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Molecular Structures of Acyclic Organophosphorus Compounds

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The structural data for acyclic organophosphorus compounds published up to 1971 have been systematically reviewed. The geometrical parameters obtained for these compounds have been classified in accordance with the concepts of the valence states of the atoms in the molecules and the types of chemical bonds. Certain general relations governing the geometrical structure of the molecules have been noted on the basis of this classification. The geometrical parameters for a specific phosphorus-element bond may vary within limits greatly exceeding the experimental error as a result of the influence of the immediate environment of the bond. However, the study of the problem of the mutual influence of atoms not linked directly is difficult owing to the lack of the necessary experimental data.
The results of the determination of the conformations of acyclic organophosphorus compounds are presented.
The bibliography includes 231 references.

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I. INTRODUCTION

Since phosphorus compounds have been recently acquiring increasing practical value, it is important to investigate the characteristics of their geometrical structures, which are not only of theoretical interest but also constitute the basis for the interpretation of the rapidly increasing volume of experimental data in various branches of chemistry. The geometrical structure of molecules is characterised by certain fundamental parameters—bond length, valence angles, and angles of internal rotation. The most widely used method of calculation of bond lengths is based on systems of covalent radii[1], but it takes into account only the differences in bond multiplicity. The introduction of corrections in accordance with the Shomaker–Stevenson equation[2] makes it possible to take into account the differences between the types of atoms. However, in this case too the calculated bond lengths frequently differs from the experimental values by an amount significantly exceeding the present level of accuracy of the experimental data (about 0.01 Å).

A more logical empirical method is the phenomenological procedure, which has been particularly widely developed by Tatevskii[3-5]. The principle of the method consists in a detailed classification of bonds in molecules based on the classical theory of structure. This classification takes into account, apart from the chemical individuality of atoms and bond multiplicities, the valence state of the linked atoms (the "type" of chemical bond) and also the effect of the immediate environment. The actual role of all these factors, which influence the fundamental geometrical molecular parameters, can be discovered by analysing the experimental data. The most complete review of the stereochemistry of phosphorus compounds is given in a collective volume "Topics in Phosphorus Chemistry"[6]†.

† The Tables published under the editorship of Sutton[7] list the results of all the structural studies up to 1960 (including the studies on phosphorus compounds). There are also a number of reviews in which the stereochemistry of individual classes of organophosphorus compounds are discussed: trihalides[8], fluorides[9], sulphides[10], compounds with a P–P bond[11], compounds of pentacoordinate phosphorus[12-16], etc. Certain problems in the stereochemistry of phosphorus compounds have been examined in the monographs of Wells[17], Van Wazer[18], and Hudson[19], and in a collective volume "Topics in Stereochemistry"[20].

However, the classification of geometrical parameters in this review is not sufficiently logical and clear-cut. In addition, and this is most important, during the five years which have elapsed since the publication of this volume, new studies have expanded and deepened our knowledge about geometrical structure.

In the present review, the geometrical parameters of acyclic organophosphorus compounds have been classified on the basis of the concepts of the classical structural theory‡. Data obtained by spectroscopic (largely microwave) and diffraction (electron diffraction and X-ray diffraction) methods for the determination of molecular geometry published up to 1971 (the data published towards the end of 1970 and the beginning of 1971 are given in the Supplement) have been compiled. More accurate results have been obtained in re-investigations of the same substances. Complexes containing phosphorus–transition element bonds and salts of phosphorus acids have been excluded from consideration.

II. THE VALENCE STATES OF THE PHOSPHORUS ATOM

The phosphorus atom in various compounds coordinates between one and six ligands, but the majority of the known phosphorus compounds have coordination numbers of 3 and 4. Although phosphorus is frequently treated as an analogue of nitrogen, it is characterised by higher coordination numbers. In this respect phosphorus is closer to the heavy Group V elements—arsenic and antimony.

During recent years, compounds with dicoordinate phosphorus stable under normal conditions were obtained and investigated for the first time. In the case of acyclic structures, these are phosphamethinecyanine cations[21-23].

A large group of the phosphorus analogues of nitrogen compounds comprises derivatives of tricoordinate phosphorus. However, tervalent nitrogen can have in this case a planar bond configuration as well as a trigonal pyramidal configuration (with a minimum valence angle of

‡ The classical theory does not always give a sufficiently complete description of the chemical structure of compounds, but it does characterise satisfactorily the coordination numbers of atoms (for example, the tetracoordinate quinquevalent phosphorus in $-\overset{|}{\underset{|}{P}}=O$, $-\overset{|}{\underset{|}{P}}\rightarrow B-$, etc.).

102°). On the other hand, the average valence angles of the phosphorus atom in such compounds vary as a rule between 90° and 100°. On passing to heavier Group V elements, a tendency towards a further decrease of the average valence angle is observed§.

A tetrahedral coordination of ligands is most characteristic of the phosphorus atom. Compounds with a tetracoordinate phosphorus atom are more stable than those with different coordination. According to the classical theory of valence, there is a double bond at the phosphorus atom in such compounds (for non-ionised structures). The actual distribution of ligands can be referred to as tetrahedral in this case only in a conventional sense, since the valence angles of phosphorus within the limits of an individual structure can vary within very wide limits—from 100° to 120°. Here a double bond is involved in the formation of the largest angles.

Table 1. The limits of variation of the length of bonds between the phosphorus atom and the atoms of non-transition elements in acyclic organophosphorus compounds (in Å; on the basis of the data in Tables 2–4 and in the Addendum).

Bond	Coordination number of phosphorus					Sum of covalent radii	
		tetracoordinate		pentacoordinate*			
	tricoordinate (single bonds)	multiple bonds	single bonds	equatorial bonds	axial bonds	according to Pauling (Ref.1)	with correction for heteropolarity of bond (Ref.2)
PH	1.41—1.44	—	1.39—1.41	—	—	1.40	1.40
PB	—	1.83—1.95	—	—	—	1.91	1.90
PC	1.77—1.94	1.65—1.78	1.74—1.88	1.78—1.85	1.99	1.87	1.83
PN	1.63—1.75	1.56—1.64	1.59—1.71	—	—	1.83	1.75
PO	1.60	1.43—1.51	1.52—1.61	—	—	1.84	1.71
PF	1.57—1.61	—	1.49—1.58	1.53—1.55	1.58—1.64	1.82	1.65
PSi	2.25	—	—	—	—	2.27	2.24
PP	2.19—2.21	—	2.16—2.24	—	—	2.20	2.20
PS	—	1.85—1.98	2.07—2.09	—	—	2.14	2.10
PCl	2.04—2.08	—	1.94—2.03	2.02—2.05	2.13—2.15	2.09	2.01
PGe	2.31	—	—	—	—	2.32	2.29
PSe	—	2.08—2.10	2.24—2.28	—	—	2.27	2.24
PBr	2.23	—	2.06—2.14	—	—	2.24	2.18
PI	2.43—2.48	—	—	—	—	2.43	2.38

*The distinction between multiple and single bonds is in many cases purely conventional owing to the effect of the environment (if the length of the given bond is adopted as a criterion of its multiplicity).

The stereochemistry of pentacoordinate phosphorus compounds has been the subject of extensive discussion[14,15,32-39]. Of the two most probable geometrical configurations—trigonal bipyramid and tetragonal pyramid—the first is regarded as energetically more favourable, but the energy difference is in many cases small[15].

§ In a spectroscopic study of the compounds $P(SiH_3)_3$,[24] $As(SiH_3)_3$, and $Sb(SiH_3)_3$,[25] it was suggested that their molecular skeleton is planar, in contrast to the analogues in which tin replaces silicon[26] and also $P(GeH_3)_3$.[27] However, this hypothesis was disproved by electron-diffraction[28,29] and a reinterpretation of the infrared and Raman spectra[30,31].

Studies on PX_5 compounds in the gas phase confirmed that the trigonal-bipyramidal structure is energetically more favourable¶.

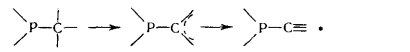
In the crystalline phase and in solution phosphorus pentahalides are present as PX_6^- anions with octahedral symmetry (tetragonal bipyramid) and tetrahedral cations PX_4^+.

As already stated, the length of a given chemical bond is determined not only by the bond type (and hence the valence state of the atoms involved in it) but also by the effect of the atoms in the immediate environment. Table 1 gives the limits of variation of the experimental phosphorus–element bond lengths in acyclic compounds for various valence states of the phosphorus atom.

III. BOND LENGTHS AND VALENCE ANGLES IN PHOSPHORUS(III) COMPOUNDS

The P—H bond length is relatively insensitive to the effect of the environment (Table 2). The difference between the values obtained by electron diffraction and spectroscopically (the microwave method) for the same molecules is systematic and is associated with the characteristics of these methods[41,42].

On the other hand, the lengths of P—C single bonds vary within wide limits, by up to 0.1 Å, which greatly exceeds the experimental error. The P—C bonds decrease in the series



As for the other element–carbon bonds, the length of each type of P–C bond varies with the type of immediate environment. Thus the length of the  bond in $P(CF_3)_3$ and CF_3PH_2 molecules is much greater (by 0.05 to 0.09 Å) than in $P(CH_3)_3$. A similar relation is observed also in derivatives with nitrosyl (CF_3NO [43] and CH_3NO [44]) and carbonyl (CF_3CHO [45] and CH_3CHO [46]) groups. However, in the $N(CF_3)_3$ molecule[47] the length of the N–C bond is smaller by 0.02 Å than in $N(CH_3)_3$ and $(CH_3)_2NH$,[48] while in C_2F_6 [49] the C–C bond is shorter by 0.05 Å than in ethane[50].

