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The Polarity and Structure of Unsaturated Derivatives of Four-coordinated Phosphorus

E.A.Ishmaeva

The results of studies on the steric and electronic structures of unsaturated organophosphorus compounds with a four-coordinated phosphorus atom by the dipole moment method are surveyed. The polarity of the C—P bonds is analysed and the problems of conjugation and unsaturation in organophosphorus compounds are discussed. The orientation of the double bond and the conformation of the aryl groups attached to the phosphorus atom are examined. Data are presented on the conformational analysis of unsaturated organophosphorus compounds.
The bibliography includes 108 references.

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I. INTRODUCTION

Studies on steric structures with the aid of molecular dipole moment (DM) data are carried out by comparing the experimental moments with values calculated by means of an additive vector scheme[1]. The validity of the additive scheme may be regarded as firmly established; deviations from additivity indicate the occurrence of intramolecular interactions in the molecule. The determination of the absolute values and directions of bond moments is an extremely difficult problem and the reliability of the results depends in many respects on its solution. An additive computational scheme for phosphorus compounds is presented in Arshinova's review[2], who also examines the contribution of the dipole moment of the lone electron pair (LEP) of the phosphorus atom to the overall polarity of the molecule and shows that, in order to calculate the magnitude and direction of the molecular moment, even for asymmetrically substituted organophosphorus compounds (OPC), there is no need to introduce the vector of the LEP moment as an independent vector for purely mathematical reasons. For symmetrically substituted molecules, the LEP dipole moment is included implicitly in phosphorus bond moments. Any additive scheme for organic molecules is based primarily on the C–H bond moment using different DM values[1]. In the calculation of the OPC dipole moments one usually employs $m(H \rightarrow C_{sp^3}) = 0.28$ D, $m(H \rightarrow C_{sp^2}) = 0.70$ D, and $m(H \rightarrow C_{sp}) = 1.10$ D, determined from the line intensities in the infrared spectra[3], which makes it possible to compare the results of calculations by different investigators.

A number of reviews are devoted to the consideration of the steric structures of different OPC.[4-6] Studies on the steric and electronic structures of OPC by the method based on the Kerr effect are considered by Arshinova[2]. This review surveys and gives a systematic account of data on the polarity and structure of unsaturated OPC with a four-coordinated phosphorus atom obtained by the dipole moment method. Compounds with $P-C_{sp^2}$ (where C_{sp^2} is a carbon atom in olefinic, carbonyl, and aromatic groups) and $P-C_{sp}$ bonds are examined; whenever necessary, data obtained by other methods are invoked (infrared, Raman, ultraviolet, and NMR spectroscopy, the Kerr effect method, and electron diffraction).

II. THE POLARITY OF THE CARBON–PHOSPHORUS BOND

The considerable advances achieved in the study of the steric and electronic structures of organic molecules by electro-optical methods have been reflected also in studies on unsaturated OPC. Table 1 presents the results of investigations of phosphorus compounds with $P-C_{sp^2}$ and $P-C_{sp}$ bonds by the dipole moment method published up to 1978 (the numbering of the compounds in Table 1 will be used henceforth in this review). Table 2 presents the available literature data for the polarities of C–P bonds obtained for different types of OPC. It shows that the C–P bond moments are not constant; furthermore, they sometimes differ not only in absolute magnitude but also as regards direction. The majority of investigators have hitherto assumed that the $C_{sp^3}-P$ bond moment is directed from the carbon to the phosphorus atom and that its absolute magnitude is ~0.6–0.8 D depending on the environment of the phosphorus atom. The $C_{sp^2}-P$ bond moment is also directed to the phosphorus atom and, in conformity with the higher electronegativity of the sp^2-hybridised carbon atom, its absolute magnitude is somewhat smaller. Its direction (from C to P) has likewise been unambiguously established by comparing the dipole moments of triphenylphosphine and its *p*-substituted derivatives[12]. The sign of the $C_{sp}-P$ bond moment is reversed, which is typical for all acetylenic compounds, including halogenoacetylenes [$m(Cl \rightarrow C_{sp}) = 0.66$ D].[40] The $P-C_{sp^3}$ and $P-C_{sp^2}$ bond moments with identical magnitudes and directions (from P to C) quoted by Mingaleva et al.[48] conflict with all other literature data. The discrepancy is probably due to the incorrect employment in the calculations of Mingaleva et al.[48] of the initial parameters: $m(P \rightarrow O)$ was assumed to be 1.2 D, although there exist rigorous data showing that it is smaller and that it has the opposite direction[51]. Despite the fact that similar values have been obtained by Ishmaeva et al.[40] and Mingaleva et al.[48], the agreement must be regarded as fortuitous, since the two teams of investigators used different initial parameters.

Thus the following sequence has been observed for the C–P bond moments: $m(C_{sp^3} \rightarrow P) > m(C_{sp^2} \rightarrow P) > m(C_{sp} \leftarrow P)$; the reversal of the sign of the $C_{sp}-P$ bond moment in this series must be regarded as legitimate. The C–P bond moments calculated taking into account the

dipole moments of the LEP of the phosphorus atom naturally differ from those where no account has been taken of the LEP. In this case a different sequence of C–P bond moments is observed[49]: $m(P \rightarrow C_{sp}) > m(P \rightarrow C_{sp^2}) > m(P \rightarrow C_{sp^3})$. In the calculation of the dipole moments of unsaturated OPC using the C–P bond moments with allowance for the LEP of the phosphorus atom, a new set of moments must be employed for all the remaining phosphorus bonds, also found taking into account the LEP. Since the absolute dipole moment of the phosphorus atom LEP is not known reliably (in any case it depends on the environment of the phosphorus atom) and the available literature data are contradictory, the present author suggests, in conformity with the evidence presented by Arshinova[2], that in the calculation of dipole moments of unsaturated OPC it is more useful to employ the moments of the C–P bonds and all other bonds without taking into account the LEP of the phosphorus atom.

Table 1. The experimental dipole moments of compounds of four-coordinated phosphorus containing an unsaturated carbon atom.

