the dipole moments of 2-ethoxy-1,3,2-dioxaphosphorinane (CVII) and its 5-spiro-analogue (CVIII) (*a*) and between the squares of the dipole moments of 2-phenoxy-1,3,2-dioxaphosphorinane (LXXXIX) and its 5-spiro-analogue (CIX) (*b*): 1) calculated values; 2) experimental values.

Table 5. The dipole moments of phosphorus bonds in 2-X-1,3,2-dioxaphosphorinanes O_2PX according to data obtained by the isoelectric map method.

Environment at P	Dipole moment	Substituent X				
		O(Ph)	Cl	O(Et)	Ph	$N(Et_2)$
O_2PX:	m_{P-O}	−0.8	−0.72	−0.32	0.06	0.65
	m_{P-X}	0.22	0.92	0.14	0.95	0.37
PX_3^*:	m_{P-X}	0	0.56	0	1.18	0.31

*See corresponding footnotes to Table 3.

The phosphorus bond dipole moments presented in Table 5 demonstrate the extreme electronic lability of phosphorus(III) compounds as a function of the environment at the phosphorus atom.

We emphasise yet again that the bond dipole moments obtained are effective values and thus reflect the nature of the redistribution of electron density. When a comparison is made with the bond polarities of symmetrically substituted phosphorus compounds, a deviation from these values is observed for exocyclic bonds. The greatest deviation $\Delta m_{P-Cl} = 0.36$ D is directed towards the chlorine atom and indicates its electron-accepting properties. The P–O ring bonds undergo much greater changes: whereas in the compound with $X = NEt_2$ there is a redistribution of electron density to the extent of approximately $0.4e$ from the phosphorus atom to the neighbouring oxygen atoms with an almost unchanged m_{P-N}, in the compound with X = Cl or OPh virtually the same electron density ($0.44e$) is transmitted from the ring oxygen atoms to the phosphorus atom. The nature of the electron redistribution for X = OEt and Ph is approximately the same. Consequently a strong geminal interaction, which depends on the nature of the atom X and is strongly reflected in the properties of the O–P bonds, is observed in the O_2P-X series. A possible mechanism for this interaction is examined below.

2. The Intramolecular Interactions and the Anisotropy of the Polarisability of the $P^{III}-Cl$ Bond

The problem of the simultaneous determination of the bond polarisability ellipsoids and molecular conformations is mathematically more complex than the determination of dipole moments. We shall consider this problem for the O_2PCl group in compound (LXX), since there are no grounds for doubting the validity of the electro-optical parameters of the carbon bonds. The group has a plane of symmetry and one must therefore determine four independent parameters: three polarisability axes and their orientations defined by the angle φ (Fig. 8). A necessary condition for the solution of this problem is an increase in the number of experimental parameters either by extending the range of isoconformational compounds or by increasing the number of methods used. As in the previous section, compound (LXX) and its spiro-analogue (LXXII) were examined and their $_mK$ constants were determined. Determinations of the depolarisation of scattered light for compound (LXX) served as an additional method.

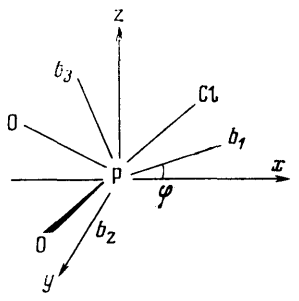


Figure 8. The directions of the axes of the polarisability ellipsoid of the O_2PCl group.

The experimental values of $_mK$ for compounds (LXX) and (LXXII) and of $_2\delta^2_\infty$ for compound (LXX) were expressed as functions of the unknown quantities γ_{P-O} and γ_{P-Cl} for the axial and equatorial conformations. The equations obtained are presented in Fig. 9 in a graphical form. The limits of the rectangle denote the region outside which the bond polarisabilities have no physical significance.

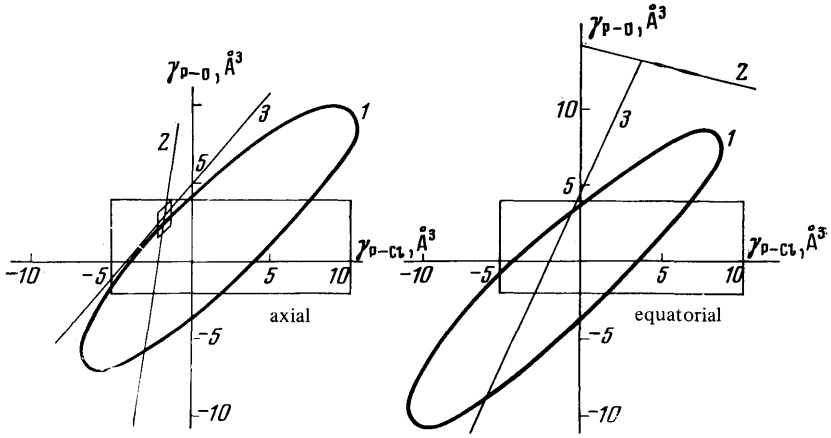


Figure 9. Dependence of γ^2 (curve *1*) and K_2 (curve *2*) for compound (LXX) and of ${}_mK$ (curve *3*) for compound (LXXII) on the anisotropy of the P–O and P–Cl bond polarisabilities; $|\gamma^2| = {}_2\delta^2_\infty (b_{xx} + b_{yy} + b_{zz})^2$.

Analysis of the graphical relation shows that a full set of values of γ_{P-O} and γ_{P-Cl} (the points of intersection of the straight lines and the ellipse) is possible only for the axial disposition of the P–Cl bond, since in this case three lines converge in one region. The tensor summation of the values $\gamma_{P-O} = 2.7$ and $\gamma_{P-Cl} = -1.7$ obtained yields the polarisability ellipsoid for the PO_2Cl group with $b_1 = 6.8$, $b_2 = 7.8$, and $b_3 = 3.0$ Å^3 and the angle $\varphi = -7$ between b_1 and the plane of the PO_2 fragment (Fig. 8). The principal axes of the polarisability ellipsoid for the PO_2Cl group may be determined more accurately without considering each bond separately and hence without introducing the hypothesis of their axial symmetry ($b_T \neq b_V$). The solution of three equations with three experimental values using the total group polarisability (17.56 Å^3) for the four unknown parameters yields two sets of polarisability ellipsoids: $b_1 = 6.437$, $b_2 = 3.369$, $b_3 = 7.537$, and $\varphi = -13°$; $b_1 = 6.783$, $b_2 = 7.871$, $b_3 = 3.135$, and $\varphi = -10°$. The second set almost coincides with the values obtained in terms of the approximation of axial symmetry, which proves the validity of the approach employed. The values obtained describe satisfactorily the structure of the 4-methyl derivative (LXIX) and of compound (LXXI).[6]