The attempt to correlate the change in P–C bond lengths with a change in the C–P–C valence angle involves difficulties. The increase of this angle on passing from methyl to phenyl derivatives is replaced by a decrease in the presence of  bonds. A characteristic feature of the P–N bond is that it is always shorter than the sum of the covalent radii (1.83 Å). In the amino-derivatives $X_2PN(CH_3)_2$, the configuration of the valence angles of the nitrogen atom is planar or nearly planar (the average valence angle of the nitrogen atom is $\bar{\alpha}_N = 117.5-120°$). In the ethyleneimine derivative $P[N(CH_2)_2]_3$, where the nitrogen atom forms part of a three-membered ring, $\bar{\alpha}_N$ is reduced to 101° and at the same time the shortening of the P–N bond is much less. A similar behaviour was noted also in a comparison of the structures of organic acid amides and *N*-acetylethyleneimine[51].

¶ It has been asserted in a spectroscopic study[40] that in the solid phase and in solution the $P(C_6H_5)_5$ molecule has the configuration of a square pyramid, which was subsequently disproved by an X-ray diffraction study of the crystalline substance (see Section IV, § 2).

Table 2. Geometrical parameters of acyclic organophosphorus compounds with tervalent phosphorus.

Formula	Bond type	r (PX), Å	XPY angle, deg	Method of investigation	References
		I. PH bond			
PH_3	>P—H	1.415 (0.005)	—	e.d./m.w.	52
PH_3	ditto	1.437 (0.004)	—	e.d.	53
PH_3	»	1.421 (0.005)	HPH 93.5	m.w.	54
CH_3PH_2	»	1.414 (0.003)	HPH 93.4	»	55
CH_3PH_2	»	1.423 (0.007)	—	e.d.	56
CF_3PH_2	»	1.43 (0.08)	HPH 96.7 (1.8)	m.w.	57
$C_3H_5PH_2$	»	1.413 (0.0002)		»	58
$(CH_3)_2PH$	»	1.419 (0.005)	HPC 97.0 (0.35)	»	59
$(CH_3)_2PH$	»	1.445 (0.02)	HPC 96.5 (assumed)	e.d.	56
F_2PH	»	1.412 (0.006)	HPF 96.3 (0.5)	m.w.	60
		II. PC bond			
HCP	P≡C—	1.5421 (0.0005)	—	m.w.	61
$P(CH_3)_3$	>P—C<	1.841 (0.003)	CPC 99.1 (0.2)	»	62
$P(CH_3)_3$	ditto	1.847 (0.003)	CPC 98.6 (0.3)	e.d.	63
$(CH_3)_2PH$	»	1.848 (0.003)	CPC 99.7 (0.3)	m.w.	59
$(CH_3)_2PH$	»	1.853 (0.003)	CPC 99.2 (0.6)	e.d.	56
CH_3PH_2	»	1.863 (0.003)	CPH 93.4	m.w.	55
CH_3PH_2	»	1.858 (0.003)	CPH 96.5 (assumed)	e.d.	56
$P(CF_3)_3$	»	1.937 (0.017)	CPC 99.6	»	64
CF_3PH_2	»	1.900 (0.006)	CPH 91.9 (1.9)	m.w.	57
$P(C_6H_5)_3$	>P—C<	1.828 (0.003)	CPC 103.0 (0.8)	X-ray	65
$P(C_6H_5)_2C_6H_4Br$	ditto	1.83	CPC 103	»	66
$(C_6H_5)_2P-C\equiv C-P(C_6H_5)_2$	»	1.832 (0.003)	CPC 102.8 (0.2)	»	67
	>P—C≡	1.765 (0.004)	CPC≡100.0 (0.2)		
$P(C\equiv C-C_6H_5)_3$	ditto	1.765 (0.01)	CPC≡100.7 (0.5)	»	68
$P(CN)_3$	»	1.78 (0.03)	CPC≡93.5 (2.0)	»	69
$P(C_3H_5)_3$	>P—C<	1.832 (0.006)	CPC 98.6 (1.3)	e.d.	70
$C_3H_5PH_2$	ditto	1.834 (0.0002)	CPH 98.3 (0.02)	m.w.	58
		III. PN bond			
$P[N(CH_3)_2]_3$	>P—N<	1.700 (0.005)	NPN 96.5 (1.0)	e.d.	71
$(CH_3)_2NPCl_2$	»	1.69 (0.03)	NPCl 100.0 (1.0)	»	72
$(CH_3)_2NPF_2$	»	1.628 (0.005)	NPF 101.6 (0.2)	X-ray	73
$P[N(CH_2)_2]_3$	>P—N<	1.75 (0.01)	NPN 97.5 (1.5)	e.d.	71
		IV. PO bond			
$P(OC_2H_5)_3$	>P—O—	1.600 (0.006)	OPO 96.5 (0.5)	e.d.	74
$P(OC_2H_5)_3$	ditto	1.600 (0.006)	OPO 100.0 (1.0)	»	74
CH_3OPCl_2	»	1.63 (assumed)	OPCl 99.0 (1.0)	»	75
		V. PF bond			
PF_3	>P—F	1.570 (0.001)	FPF 97.8 (0.2)	e.d./m.w.	76
F_2PH	ditto	1.582 (0.002)	FPF 99.0 (0.2)	m.w.	60
$(CH_3)_2NPF_2$	»	1.610 (0.004)	FPF 91.5 (0.3)	X-ray	73
$PFCl_2$	»	1.55 (0.05)	102 (mean)	e.d.	77
		VI. PSi bond			
$P(SiH_3)_3$	>P—Si—	2.248 (0.003)	SiPSi 96.45 (0.5)	e.d.	28
		VII. PP bond			
P_2I_4	>P—P<	2.212 (0.06)	PPI 94	X-ray	78
		VIII. PCl bond			
PCl_3	>P—Cl	2.043 (0.003)	ClPCl 100.1 (0.35)	m.w.	79
PCl_3	ditto	2.042 (0.002)	ClPCl 100.2 (0.15)	e.d.	80
$(CH_3)_2NPCl_2$	»	2.083 (0.005)	ClPCl 98.0 (1.0)	»	72
CH_3OPCl_2	»	2.084 (0.005)	ClPCl 99.3 (1.0)	»	75
$PFCl_2$	»	2.02 (0.03)	102 (mean)	»	77
		IX. PGe bond			
$P(GeH_3)_3$	>P—Ge—	2.308 (0.003)	GePGe 95.4 (0.05)	»	29

Table 2 continued.

Formula	Bond type	r (PX), Å	XPY angle, deg	Method of investigation	References
		X. PBr bond			
PBr_3	>P—Br	2.23 (0.01)	BrPBr 100 (2.0)	»	81
		XI. PI bond			
PI_3	>P—I	2.43 (0.04)	IPI 102 (2)	»	82
P_2I_4	ditto	2.475 (0.028)	IPI 102.3	X-ray	78

*Compounds with more than one type of bond at the phosphorus atom are quoted in several places according to the number of bond types. To avoid unnecessary repetition, in each case only those angles are quoted in the formation of which the given bond is involved. Here and henceforth the following notation is employed: e.d. = electron diffraction; m.w. = microwave spectroscopy; X-ray = X-ray diffraction.

It is interesting that, in contrast to the >P—N< and >P—N< bonds, the >P—C— and >P—C< bonds are hardly different in length. This is evidence of a difference in the type of interaction of tricoordinate phosphorus with nitrogen and carbon.

When two amino-groups in $P[N(CH_3)_2]_3$ are replaced by halogen atoms (chlorine, fluorine), there is a tendency towards a decrease of the P—N bond length, which is particularly pronounced in the case of the fluoro-derivative.

The effect of the amino-group on the phosphorus—halogen bond is in turn shown by a considerable increase in the length of the latter. Thus the P—Cl bond in $(CH_3)_2NPCl_2$ is longer by 0.04 Å compared with the value found for PCl_3 and the P—F bond in $(CH_3)_2NPF_2$ is longer by the same amount compared with the value found in PF_3.

The effect of the methoxy-group is similar. The P—Cl bond in CH_3OPCl_2 is also longer by 0.04 Å than in PCl_3.

A tendency towards a decrease of the >P— element bond length compared with the sum of the covalent radii on passing along a series of elements in the Periods from left to right and in the Groups from below upwards is noteworthy (Table 1).

IV. BOND LENGTHS AND VALENCE ANGLES IN PHOSPHORUS(V) COMPOUNDS

1. Structures with a Tetracoordinate Phosphorus Atom

The vast majority of data presented in this section were obtained by X-ray diffraction studies on crystals. The structure of the molecules in crystals may be modified under the influence of the crystal lattice forces, intermolecular hydrogen bonds, etc. Moreover, the accuracy of the X-ray method for the determination of the fundamental geometrical parameters is lower than that of the electron diffraction and microwave methods. Therefore here

a detailed determination of the geometrical structure is even more complicated than in the case analysed above.

Quinquevalent tetracoordinate phosphorus forms, in contrast to tervalent phosphorus, a multiplicity of stable compounds with double bonds (as understood in the classical theory structure) (Tables 1 and 3A). The lengths of these bonds vary within wide limits (by as much as 0.15 Å) but in general are shorter than the lengths of single bonds formed by tetracoordinate phosphorus (Tables 1 and 3B).