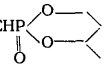
No. of cpd.	Compound	Solvent*	μ, D	References
	Compounds with a P^V–$C_{sp}2$ (olefin) bond			
(I)	CH_2=CHP (O) $(OC_2H_5)_2$	b	2.95	7,8,
		b	2.91	9
(II)	CH_2=CHP (S) $(OC_2H_5)_2$	c	2.76	10
(III)	CH_2=CHP (O) $(C_2H_5)_2$	c	4.55	11
(IV)	CH_2=CHP (S) $(C_2H_5)_2$	c	4.08	10
(V)	CH_2=CHP (O) $(C_6H_5)_2$	b	4.34	11
(VI)	CH_2=CHP (O) (C_2H_5) (C_6H_5)	b	4.31	11
(VII)	CH_2=CHP (O) Cl_2	c	3.52	10
		d	3.56	10
(VIII)	CH_2=CHP (S) Cl_2	d	3.11	10
(IX)	CH_2=C $(CH_3)_2$ P (O) $(OC_2H_5)_2$	c	2.90	11
(X)	CH_2=C (CN) P (O) $(OC_2H_5)_2$	c	3.51	11
(XI)	CH_2=C (Br) P (O) $(OC_2H_5)_2$	c	2.59	11
(XII)	CH_3CH=CHP (O) $(OC_2H_5)_2$	b	2.92	9,12
(XIII)	C_2H_5CH=CHP (O) $(OC_2H_5)_2$ (*cis*)	b	2.89	9
(XIV)	C_2H_5CH=CHP (O) $(OC_2H_5)_2$ (10% (*cis*), 90% *trans*)	b	3.03	9
(XV)	iso-C_3H_7CH=CHP (O) $(OC_2H_5)_2$ (90% (*cis*), 10% *trans*)	b	2.90	9
(XVI)	NCCH=CHP (O) $(OC_2H_5)_2$ *trans*)	c	3.99—4.02	••
(XVII)	n-C_4H_9OCH=CHP (O) $(OC_2H_5)_2$ (*trans*)	b	3.38	11
(XVIII)	n-C_4H_9SCH=CHP (O) $(OC_2H_5)_2$ (*trans*)	b	3.42	••
(XIX)	n-C_4H_9OCH=CHP 	b	4.10	••
(XX)	C_2H_5OCH=CHP (O) $(OC_6H_5)_2$	b	4.04	••
(XXI)	n-C_4H_9OCH=CHP (O) $(C_6H_5)_2$ (*trans*)	b	4.36	13
(XXII)	n-C_4H_9OCH=CHP (O) Cl_2	c	4.46	11
(XXIII)	$(C_6H_5O)_2$P (O) CH=CHP (O) $(OC_2H_5)_2$	c	3.52	••
(XXIV)	CH_3CH=C (CH_3) P (O) $(OC_2H_5)_2$	b	2.85	9
(XXV)	Cl (CH_3) C=CHP (O) $(OC_2H_5)_2$ (*cis*)		3.35	14,15
(XXVI)	Cl (CH_3) C=CHP (O) $(OC_2H_5)_2$ (*trans*)	—	2.92	15
(XXVII)	Cl(t-C_4H_9) C=CHP (O) $(OC_2H_5)_2$ (*cis*)	—	3.51	15
(XXVIII)	Cl(t-C_4H_9) C=CHP (O) $(OC_2H_5)_2$ (*trans*)	—	2.92	15
(XXIX)	Cl (C_6H_5) C=CHP (O) $(OC_2H_5)_2$	—	3.68	14
(XXX)	ClCH=C (CH_3) P (O) $(OC_2H_5)_2$ (*trans*)	—	3.11	15
(XXXI)	Cl (OC_2H_5) C=CHP (O) $(OC_2H_5)_2$ (mixture of *cis* and *trans*)	—	3.54	15
(XXXII)	CH_2=CH—CH=CHP (O) $(OC_2H_5)_2$ (*trans*)	b	3.04	7,8
			2.92	9
(XXXIII)	CH_2=CH—CH=CHP (S) $(OC_2H_5)_2$ (*trans*)	b	2.91	7
(XXXIV)	CH_3CH=CHCH=CHP (O) $(OC_2H_5)_2$ (*trans*)	b	3.07	9
(XXXV)	CH_2=CHC (CH_3)=CHP (O) $(OC_2H_5)_2$ (*cis*:*trans* = 1:1)	b	2.94	9
(XXXVI)	CH_2=CHC (Cl)=CHP (O) $(OC_2H_5)_2$	—	2.84	14
(XXXVII)	C_6H_5CH=CHP (O) $(OC_2H_5)_2$	b	3.68	12,16
		b	3.13	17
		c	3.18	17
(XXXVIII)	C_6H_5CH=CHP (O) Cl_2	c	4.30	17
(XXXIX)	C_6H_5CH=CHP (S) $(CH_3)_2$	b	4.79	12,18
(XL)	C_6H_5CH=CHP (S) $(C_6H_5)_2$	b	4.80	12,18
(XLI)	$(C_6H_5CH$=$CH)_3PS$	b	4.80	12,18
(XLII)	C_6H_5CH=C (CN) P (O) $(OC_2H_5)_2$	c	2.58	8
(XLIII)	*p*-ClC_6H_4CH=CHP (O) $(OC_2H_5)_2$	c	2.87	17
(XLIV)	*p*-ClC_6H_4CH=CHP (O) Cl_2	c	3.14	17
(XLV)	*p*-ClC_6H_4CH=C (CN) P (O) $(OC_2H_5)_2$	c	2.67	8,17
(XLVI)	*p*-BrC_6H_4CH=C (CN) P (O) $(OC_2H_5)_2$	c	2.62	8,17
(XLVII)	*p*-$NO_2C_6H_4CH$=C (CN) P (O) $(OC_2H_5)_2$	b	4.78	8,17

Table 1 (contd.).