The axes of the bond polarisability ellipsoids may be determined by the joint examination of data derived by two related methods—double refraction and the depolarisation of Rayleigh light scattering—for the same compound. Thus the graphical representation of experimental values of ${}_mK$ and $10^{-3}\ {}_2\delta^2_\infty$ for 2-chloro-1,3,2-dioxaphospholane as a function of the unknown γ_{P-O} and γ_{P-Cl} showed[6] that the only possible solution, where the ellipse and the straight line intersect, corresponds to the axial position of the chlorine atom with $\gamma_{P-O} = 1.93$ and $\gamma_{P-Cl} = 0.37$ Å^3.[6]

The successive application of the methods considered above for the determination of the anisotropy of bond polarisabilities can also lead to satisfactory results. For example, the analytical solution of the system of two equations for the axial and equatorial conformations of 2-chloro-1,3,2-dithiaphosphorinane (CIII), the experimental values ${}_mK = 78$ and ${}_2\delta^2_\infty = 4.6 \times 10^{-3}$ for which were expressed as functions of the unknown γ_{P-S} and γ_{P-Cl}, led to four possible versions: (1) 0.65 and −1.33 and (2) −3.04 and −0.76 Å^3 for the axial conformation and (3) 2.97 and 2.18 and (4) −3.97 and −1.84 Å^3 respectively for the equatorial conformation. The latter solution is unlikely owing to the high negative values of γ. The choice from the three remaining solutions (i.e. the determination of the third structural parameter) was made by examining the values of ${}_mK$ for 2-phenyl-1,3,2-dithiaphosphorinane (CIV): the high negative value ${}_mK = -344$ may be obtained in only one case—when the P–Ph bond is axial, $\gamma_{P-S} = 0.65$ Å^3, and the plane of the benzene ring is perpendicular to the plane of symmetry of the molecule. Using the average bond polarisabilities (Table 2), it is possible to calculate the components of the polarisability tensor of the P–S bond: $b_L = 3.24$ and $b_T = b_V = 2.59$ Å^3; the corresponding values for the P–Cl bond are $b_L = 2.46$ and $b_T = b_V = 3.79$ Å^3.

The anisotropies of phosphorus bond polarisabilities in methyl phosphorodichloridite (IV) were calculated for the observed electron-diffraction structure[89] (angle of deviation of the methoxy-group from the *cis*-position $\varphi = 17°$): $\gamma_{P-O} = 1.54$ and $\gamma_{P-Cl} = 1.78$ Å^3.[36] The latter value is intermediate between the corresponding parameters for phosphorus trichloride and cyclic phosphoromonochloridites. The P–Cl bond length also varies in parallel with γ_{P-Cl}.[6] The observed parallel variation may be useful in the determination of the values of γ_{P-Cl} for the substituted phosphites $PCl_n(OR)_{3-n}$.[6]

All the facts presented above show that the environment of the phosphorus(III) atom has a marked influence on the system of mobile electrons. This precludes the use of homogeneous electro-optical characteristics even for compounds of the same class but conformationally inhomogeneous. A change in the anisotropy of the phosphorus bond polarisabilities has been observed[6] in 2-chloro-1,3,2-dioxaphospholane and its 4,4,5,5-tetramethyl analogue (LXI). The cause of this is associated with the difference between the conformations: the first compound has the form of an envelope with an axial P–Cl bond and the second has the form of a half-chair; as a result of this, the P–Cl bond length[90,91] and the shielding of the phosphorus nucleus[6] are altered. Thus, phosphorus(III) compounds require a special non-trivial approach, where all the unknown structural and bond parameters are found simultaneously for a series of isoconformational compounds.

The cause of such unusual mobility of the electron cloud of phosphorus(III) has not so far been elucidated, but it is apparently associated with intramolecular interactions. Analogous deviations from the additivity of polarisability for an asymmetric environment have been observed in α-chloromethyl ether [92] and methanesulphonyl chloride [3]. The anomalous behaviour of α-chloroethers [93] and compounds of Group IV elements with α-carbofunctional groups [94] is manifested also in other properties and can be explained by intramolecular coordination of the type of a three-centre bond formed by σ electrons (the so called α-effect [93]). The involvement of the oxygen LEP creates an excess of π electrons at the chlorine atom and the ^{35}Cl NQR frequency falls compared with alkyl chlorides. An analogous decrease of frequencies has been observed [86] also for the asymmetric phosphorochloridites $ROPCl_2$ and $(RO)_2PCl$ compared with phosphorus trichloride. The variation of the frequencies and of the P–Cl bond length cannot be explained by the involvement of the vacant *d* orbitals of the phosphorus atom, since this should have led to a deficiency of electrons at the chlorine atom [86].

Other, alternative mechanisms of the observed effect have also been proposed: direct interaction of the geminal atoms in the direction of the field [95] and hyperconjugation of the LEP of the oxygen atom with the C–Cl bond [96]. The possibility of the σ, π conjugation for the phosphorus atom has been discussed recently [97]; it was noted that hyperconjugation with σ-bonds formed by the elements in the Third Period should be observed. By analogy with pyranoid derivatives, for the axial position of the P–Cl bond the oxygen *p* orbital is disposed in a manner "convenient" for overlapping with the antibonding σ^* orbital of the P–Cl bond. This type of delocalisation strengthens the P–O bond and weakens the P–Cl bond. In fact, the P–Cl bond length in 2-chloro-1,3,2-dioxaphosphorinane (2.128 Å) is much greater than in phosphorus trichloride (2.043 Å). [86] The formation of many-centre bonds is also stereospecific and is possible only for the axial conformation. Whatever the mechanism of the observed interaction, it should lead to an increase of the perpendicular component of the polarisability ($b_T = b_V$) of the bond with the chlorine atom: this was observed in phosphorochlorodites, 2-chloro-1,3,2-dithiaphosphorinanes, chloro- and bromoarsenites [99,100], and α-chloroethers [92]. The concept of the delocalisation of the LEP of the oxygen atom to the antibonding orbital of the exocyclic bond explains, within the framework of the general theory of molecular orbitals, the anomeric effect [98,101] and the *gauche*-effect [101,102], i.e. the stabilisation of the conformations which were established above for phosphorus(III)-containing heterocycles; the present author therefore believes that this concept is preferable, although it does leave many problems unsolved.