Recently new more reliable X-ray diffraction data on the P=C bond length in phosphoranylidines have been published. The P=C bond lengths in the $(C_6H_5)_3P{=}C{=}C{=}O$, $(C_6H_5)_3P{=}C{=}C{=}S$, and $(C_6H_5)_3P{=}CH_2$ molecules were found to be appreciably shorter than in other ylidines. In the oxygen derivative the P=C=C angle is 145.0°, which is unusual for carbon, since theoretically the cumulene chain should be linear, as in carbon dioxide[83], keten[84], etc. In the thio-derivative, the length of the P=C bond is greater by 0.04 Å and the P=C=C angle is greater by 22.5°C than in the oxygen derivative. In $(C_6H_5)_3P{=}CH_2$ the P=C bond length is intermediate in the above set of three compounds. Electron diffraction data indicate a pronounced dependence of the P=O bond length on the nature of the environment. It increases by 0.04 Å on passing from $POCl_3$ to $(CH_3)_3PO$, which is accompanied by a decrease of the O–P–X angle. A similar increase of the P=O bond length occurs when one of the chlorine atoms of $POCl_3$ is replaced by C_6H_5 or $(CH_3)_2N$ groups.

It is striking that complex formation involving POX_3 (X = Cl, CH_3, C_6H_5, etc.) molecules proceeds via the phosphoryl bond and is accompanied by an increase in its length.

The single bonds in compounds of tetracoordinate phosphorus are as a rule shorter and the valence angles between them are larger than the corresponding bonds and angles in compounds with tricoordinate phosphorus (Tables 1, 2, and 3B). This relation holds satisfactorily for P–C bonds with carbon atoms in various valence states and in the majority of other cases. At the same time the P–P bond length remains constant (albeit within the limits of a considerable experimental error) for both valence states of the phosphorus atoms and is equal to the sum of the covalent radii. Some of the features of the mutual influence of atoms found in compounds of tricoordinate phosphorus (Section III) are characteristic also of compounds with tetracoordinate phosphorus. In particular, this is confirmed by the shortening of the C–N bond under the influence of fluorine atoms in the $(CH_3)_2NPF_2.B_4H_8$ molecule by 0.06 Å compared with the length of this bond in $(NH_2)_3P.BH_3$. The P–F bond length in the first molecule then proved to be significantly greater than in the absence of the amino-group (an increase by up to 0.07 Å compared with the P–F bond length in $PF_3.B_4F_6$). The effect of the amino-group on the PCl bond length is similar.

The sensitivity of the P–Cl bond to the influence of substituents is characterised by a marked tendency towards an increase in its length on passing along the series $POCl_3 \rightarrow PSCl_3 \rightarrow C_6H_5POCl_2 \rightarrow (CH_3)_2NPOCl_2$ [in the case of tricoordinate phosphorus we have similarly $PCl_3 \rightarrow (CH_3)_2NPCl_2$, CH_3OPCl_2]. The increase of the phosphorus–halogen bond length is accompanied as a rule by a decrease of the halogen–phosphorus–halogen valence angles formed by these bonds.

Complex formation via the P=O or P=S multiple bonds evidently has little effect on the P–C bond length, while the P–Cl bond length becomes appreciably reduced under these conditions.

We also have the following interesting facts.

1. The average $=\overset{|}{\underset{|}{P}}-N\diagup\diagdown$ bond length is greater by only 0.015 Å than the $-\overset{|}{\underset{|}{P}}=N-$ bond length in the $(C_6H_5)_2P(F){=}NCH_3$ molecule (Table 3A). The P–F bond is unusually short in this molecule (1.488 Å).

2. In the compound $PS[N(CH_2)_2]_3$ the $=\overset{|}{\underset{|}{P}}-N\diagup\diagdown$ bond length proved to be the same, within the limits of experimental error, as that of the $=\overset{|}{\underset{|}{P}}-N\diagup\diagdown$ bond. In contrast, as already mentioned, in compounds of tricoordinate phosphorus the $\diagup P-N\diagup\diagdown$ bond length is greater by 0.05 Å than that of the $\diagup P-N\diagdown$ bond (Table 2). The relative magnitudes of the average valence angles at the nitrogen atoms in $-N\diagup\diagdown$ and $-N\diagup$ are the same in both cases (100–101° and 116–120°).

3. In the compound $\begin{matrix}(NH_2)_2P(S)\\ \diagdown\\ \quad N-CH_3\\ \diagup\\ NH_2(NHCH_3)P(S)\end{matrix}$, the lengths of the bonds between the phosphorus atoms and the central nitrogen atom (1.708 Å—the maximum value known for the P–N bond length involving tetracoordinate phosphorus†) is greater by 0.06 Å than the lengths of the remaining P–N bonds in this molecule‡. The central nitrogen atom has in this case a planar bond configuration.

For comparison, we recall that the length of the Si–N bond also increases with the number of Si atoms linked to the N atom in the sequence $ClSi[N(CH_3)_2]_3$ (1.715 Å) [85] → $CH_3N(SiH_3)_2$ (1.726 Å) [86] → $N(SiH_3)_3$ (1.738 Å).[87]

2. Structures with a Pentacoordinate Phosphorus Atom

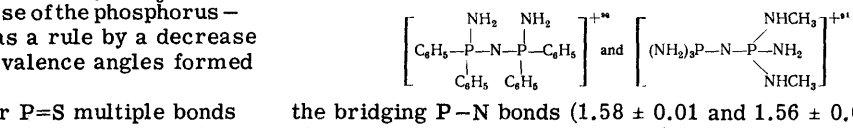
These compounds are relatively unstable. In particular, the stability of pentahalides diminishes significantly with increasing atomic weight of the halogen. The pentaiodide is altogether unknown and the chloride and bromide are ionised in the crystal to $[PCl_4]^+[PCl_6]^-$ and $[PBr_4]^+Br^-$.

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† The P–N bond length in the $Na^+[PO_3NH_3]^-$ crystal structure, which is 1.77 ± 0.02 Å, was determined by Cruickshank[88] as the length of a single P–N bond. It is close to the sum of the covalent radii of the phosphorus and nitrogen atoms with the Shomaker–Stevenson correction (1.75 Å).

In the $Ca_{1.5}C_3H_3N_2(PO_3)_2.6H_2O$ crystal structure, where the nitrogen atoms form part of an aromatic group, the average length of the P–N bonds outside the ring is 1.786 ± 0.006 Å.[89] The authors of this investigation claim that they found the length of a single P–N bond.

‡ In the cations



and

the bridging P–N bonds (1.58 ± 0.01 and 1.56 ± 0.02 Å) are shorter than the terminal bonds (1.65 ± 0.01 and 1.63 ± 0.02 Å). The P–N–P angles in these structures are 136° ± 1° and 129.2°.

Table 3. Geometrical parameters of acyclic organophosphorus compounds with tetracoordinate phosphorus.