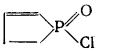
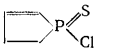
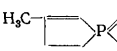
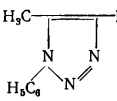
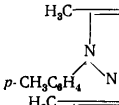
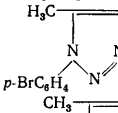
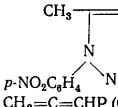
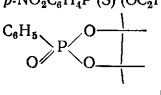
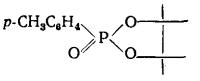
No. of cpd.	Compound	Solvent*	μ, D	References
(XLVIII)	*m*-$NO_2C_6H_4CH$=C (CN) P (O) $(OC_2H_5)_2$	b	4.14	8,17
(XLIX)	*p*-$CH_3OC_6H_4CH$=C (CN) P (O) $(OC_2H_5)_2$	c	3.30	8,17
(L)	*p*-$(CH_3)_2NC_6H_4CH$=C (CN) P (O) $(OC_2H_5)_2$	b	4.08	8,17
(LI)		—	4.69	19
(LII)		—	3.56	19
(LIII)		—	5.37	19
(LIV)		—	4.95	19
(LV)		—	4.58	19
(LVI)		b	4.76	20
(LVII)		b	4.33	20
(LVIII)		b	2.27	20
(LIX)		b	2.42	20
(LX)	CH_2=C=CHP (O) $(OC_2H_5)_2$	b	3.14	9
(LXI)	CH_3CH=C=CHP (O) $(OC_2H_5)_2$	b	3.32	9
(LXII)	$(CH_3)_2C$=C=CHP (O) $(OCH_3)_2$	b	3.46	9
(LXIII)	$(CH_3)_2C$=C=CHP (O) $(OC_2H_5)_2$	b	3.38	9
(LXIV)	CH_2=C=C(CH_3) P (O) $(OCH_3)_2$	b	3.14	9
(LXV)	CH_2=C=C (CH_3) P (O) $(OC_2H_5)_2$	b	3.07	9
	Compounds with a P^V–$C_{sp}2$ (carbonyl) bond			
(LXVI)	CH_3C (O) P (O) $(OC_2H_5)_2$	c	3.10	21
(LXVII)	C_6H_5C (O) P (O) $(OCH_3)_2$	c	2.93	12
(LXVIII)	C_6H_5C (O) P (O) $(OC_2H_5)_2$	c	2.76	21
(LXIX)	C_6H_5C (O) P (O) (C_2H_5) (OC_2H_5)	c	2.44	21
(LXX)	C_6H_5C (O) P (O) (C_6H_5) (OC_2H_5)	c	2.72	21
(LXXI)	C_6H_5C (O) P (O) $(C_2H_5)_2$	c	2.28	21
(LXXII)	C_6H_5C (O) P (O) $(C_6H_5)_2$	b	2.69	21
(LXXIII)	*p*-$CH_3C_6H_4C$ (O) P (O) $(OC_2H_5)_2$	c	2.88	21
(LXXIV)	*p*-$CH_3OC_6H_4C$ (O) P (O) $(OC_2H_5)_2$	c	3.35	21
(LXXV)	*p*-FC_6H_4C (O) P (O) $(OC_2H_5)_2$	c	2.73	••
(LXXVI)	*p*-ClC_6H_4C (O) P (O) $(OC_2H_5)_2$	c	2.79	21
(LXXVII)	*o*-ClC_6H_4C (O) P (O) $(OC_2H_5)_2$	c	3.11	21
(LXXVIII)	(*m*-ClC_6H_4C (O) P (O) $(OC_2H_5)_2$	c	2.77	21
(LXXIX)	(*p*-BrC_6H_4C (O) P (O) $(OC_2H_5)_2$	c	2.80	21
(LXXX)	(*m*-BrC_6H_4C (O) P (O) $(OC_2H_5)_2$	c	2.88	21
(LXXXI)	(*p*-$NO_2C_6H_4C$ (O) P (O) $(OC_2H_5)_2$	b	4.84	21
(LXXXII)	$(C_2H_5)_2NC$ (O) P (O) $(OC_2H_5)_2$	b	2.91	12,22
		—	2.93	12
(LXXXIII)	$(C_2H_5)_2NC$ (O) P (O) $(OC_3H_7)_2$	b	3.02	12,22
(LXXXIV)	$(C_2H_5)_2NC$ (O) P (O) $(OC_3H_7$-iso$)_2$	b	2.88	12,22
(LXXXV)	$(C_2H_5)_2NC$ (O) P (O) $(OC_4H_9)_2$	b	3.09	12,22
(LXXXVI)	$(C_2H_5)_2NC$ (O) P (O) $(OC_6H_{11}$-iso$)_2$	b	2.92	12,22
(LXXXVII)	$(C_2H_5)_2NC$ (O) P (O) $(OC_6H_{13})_2$	b	2.94	12,22
	Compounds with a P^V–$C_{sp}2$ (aryl) bond			
(LXXXVIII)	C_6H_5P (O) $(OCH_3)_2$	c	2.95	23
(LXXXIX)	C_6H_5P (O) $(OC_2H_5)_2$	c	3.04	24
(XC)	C_6H_5P (O) Cl_2	c	3.99	24
(XCI)	*p*-$CH_3C_6H_4P$ (O) $(OCH_3)_2$	c	3.37	23
(XCII)	*p*-$CH_3C_6H_4P$ (O) $(OC_2H_5)_2$	c	3.23	24
(XCIII)	*p*-$CH_3OC_6H_4P$ (O) $(OCH_3)_2$	c	3.39	23
(XCIV)	*p*-$CH_3OC_6H_4P$ (O) $(OC_2H_5)_2$	c	3.31	24
(XCV)	*p*-ClC_6H_4P (O) $(OCH_3)_2$	c	2.63	23
(XCVI)	*p*-ClC_6H_4P (O) $(OC_2H_5)_2$	c	2.83	24
(XCVII)	*p*-BrC_6H_4P (O) $(OC_2H_5)_2$	c	2.81	24
(XCVIII)	*p*-$NO_2C_6H_4P$ (S) $(OC_2H_5)_2$	b	4.98	12
(XCIX)		c	5.18	25
(C)		c	5.13	25

Table 1 (contd.).