3. The Anisotropy of the Polarisability of P^{III}–O Bonds.

The above analysis of the bond dipole moments in 2-X-1,3,2-dioxaphosphorinanes showed that the P–O bonds within the ring undergo the greatest changes. The redistribution of electron density should lead to an alteration of the anisotropy of the polarisability. The value $\gamma_{P-O} = -0.59$ Å^3, most widely used in the literature, was obtained by Le Fevre [1] on the basis of $_mK$ for the bicyclic phosphite (C), determined in dioxan, but it is inconsistent with the values of $_mK$ for compounds of the 1,3,2-dioxaphosphorinane series. Thus the value of γ_{P-O} for 2-chloro-1,3,2-dioxaphosphorinane (2.7 Å^3), 2-chloro-1,3,2-dioxaphospholane (1.93 Å^3), and methyl phosphorodichloridite (1.54 Å^3) were presented in the previous section. The determination of the steric structures (see Section I) of the 2-alkoxy- [84] and 2-phenoxy-derivatives [129] of compound (LXXXIX) and of 2-phenyl-1,3,2-dioxaphosphorinanes (XCIX) makes it possible to calculate the phosphorus bond polarisability eliipsoids. For the axial *gauche*-conformation of the methoxy-group [84], $\gamma_{P-O} = -0.25$ Å^3 in compound (LXXXV). [129] The phenoxy-group in compound (XCII) has the axial *cis*-orientation and its benzene ring is arranged at right angles to the plane of symmetry of the molecule [129]; the anisotropies of the exocyclic and ring P–O bond polarisabilities, calculated for this structure, are respectively 2.35 and 3.11 Å^3. [129]

The axial orientation of the phenyl group in 5,5-dimethyl-2-phenyl-1,3,2-dioxaphosphorinane (XCIX) was demonstrated in Section III. Such a bulky substituent can occupy the axial position only when the plane of the benzene ring is perpendicular to the plane of symmetry of the molecule (as was found for 2-phenyl-1,3,2-dithiaphosphorinane in Section III, by Martin and Robert [103], and from the analysis of ^{1}H NMR spectra [104] and X-ray diffraction data [105]). When $_mK_{exp} = -298$ is expressed as a function of two unknown parameters, the following relation is obtained:

$$13.43\gamma_{P-O} + 0.78\gamma_{P-C(Ph)} = 26.43,$$

the analysis of which shows that reasonable solutions are possible only for positive values of γ, γ_{P-O} being capable of variation over the very narrow range 1.8–2.0 Å^3, whereas the range of the corresponding solutions for $\gamma_{P-C(Ph)}$ is somewhat wider—from 0.6 to 2.9 Å^3. A positive value of $\gamma_{P-C_{sp^2}(Ph)}$ is also obtained on the hypothesis that the anisotropies of the $P-C_{sp^3}$ and $P-C_{sp^2}$ bond polarisabilities are close, differing by the exaltation of the total polarisability. The latter is expressed in terms of the difference between the refractions (Table 2). Then $b_L = 3.28$ and $b_T = 0.79$ Å^3. The value $\gamma = 2.49$ Å^3 obtained appears more reliable than the value calculated by Le Fevre [1] on the basis of the empirical relation between b_L and the bond length ($\gamma = -0.3$ Å^3, Table 4).

The data presented show that γ_{P-O} is positive in most cases. We may note the similarity of γ_{P-O} and m_{P-O} for phenoxy-derivatives and 2-chloro-1,3,2-dioxaphosphorinane, which shows that the electronic interactions are related.

The determination of the anisotropy of the P–O bond polarisability permits the solution of complex conformational problems associated with the determination of several structural parameters, one or two of which vary continuously. In such cases, the combined and successive application of related methods to a series of isoconformational compounds is most effective. This procedure has been partly demonstrated above in the analysis of molecular and bond dipole moments and of the anisotropies of the P–O bond polarisabilities in 2-phenoxy-1,3,2-dioxaphosphorinanes. The last stage in the structural study of such molecules involves the determination of the angle of rotation of the benzene ring, which may be found from the $_mK$ data for compounds (LXXXIX)–(XCI). The calculations were made for the *cis*-axial orientation of the phenoxy-group found above, with the parallel and perpendicular arrangements of the plane of the benzene ring relative to the plane of the $P-O-C_{aryl}$ bonds. The following values were used for the $O-C_6H_4-Br-p$ and $O-C_6H_4-NO_2-p$ fragments: $b_1 = 18.23$, $b_2 = 13.47$, and $b_3 = 9.38$ Å^3, calculated from Le Fevre's data [1], and $b_1 = 18.99$, $b_2 = 12.62$, and $b_3 = 7.62$ Å^3. [106] The smallest calculated values were obtained for the perpendicular conformation and agree best with experiment.

In phenyl *o*-phenylene phosphites, the structural problem reduces to the determination of the following unknowns: the angle of the non-planarity of the five-membered ring Ψ, the position of the exocyclic bond, the angle of rotation relative to the P–O bond φ, and the angle of rotation of the benzene ring of the phenoxy-group θ, the first and last parameters varying continuously (Fig. 10).

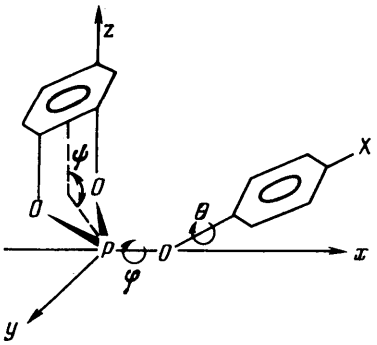


Figure 10. Determination of the steric structure of *o*-phenylene phenyl phosphites.