A. Multiple bonds

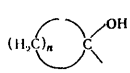
Formula	Bond type	r (P = X), r (P→X), Å	YP = X angle, deg	Method of investigation	References
1	2	3	4	5	6
I. PB bond					
$PF_3 \cdot BH_3$		1.836 (0.012)		m.w.	92
$HF_2P \cdot BH_3$	ditto	1.832 (0.009)	{FPB 117.7 (0.3) HPB 120.1 (0.6)	ditto	93
$PF_3 \cdot B_4F_6$	»	1.825 (0.015)	FPB 116.2 (1.0)	X-ray	94
$(NH_2)_3P \cdot BH_3$	»	1.887 (0.015)	NPB 115 (mean)	ditto	95
$(CH_3)_2NPF_2 \cdot B_4H_8$	»	1.856 (0.008)	{NPB 117.6 (0.3) FPB 115.0 (mean)	»	96
$(CH_3)_4P_2 \cdot 2BH_3$	»	1.951 (0.021)	{CPB 114.8 (1.4) PPB 112 (mean)	»	97
II. P=C bond					
$(C_6H_5)_3P{=}CH_2$		1.661 (0.008)	CP=C 113.5 (0.3)	»	98
$(C_6H_5)_3P{=}C{=}C{=}O$		1.648 (0.007)	CP=C 111.5 (0.4)	»	99
$(C_6H_5)_3P{=}C{=}C{=}S$	ditto	1.677 (0.008)	CP=C 110.8 (0.4)	»	100
$(C_6H_5)_3P{=}C(CH_3O_2C)-C(CO_2CH_3){=}N-C_6H_4Br$		1.70 (0.03)		»	101
$(C_6H_5)_3P{=}CH-SO_2-O-C_6H_4CH_3$	ditto	1.71 (0.02)	CP=C 107	»	102
$(C_6H_5)_3P{=}C(Cl)-C(=O)C_6H_5$	»	1.74 (0.01)	CP=C 106	»	103
$(C_6H_5)_3P{=}R{=}P(C_6H_5)_3$ ("blue substance")	»	1.74 (mean)	approx. tetrahedral val. angles at P	»	104
$(C_6H_5)_3P{=}R$ ("dark-green substance")	»	1.77 (0.02)	CP = C 111	»	105
$(C_6H_5)_3P \cdot CS_2$	»	1.78 (0.03)	approx. tetrahedral val. angles at P	»	106
$(C_6H_5)_3P{=}C(P(C_6H_5)_3)C(CF_3)_2O$	»	1.75 (0.02)	CP = C 114.1 (mean)	»	107
III. P=N bond					
$(C_6H_5)_2P(F){=}NCH_3$		1.641 (0.002)	{FP=N 118.7 (0.1) CP=N 104.3 (0.1)	»	108
$(C_6H_5)_3P{=}NR$ ("pale-green substance")	ditto	1.630 (0.005)	CP=N 110	»	109
$(C_6H_5)_3P{=}NR$ ("brown substance")	»	1.56 (0.02)	CP=N 112 (3)	»	110
IV. P=O bond					
$(CH_3)_3PO$		1.479	CP=O 112.3	e.d.	111
$(CH_3)_2P(O)OH$	ditto	1.495 (0.005)	{CP=O 111.5 (0.5) OP=O 112.7 (0.2)	X-ray	112
$(CH_3)_2NPO(C_6H_5)_2$	»	1.47	CP=O 117.6	ditto	113
$(C_6H_5)_2P(O)OH$	»	1.45	CP=O 111	»	114
$R-PO(OCH_3)_2$ R = hydrocarbon rings	»	1.473 (0.008)	{CP=O 114.0 (1.0) OP=O (mean)	»	115
 where n = 8,9,11 or 12)					
$PO(NH_2)_3$	»	1.510 (0.003)	NP=O 112 (mean)	»	116
$\{PO[N(CH_3)_2]_2\}_2C_4H_4$	»	1.476 (0.004)	{NP=O 112.0 CP=O 110.9	»	117
$(HO)_3PO$	»	1.52 (0.03)	OP=O 113	»	118
$(HO)_3PO \cdot {}^1/_2H_2O$	»	1.490 (0.005)	OP=O 111.8 (0.3)	»	119
$HP(OH)_2O$	»	1.47 (0.03)	OP=O 115		120
$(ClC_6H_4O)_2PO(OH)$	»	1.497 (0.009)	OP=O 112 (mean)	»	121
$(C_6H_5CH_2O)_2PO(OH)$	»	1.47 (0.01)	OP=O 113 (mean)	»	122
$(C_6H_4NO_2)_3PO_4$	»	1.438 (0.005)	OP=O 115 (mean)	»	123
$(C_6H_5O)_3PO$	»	1.432 (0.01)	OP=O 115 (mean)	»	124
POF_3	»	1.436 (0.006)	FP=O 117.0 (0.2)	e.d.	127
$HPOF_2$	»	1.437 (0.006)	{HP=O 117.9 (2.0) FP=O 116.3 (1.0)	m.w.	126
$POCl_3$	»	1.449 (0.005)	ClP=O 114.7 (0.2)	e.d.	127
CH_3POCl_2	»	1.448 (0.005)	{ClP=O 114.5 (0.5) CP=O 117.4 (1.0)	ditto	128
$C_6H_5POCl_2$	»	1.47 (0.01)	{ClP=O 116 (1) CP=O 116 (2)	»	129
$(CH_3)_2NPOCl_2$	»	1.47 (0.02)	ClP=O 116	»	72
$POBr_3$	»	1.442 (0.02)	BrP=O 115 (2)	X-ray	130

Table 3 (continued).

Formula	Bond type	r (P=X), Å	YP = X angle, deg	Method of investigation	References
$POBr_3$	$-\overset{\vert}{P}=O$	1.41 (0.07)	—	e.d.	131
$(CH_3)_3PO \cdot SbCl_5$	ditto	1.56 (0.04)	—	X-ray	132
$[(C_6H_5)_3PO \cdot SeOCl_2]_2$	»	1.51 (0.01)	OP=O 112	»	133
$POCl_3 \cdot SbCl_5$	»	1.46 (0.02)	OP=O 111.5 (0.7)	»	132
$POCl_3 \cdot NbCl_5$	»	1.45 (0.02)	—	»	132
		V. P=S bond			
$C_2H_5)_3PS$	$-\overset{\vert}{P}=S$	1.86 (0.03)	CP=S 112	»	134
$(CH_3)_4P_2S_2$	ditto	1.96	CP=S 115 PP=S 113	»	135
$(C_2H_5)_4P_2S_2$	»	1.94 (0.01)	CP=S 115.0 (1.0) PP=S 112.8 (1.0)	»	136
$(CH_3)_2(C_6H_5)_2P_2S_2$	»	1.98 (0.02)	CP=S 115 (mean)	»	137
$[(C_2H_5)_2P(S)Se]_2$	»	1.932 (0.01)	CP=S 117.0 (0.5) SeP=S 104.1 (0.5)	»	138
$[(C_2H_5)_2P(S)Se]_2Te$	»	1.926 (0.01)	CP=S 116.0 (1.0) SeP=S 103.8 (0.6)	»	139
$(C_6H_5)_2P(S)OCH_3$	»	1.936 (0.006)	OP=S 115.6 (0.4) CP=S 113.9 (0.8)	»	140
$(NH_2)_2P(S)$ $NHCH_3(NH_2)P(S)$	»	1.958 (0.005)	NP=S 112 (mean)	»	141
$P(S)[N(CH_2)_2]_3$	»	1.910 (0.015)	NP=S 118.0 (1.5)	»	142
$[(CH_3O)_2PS_2]_2Te$	»	1.923 (0.007)	OP=S 117.0 (0.3) SP=S 107.0 (0.3)	»	143
PSF_3	»	1.87 (0.03)	—	e.d./m.w.	125
PSF_3	»	1.87	—	m.w.	144
PSF_3	»	1.85 (0.02)	—	e.d.	145
$PSCl_3$	»	1.885 (0.005)	ClP=S 116.6 (0.2)	ditto	127
$PSBr_3$	»	1.890 (0.06)	—	»	131
$2(C_6H_5)_3PS \cdot 3I_2$	»	2.01 (0.03)	CP=S 113	X-ray	146
		VI. P=Se bond			
$[(C_2H_5)_2PSe_2]_2Se$	$-\overset{\vert}{P}=Se$	2.095 (0.006)	CP=Se 116.6 (1.0) SeP=Se 103.1 (0.3)	ditto	147
$(C_6H_5)_2P(Se)OCH_3$	ditto	2.081 (0.008)	CP=Se 114.2 (0.9) OP=Se 115.9 (0.6)	»	140
$[(C_6H_5)_3P(Se) \cdot HgCl_2]_2$	»	2.169 (0.006)	CP=Se 110.0 (0.4)	»	148

B. Single bonds

Formula	Bond type	r (PY), Å	YPY angle, deg	Method of investigation	References
		I. PH bond			
$HPOF_2$	$=\overset{\vert}{P}-H$	1.387 (0.01)	HPF 101.9 (1.5)	m.w.	126
$HF_2P \cdot BH_3$	$\leftarrow\overset{\vert}{P}-H$	1.409 (0.004)	HPF 98.6 (0.3)	ditto	93
		II. PC bond			
$(CH_3)_3PO$	$=\overset{\vert}{P}-C-$	1.813	CPC 106	e.d.	111
$(CH_3)_2P(O)OH$	ditto	1.780 (0.006)	CPC 107.3 (0.3)	X-ray	112
CH_3POCl_2	»	1.80 (0.025)	CPCl 103.3 (0.5)	e.d.	128
$(CH_3)_4P_2 \cdot 2BH_3$	$\leftarrow\overset{\vert}{P}-C-$	1.827 (0.010)	CPC 106.0 (0.6) PPC 104.4 (1.0)	X-ray	97
$(CH_3)_4P_2S_2$	$=\overset{\vert}{P}-C-$	1.74	CPC 105 PPC 105	ditto	135
$(CH_3)_2(C_6H_5)_2P_2S_2$	$=\overset{\vert}{P}-C$	1.82 (0.02)		»	137
	$=\overset{\vert}{P}-C-$	1.88 (0.02)			
$(C_2H_5)_3P \cdot CS_2$	ditto	1.82 (0.03)		»	106
$(C_2H_5)_3PS$	»	1.87 (0.04)	CPC 107	»	134
$(C_2H_5)_4P_2S_2$	»	1.83 (0.02)	CPC 107.3 (1.0) PPC 102.2 (1.0)	»	136
$[(C_2H_5)_2P(S)Se]_2$	»	1.83 (0.04)	CPC 105 SePC 105	»	138
$[(C_2H_5)_2P(S)Se]_2Te$	»	1.82 (0.04)	CPC 103.9 (2.0) SePC 108.5 (1.5)	»	139
$[(C_2H_5)_2PSe_2]_2Se$	»	1.825 (0.03)	CPC 103.3 (1.8) SePC 108.5 (1.0)	»	147
R—PO$(OCH_3)_2$ (for R, see Table 3A)	$=\overset{\vert}{P}-C_{ring}$	1.834 (0.009)	CPO 106.0 (mean)	»	115
$(C_6H_5)_3P=C=C=S$	$=\overset{\vert}{P}-C$	1.795 (0.007)	CPC 108.1 (0.4)	»	100
$(C_6H_5)_3P=C=C=O$	ditto	1.805 (0.006)	CPC 107.3 (0.3)	»	99

Table 3 (continued).