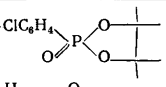
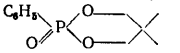
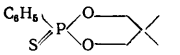
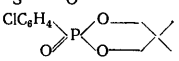
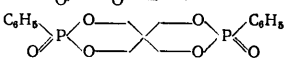
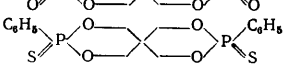
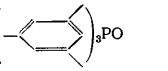
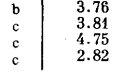
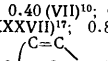
No. of cpd.	Compound	Solvent*	μ, D	References
(CI)		c	5.32	25
(CII)		b c d	4.59; 5.73 4.36; 4.51 4.96	25,26 25,27 27
(CIII)		d	4.21	27
(CIV)		c	4.46	25
(CV)		d	3.82	27
(CVI)		d	3,28	27
(CVII)	$C_6H_5(CH_3)P(O)OCH_3$	b c	3.79—3,82 3.80	28 29
(CVIII)	$C_6H_5(CH_3)P(O)OC_6H_5$	c	3.88	29
(CIX)	$C_6H_5(CH_3)P(O)OC_6H_4NO_2$-*n*	c	6.25	29
(CX)	*p*-$ClC_6H_4(CH_3)P(O)OCH_3$	b	3.06—3.10	28
(CXI)	*p*-$CH_3C_6H_4P(O)(CH_3)_2$	c	4,30	30
(CXII)	*p*-$CH_3C_6H_4P(O)(C_4H_9$-*t*$)_2$	c	4.85	30
(CXIII)	*p*-$CNC_6H_4P(O)(CH_3)_2$	d	4.60	30
(CXIV)	$(C_6H_5)_2P(O)OC_2H_5$	b	3.65—3.70	28
(CXV)	$(C_6H_5)_2P(S)SCH_3$	b	4.01—4.06	31
(CXVI)	$(C_6H_5)_2P(S)SSP(S)(C_6H_5)_2$	b	4.18—4.26	31
(CXVII)	*p*-$ClC_6H_4)_2P(O)OC_2H_5$	b	3.12—3.18	28
(CXVIII)	*p*-$ClC_6H_4)_2P(S)SCH_3$	b	2.89—2.96	31
(CXIX)	*p*-$ClC_6H_4)_2P(S)SSP(S)(C_6H_4Cl$-*n*$)_2$	b	2.28—2.46	31
(CXX)	*p*-$ClC_6H_4)_2P(S)SH$	b	2.62—2.70	31
(CXXI)	$(C_6H_5)_2P(O)CH_2CN$	b	3.76	32
(CXXII)	$(C_6H_5)_2P(O)CCl_3$	c	3.81	33
(CXXIII)	*p*-$CH_3C_6H_4)_2P(O)CCl_3$	c	4.75	33
(CXXIV)	*p*-$ClC_6H_4)_2P(O)CCl_3$	c	2.82	33
	Symmetrical triarylphosphine oxides			
(CXXV)	$(C_6H_5)_3PO$	*p*-x b d	4.403 4.49; 4.44; 4.42; 4.53 4.55	12 12,34, 35,36,37 12
(CXXVI)	$(C_6H_5)_3PS$	b c	4.89; 4.79; 4.83 3.14	12,37,38 35
(CXXVII)	*p*-$ClC_6H_4)_3PO$	b	2.95; 3.01	12,37
(CXXVIII)	*p*-$ClC_6H_4)_3PS$	b	3.14	37
(CXXIX)	*m*-$ClC_6H_4)_3PO$	b c	4.41 4.78	37 35
(CXXX)	*m*-$ClC_6H_4)_3PS$	b	4.60	37
(CXXXI)	*p*-$FC_6H_4)_3PO$	b	2.98	37
(CXXXII)	*p*-$FC_6H_4)_3PS$	b	3.23	37
(CXXXIII)	*m*-$FC_6H_4)_3PO$	b	4.30	37
(CXXXIV)	*m*-$FC_6H_4)_3PS$	b	4.51	37
(CXXXV)	*p*-$CH_3C_6H_4)_3PO$	c	5.02	35
(CXXXVI)	*m*-$CH_3C_6H_4)_3PO$	b c	4.88 4.57	36 35
(CXXXVII)		b	4.18	36
	Asymmetric triarylphosphine oxides			
(CXXXVIII)	$(C_6H_5)_2P(O)C_6H_4OCH_3$-*p*	d	4.83	12
(CXXXIX)	$(C_6H_5)_2P(S)C_6H_4OCH_3$-*p*	d	5.19	12
(CXL)	$(C_6H_5)_2P(O)C_6H_4Cl$-*p*	d	4.37	12
(CXLI)	$(C_6H_5)_2P(S)C_6H_4Cl$-*p*	d	4.84	12
(CXLII)	$(C_6H_5)_2P(O)C_6H_4Br$-*p*	d	4.57	12
(CXLIII)	$(C_6H_5)_2P(S)C_6H_4Br$-*p*	d	4.71	12
(CXLIV)	$(C_6H_5)_2P(O)C_6H_4N(CH_3)_2$-*p*	d	5.71	12
(CXLV)	$(C_6H_5)_2P(S)C_6H_4N(CH_3)_2$-*p*	d	6.42	12
	Compounds with a P^V–C_{sp} bond			
(CXLVI)	$HC{\equiv}CP(O)(OC_2H_5)_2$	b	3.64; 3.86	39,40
(CXLVII)	$CH_3C{\equiv}CP(O)(OC_2H_5)_2$	c b	3.69 3.78; 3.94	40 12,39,40
(CXLVIII)	$CH_3C{\equiv}CP(O)(OC_4H_9)_2$	b	3.93	12,41
(CXLIX)	$CH_3C{\equiv}CP(S)(CH_3)_2$	b	4.90	42
(CL)	$CH_3C{\equiv}CP(O)(C_2H_5)_2$	c	4.59	40
(CLI)	$CH_3C{\equiv}CP(O)(C_6H_5)_2$	c	4.48	40
(CLII)	$CH_3C{\equiv}CP(O)Cl_2$	c	3.92	40
(CLIII)	$ClC{\equiv}CP(O)(OC_2H_5)_2$	b	3.44; 3.54	39,40
(CLIV)	$BrC{\equiv}CP(O)(OC_2H_5)_2$	b	3.66	39
(CLV)	$(C_2H_5)_2NC{\equiv}CP(O)(OC_2H_5)_2$	— b	5.06 3.71	43 **
(CLVI)	$CH_2{=}CHC{\equiv}CP(O)(OC_2H_5)_2$	b	3.88	44
(CLVII)	$CH_2{=}CHC{\equiv}CP(S)(CH_3)_2$	b	4.73	42
(CLVIII)	$CH_2{=}C(CH_3)C{\equiv}CP(O)(OC_2H_5)_2$	b	3.84	44
(CLIX)	$CH_3CH{=}CHC{\equiv}CP(O)(OC_2H_5)_2$	b	4.06	12,44
(CLX)	$C_2H_5C{\equiv}CC{\equiv}CP(O)(OC_2H_5)_2$	b	4.39	16
(CLXI)	$C_6H_5C{\equiv}CP(O)(OC_2H_5)_2$	b	4.17	12,16
(CLXII)	$C_6H_5C{\equiv}CP(S)(CH_3)_2$	b	4.91	12,42
(CLXIII)	$(CH_3C{\equiv}C)_2P(O)CH_3$	b	4.98	12,42
(CLXIV)	$(C_6H_5C{\equiv}C)_2P(O)CH_3$	b	5.18	12,42

Table 1 (contd.).

No. of cpd.	Compound	Solvent*	μ, D	References
(CLXV)	$(C_6H_5C{\equiv}C)_2P(S)CH_3$	b	5.14	12,42
(CLXVI)	$(C_6H_5C{\equiv}C)_2P(S)C_6H_5$	b	5.20	12,42
(CLXVII)	$(C_6H_5C{\equiv}C)_2P(S)CH{=}CHC_6H_5$	b	5.12	12,42
(CLXVIII)	$(CH_3C{\equiv}C)_3PS$	b	5.20	42
(CLXIX)	$(C_6H_5C{\equiv}C)_3PS$	b	5.32	42
(CLXX)	$(p$-$CH_3C_6H_4C{\equiv}C)_3PS$	b	5.47	42
(CLXXI)	$[o,p$-$(CH_3)_2C_6H_3C{\equiv}C]_3PS$	b	5.78	42

*Solvent: b = benzene; c = carbon tetrachlorides; d = dioxan; *p*-x = *p*-xylene.
**Data of the author of the review.

Table 2. The dipole moments (in D) $m(C_{sp^3}-P)$, $m(C_{sp^2}-P)$, and $m(C_{sp}-P)$.

Bond	Without allowance for the P atom LEP dipole moment	With allowance for P atom LEP dipole moment
$C_{sp^3}-P$	0.55 (Me_3P)[45–46]; 0.81 (Et_3P)[8]; 0.94 (Et_2POEt)[50]; 1.11* (Et_3P)[47]; —0.7 (av.)[48]	—0.1  [49]
C_{sp^3} (olefin)-P	0.30 (V)[11]; 0.37 (VI)[11]; 0.40 (VII)[10]; 0.56 (I)[6]; 0.60 (IV)[10]; 0.82 (XXXVII)[17]; 0.83 (III)[11]; —0.09 (VIII)[10]; —0.9  [48]	—0.7  [49]
C_{sp^3} (phenyl)-P	0.38—0.39 (Ph_3P)[21,37,47]; 0.69 (XC)[24]; 0.70 (LXXXIX)[24]; 0.7** (Ph_3P)[50]; 1.40*** from data in Ref.31	—0.4 (Ph_3P)[49]
$C_{sp}-P$	—0.20 (CL)[40]; —0.30 (CLII)[40]; —0.30 (av.)[40]; —0.43 (CLI)[40]; ~—0.7 (av.)[48]	—1.3  [49]

*The authors [17] evidently have in mind the group moment of the Et–P bond, so that $m(C_{sp^3}-P) = 1.11-0.28 = 0.83$ D.
**Here it is assumed that $m(H-C_{sp^2}) = 0.31$ D.
***Here $m(H-C_{sp^2}) = 0$; in all other instances the authors employed the values of $m(H-C)$ quoted by Gribov and Popov [3].