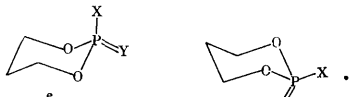
The joint examination of the dipole moment of phenyl *o*-phenylene phosphite (LXVII) itself and of its *p*-bromo- and *p*-methoxy-derivatives permits the determination of the dihedral angle of the bending of the five-membered ring (155°) corresponding to the axial position of the exocyclic bond, and the *gauche*-orientation of the phenoxy-group may be demonstrated[8]. The angle of rotation of the benzene ring was calculated from the Kerr effect data for the observed conformation[8]. The angle was varied from 0° (when the plane of the benzene ring and the plane formed by the P–O–C bonds coincide) to 180° in 30° steps. The positive direction of rotation was assumed to be that in which the position of the aryl group closest to the phosphorus moves away from the oxygen atom. A 35° angle corresponds to the experimental value of ${}_{m}K$. The strong steric interactions in the *oop*-tri-t-butyl derivative (LXVIII) induce a reorientation of the benzene ring: the experimental value of ${}_{m}K$ changes sign [157 for compound (LXVII) and −35.5 for compound (LXVIII)], which corresponds to an additional displacement of the benzene ring from the initial plane: the angle increases to 90°.[8]

IV. THE STRUCTURES OF FOUR-COORDINATED PHOSPHORUS COMPOUNDS

Since four-coordinated phosphorus forms highly polar and anisotropic bonds (Tables 3 and 4), the dipole moments and the values of ${}_{m}K$ are very sensitive to conformational changes. In view of the necessity to test the validity of and to refine the additive values for phosphorus(IV) bonds, studies were begun on systems which are simple as regards conformation and where the probable number of rotational isomers does not exceed two. 1,3,2-Dioxaphosphorinanes, investigated by a wide variety of physical methods, may be included among them. Comparison of the results of several investigations may serve as a criterion of the validity of the methods of calculation employed. Conformational analysis of heterocyclic molecules is a problem of independent interest—the study of the influence of the nature of the substitutent at the phosphorus atom on the structure of the molecule as a whole.

1. Conformational Analysis of Heterocyclic Molecules

Owing to the absence† of rotational isomerism in the exocyclic part of the molecule, the set of the probable conformations of the acid chlorides and methyl derivatives of 1,3,2-dioxaphosphorinanes is reduced to a minimum: there are two chair forms with the axial (a) or equatorial (e) orientations of the P=Y bond:



The existence of conformations other than the chair conformations has not been confirmed by NMR data[107,108]

Table 6 presents the experimental and calculated values (the standard parameters found from the constants ${}_{m}K$ for symmetrically substituted compounds were used for the phosphorus bonds: $\gamma_{P-O} = -0.59$; $\gamma_{P-C} = 1.49$; $\gamma_{P-Cl} = 2.66$ Å^3, subject to the conditions that $\gamma_{C-C} = 0.71$ and $\gamma_{C-O} = 0.43$ Å^3.[1] We shall compare initially data for the thiono-derivatives (LXXVI) and (LXXVII), on the one hand, and (LXXXI) and (LXXXII), on the other. While the polarities of the acid chlorides (LXXVI) and (LXXVII) are similar, the dipole moments of compounds (LXXXI) and (LXXXII) differ markedly, which indicates a difference between their conformations. The dipole moments and the constants ${}_{m}K$ found for compounds (LXXXII) and (LXXVII) are closest to the values calculated for the chair form with an equatorial thiophosphoryl group (Table 6). The stabilisation of one conformer is possible for the *cis*-configuration of the 4-methyl group and the P=Y bond. The constant ${}_{m}K$ for this structure agrees with the experimental value for compound (LXXXII). The satisfactory agreement confirms the applicability of the additive P–O, P=S, and P–C bond polarisabilities and makes it possible to determine the structure of compound (LXXXI), which exists in the form of an equilibrium mixture of two chair forms, where the conformation with the thiophosphoryl group in the axial position predominates (mole fraction 0.8).

The phosphorochlorothioate (LXXVI) is conformationally homogeneous[111] and, according to dipole moment measurements, has the chair form with an equatorial thiophosphoryl group[30]. However, all the calculated values of ${}_{m}K$ proved to be much lower than the experimental results[30]; for this reason, the effective anisotropy of the P–Cl bond polarisability, determined from the experimental ${}_{m}K$ for this compound ($\gamma_{P-Cl} = -1.31$ Å^3), was considered. The value obtained led to the identification of the equatorial conformation (for the P=Y bond) of the 4-methyl analogue (LXXVII) [30] and the phosphorochloridate (LXXV).[29]

In connection with the study of the problem of internal rotation about the O–P bond, it was of greatest interest to investigate compounds symmetrically substituted relative to the phosphorus atom—2-alkoxy-derivatives of

†The rotation of the methyl group does not affect the calculated dipole moment and the constant ${}_{m}K$.

Table 6. The calculated and experimental parameters for 1,3,2-dioxaphosphorinanes with phosphorus(IV).

Substituents		Compound	Parameter	Experimental value	Calculated*	
at P atom	at $C_{(4)}$ atom				P = Y (e)	P = Y (a)
CH_3, S	H	LXXXI	μ, *D*	3.90	5.89	3.92
			$_mK$	436	1287	204
CH_3, S	CH_3	LXXXII	μ, *D*	5.37	5.89	3.92
			$_mK$	1175	1273 (a); 1168 (e)	243 (a); 202 (e)
Cl, S	H	LXXVI	μ, *D*	5.30	5.46	4.22
			$_mK$	1356	714	—110
Cl, S	CH_3	LXXVII	μ, *D*	5.54	5.46	4.22
			$_mK$	1195	1341 (a); 1294 (e)	111 (a); 74 (e)
Cl, O	H	LXXV	μ, *D*	5.89	5.77	3.81
			$_mK$	556	753	123
H, O	CH_3**	LXCIV	μ, *D*	5.77	5.85	3.78
			$_mK$	541	—	—
H, O	CH_3**	LXCV	μ, *D*	4.19	5.85	3.78
			$_mK$	160	—	—
CH_3, O	CH_3**	LXXX	μ, *D*	6.36	6.06	3.97
			$_mK$	346	—	—
CH_3O, O	CH_3**	LXXXV	μ, *D*	6.07	5.41 (*c*); 7.6 (*t*); 5.91 (*g*)	3.14 (*c*); 5.22 (*t*); 3.75 (*g*)
			$_mK$	344	390 (*c*); 978 (*t*); 354 (*g*)	60 (*c*); 182 (*t*); 1 (*g*)
CH_3O, O	CH_3**	LXXXVI	μ, *D*	4.46	5.41 (*c*); 7.6 (*t*); 5.91 (*g*)	3.14 (*c*); 5.22 (*t*); 3.75 (*g*)
			$_mK$	165	390 (*c*); 978 (*t*); 354 (*g*)	60 (*c*); 182 (*t*); 1 (*g*)
CH_3O, S	CH_3**	LXXXVII	μ, *D*	5.51	509 (*c*); 6.89 (*t*); 5.58 (*g*)	2.85 (*c*); 4.94 (*t*); 3.50 (*g*)
			$_mK$	929	1016 (*c*); 2173 (*t*); 848 (*t*)	177 (*c*); 531 (*t*); 170 (*g*)
CH_3O, S	CH_3**	LXXXVIII	μ, *D*	3.93	5.09 (*c*); 6.89 (*t*); 5.58 (*g*)	2.85 (*c*); 4.94 (*t*); 3.50 (*g*)
			$_mK$	298	1016 (*c*); 2173 (*t*); 848 (*t*)	177 (*c*); 531 (*t*); 170 (*g*)