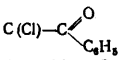
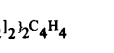
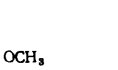
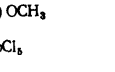
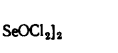
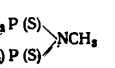
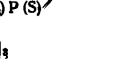
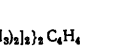
Formula	Bond type	r (PY), Å	YPY, angle, deg	Method of investigation	References
$(C_6H_5)_3P=C(Cl)-C(=O)C_6H_5$		1.81 (0.02)	—	»	103
$(C_6H_5)_3P=CH-SO_2-O-C_6H_4CH_3$	ditto	1.81 (0.02)	CPC 112 (mean)	»	102
$(C_6H_5)_3P=R$ ("dark-green substance")	»	1.81 (0.02)	CPC 108	»	105
$(C_6H_5)_3P=R=P(C_6H_5)_3$ ("pale-blue substance")	»	1.816 (0.015)	approx. tetrahedral val. angles at P	»	104
$(C_6H_5)_3P=CH_2$	»	1.823 (0.01)	CPC 105.0	»	98
$(C_6H_5)_3P=C(CH_2O_2C)(CO_2CH_3)-C=N-C_6H_4Br$	»	1.83 (0.025)			101
$(C_6H_5)_3P=C(P(C_6H_5)_3)(C(CF_3)_2)O$	»	1.85 (0.02)	CPC 104.4 (mean)	»	107
$(C_6H_5)_3P=NR$ ("pale-green substance")	»	1.792 (0.007)	CPC 109	»	109
$(C_6H_5)_3P=NR$ ("brown substance")	»	1.809 (0.012)	CPC 107 (3)	»	110
$F(C_6H_5)_2P=NCH_3$	»	1.806 (0.003)	CPC 107.1 (0.1)	»	108
$(CH_3)_2N(C_6H_5)_2PO$	»	1.805	CPC 105 (mean)	»	113
$HO(C_6H_5)_2PO$	»	1.81 (0.03)	CPC 108	»	114
$\{PO[N(CH_3)_2]_2\}_2C_4H_4$		1.809 (0.005)	NPC 107.2	»	117
$C_6H_5POCl_2$		1.76 (0.02)	—	e.d.	129
$(C_6H_5)_2P(S)OCH_3$	ditto	1.81 (0.02)	CPC 105.7 (0.7) OPC 103.2 (1.0)	X-ray	140
$(C_6H_5)_2P(Se)OCH_3$	»	1.81 (0.03)	CPC 104.8 (1.2) OPC 103.0 (1.7)	ditto	140
$(CH_3)_3PO\cdot SbCl_5$		1.81 (0.08)	CPC 109	»	132
$[(C_6H_5)_3PO\cdot SeOCl_2]_2$		1.80 (0.01)	CPC 107	»	133
$2(C_6H_5)_3PS\cdot 3I_2$	ditto	1.82 (mean)	CPC 106	»	146
$[(C_6H_5)_3P(Se)\cdot HgCl_2]_3$	»	1.81 (0.02)	CPC 109	»	148
		III. PN bond			
$(NH_2)_3P\cdot BH_3$		1.653 (0.01)	NPN 108 (mean)	»	95
$PO(NH_2)_3$		1.656 (0.01)	NPN 106.5 (mean)	»	116
$(NH_2)_3P(S)-NCH_3$ $NH_2(NHCH_3)P(S)$		1.65 (0.02) 1.708 (0.015)	NPN 107 (2)	»	141
$PS[N(CH_3)_2]_3$		1.64 (0.02)	NPN 100.0 (1.5)	»	142
$\{PO[N(CH_3)_2]_2\}_2C_6H_4$		1.647 (0.006)	NPN 106.9 CPN 107.2	»	117
$(CH_3)_2NPO(C_6H_5)_2$	»	1.67		»	113
$(CH_3)_2NPOCl_2$	»	1.67 (0.04)	ClPN 102 (1)	e.d.	72
$(CH_3)_2NPF_2\cdot B_4H_8$		1.593 (0.006)	FPN 105 (2)	X-ray	96
		IV. PO Bond			
$(HO)_3PO$		1.57 (0.03)	OPO 106	ditto	118
$(HO)_3PO\cdot{}^1/_2H_2O$	ditto	1.552 (0.006)	OPO 107 (3)	»	119
$(C_6H_5O)_3PO$	»	1.567 (0.023)	OPO 100	»	124
$(C_6H_4NO_2)_3PO_4$	»	1.572 (0.005)	OPO 103.1	»	123
$(C_6H_5CH_2O)_2P(O)OH$	»	1.555 (0.01) (P—OR) 1.545 (0.01) (P—OH)	OPO 105	»	122
$(ClC_6H_4O)_2P(O)OH$	»	1.497(0.009) (mean)	OPO 108	»	121
$HPO(OH)_2$	»	1.54 (0.03)	OPO 102	»	120
$(CH_3)_2P(O)OH$	»	1.559 (0.005)	OPC 107 (2)	»	112
$(C_6H_5)_2P(S)OCH_3$	»	1.60 (0.02)	OPC 103.2 (1.0)	»	140
$(C_6H_5)_2P(Se)OCH_3$	»	1.61 (0.03)	OPC 103.0 (1.0)	»	140
$[(CH_3O)_2PS_2]_2Te$	»	1.58 (0.02)		»	143
$(CH_3O)_2P(O)R$ (For R see Table 3A)	»	1.572 (0.010)	OPO 102.7 (0.4)	»	115
		V. PF bond			
$PF_3\cdot BH_3$		1.538 (0.008)	FPF 99.8 (1.0)	m.w.	92
$PF_3\cdot B_4F_6$	ditto	1.510 (0.015)	FPF 101.7 (1.0)	X-ray	94
POF_3		1.524 (0.003)	FPF 101.3 (0.2)	e.d.	127
PSF_3		1.53 (0.02)	FPF 100.3 (2.0)	e.d./m.w.	125
$HF_2P\cdot BH_3$		1.552 (0.006)	FPF 100.0 (0.5)	m.w.	93
$HPOF_2$	ditto	1.539 (0.003)	FPF 99.8 (0.5)	ditto	126
	»	1.583 (0.005)	FPF 96.4 (0.3)	X-ray	96
	»	1.488 (0.002)	FPC 110.7 (0.1)	ditto	108

Table 3 (continued).

Formula	Bond type	r (PY), Å	YPY angle, deg	Method of investigation	References
		VI. PP bond			
$(CH_3)_4P_2 \cdot 2BH_3$		2.205 (0.005)	PPC 104.4 (1.0)	X-ray	97
$(CH_3)_4P_2S_2$		2.18	PPC 105	ditto	135
$(C_2H_5)_4P_2S_2$	ditto	2.22 (0.01)	PPC 102.2	»	136
$(CH_3)_2(C_6H_5)_2P_2S_2$	»	2.21 (0.02)	PPC 103.5	»	137
		VII. PS bond			
$[(CH_3O)_2PS_2]_2Te$		2.09 (0.01)		»	143
		VIII. PCl bond			
$POCl_3$		1.993 (0.003)	ClPCl 103.3 (0.2)	e.d.	127
$PSCl_3$	ditto	2.011 (0.003)	ClPCl 101.8 (0.2)	»	127
CH_3POCl_2	»	2.032 (0.009)	ClPCl 101.8 (0.5)	»	128
$C_6H_5POCl_2$	»	2.025 (0.005)	ClPCl 102 (2)	»	129
$(CH_3)_2NPOCl_2$	»	2.033 (0.008)	ClPCl 102 (1)	»	72
$POCl_3 \cdot SbCl_5$	»	1.96 (0.01)	ClPCl 106.5 (0.4)	X-ray	132
$POCl_3 \cdot NbCl_5$	»	1.94 (0.01)		ditto	132
		IX. PSe bond			
$[(C_2H_5)_2P(S)Se]_2$		2.275 (0.011)	SePC 107	»	138
$[(C_2H_5)_2P(S)Se]_2Te$	ditto	2.258 (0.01)	SePC 108.5 (1.5)	»	169
$[(C_2H_5)_2PSe_2]_2Se$	»	2.239 (0.007)	SePC 108.5 (1.0)	»	147
		X. PBr bond			
$POBr_3$		2.14 (0.01)	BrPBr 107 (mean)	»	130
$POBr_3$	ditto	2.06 (0.03)	BrPBr 108 (3)	e.d	131
$PSBr_3$	»	2.13 (0.03)	BrPBr 106.3	ditto	131

According to Raman spectra [149], in the gas phase the pentachloride also dissociates $PCl_5 \rightarrow PcL_3 + Cl_2$, to an extent which is determined by the temperature and pressure.

Table 4. Bond lengths in acyclic compounds of pentacoordinate phosphorus.

Formula	r (Pc), Å		r (P — Hal), Å		Method of investigation	Refs.
	axial	equatorial	axial	equatorial		
$P(C_6H_5)_5$	1.987 (0.006)	1.850 (0.02)	—	—	X-ray	169
$(CH_3)_2PF_3$	—	1.798 (0.004)	1.643 (0.003)	1.553 (0.006)	e.d.	162
CH_3PF_4	—	1.780 (0.005)	1.612 (0.004)	1.543 (0.004)	ditto	162
HPF_4	—	—	1.594 (0.005)	1.55 (0.03)	m.w.	158
PF_5	—	—	1.577 (0.005)	1.534 (0.004)	e.d.	170
PF_3Cl_2	—	—	(2.05 ± ±0.03)	(1.59 ± ±0.03)	ditto	77
PCl_5	—	—	2.124 (0.009)	2.020 (0.007)	»	171

In the gas phase the molecules of PF_5, PCl_5, and their derivatives have the configuration of a regular (D_{3h} symmetry) or nearly regular trigonal bipyramid. An empirical rule, according to which the more electronegative or a large series of substituents occupy axial positions in this configuration, was established on the basis of NMR, infrared, and Raman spectroscopic data [12,13]. There are no exceptions to this rule for acyclic structures, at least in the gas phase§.