The $C_{sp^2}-P$ bond moments are subject to the particularly strong influence of the substituents both at the phosphorus atom and in the unsaturated group (there are very few data for $C_{sp}-P$ bonds). An additional illustration of the foregoing considerations is provided by the experimental dipole moments of the following compounds: 2.91–2.95 D [7–9] for (I), 2.92–3.04 D [7–9] for (**XXXII**), and 3.13–3.18 D [17] and 3.68 D [16] for (**XXXVII**). With increase of the length of the π-electron system at the phosphorus atom, the experimental dipole moment increases, although calculation based on the additive scheme yields the same value for different compounds. The conjugation in buta-1,3-dienylphosphonates, buta-1,3-dienylphosphonothioates [8,52], and styrylphosphonates [53,54] (in which the C=C and P=O groups are in the *trans*-positions) has been detected by infrared and Raman spectroscopic methods. Consequently a theoretical calculation of the dipole moments of unsaturated OPC using the same value of $m(C_{sp^2}-P)$ is possible only for compounds with analogous structures. $m(R-P)$ (where R is an unsaturated group), which is equal

to the sum of the $R'-C_{sp^2}$ and $C_{sp^2}-P$ bond moments, the conjugation moment of the π-electron system incorporating the phosphorus atom, and the interaction moment arising when substituents ($R' = H$, CH_3, etc.) are introduced into the π-electron system, may be calculated with the aid of data for model compounds for each series of unsaturated OPC:

$$m(R-P) = m(R'-C_{sp^2}) + m(C_{sp^2}-P) + m_{conjug.} + m_{interact.}$$

The conjugation moment and the intrinsic moment of the $C_{sp^2}-P$ bond cannot be calculated separately; the instances where it is possible to isolate the interaction moments will be discussed below. Thus the $C_{sp^2}-P$ bond moments determined are not the true moments, representing effective quantities which include the conjugation moment and frequently also the interaction moment. However, these moments may be used to estimate the conjugation effects in series of analogous compounds when only one end of the conjugated system is altered.

An additional difficulty in the study of unsaturated phosphonates is the necessity to know the magnitude and direction of the dipole moment of the irregular $P(O)(OR)_2$ group. The latter had been calculated by Mingaleva et al.[48], but was subsequently re-evaluated, for reasons stated, by Ishmaeva et al.[8] (2.30 D was obtained). The vector of the effective dipole moment of this group forms an angle of 72° with the C–P bond, which corresponds to the *gauche*-orientation (with some distortion in the direction of *cis*-orientation) of the ethyl groups in relation to the P–O bond.

Table 3. The effective values of $m(C_{sp^2}-P)$ in phosphonates[8,17].

Compound	$m(C_{sp^2}\rightarrow P)$, D
(I)	0.56
(XXXII)	0.70
(LXXXVIII)	0.69
(XXXVII)	0.82

The determination of the magnitude and direction of the effective dipole moment of the dialkylphosphono-group made it possible to estimate the effective $C_{sp^2}-P$ bond moments in various unsaturated phosphonates (Table 3). The high $P-C_{sp^2}$ bond moments, with the moment directed towards the carbon atom, which are obtained on solving a quadratic equation, can apparently be excluded from consideration, since these data do not agree with the electronegativities of the C and P atoms and also conflict with ideas concerning the polarity of single bonds involving phosphorus. Table 3 shows that the C–P bond moments in unsaturated phosphonates unsubstituted in the π-electron system vary relatively little (~0.6–0.8 D).

The $C_{sp^2}-P$ bond orders in vinylphosphine oxides and sulphides vary within wide limits (Table 4). The effective $C_{sp^2}-P$ bond orders in compounds (III)–(VI), listed in Table 4, can be satisfactorily accounted for by steric effects and are consistent with the ideas concerning the electronic influence of phosphorus-containing substituents[55]. The variation of the $C_{sp^2}-P$ bond moment may serve as evidence for the variation of conjugation in the π-electron system. Accordingly, one may expect a higher value of $m(C_{sp^2}-P)$ for buta-1,3-dienylphosphonate (XXXII) than for vinylphosphonate (I) and a higher value for styrylphosphonate (XXXVII) than for phenylphosphonate (LXXXIX), which is in fact observed (Table 3). The determination of the effective values of $m(C_{sp^2}-P)$ made it possible to estimate the moments of the interaction of the vinyl and phenyl groups with the diethylphosphono-group in esters of buta-1,3-dienyl- and styryl-phosphonic acids, which are respectively 0.14 and 0.23 D.[17] Evidently there is some electron transfer in the π-electron system, which leads to the orientation of the overall moment of the hydrocarbon groups towards the phosphorus atom. The moment of the interaction with the sulphur-containing compound (XXXIII) also proved to be close to these values (0.20 D). The interaction moment obtained for compound (XLIII) (1.12 D) indicates an appreciable involvement of the phosphorus-containing group in the direct polar conjugation of the overall chain.

Table 4. The effective values of $m(C_{sp^2}-P)$ in vinylphosphine oxides and sulphides[10-11].

Cpd.	$m(C_{sp^2}\rightarrow P)$, D	Cpd.	$m(C_{sp^2}\rightarrow P)$, D
(III)	0.83	(V)	0.30
(IV)	0.60	(VII)	0.40
(VI)	0.37	(VIII)	−0.09

The interaction moments may be determined also for *p*-substituted phenylphosphonates (Table 5). The values calculated for them do not agree with experiment, which is due to the interaction of the *p*-substituents in the phenyl group with the $P(O)(OR)_2$ group. The interaction moments directed along the $C_{sp^2}-P$ bond reach values ≥ 1 D, which indicates an appreciable involvement of the phosphorus-containing fragment in the overall conjugation chain. An excellent correlation has been found ($r = 0.999$) between the experimental dipole moments of *p*-substituted phenylphosphonates and the Hammett σ constants, which indicates an interaction involving conjugation. The experimental dipole moments of *p*-substituted benzoylphosphonates[21] exceed the calculated values by 0.6–0.7 D. Although it is not possible to separate the influence of the C–O and P–O groups and to calculate the interaction moments, nevertheless, the significant influence of the phosphorus-containing group in this instance may be recognised. It follows from the fact that the interaction moment in *p*-methoxyacetophenone is only 0.24 D while in *p*-chloro- and *p*-bromo-acetophenones the experimental values are actually somewhat lower than those calculated assuming additivity. This conclusion is confirmed by the results obtained in infrared and ultraviolet spectroscopic studies on benzoylphosphonates[56-64].