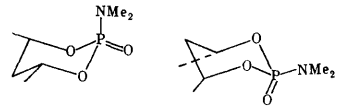
*(a) represents the axial position of the methyl group at $C_{(4)}$ and (e) represents the corresponding equatorial position. **In conformity with the analysis of ^{1}H NMR spectra [31,109,110], only the equatorial orientation of the methyl group at $C_{(4)}$ was considered for these compounds; (*c*), (*t*), and (*g*) represent calculations for the *cis*-, *trans*-, and *gauche*-conformations of the OCH_3 group.

1,3,2-dioxaphosphorinanes. The probability of conformational equilibrium between two chair forms (which would greatly complicate the solution of the conformational problem) was ruled out by the introduction of the 4-methyl group into the ring. Oxidation and addition of sulphur to the *cis*- and *trans*-isomers of 2-methoxy-4-methyl-1,3,2-dioxaphosphorinane yielded two pairs of geometrical isomers of the corresponding phosphates and phosphorothioates, for which the dipole moments and the constants $_mK$ were determined and calculated (Table 6). Joint analysis of the results obtained by spectroscopic methods (^{1}H NMR, infrared, and Raman spectroscopy) and of the dipole moments and the constants $_mK$ made it possible tp identify the structures produced [the multiple bond is in the equatorial and axial positions respectively in the *cis*- and *trans*-isomers of compounds (LXXXV) and (LXXXVII)] and to reach a conclusion about the stereospecificity of the chemical reactions investigated [31].

Earlier studies [29,30] of the Kerr effect in 1,3,2-dioxaphosphorinanes containing phosphorus(IV) were based on a preliminary analysis of the initial bond parameters and, where necessary, effective quantities were considered. The determination of the fundamental characteristics of the steric structures of compounds of this class (the greater tendency towards equilibrium between two chair forms compared with tervalent phosphorus analogues, the dependence of the conformation of the heterocycle on the nature of the exocyclic substituent, and the general nature of the conformational behaviour of compounds with phosphoryl and thiophosphoryl groups) makes it possible to analyse in greater detail the electrical and the electro-optical parameters of the phosphorus bonds. It was noted above that it is necessary to compare for this purpose the corresponding compounds with three- and four-coordinated phosphorus.

Section III presented the necessary data for 2-X-1,3,2-dioxaphosphorinanes with X = Cl, OAlk, NR_2, etc.

On the basis of the polarities of the *cis*- and *trans*-isomers of *cis*-4,6-dimethyl-2-dimethylamino-1,3,2-dioxaphosphorinane and their known steric structures [112], it is possible to determine the polarity of the phosphoryl group: 3.33 and 3.60 D were obtained for its equatorial and axial positions respectively [113].



μ = 5.80 D μ = 4.05 D

The difference between the dipole moments indicates the stereospecificity of the intramolecular interactions: the lower dipole moment of the equatorial phosphoryl group is apparently associated with the more pronounced conjugation between this group and the lone electron pairs of the ring oxygen atoms. Indeed, according to quantum-mechanical calculations, the multiplicity of the equatorial P=Y bond is greater than that of the axial bond [113]. The non-equivalence of the bond dipole moments in the two chair conformations was also noted for 2-methyl-2-thiono-1,3,2-dioxaphosphorinane. [30]

The identification of the conformations of two stereoisomeric 2-hydro-4-methyl-2-oxo-1,3,2-dioxaphosphorinanes (XCIV) and (XCV) [109,110] made it possible to revise the parameters of the polarity and polarisability of the phosphorus bonds [130] and to calculate the previously unknown anisotropy of the P–H bond polarisability, namely $\gamma_{P-H} = -1.1$ Å^3. [130]

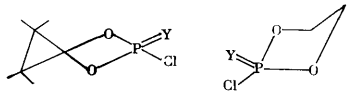


(XCIV): μ = 5.77 D; $_mK$ = 541; $m_{P=O}$ = 2.95 D, $\gamma_{P=O}$ = 0.81 Å^3; (XCV): μ = 4.19 D; $_mK$ = 160; $m_{P=O}$ = 3.48 D, $\gamma_{P=O}$ = 0.3 Å^3.

The values obtained proved useful for the investigation of the steric structures of compounds (XCVI)–(XCVIII), which are involved in a complex conformational equilibrium[127].

Spectroscopic study of the phosphorochloridate (LXXV)[114] and the phosphorochlorothioate (LXXVI) [111], demonstrated their conformational homogeneity; the dipole moments and analysis of the ^{1}H NMR spectra indicate a chair conformation with the equatorial position of the double bond. The parameters determined for this structure have the following values: $m_{P=O}$ = 2.40 D, $\gamma_{P=O}$ = 1.34 Å^3, $m_{P=S}$ = 2.10 D, and $\gamma_{P=S}$ = 3.06 Å^3 (Arshinova et al.[126]) (they differ somewhat from the values quoted by Arbuzov and Arshinova[5], who carried out the calculation on the basis of $\gamma_{P=O}$ and γ_{P-Cl} calculated for $_mK$ in dioxan solutions).