§ Analysis of the vibrational spectra [150,151], measurements of the dipole moments [151,152], and also NQR and NMR data [153] show that the molecules of all the members of the PCl_nF_{5-n} series exist in the trigonal-bipyramidal configuration with the F atoms in the axial positions. The vibrational spectra of CF_3PCl_4 [154] and $(CF_3)_2PCl_3$ [155] and the ^{19}F NMR spectra of CF_3PCl_3F [156] show that the more electronegative $-CF_3-$ groups (compared with chlorine) are also in the axial positions. The trigonal-bipyramidal structure of the HPF_4 molecule with an equatorial H atom has been established from infrared [157] and microwave spectra [158]. Finally, the validity of the above rule is confirmed by the vibrational spectra of compounds in the series CH_3PF_4, [159] CCl_4PF_4, [160] and CF_3PF_4, [161] according to which the CX_3 groups are localised in the equatorial positions (C_{2V} symmetry). For the methyl derivatives CH_3PF_4 and $(CH_3)_2PF_3$, this was also found by electron diffraction [162].

However, there is a divergence in views concerning CF_3PF_4. Thus in a microwave study [163] it was asserted that the CF_3 group occupies an axial position (C_{3V} symmetry). However, no details of the structure are quoted and the authors do not exclude the possibility of the presence of conformations other than C_{3V}. Earlier an axially substituted model of the CF_3PF_4 molecule was preferred on the basis of NMR spectra [12].

Some evidence for the possibility of the existence of conformational isomers in the case of the CF_3PF_4 molecule (together with the basic structure having the C_{2V} symmetry) was noted in the interpretation of the vibrational spectra [161].

According to electron-diffraction data (Table 4), the non-equivalence of the axial and equatorial bonds increases from 0.043 ± 0.008 Å in PF_5 to 0.104 ± 0.01 Å in PCl_5. It has also been established that, with increase of the number of CH_3 substituents, there is an increase in the length of both axial and equatorial P–F bonds, the length of the axial bond increasing faster. Therefore, on the basis of a calculation of the ratio of the lengths of the P–F axial bonds in PF_5 (adopted as unity by convention) and in substituted fluorophosphoranes, the ionic structure $[R_4P]^+F^-$ was proposed[164] for $(CH_3)_4PF$. However, there is so far no evidence for the existence of ionic structures of pentacoordinate phosphorus fluorides comparable to those found in the chlorides[165-168]. The mixed halide PF_3Cl_2 was investigated by electron diffraction as early as the end of the 1930's. It was established that the F atoms are equivalent and are therefore in the equatorial positions, but the lengths of the P–F (1.59 Å) and P–Cl (2.05 Å). bonds found throw doubt on the correctness of this conclusion. The vibrational spectra indicate that both axial positions in PF_3Cl_2 are occupied by F atoms[13,150]. The general tendency is probably as follows: the lengths of the axial bonds in the trigonal-bipyramidal structures vary approximately between the same limits as the lengths of the corresponding bonds of tricoordinate phosphorus; the lengths of the equatorial bonds are closer to those of single tetracoordinate phosphorus bonds (Table 1).

V. INTERNAL ROTATION AND CONFORMATIONAL ISOMERISM IN ACYCLIC ORGANOPHOSPHORUS COMPOUNDS

The study of intramolecular rotation and conformational isomerism has recently become a central problem in the theory of chemical structure. However, the only possible realistic approach to this problem still consists in the accumulation and analysis of experimental data. There are no general approximate hypotheses which would account for the characteristics of intramolecular rotation. The applicability of each of the numerous empirical methods of calculation of potential barriers is limited to special cases, since these methods do not have a rigorous physical basis. In many cases the geometry of stable conformations of organophosphorus compounds can be satisfactorily accounted for by the mutual repulsion of the non-bonded atoms in the molecule. Owing to the considerable differences between the types of intermolecular interactions, the ratio of the rotational isomers in the mixture may be various depending on the state of aggregation of the substance.

1. Compounds with a P–B bond

An ethane-like staggered conformation, corresponding to minimum steric interactions, is characteristic of compounds of the type $X_3P.BY_3$ [X = H, F, $N(CH_3)_2$; Y = H] in the vapour (according to microwave data[92,93]) and in the crystalline phase (according to vibrational spectra[172] and X-ray diffraction[95]). The barrier to internal rotation (V_3) is 3.24 ± 0.15 kcal mole^{-1} in the $F_3P.BH_3$ molecule[92] and about 3.6–4.5 kcal mole^{-1} in the $HF_2P.BH_3$ molecule[93], i.e. is close to the value in ethane.

2. Compounds with a P–C bond

In the molecules of methylphosphines $P(CH_3)_3$ and $PH(CH_3)_2$ in the vapour phase, the mutual orientation of the methyl groups is also staggered and $V \leqslant 1$ kcal mole^{-1} according to electron diffraction data[56,63] and 2.6 ± 0.5 kcal mole^{-1} according to microwave data[59,62]. Microwave data show that the barriers to rotation in CH_3PH_2 (about 2 kcal mole^{-1}) [55] and CF_3PH_2 (2.36 ± 0.08 kcal mole^{-1}) [57] are approximately the same.

An electron diffraction study of $P(C_3H_5)_3$ vapour[70] showed that the deviation of each of the three cyclopropyl groups from its position in the staggered configuration with C_{3V} symmetry is different (9.5°, −13°, −15°) and "the attempt to interpret the data using the hypothesis that a mixture of molecules with different conformations is present proved fruitless".

Crystalline triphenylphosphine $P(C_6H_5)_3$ was shown by X-ray diffraction[65] to have the C_3 propeller-like conformation with angles between normals to the plane of the base of the phosphorus pyramid and to the plane of the phenyl rings of the order of 60°. In the vapour phase the $(CH_3)_3PO$ molecule[111] has the C_{3V} symmetry with the *trans*-disposition of H atoms relative to the oxygen atom.

Vibration spectra[173] showed that in the liquid phase the more complex structures $CH_2YP(=O)X_2$ (X = F or Cl; Y = Cl, CH_3, or CH_2Cl) exist as mixtures of *trans*- and gauche-conformers with C_S and C_1 symmetry.

In the solid phase of the fluorides, conformers with the C_1 symmetry remain, while in the solid phase of the chlorides the remaining conformers have the higher C_S symmetry.

An electron diffraction study of the vapour of $C_6H_5P(=O)Cl_2$ showed[129] that the most probable conformation of this compound involves a coplanar disposition of the phenyl ring and the P=O bond. This conformation corresponds to minimum steric interaction. Here the barrier to rotation about the P–C bond is approximately 1 kcal mole^{-1}.

The internal rotation of CH_3 groups in the molecules of the pentacoordinate phosphorus compounds CH_3PF_4 and $(CH_3)_2PF_3$ could not be characterised by electron diffraction[162]. The barrier to rotation in CH_3PF_4 is very low (about 10 cal mole^{-1}), which leads to the hypothesis of free rotation. At the same time the barrier to internal rotation in the CF_3PF_4 molecule is 5.0 ± 1.5 kcal mole^{-1} according to microwave data[183].

3. Compounds with a P–N bond

According to low-temperature NMR spectra[174-178], the usual barrier to rotation relative to the P–N bond in the series of aminophosphines $R_1R_2NPR_3R_4$ ($R_1 = CH_3$; R_2 = H, CH_3, or $C_6H_5CH_2$; R_3 = Cl, C_6H_5, or CF_3; R_4 = Cl, C_6H_5, or CF_3) varies in the range from about 9 to 14 kcal mole^{-1}¶. This value is higher than for P–B and P–C bonds (see above). It has also been shown[174] that, particularly in aminophosphines with geminal substitution at the phosphorus atom ($R_3 = R_4$ = Cl or C_6H_5), the barrier depends on the dimensions of the R_1 and R_2 substituents linked to the nitrogen atom. When one of the substituents has a branched chain (for example, $R_1 = C_6H_5CH_2$ and $R_2 = CH_3$), the barrier is higher by 2–3 kcal mole^{-1} (up to about 14 kcal mole^{-1}) than for $R_1 = R_2 = CH_3$ (about 11 kcal mole^{-1}).

Recent studies indicate the possibility of rotational isomerism relative to the P–N bond in compounds with

¶ According to an estimate based on infrared spectra[179], in the compound $CH_3NH-P(CF_3)_2$ the barrier to internal rotation is about 20 kcal mole^{-1}. However, this value is disputed in another study[176].

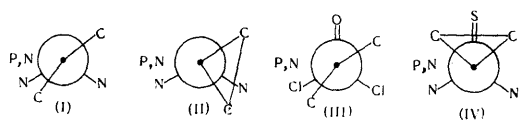
tricoordinate phosphorus[179,180]. This possibility follows in particular from the NMR spectra[180] of the compound $C_6H_{12}NPF_2$. The existence of two *gauche*-isomers has been postulated on the basis of infrared spectra[179] for the compound $CH_3NH-P(CF_3)_2$ in the gas phase, in the liquid, and in benzene solution: the first with a hydrogen atom and the second (in a smaller amount) with a methyl group between CF_3 groups; in this case free rotation obtains at temperatures above 88°C. However, the authors of the investigation[176] believe that in the latter case the characteristics of the infrared spectra cannot be interpreted similarly, i.e. in the sense of the existence of a mixture of isomers. They found that *N*-deuterated specimens $CH_3ND-P(CF_3)_2$ contains two isomers in proportions of 4:1 only below −120°C and on the basis of steric considerations it was postulated that the isomer with the deuterium atom between the CF_3 groups should predominate.

