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Molecular Structures of Cyclic Organophosphorus Compounds

L.S.Khaikin and L.V.Vilkov

The structural data for various classes of cyclic organophosphorus compounds published up to 1972 are systematically reviewed. The geometrical parameters are classified in accordance with the concepts of the valence states of atoms in the molecule and the types of chemical bonds. The dependence of bond lengths and valence angles in various cyclic systems on the number of atoms in the latter is discussed. Endocyclic parameters are compared with exocyclic parameters and also with the corresponding parameters of acyclic structures. Such comparison makes it possible, in particular, to characterise the influence of exocyclic substituents on cyclic systems which is sometimes reflected in a considerable change of the geometrical parameters. The results of studies on the conformational relations in cyclic phosphorus-containing structures are described.
The bibliography includes 274 references.

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I. INTRODUCTION

Among organophosphorus compounds, cyclic derivatives are fairly common. Much information concerning the geometrical parameters and conformational characteristics of these compounds has now accumulated and a systematic account of such data is a timely and important task. We attempted to carry this out using as a theoretical basis for the classification of the geometrical parameters the concepts of the valence state of atoms in the molecule and the types of chemical bonds (in the sense of the classical theory of structure) [1-3]. The review gives a compilation of experimental spectroscopic and diffraction data employed to determine molecular geometry and published up to 1972.

The vast majority of these data appeared after the publication of fundamental reviews on the stereochemistry of phosphorus compounds in the compilations "Topics in Phosphorus Chemistry" [4] and "Topics in Stereochemistry" [5] and also reviews on the stereochemistry of phosphorus sulphides [6], compounds with a PP bond [7], phosphonitriles [8,9], and cyclophosphazanes [10].

Data quoted in our earlier review [11] are used for comparison with the geometrical parameters of cyclic structures. Owing to lack of space, the geometrical isomerism determined by the orientation of exocyclic substituents around the phosphorus atom and other ring atoms is not discussed, although this problem is undoubtedly closely related to that of the conformation of cyclic structures.

II. PHOSPHINOBORINES [(I)-(III)]

The phosphinoborine cyclic systems consist of PB bonds, both atoms being tetracoordinate (Table 1). The comparatively scanty information concerning the structure of phosphinoborines at present available precludes a sufficiently far-reaching analysis of their chemical structure. The lengths of the PB bonds in the rings are the same in each structure within the limits of experimental error. Exocyclic PC bonds have the usual length for single bonds formed by tetracoordinate phosphorus. However, regardless of the complexity of the ring, the length of the PB bond in phosphinoborines is greater than the sum of Pauling's covalent radii (1.91 Å) [12] and also somewhat greater than the length of the analogous bond in acyclic structures (1.83-1.95 Å). Although the phosphorus atom in phosphinoborines is formally pentacovalent, the way this property is reflected in the length of the PB bonds, which cannot be regarded as single bonds, is at least unusual.

The endocyclic valence angles are determined to a considerable degree by the dimensions of the ring system. It is striking that, with increase of the number of PB units in the ring, the endocyclic BPB phosphorus valence angle increases apparently to a greater extent than the PBP boron valence angle.

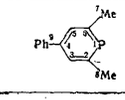
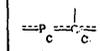
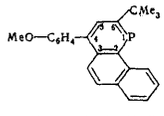
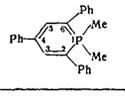
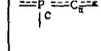
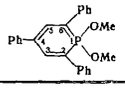
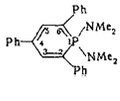
The structures of phosphinoborines have been investigated only in the crystalline state and the conformations of their ring systems have been found to be non-planar under these conditions.

Table 1. Phosphinoborines*.