The dipole moments and the constants $_mK$ for 2-chloro-2-oxo- and 2-chloro-2-thiono-1,3,2-dioxaphospholanes (LVII)–(LXVI) [126] were analysed on the basis of the results. According to Arshinova et al.[126], the 4,4,5,5-tetramethyl derivatives have the half-chair conformation; for the remaining compounds investigated, the envelope ring conformation, with the carbon atom displaced from the plane of the ring, is believed to be the most probable. The multiple bond is oriented preferentially pseudoaxially:



(LXI), (LXVI) (LVII), (LXII)

Four-membered rings constitute a more complex case for the conformational analysis of heterocycles, since one of the structural parameters (the angle of ring nonplanarity) varies continuously. The dipole moment and the constant $_mK$ for 3-chloro-3-thiono-1,3-thiaphosphetan (XLIX) were calculated as functions of the dihedral ring bending angle θ, which was varied from 120°, when the P=Y bond is arranged pseudoequatorially, to 180°, when the ring is planar, and further to 240°, when the P=Y bond becomes pseudoaxial[24]. Electron diffraction data for the geometry of 3-chloro-3-oxo-1,3-thiaphosphetan were used in the calculation[115] and the parameters found for thietan were used for the C–S bond: 0.86 D; b_L = 2.05; b_T = 1.61 Å^3.[116] The experimental dipole moment of compound (XLIX), which is 2.18 D, agrees with the calculated minimum value (2.17–2.20 D) for θ = 130 to 150°. Joint examination of the dipole moment and the constant $_mK$ shows that the angle is 135°.[24] In the 3-oxo-derivative, the oxygen atom, whose bulk is smaller, may also occupy the pseudoaxial position, which leads to the coexistence of a whole set of conformers. Calculation of the energies of the conformations by Hoffmann's method confirmed this hypothesis[24].

In the corresponding 3-methoxy-1,3-thiaphosphetans (L) and (LI), the conformational problem is complicated owing to the rotational isomerism of the methyl group relative to the P–O bond. The number of possible conformations increases by a factor of three and simple comparison of the calculated and experimental parameters does not allow an unambiguous choice[25]. The procedure involving the joint application of two related methods, proposed by Vereshchagin et al.[116], in which one plots the calculated $_mK$ against the square of the dipole moment, is particularly useful in such situations. The point corresponding to the experimental values defines the required parameters. Fig. 11 illustrates the graphical relations obtained. The positions of the experimental points identify unambiguously the conformations of compound (L) and (LI). Both substances have the same dihedral ring bending angle (135–140°) as the value found for the acid chloride (XLIX) and the pseudoaxial methoxy-groups have the *gauche*-orientation. An analogous structure was found also for the phenoxy-derivatives[25].

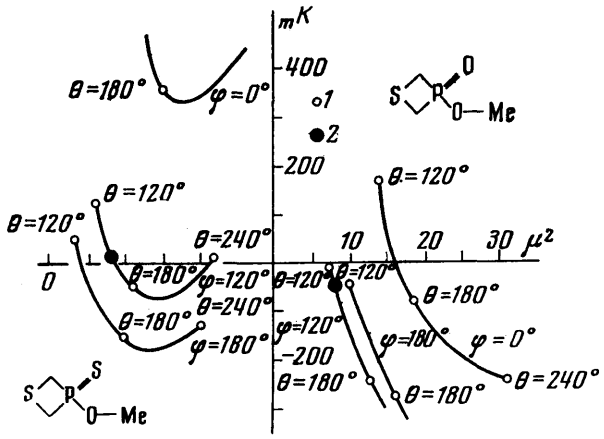


Figure 11. Graphical relation between the Kerr constants and the squares of the dipole moments of 3-methoxy-1,3-thiaphosphetans; θ is the dihedral angle of the nonplanarity of the four-membered ring and φ the angle determining the rotation relative to the P–O bond: 1) calculated values; 2) experimental values.

The examples examined show how effective is the joint graphical interpretation of data derived by two related methods. Problems which are insoluble by each method separately can be solved unambiguously by means of a graphical comparison. Other examples If the combined application of physical methods, which lead to new possibilities in the conformational analysis of complex systems, are given below.

2. Internal Rotation in Acyclic Compounds

The main difficulty in the employment of the Kerr effect in structural studies on acyclic molecules is due to the uncertainty of the bond parameters. The problem of their selection for compounds which are asymmetrically substituted relative to the phosphorus atom has been analysed[6] in relation to dichloromethylphosphine oxide (XXVI) and sulphide (XXVIII) as examples. In the former case, the dipole moment and the constant $_mK$ can be expressed in terms of the parameters determined for phosphoryl chloride. In the latter case [compound (XXVIII)], there is no additivity and the determination of the bond characteristics requires the use of an additional compound having the same environment at the phosphorus atom but a different direction of the dipole moment. Dichloro-(trichloromethyl)phosphinesulphide (XXIX) has such properties. Joint examination of the constants $_mK$ for both compounds leads to the following values: γ_{P-Cl} = 3.12 and $\gamma_{P=S}$ = 4.39 Å^3; these differ appreciably from the

values found for symmetrically substituted compounds. We shall therefore consider henceforth substances where the four-coordinated phosphorus atom has the same immediate environment.

The infrared spectra, dipole moments, and the constants $_mK$ of chloromethyldiphenylphosphine (XXII) indicate the existence of two conformers in proportions of 0.9 : 1.[13] Comparison of the dipole moments and the constants $_mK$ with the calculated values makes it possible to identify these structures: *trans*-, *gauche*- ($_mK$ = 55 for the *trans*-disposition relative to the P=O bond and −58 for the *gauche*-disposition, the experimental value being 44). The agreement between the conclusions obtained by the three methods confirms the validity of the chosen model and makes it possible to investigate more complex systems, where one considers the rotation of two irregular groups of the type $CH_3P(O)(CH_2X)_2$ in compounds (XXIII) and (XXIV). These substances are interesting from the standpoint of the observation of the mutual influence of the rotating groups. They have a large number of possible conformations, of which there are six for the *gauche*- and *trans*-dispositions of the bonds. Analysis of the infrared bands in the spectra of crystalline compounds (XXIII) and (XXIV) and their solutions with different dielectric constants of the medium led to the conclusion that two conformers are in thermodynamic equilibrium. On the plot of the square of the dipole moment against $_mK$, the experimental point for compound (XXIII) ($_mK$ = 33.6) corresponds best to equilibrium between the *trans*,*trans*- ($_mK$ = 7.9) and *trans*,*gauche*-forms (the calculated value for the latter is 101 and 122 respectively for the clockwise or anticlockwise 60° rotation of the C–C bond relative to the eclipsed position) (Fig. 12)[14]. The replacement of chlorine atoms by bromine in the halogenomethyl groups led to an appreciable alteration of the preferred conformations: the conformer with the *trans*-orientation of the C–Br bond was displaced from the equilibrium. The *trans*,*gauche*-form ($_mK$ = 1.67), which exists in equilibrium with the *gauche*,*gauche*-form ($_mK$ = −240) is the most stable; the experimental values is 74.[15]

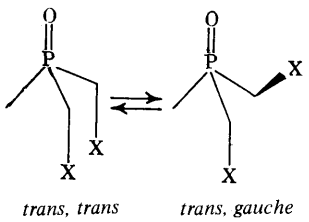


Figure 12. The preferred conformations of acyclic molecules.