The problem of the energy favouring a particular conformer is controversial. As in the examples examined above, on the basis of NMR spectra[180] preference is given to the *gauche*-conformation of $C_6H_5(CH_3)NPF_2$ as the more favourable. The same conformation was found by X-ray diffraction for the $(CH_3)_2NPF_2$ molecule[73].

At the same time the authors of one of the NMR investigations[174] assert that at least symmetrically substituted aminophosphines $(CH_3)_2NP(C_6H_5)_2$ and $(CH_3)_2NPCl_2$ exist in the sterically less favourable *anti*-conformation. This conclusion was disproved by another NMR study[176] in which preference was given to the *gauche*-conformation of the $(CH_3)_2NPCl_2$ molecule.

On the other hand, electron diffraction showed that in the vapour phase $(CH_3)_2NPCl_2$ has the *anti*-conformation. Moreover, the *anti*-conformation is the most stable in the case of diphosphines (see below) and hydrazine derivatives.

The rotational forms of the $P[N(CH_3)_2]_3$ and $P[N(CH_2)_2]_3$ molecules in the vapour phase found by electron diffraction[71],

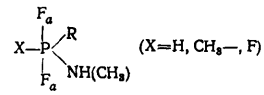


are also not the most favourable from the standpoint of steric interactions (models I and II).

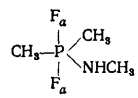
There are comparatively few experimental data for compounds of tetracoordinate phosphorus. Electron diffraction showed[72] that in the vapour phase the $(CH_3)_2NP(=O)Cl_2$ molecules has an asymmetric conformation (model III), the existence of which are confirmed by NQR spectra[181]. On the other hand, X-ray diffraction showed[142] that the $P(=S)[N(CH_2)_2]_3$ molecule has a conformation close to C_{3V} (model IV).

Vibrational spectra demonstrated[182-184] that the monosubstituted amides $RNHP(=S)Cl_2$ exist as mixtures of two rotational isomers in the liquid phase and in solutions. Under these conditions, the disubstituted amides $R_2NP(=S).Cl_2$ exist in a single conformation[182]. It has been noted that the presence of only one isomeric form of $R_2NP(=S)Cl_2$ cannot be explained by steric hindrance to the rotation of the R_2N group about the P–N bond. The geometrical parameters of the fragments about the nitrogen atom in di- and mono-substituted amides are close in magnitude and therefore the steric hindrance should be approximately the same.

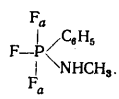
The barriers to the rotation of $NHCH_3$ groups in compounds of pentacoordinate phosphorus of the type



were determined from NMR spectra[185,186]. They vary from 5.0 ± 1.5 kcal mole^{-1} in



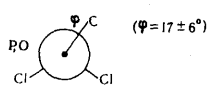
to 12 ± 1.0 kcal mole^{-1} in



These high values are attributed to the existence of intramolecular hydrogen bonds between the $NHCH_3$ groups and one of the axial F_a atoms, as shown by the observed nonequivalence of F_a atoms.

4. Compounds with a P–O bond

Only one conformer of the CH_3OPCl_2 molecule in the vapour and liquid phases with the C_S symmetry was found from vibrational spectra[187]. The barrier to rotation is 1.0 kcal mole^{-1} (1.6 kcal mole^{-1} for the deuterated derivative). It proved impossible to make a choice between the two possible orientations of the methoxy-group. According to electron diffraction data[75], the statistical mean conformation of this molecule in the vapour phase is somewhat distorted relative to C_S:



and is close to the form more favourable from the standpoint of steric interactions.

It follows from the vibrational spectra[188] of $(CH_3O)_3P=S$ that at least two conformers exist in the liquid phase and only one in the crystalline phase. The structure of this molecule in the crystalline phase has not been investigated but X-ray diffraction showed[134] that $(C_2H_5)_3P=S$ has a conformation with C_3 symmetry and the angle $\varphi < 90°$ (see above). The vibrational spectra obtained for the compounds $ROP(=Y)X_2$ (R = CH_3 or C_2H_5; X = F or Cl; Y = O or S) in the vapour, liquid, and solid phases and in solutions[189-194] indicate the presence of at least two conformers in all cases. The specific conformations were not established on the basis of the spectra but it is suggested that one of them has the C_S symmetry.

It has been shown[194] that, on the assumption of the occurrence of attraction (but not repulsion) between the CH_3 group and the Cl and S atoms, it is possible to select two models ($\varphi = 0°$ and $\varphi = 120°$) for the $CH_3OP(S)Cl_2$ molecule, whereupon the calculated frequencies agree with the experimental values for solutions of this substance.

5. Compounds with the P–P bond

From the standpoint of steric interactions, the *anti*-conformation (C_{2h} symmetry) and the *gauche*-conformation (C_2 symmetry) are the most probable for molecules of the type P_2X_4.[11] The halogeno-derivatives probably have the *anti*-conformation, which is the less favourable of the two. This has been demonstrated spectroscopically for P_2Cl_4 in all three phases[195]. Preference is also given to the *anti*-conformation of the P_2F_4 molecule[186]. The problem of the possible change in the conformation of the P_2I_4 molecule on passing from one phase to another was discussed for some time. C_{2h} symmetry was found for crystalline P_2I_4 from Raman spectra[197] and by X-ray diffraction[78]. At the same time measurements of the dipole moments[198] and interpretation of the infrared spectra[197,199] led to the assertion that, in contrast to the crystalline phase, in CS_2 solution this molecule has the C_2 symmetry. However, a subsequent repetition of the spectroscopic study[200] showed that P_2I_4 retains the C_{2h} symmetry also in CS_2 solution and an anomaly in the infrared spectra of the solutions was explained[201] by the equilibrium $3P_2I_4 \rightleftharpoons 4PI_3 + \frac{1}{2}P_4$.

The vibrational spectra of P_2H_4 in the vapour, liquid, and solid phases[202-204] have nevertheless been interpreted on the basis of the *gauche*-conformation. The spectrum of the liquid phase[203] was complicated by the presence of the decomposition products of the compound. At the same time the NMR spectrum[205] demonstrated the equivalence of the hydrogen atoms in P_2H_4. Although the author of the investigation interprets this phenomenon as evidence for rapid interconversion of different conformers, it is also consistent with the possible existence of fixed *anti*- or eclipsed (*cis*-) conformations.

Interpretation of the infrared spectra of $P_2(CH_3)_4$ showed[206] that only the *anti*-conformation exists in the crystalline phase, while in the liquid phase both *anti*- and *gauche*-conformers are present. It proved impossible to arrive at any conclusion concerning the conformation of this molecule in the gas phase. The ^1H NMR spectra[207] of the liquid phase of $P_2(CH_3)_4$ are inconsistent with the existence of the *anti*-conformer.

The *trans*-conformation with C_{2h} symmetry has been found for a number of structures of the type $R_4P_2(=S)_2$ (R = CH_3, C_2H_5, or C_6H_5) in both the crystalline phase (by X-ray diffraction[135-137] and from infrared spectra[208-212]) and in the liquid phase and in dilute solution (from infrared spectra[212]). Certain differences between the spectra of diphosphine disulphides in the crystalline and liquid phases are attributed[11] to the possibility of hindered rotation about the P–C bonds. However, three conformations of $(CH_3)_4P_2.2BH_3$ were found in the most stable of the crystalline modifications of this substance[97].

6. "Pseudorotation" in Compounds of Pentacoordinate Phosphorus

The NMR spectra of phosphorus pentafluoride (PF_5) and a number of its derivatives $PX_{5-n}F_n$ are evidence of the equivalence of the F nuclei in these compounds[12-16,213]. In particular, the equivalence in the compounds PXF_4 might correspond to an actual equilibrium configuration of the type of a tetragonal pyramid with C_{4v} symmetry. However, as already mentioned above, only the trigonal-bipyramidal configuration is characteristic of compounds of pentacoordinate phosphorus.

To account for the effect observed in the NMR spectra, the concept of "pseudorotation"—an intramolecular process as a result of which two equatorial atoms are transferred to axial positions and conversely—has been resorted to[15,16,214]. The process is accompanied by a deformation of the valence angles:



As a result, the initial trigonal bipyramid is rotated by 90° relative to the equatorial bond distinguished in the diagram. Such inversion is analogous in a certain sense to the inversion in the ammonia molecule[215] and may be caused by intramolecular vibrations[216]. Calculations yield the following values for the energy barrier to "pseudorotation" (kcal mole^{-1}): 7.6 for PF_5, 10.9 for $PClF_4$, 15.0 for CH_3PF_4, and 13.5 for PCl_5. A systematic analysis of the possible isomeric forms caused by "pseudorotation" in trigonal-bipyramidal molecules has been carried out[217].

At the same time it should be noted that the available data do not as yet allow an unambiguous determination of the true mechanism of the above intramolecular inversion. The Raman spectra obtained[218] for gaseous and liquid PF_5 do not prove the mechanism of this process as described above but they are not inconsistent with it either. In certain specific cases other possible mechanisms of such rearrangements have been postulated[16,219].