Thus the π-electron system in the unsaturated OPC investigated interacts with the phosphorus-containing groups. The problem of the involvement in conjugation of the tetrahedral phosphorus atom has been frequently discussed in the literature[7,16,21,24,52-54,56,65-74]. It has been suggested that the conjugation is both of the $\pi-\pi$ and $p\pi-d\pi$ type, but the mechanism of the interaction of unsaturated systems with phosphorus-containing groups still cannot be regarded as accurately established. The

hypothesis of the $p_\pi - d_\pi$ interaction in these systems, widely used by chemists, has been questioned[75], because the *d* orbitals of the phosphorus atom are fairly diffuse and energetically unsuitable and their appreciable overlapping with the orbitals of the groups attached to phosphorus is unlikely, i.e. the quantitative aspect of the problem of the role of the $p_\pi - d_\pi$ interaction remains controversial[6]. There is nevertheless no doubt that electron delocalisation takes place in OPC molecules containing unsaturated groups with participation of the phosphorus atom or the entire phosphorus-containing group, which the present author attempted to demonstrate by the dipole moment method.

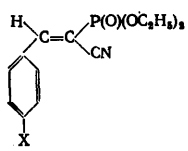
Table 5. The dipole moments of p-$XC_6H_4P(O)(OC_2H_5)_2$.[24]

Compound	X	μ_{exp}, D	μ_{calc}, D	m_{react}, D
(XCII)	CH_3	3,23	3.30	—0,10
(XCVI)	Cl	2,83	2,25	1.27
(XCVII)	Br	2.81	2,26	1,22
(XCIV)	CH_3O	3.31	3,21	0,98

III. THE STERIC ORIENTATION OF THE DOUBLE BOND AT THE PHOSPHORUS ATOM

Another important task in the study of unsaturated OPC is investigation of their steric structure. There are very few electron diffraction or X-ray diffraction literature data for these compounds (see reviews[4-6]) and they are mainly concerned with compounds containing a $P-C_{sp^2}$ bond (phenyl) (see, for example, Refs. 76-80). There have been several studies on compounds with a $P-C_{sp^2}$ (olefin) bond[81-83] and acyclic OPC with a $P-C_{sp^2}$ (olefin) bond have been investigated in only one study[82] in relation to vinylphosphonic dichloride and divinylphosphinic chloride. It has been shown[82] that the main conformation of both compounds is one with the *cis*- (or nearly *cis*-) disposition of the C=C and P=O bonds, which are virtually coplanar. There is also other evidence for the preferential disposition of the C=C and P=O bonds in a single plane[52,84,85].

The dipole moment method is important and fairly reliable for the determination of the configurations of unsaturated OPC. For example, it has been established by the dipole moment method, in agreement with NMR data[86], that the benzene ring and the diethylphosphono-group in α-cyanostyrylphosphonates are in the *trans*-positions[17] (Table 6):



Furthermore, the dipole moment method makes it possible to investigate the conformational isomerism relative to the $P-C_{sp^2}$ and other bonds involving phosphorus (P–O, P–S, P–Se, etc.). Estimation of the polarity of the $P-C_{sp^2}$ bond in styrylphosphonic acid esters made it possible to assess the conformational isomerism of α-cyanostyrylphosphonates, i.e. to examine the rotation about the $P-C_{sp^2}$ (olefin) bond[17]. The presence of the cyano-group in these compounds is responsible for the different polarities of the *s-cis*- and *s-trans*-conformers:

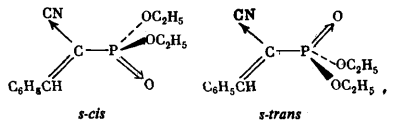


Table 6. The dipole moments of p-$XC_6H_4CH=C(CN)P(O)(OC_2H_5)_2$.[17]

Compound	X	μ_{exp}, D	μ_{calc}, D	
			trans	*cis*
(XLV)	Cl	2.67	2,73	1.99
(XLVI)	Br	2.62	2.74	1.96
(XLVII)	NO_2	4.78	4.53	3.40

Comparison of the dipole moments calculated for the two conformers with the experimental dipole moment of diethyl-α-cyanostyrylphosphonate (XLII) indicates the preferential (approximately 80%) occurrence of the *s-cis*-form, i.e. the conformer with the antiparallel direction of the dipoles of the substituents (CN and P=O). The conformational isomerism in relation to the $P-C_{sp^2}$ bond in α- and β-substituted vinylphosphonates has been investigated[10,11]:

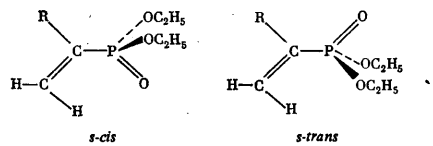


Table 7. The dipole moments of $CH_2=C(R)P(O)(OC_2H_5)_2$.[11]

Compound	R	μ_{exp}, D	μ_{calc}, D		
			s-trans	*s-cis*	n_{s-cis}, %
(IX)	CH_3	2.90	2.86	3.30	10
(X)	CN	3.51	5.24	0.88	60
(XI)	Br	2,59	3.64	1.60	60

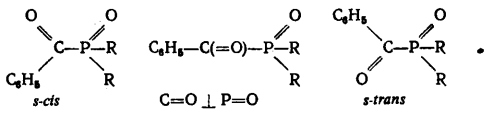
Table 7 presents the experimental and calculated dipole moments of α-substituted vinylphosphonates. The tabulated data show that the conformer with the antiparallel directions of the dipoles is more stable in all the compounds. The preferred *s-trans*-form of α-methylvinylphosphonic dichloride has also been detected by infrared spectroscopy[87]. The *s-cis*–*s-trans* isomerism of vinylphosphonates with an irregular substituent in the β-position

and a non-uniform distribution of conformations can likewise be investigated, since the dipole moments of the two isomers are different. According to ^{1}H NMR data[13], the RO and P=O groups in β-alkoxyvinylphosphonates are in the *trans*-positions relative to the C=C bond. Comparison of the calculated and experimental dipole moments of these compounds (Table 8) shows that the conformer with the *s-trans*-disposition of the C=C and P=O bonds predominates in all the compounds[13].

Table 8. The dipole moments of $C_4H_9OCH{=}CHP(O)R_2$.[13]

Compound	R	μ_{exp}, D	μ_{calc}, D		n_s-trans, %
			s-trans	*s*-cis	
(XVII)	OC_2H_5	3.41	3.46	3.97	100
(XXII)	Cl	4.46	4.39	4.92	90
(XXI)	C_6H_5	4.36	4.18	4.70	70

The isomerism relative to the $P-C_{sp^2}$ (carbonyl) bond has been investigated for benzoylphosphine oxides as an example[21]. The latter are convenient subjects for the examination of rotation about the $P-C_{sp^2}$ bond in contrast to the unsubstituted vinyl- and buta-1,3-dienyl-phosphonates, where the polarities of the *s-cis*- and *s-trans*-conformers are independent of rotation about the bond. There is as yet no unanimous view in the literature concerning the relative positions of the C=O and P=O groups. A structure with the C=O and P=O groups in mutually perpendicular planes has been suggested[88]. According to other data[67], a planar disposition of the π-electron system and the P=O bond is the most favourable; in this case there is a possibility of two rotational isomers with the *s-cis*- and *s-trans*-dispositions of the C=O and P=O groups:



s-cis *s-trans*

Table 9 presents the experimental and calculated dipole moments of benzoyldiethylphosphine oxide (LXXI) and benzoyldiphenylphosphine oxide (LXXII).[21] If the C=O and P=O groups were located in mutually perpendicular planes, the experimental dipole moments of (LXXI) and (LXXII) would be close to 4.59 D, whereas in fact they are consistent with an equilibrium between *s-cis*- and *s-trans*-forms, where the content of the latter is approximately 90–95%. When the experimental and calculated dipole moments of benzoylphosphinates[21] are examined, the *s-trans*-conformation also proves to be preferred (approximately 90–95%), i.e. there is virtually no rotation about the $C_{sp^2}-P$ bond. It is noteworthy that the strong dipoles of the substituting groups in the preferred conformations (C≡N and P=O, C=O and P=O) are oriented antiparallel, which indicates a significant influence of electrostatic factors on the steric structure. There is a conformational equilibrium in benzoylphosphonates between the *s-cis*- and *s-trans*-forms, with the latter predominating slightly (~60%).[21]