The much more complex case of the rotation of three irregular halogenomethyl groups was investigated in relation to the trihalogenomethylphosphine oxides (XXI) and (XXV). When the eclipsed forms are excluded, the number of conformers is seven. The combined application of the data obtained by several physical methods (infrared spectroscopy, dipole moment measurements, and the Kerr effect) for dihalogenomethyl derivatives showed[12,15] that the replacement of the halogen also alters the composition of the conformational equilibrium mixture. Whereas the proportions of the *trans*, *trans*, *trans*- and *gauche*, *gauche*, *gauche*-forms are 0.8 : 0.2 for X = Cl,[12] in the case of the bromo-derivative the first of these forms is displaced from equilibrium and the *trans*, *trans*, *gauche*-conformer predominates[15].

The problem of the internal rotation about the P-heteroatom bonds is of interest as regards conformations. The greatest number of studies have been concerned with the P–O bond, despite the fact that the nature of the potential energy curve for this bond has still not been finally established. As mentioned above, the study of the structures of the methyl phosphinate esters (L) and (LI) and of their structural analogues with the phenyl group led to the conclusion that only the *gauche*-conformer in relation to the phosphoryl or thiophosphoryl linkage exists. The *gauche*-orientation of the methoxy-group has been established for the *cis*-isomers of 1,3-butylene phosphates (LXXXIII) and phosphorothioates (LXXXV)[31] (Table 6). In all the cases quoted, the alkoxy-group occupies the axial position, where the steric interaction with hydrogen atoms may constitute a significant obstacle to the realisation of the conformation which is more stable from the standpoint of the electronic properties. Indeed, for the equatorial orientation of the P–OR group in the corresponding *trans*-isomers of compounds (LXXXIV) and (LXXXVI), conformational equilibrium between the *trans*- and *gauche*-forms was observed (Table 6). The equilibrium was confirmed by infrared and Raman spectra[31]. In five-membered rings, the steric interactions of the exocyclic P–OR bond with the remainder of the molecule may be greatly reduced owing to the planar structure of the 1,3,2-dioxaphospholen[117,118] or phospholen[49] ring or, in the case of the envelope conformation, of the 1,3,2-dioxaphospholan ring with the carbon atom at the apex[119]. This also leads to the *trans*-orientation being greatly preferred.

Among acyclic molecules, the trialkyl phosphates (X), (XV), and (XVII), whose dipole moment spectra and, for the last two compounds, also the constants $_mK$ have been investigated[9,10], are closest to the systems investigated. Graphical comparison of the squares of the dipole moments and the constants $_mK$ for compound (XVII), taking into account the populations of the conformations known from the infrared spectra, showed that the *gauche*, *gauche*, *cis*-form predominates in the conformational equilibrium[9]. This conclusion is disputed by Egorov et al.[50], whose analysis of the dipole moments led to the detection of the equilibrium between the *trans*, *trans*, *gauche*- and *trans*, *trans*, *trans*-conformers, the dipole moments being calculated from the bond dipole moments, which have been criticised[10]. The conclusion reached by Raevskii et al.[9] also appears unlikely. It is didficult to imagine an equilibrium mixture of *cis*, and *gauche*-forms, between which there is no energy barrier according to quantum-mechanical calculations[120–122]. It is more correct to consider intermediate forms with a torsional angle ranging from 120° (*gauche*) to 180° (*cis*) and further to 240° (*gauche*) in the "cisoid" conformations. Instead of the formal sixteen structures, one can then postulate six. After revising the structure of trialkyl phosphorothioates from these standpoints, the authors[10] concluded that the conformer with the cisoid or *gauche*-disposition of all the OR groups predominates in the thermodynamic equilibrium between the conformers of compound (XVII). The *gauche*,*gauche*, *gauche*-conformer of compound (XV) is fully stabilised.

3. The Conjugation Effects

Measurements of Kerr constants and light scattering constitute a unique procedure for the investigation of the rotation of the plane of the benzene ring relative to the element–phenyl bond. On the basis of data derived by these two methods, it is possible to determine reliably the conformations of aromatic compounds in solutions, since the anisotropy of the polarisability of the phenyl group is very large [1–3]. At the phosphorus atom, the conjugations with the lone electron pair, the multiple bond, or the vacant *d* orbitals have different stereospecificities so that the solution of this type of conformational problem yields directly information about the strength and nature of the possible conjugation effects, which are determined by the orientation of the aryl groups.

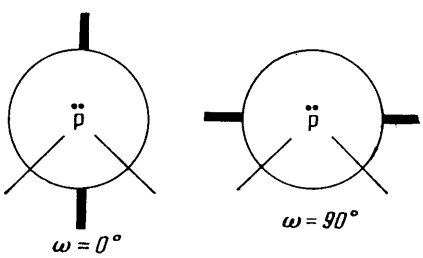


Figure 13. The rotation of the benzene ring relative to the Ph–P bond.