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The molecular structures of organophosphorus compounds have been examined in this review on the basis of the classical theory of structure. The aim was not to investigate the agreement between approximate electronic concepts, in particular the concept of $p_\pi - d_\pi$ interactions, and the characteristics of geometrical structure. This problem is complex and controversial[220] and requires special analysis.

The characteristics of the geometrical structure of molecules revealed by the analysis of experimental data permit the prediction of the structural parameters for compounds which have not yet been investigated and also make it possible to study the dependence of various properties of materials on their molecular structure.

Structural information is now available for organophosphorus compounds in which the phosphorus atom has different coordination numbers. The length of the phosphorus–element bond depends both on the valence state of the atoms involved in the bond and on the atoms in its immediate environment. The valence angles at the phosphorus atom are fairly characteristic of the given coordination number of phosphorus.

The characteristics of the molecular conformations determined by the rotation about the phosphorus–element bond are less well defined. Steric interactions play a considerable role but do not determine the conformation of the molecules in all cases.

ADDENDUM

After the review had been sent to the printers, a number of new studies on the structure of acyclic organophosphorus compounds were published. In many cases (concerning the reinvestigation of certain structures or more detailed reports with revision of earlier data) the appropriate corrections were introduced into the main text. In addition the following data merit consideration.

The electron diffraction study of the structure of tetramethyldiphosphine[221] $P_2(CH_3)_4$ evidently terminates the controversy concerning the most favourable conformation of this molecule (see above). In the gas phase $P_2(CH_3)_4$ was found to have a conformation close to the *anti*-form. The angle of deviation from the *anti*-form (16°) is less than the error in the determination of the angle in the above study (23°). Among other parameters found for the tetramethyldiphosphine molecule, we have the following:

$r(P\text{---}P) = 2.192\ (0.009)$ A, $\angle CPC = 99.6\ (1.0)°$,

$r(P\text{—}C\text{—}) = 1.853\ (0.003)$ A, $\angle PPC = 101.1\ (0.7)°$.

The authors of the investigation note that the geometrical parameters of diphosphine are close to those found for their analogues—monophosphines (see, in particular, Table 2).

The vibrational spectra of $N[P(CF_3)_2]_3$ are inconsistent with the planar configuration of the NP_3 fragment and have been interpreted on the basis of its pyramidal structure[222]. The infrared spectrum of the compound in the vapour phase obtained somewhat earlier[223] apparently did not contradict the hypothesis that the NP_3 fragment is planar. However, it has been noted[222] that certain important frequencies were too weak, as a result of which many ambiguities remained. Since, as stated by Hendra et al.[222], conformational analysis did not confirm the planarity of the NP_3 fragment, additional infrared spectra and laser Raman spectra in the liquid phase were measured. The study of all the available spectra[222,223] showed that the nitrogen atom in the compound can indeed be regarded as located outside the P_3 plane. As the same time one cannot exclude the possibility of an equilibrium between the planar and pyramidal structures.

The authors believe that in the pyramidal configuration of the $N[P(CF_3)_2]_3$ molecule the role of the F atoms, despite their electron-accepting properties, is more likely to involve a weakening of the P–N bonds than their strengthening. In this connection it is interesting to recall that in the compound

$(NH_2)_2P(S)$ \
 N—CH_3 ,
$NH_2(NHCH_3)P(S)$ /

investigated by X-ray diffraction in the crystalline phase[141], the length of the bonds between the P atoms and the central N atom is greater by 0.06 Å than that of the remaining $=P-N<$ bonds. However, the central N atom has a planar bond configuration.

An X-ray diffraction study of the structure of triethynyl phosphine[224] $P(C{\equiv}CH)_3$ showed that in the crystalline phase this molecule has the C_{3v} symmetry. The mean values of the principal geometrical parameters are as follows: $r(>P-C{\equiv}) = 1.75$ Å; $<CPC = 101°$. A characteristic feature is the non-linearity of the P–C≡C fragment (the angle of deviation from linearity reaches up to 11°). A similar effect was noted also in the structures $P(C{\equiv}C-C_6H_5)_3$ [68] and $P(C{\equiv}N)_3$,[69] investigated previously by X-ray diffraction.

Analysis of the infrared spectra obtained in all three phases is evidence of the presence of two rotational isomers with C_S symmetry in compounds of the series $(CF_3)_2PXY$ (where X = O or S and Y = H or D).[225]

An X-ray diffraction study of the structure of triphenylphosphine oxide[226] $(C_6H_5)_3P{=}O$ furnished a criterion allowing a quantitative estimation of the effect of the environment on the length of the bond of the type

$=P-C<$

The length of this bond in the $(C_6H_5)_3P{=}O$ molecule is 1.76 (0.01) Å, i.e. the same as the value found by electron diffraction for the $C_6H_5P(=O)Cl_2$ molecule (see Table 3B). It is striking that the $=P-C-$ bond also remains unchanged, within the limits of experimental error, on passing from the $(CH_3)_3P{=}O$ molecule to $CH_3P(O)Cl_2$ (Table 3B). However, in the series

$(C_6H_5)_3P{=}O \rightarrow (C_6H_5)_3P{=}NR \rightarrow (C_6H_5)_3P{=}C{=}C{=}X \rightarrow (C_6H_5)_3P{=}CH_2$

the length of the $=P-C<$ bond increases to 1.82 Å (Table 3B). The remaining parameters of the $(C_6H_5)_3P{=}O$ molecule have the following values:

$r(-P{=}O) = 1.46(0.01)$ A, $\angle CPC = 107.1\ (0.7)°$, $\angle CP(=O) = 111.7\ (0.6)°$.

The length of the single P–S bond was determined for only the second time in an X-ray diffraction study of the structure of the $[(iso\text{-}C_3H_7O)_2PS_2]_2$ molecule[227]. In this molecule $r(-P{=}S) = 1.908\ (0.003)$ Å is shorter than $r(=P-S) = 2.072\ (0.002)$ Å by about 0.16 Å, i.e. by the same amount as in the $[(CH_3O)_2PS_2]_2Te$ molecule (Table 3). The remaining parameters found in this investigation[224] are as follows:

$r(=P-O) = 1.561\ (0.005)$ A,

$\angle OPO = 96.6\ (0.2)°$, $\angle OP{=}S = 119.3\ (0.2)°$,

$\angle SPO = 108.2\ (0.2)°$, $\angle SP{=}S = 104.8\ (0.1)°$.

The shortening of $r(-P{=}O)$ compared with $r(=P-O-)$ found by an X-ray diffraction study of the structure of $(CH_3O)_2P(=O)R$ (where R = 3-hydroxy-2,2,5,5-tetramethyltetrahydrofuryl),[228] is only about 0.11 Å. The parameters of this structure are as follows:

$r(-P{=}O) = 1.471\ (0.007)$ A, $\angle OPO = 102.3\ (0.4)°$,

$r(=P-O-) = 1.581\ (0.009)$ A, $\angle OPC = 106.5\ (0.4)°$,

$r(=P-C-_{ring}) = 1.812\ (0.009)$ A, $\angle OP{=}O = 114.4\ (0.4)°$,

$\angle CP{=}O = 112.0\ (0.4)°$.

According to vibrational spectra[229], the $C_6H_5S-PF_4$ molecule has an equatorially substituted trigonal-bipyramidal structure.

An X-ray diffraction reinvestigation of the structure of $(CH_3)_4P_2S_2$ (see the data[135] in Table 3) showed[230] that the crystal unit cell of the substance contains two types of molecules with the following parameters:

	Molecule (I)	Molecule (II)
$r(=P-P=)$	2.245 (0.006) A	2.161 (0.004) A
$r(-P{=}S)$	1.951 (0.003) A	1.970 (0.004) A
$r(=P-C-)$	1.800 (0.008) A	1.820 (0.008) A
$\angle CP{=}S$	115.0 (0.3)°	115.0 (0.3)°
$\angle PP{=}S$	111.0 (0.2)°	112.0 (0.2)°
$\angle CPC$	103.5 (0.4)°	105.3 (0.4)°.
$\angle PPC$	105.6 (0.3)°	104.3 (0.4)°.

The authors failed to find any cause of the observed differences between the bond lengths in molecules (I) and (II) other than the effect of steric factors.

An electron diffraction study showed[231] that in the gas phase the $(CH_3)_2NPF_2$ and H_2NPF_2 molecules have the *gauche*-conformation [the $(CH_3)_2NPF_2$ molecule has the *gauche*-conformation also in the crystalline phase[73]]. The following fundamental geometrical parameters of these molecules have been quoted:

	$(CH_3)_2NPF_2$	H_2NPF_2
$r(>P-F)$	1.589 (0.003) Å	1.581 (0.003) Å
$r(>P-N<)$	1.684 (0.008) Å	1.661 (0.007) Å
$\angle$ FPN	97 (4)°	101.0 (1.1)°
$\angle$ FPF	99 (3)°	95.3 (1.1)°

It was found that the configuration of the valence angles at the nitrogen atom in the above compound is non-planar in the gas phase (the sum of the valence angles is equal to 348.4° and 346° respectively), while in the crystalline phase the PNC_2 fragment in the $(CH_3)_2NPF_2$ molecule is planar. It was noted that in $(CH_3)_2NPF_2$ the P–N bond length found in the gas phase is higher by 0.056 Å than the value found in the crystalline phase, while the P–F bond length is smaller by 0.021 Å (Table 2).

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