The conclusion that the O=C–P=O system is not rigid has been questioned[89]. The authors[89] studied benzoylphosphonates by infrared spectroscopy and concluded that there is no rotation about the $P-C_{sp^2}$ bond, because the absorption band of the carbonyl group is not split. The *s-trans*-form (which predominates for benzoylphosphinates and benzoylphosphine oxides also according to dipole moment data) has been suggested as the only isomer of these compounds. If it is supposed that there is a non-planar *gauche*-disposition of the C=O and P=O groups in benzoylphosphonate (LXVIII), the dipole moment calculated for this form is found to be close to the experimental value. However, the occurrence of this form has been rejected[89].

Table 9. The dipole moments of benzoyldiethylphosphine oxide and benzoyldiphenylphosphine oxide[21].

Compound	μ_{exp}, D	μ_{calc}, D			n_s-trans, %
		s-cis	C=O ⊥ P=O	*s-trans*	
(LXXI)	2.28	6.25	4.59	1.73	95
(LXXII)	2.69	6.25	4.59	1.73	90

The available literature data concerning the mutual disposition of the C=O and P=O groups in benzoylphosphonates[21,88,89] are probably insufficient for a final conclusion. At any rate, the absence of the splitting of the ν(C=O) band is not adequate evidence for the rigidity of the O=C–P=O system, because the forms involved in equilibrium may have similar spectroscopic characteristics, and may be indistinguishable in the infrared spectra. Nor can one explain the difference between the calculated dipole moment (0.78 D)[21] of the *s-trans*-form of benzoylphosphonate (LXVIII) and the experimental value (3.10 D) by a deviation from additivity owing to the interactions of the carbonyl and phosphoryl groups (as was done by Laskorin et al.[89]). Experiment showed that, even in the presence of direct polar conjugation, the difference between the experimental and calculated dipole moments does not exceed 1–1.5 D. Furthermore, an analogous interaction occurs also in benzoylphosphine oxide and benzoylphosphinates, for which the results obtained by the dipole moment and infrared spectroscopic methods are virtually identical. It would be very useful to apply another independent method to this problem.

IV. THE CONFORMATION OF ARYL DERIVATIVES OF FOUR-COORDINATED PHOSPHORUS

The internal rotation of the hydrocarbon groups does not affect the magnitude and direction of the molecular dipole moment in terms of the approximation of the additive scheme. Their steric orientation may be established on the basis of molar Kerr constants (*mK*).[2] The first compound with the $C_{sp^2}-P^V$ bond investigated by this method was triphenylphosphine oxide[38]. The additive scheme for the anisotropy of the phosphorus bond polarisability has been analysed[2]. The available literature data show that one aryl group linked to the phosphorus atom (both tervalent and quinquevalent)[76,91] is located in the plane incorporating the axis of the CPX_2 (X = R or Hal) pyramid,

i.e. is coplanar with the hybridised LEP of the phosphorus atom or with the phosphoryl group (Fig. 1).

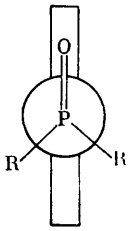


Figure 1. Conformation of dialkylarylphosphine oxides [91].

However, the aryl group in *p*-substituted arylphosphonates [23] is to a large extent displaced from the C_{sp^2}–P–O plane. Two regions of energetically favourable positions with rotation away from this plane to one side or the other ($\varphi = \pm 50°$), resembling the eclipsing of single P–O bonds (Fig. 2), have been observed for this group. It is of interest that, in the study of complexes of *O,O*-diethyl phenylphosphonite with different metals, a non-planar structure was also discovered ($\varphi = 55–75°$). [92] Thus the conjugation in *p*-substituted arylphosphonates [24] apparently cannot be of the $\pi-\pi$ type and is better explained by a $p\pi-d\pi$ interaction. The conjugation between the phenyl and P=O groups has been confirmed by a study of the infrared spectra of cyclohexylphenylphosphine oxides. [93] The rotation about the P–C_{sp^2} (phenyl) bond in 2-oxo-(thiono)-2-phenyl-1,3,2-dioxaphosphorinanes (CII) and (CIII) and their spiro-analogues (CV) and (CVI) has been investigated [27], and it has been found that the conformer with an equatorial phenyl group predominates in these compounds (80%), the plane of the benzene ring being parallel to the LEP of the phosphorus atom or the P=O and P=S bonds. The plane of the benzene ring in the conformer with an axial phenyl group is perpendicular to the molecular symmetry plane in derivatives of both three- and four-coordinated phosphorus.

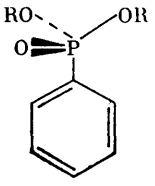


Figure 2. Orientation of the aryl fragment in *O,O*-dialkyl arylphosphonates [23].

The rotation of two aryl groups in OPC has been examined in relation to propynyl and trichloromethyldiphenylphosphine oxides [33,40]. The angular variation of the calculated Kerr constant for compound (CLI) is very pronounced (Fig. 3), which made it possible to determine the conformation of this compound with a high accuracy.

Owing to their linearity, the P=O bond and the P–C≡C group gives rise to the same steric hindrance to the rotation of substituents at the phosphorus atom; nevertheless a structure obtains in which the planes of the phenyl groups nearly eclipse the C≡C bond.

The experimental values of mK for diphenyltrichloromethylphosphine oxide (CXXII), trichloromethylditolylphosphine oxide (CXXIII), and di-*p*-chlorophenyltrichloromethylphosphine oxide (CXXIV) [33] correspond to the values calculated for an angle of rotation of 15°. Hence the conclusion that the conformations of the molecules investigated are close to the sterically least hindered conformation in which the plane of each aromatic ring is perpendicular to the C_{sp^2}–P–C_{sp^2} plane with a possible deviation by an angle up to 15°, which leads to the eclipsing of the phosphoryl group. The conformation established by Ishmaeva et al. [33] was explained by a balance between the energies of the steric interactions of the hydrogen atom in the *o*-position, within the pyramid formed by phosphorus bonds, with the analogous hydrogen atom in a neighbouring aryl group, on the one hand, and the trichloromethyl group, on the other. Thus the benzene rings in propynyl- and trichloromethyl-diphenylphosphine oxides are rotated by a small angle in different directions from the same initial position. However, in principle, similar results have been obtained for these compounds, i.e. the replacement of the linear propynyl group by the bulky trichloromethyl group has little influence on the conformations of the compounds.