In this sense, monoaryl derivatives are of greatest interest, since additional aromatic groups at the phosphorus atom can lead to the steric repulsion of the substituents in the *o*-positions of the aryl groups. It was shown above for 2-phenyl-1,3,2-dioxaphosphorinane (XCIX) and 2-phenyl-1,3,2-dithiaphosphorinane (CIV) that the most preferred conformation is one where the plane of the benzene ring is perpendicular to the plane of symmetry of the molecule ($\omega = 90°$ in Fig. 13), but the *syn*-axial interactions [the 2-phenyl groups in compounds (XCIX) and (CIV) are arranged axially] prevents the realisation of the alternative conformation, so that it is desirable to examine less sterically overloaded molecules of the type PX_2Ph and their oxides. Such phosphines [compounds (XXXI)–(XXXV) and (XLIV)–(XLVI)] have been investigated [18,19]. In the calculation for the C_{sp^2}–P bond, the value $\gamma = -0.3$ Å^3, obtained by a semiempirical method, was used. For the two conformations with $\omega = 0$ and 90°, the authors [18,19] obtained the following values of the Kerr constant (the values of $10^{11}{}_mK_0°$, $10^{11}{}_mK_{90°}$, $10^{11}{}_mK_{exp}$ are quoted): 3, −4, and 1 for (XXI); 4, −3, and 5 ± 2 for (XXXII); 96, 90, and 132 for (XXXIII); 6, −8, and 2 for (XXXIV); 7, −17, and 10 ± 3 for (XXXV); 33.4, −73.8, and 30 for the oxide (XLIV); 24.2, −85.9, and 24.9 for the oxide (XLV); 35.3, −46.7, and 44.4 for the oxide (XLVI). In all cases the plane of the benzene ring coincides, according to these data, with bisector of the RPR angle ($\omega = 0°$) and the LEP of phosphorus(III) or the phosphoryl group in the case of phosphine oxides is thus coplanar with the benzene ring, which rules out the possibility of the $p-\pi$ interaction with the LEP. We may note that the conformation with $\omega = 0°$ differs in principal from the conformation of dimethylaniline [123] and its derivatives, where the molecule is a flattened pyramid and $\omega = 90°$. *p*-Aminobenzoic acid has a similar structure [124]. The change in the conjugation of the aromatic system with the LEP of phosphorus(III) and nitrogen(III) may play a definite role in the alteration of the conformations of the phenyl derivatives of these elements. According to Raevskii et al.[18], the energy of the $p-\pi$ conjugation in phosphorus(III) compounds is insignificant owing to the considerable amount of *s* character of the phosphorus(III) LEP orbital and cannot compete with the energy of the steric interactions between the hydrogen atoms of the phenyl group and the substituents at the phosphorus atom.

When two aryl groups are present, the *o*-hydrogen atoms in the observed bisector conformation, located within the pyramid, approach one another and suffer steric repulsion, so that there is a possibility of the displacement of the two aromatic rings from the plane. Having adopted an initial situation in which the plane of each aryl group is perpendicular to the C_{sp^2}–P–C_{sp^2} plane and having analysed the graphical relation between ${}_mK$ and the angles of rotation of the phenyl groups, the authors [22] concluded that the conformation of the molecules of compounds (XLI)–(XLIII) is close to that where each aromatic ring is perpendicular to the C_{sp^2}–P–C_{sp^2} plane, with a possible deivation up to 15° in the direction leading to the eclipsing of the phosphoryl group. The occurrence of the bisector conformation ($\omega = 32°$) is hindered by the strong steric interaction between the inner *o*-hydrogen atoms.

The steric repulsion of the *o*-hydrogen atoms within the pyramid increases by a factor of three on passing to the triaryl derivatives, so that one may expect an even greater twisting of the molecules. The symmetrically substituted triphenylphosphine (XXX), its oxide (XXXVI), and its sulphide (XLII) were investigated for the first time by Le Fevre [17,20], but the constants ${}_mK$ were determined in benzene. Since the subsequent measurement of ${}_mK$ for compound (XXXVI) in carbon tetrachloride [21] led to significantly different results, we shall consider only the latter study. Comparison of the experimental ${}_mK$ and the values calculated assuming C_3 symmetry for compounds (XXXVI)–(XL) yielded the following angles of rotation of the benzene ring: 55°, 65°, 49°, 60°, and 52° respectively. According to the authors [21], the introduction of substituents such as the chlorine atom of the methyl group causes flattening, which may be accounted for by the conjugation of the aromatic rings with the phosphorus *d* orbitals; the influence of the direct polar conjugation with the phosphoryl group is significant in *p*-chloro-derivatives.

The Kerr effect method may be useful in the study of the steric and electronic structures of organophosphorus compounds. The joint application of the Kerr effect and other physical methods is particularly promising, gives rise to wide possibilities, and makes it possible to investigate complex conformational problems associated with the determination of several unknown parameters. The combined use of several methods permitted systematic and specific investigations of the influence of the nature of substituents at the phosphorus atom on the conformation of the molecule and of the nature of the hindered rotation relative to the P–O, P–C, P–Ph, etc. bonds in compounds of three- and four-coordinated phosphorus.

Organophosphorus compounds, which are distinguished by a wide variety of intramolecular interactions, are excellent objects for the investigation of such interactions by electro-optical methods. The graphical isoelectric and isoanisotropic map methods make it possible to

estimate quantitatively the electron redistributions occurring in the molecules being compared and hence provide a justification for conclusions concerning the nature, magnitude, and direction of the electronic effects. The conclusion concerning the extreme electronic lability of phosphorus(III) compounds, which makes it virtually impossible to employ the usual additive scheme in calculations on asymmetrically substituted compounds, is of interest in this sense.

The determination of the additive bond characteristics and the development of methods for their determination permit the study of systems where the phosphorus atom has a different coordination. Compounds of five-coordinated phosphorus and heteroaromatic systems are of special interest for the investigation of steric and electronic structures. The different coordination causes a radical alteration of the nature of the intramolecular interactions [with the phosphorus(III) lone electron pair, with the multiple bonds involving phosphorus(II) and phosphorus(IV), and with the *d* orbitals of phosphurus(V)], so that comparison of the conformations and internal rotations for identical phosphorus bonds in the P^{III}–P^{IV}–P^{V} series (and in certain cases also for P^{II} and P^{VI}) leads to the prospect of the direct investigation of the influence of intramolecular interactions on molecular conformation.

Simultaneous examination of the electrical and electro-optical properties of conjugated and heteroaromatic phosphorus compounds permits the determination of the nature of the distribution of electron density and of the direction of the exaltation of polarisability induced by the introduction of the phosphorus atom. Such studies have been carried out for pyridine and its derivatives [125]. Comparison with phosphorus-containing analogues will make it possible to investigate the conjugation problem in detail.

Further development of research on the application of the Kerr effect to organophosphorus compounds will involve the formulation in greater detail and extension of the additive system of bond and group polarities and polarisabilities. The lack of rigorously tested parameters for many phosphorus bonds is a serious obstacle. The creation of new methods and the development of earlier non-trivial methods for the simultaneous determination of bond and structural characteristics should be of great assistance.

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Butlerov Chemical Institute
at the Ul'yanov-Lenin Kazan
State University