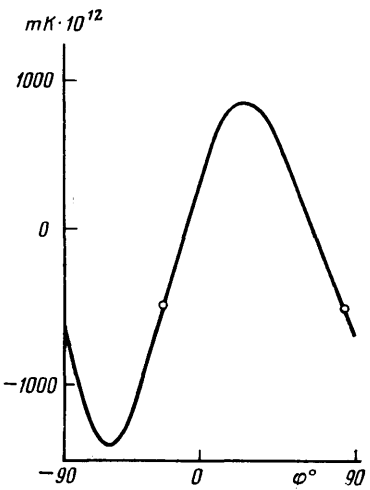


Figure 3. Conformational dependence of the Kerr constant for diphenylpropynylphosphine oxide (CLI) [40] (the circles on the curves represent experimental values).

The rotation of three aryl groups in triarylphosphine oxide molecules has been investigated [35,38,94]. Comparison of the experimental mK and the values calculated on the assumption of C_3 symmetry for unsubstituted triphenylphosphine oxide (CXXV) and its *p*-chloro-derivative (CXXVII), *m*-chloro-derivative (CXXIX), *p*-methyl-derivative (CXXXV), and *m*-methyl-derivative (CXXXVI) [35]

led to the following angles of rotation of the benzene ring: 55°, 65°, 49°, 60°, and 52° respectively (Fig. 4). The halogen atom and the methyl group in the *p*-position lead to some flattening of the molecules compared with unsubstituted triphenylphosphine oxide. The authors [35] suggest that this may be accounted for from the standpoint of the $p_\pi - d_\pi$ conjugation of aromatic rings with the phosphorus atom. The possibility of a similar interaction has been pointed out in other studies [95,96].

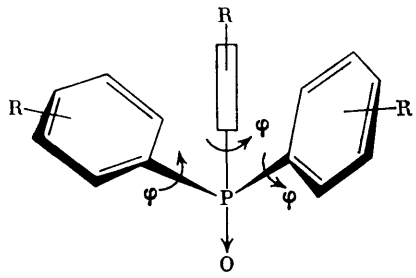


Figure 4. The conformation of triarylphosphine oxides [35].

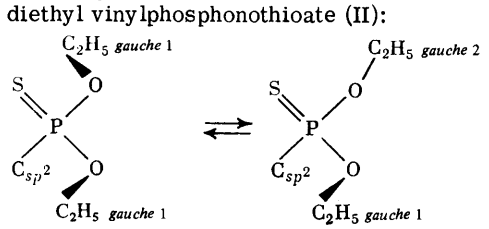
The data concerning the barriers to the rotation about the C_{sp^2}–P bonds are scanty. The rotational barriers have been estimated [87,97] from the torsional vibration frequencies of compounds (VII) and (XC): V = 4–6 kcal mole^{-1}.

V. CONFORMATIONAL ISOMERISM IN RELATION TO SINGLE BONDS IN UNSATURATED ORGANOPHOSPHORUS COMPOUNDS

It is now well known that, on rotation about single bonds in compounds of four-coordinated phosphorus, the *gauche*- or *trans*-form predominates [98–105], regardless of the bond (P–O, P–S, or P–Se) about which rotation takes place. Significant differences between compounds containing one, two, or three [106] irregular groups have not been observed. The same forms as in 2-alkoxy (methylthio, methylseleno)-2-oxo(thiono)-1,3,2-dioxaphosphorinanes [100,102,105] are produced in acyclic derivatives [104].

Data concerning conformational isomerism in relation to single bonds in unsaturated OPC are still very few [10,40]. However, they too indicate the preferred *gauche*- or *trans*-orientation to the alkyl and P=O or P=S group.

It has been found [10] that conformational equilibrium between two forms with the *gauche*-orientation of the alkyl and P=S groups (apparently with some distortion owing to a tendency towards the formation of the *cis*-form) obtains in diethyl vinylphosphonothioate (II):



As for diethyl ethynylphosphonate (CXLVI) and propynylphosphonate (CXLVII), the experimental dipole moments agree with the values calculated for structures with the *gauche*-disposition of the alkyl and P–O groups [39].

The study of the rotation about the C_{sp^3}–P bond in diethylpropynylphosphine oxide (CL) by the method based on the Kerr effect [40] led to the conclusion that the C–CH_3 bonds in the ethyl groups are only in the *gauche*-positions relative to the P=O group (Fig. 5). The experimental value $mK = -176 \times 10^{-12}$ for (CL) is rigorously consistent with calculations for the $gauche_1$, $gauche_1$-conformation (-180×10^{-12}) and the $gauche_1$, $gauche_2$-conformation (-178×10^{-12}). Analogous data for the structures of irregular methoxy-groups have been obtained for arylphosphonates [23]. A conformational equilibrium of the two forms of the above compounds has been demonstrated by infrared spectroscopy. These forms have been identified by the dipole moment method; the calculated and experimental data were treated by Exner's method [107], which led to the conclusion that the *gauche*-orientation of the methyl and P=O groups is preferred, with some distortion (up to 20°) towards the *cis*-form. The possibility, in principle, of such distortion has been confirmed also by quantum-chemical calculations [108].

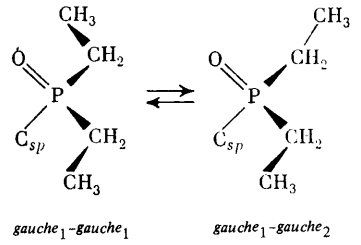


Figure 5. The orientation of the methyl groups and the P=O bond in the molecule of diethylpropynylphosphine oxide (CL). [40]

The rotation about the P–O bond in alkyl and aryl methylphenyl- and diphenyl-phosphinates [28,29] leads to conformers with the *gauche*-orientation of the alkyl or phenyl and phosphoryl groups. It is believed [28] that the increment in the refraction of the C_6H_5–P^V group (1.0 cm^3) arises owing to the conjugation of the benzene ring with the P=O group, while the second benzene ring, linked to the phosphorus atom, does not give rise to an analogous effect [28]. The *gauche*-orientation is preferred also in the esters of diphenylphosphinodithioic acid (CXI), di(*p*-chlorophenyl)phosphinodithioic acid (CXIV), [31] and di(*p*-chlorophenyl)phosphinodithioic acid (CXVI). [31]

Thus rotation about single P–O, P–S, and P–C_{sp^3} bonds in unsaturated OPC containing a four-coordinated phosphorus atom obeys rules common to organophosphorus compounds.

Summarising the discussion of the steric and electronic structures of unsaturated OPC with a four-coordinated phosphorus atom, one may note that the phosphorus atom is involved in a mesomeric type interaction. The steric orientation of the π-electron system is evidently to a large extent determined by these interactions, while the relative

stabilities of the conformers involved in the equilibrium are controlled by polar factors. The presence of π-electron systems has hardly any influence on the conformations of the irregular groups attached to the phosphorus atom, which permits a comparison of the physical and chemical properties in large series of organophosphorus compounds.

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Ul'yanov Lenin Kazan State
University