Compound	Ring conformation	Endocyclic bonds		Exocyclic bonds		Endocyclic valence angles		Exocyclic valence angles		Research technique	References
		bond type	bond length, Å	bond type	bond length, Å	angle	magnitude, deg	angle	magnitude, deg		
$(Ph_2PBI_2)_2$ (I)	non-planar		2.00 (0.03)		1.81 (0.02)	BPB PBP	88.0 88.1	CPC	103.5	X-ray	13
$(Me_2PBH_2)_3$ (II)	chair	ditto	1.935 (0.009)		1.837 (0.007)	BPB PBP	118.1 (1.2) 112.2 (0.9)	CPC BPC	100.4 (0.9) 109.1 (0.6)	ditto	14
$(Me_2PBH_2)_4$ (III)	saddle	»	1.932 (0.024)	ditto	1.868 (0.012)	BPB PBP	125** 104**	CPC BPC	104.2 (1.7) 110.2 (0.7)	»	15

*Here and henceforth the subscript c denotes atoms forming part of the ring system.
**This value is quoted by Goldstein and Jacobson [16].

Table 2. Phosphabenzenes.

Compound	Rhg conformation	Endocyclic bonds		Exocyclic bonds		Endocyclic valence angles		Exocyclic valence angles		Method	Refs.
		bond type	bond length, Å	bond type	bond length, Å	angle	magnitude, deg	angle	magnitude, deg		
 (IV)	planar		1.743 (0.005)	—	—	CPC PCC	102.4 (0.2) 122.9 (0.4)	—	—	X-ray	20
 (V)	ditto	ditto	1.75	—	—	CPC PCC	103 124 (mean)	—	—	ditto	21
 (VI)	»		1.749 (0.005)		1.806 (0.006)	CPC PCC	104.72 (0.23) 119.90 (0.35)	CPC C PC c	101.32 (0.27) 112.8 (mean)	»	22
 (VII)	»	ditto	1.72 (0.02)		1.58 (0.02)	CPC PCC	107 (2) 120 (2)	OPO C PO c	93 (2) 114 (2)	»	23
 (VIII)	»	»	1.739 (0.004)		1.659 (0.003)	CPC PCC	105.0 (0.2) 119.9 (0.3)	NPN C PN c	101.6 (0.2) 112.6 (mean)	»	24

III. PHOSPHABENZENES [(IV)–(VIII)]

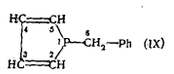
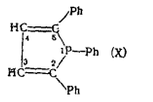
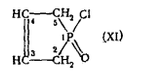
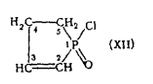
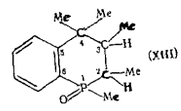
Compounds of this class are derivatives of benzene in which a phosphorus atom replaces one of the carbon atoms of the benzene ring (Table 2). The planar six-membered phosphabenzene ring is one of the first structures where the phosphorus atom was obtained in a dicoordinate state†.

† The existence of dicoordinate phosphorus in the perchlorates of phosphamethinecyanine derivatives was known previously [17–19]. In the cations $[(C_9H_9NS)_2P]^+$ [18] and $[(C_{11}H_{10}N)_2P]^+$, [19] the phosphorus atom forms two PC bonds in each case. In the first case, the cation is almost planar and has a symmetrical structure [r(PC) = 1.76 ± 0.01 Å, ∠CPC = 104.6°]. In the second case, the cation was found to be asymmetric, which is shown by a difference between the angles of rotation of the $C_{11}H_{10}N$ residues about the PC bonds and by the non-equivalence of the bonds themselves [r(PC) = 1.77 ± 0.01 and 1.81 ± 0.01 Å; ∠CPC = 100.4°].

According to X-ray diffraction data, both endocyclic PC bonds in (IV) and (V) have the same length, which is intermediate between the average lengths of $-\overset{|}{\underset{|}{P}}=C\diagdown$ bonds (1.65–1.78 Å) of single PC bonds (1.74–1.94 Å) in acyclic structures [11]. The four CC bonds in the ring also have the same length (1.388 ± 0.009 Å). The planarity of the six-membered cyclic system is achieved by an increase of the PCC and CCC angles to 122–126°, while the CPC angle is relatively small (102–103°).

In compound (IV), the displacement of the atoms in the heterocycle from the optimum mean-square plane does not exceed 0.005 Å. The displacement of the exocyclic $C_{(7)}$, $C_{(8)}$, and $C_{(9)}$ atoms from the plane of the ring is not more than 0.024 Å. All these data suggest that the phosphabenzene ring system is aromatic. The NMR and ultraviolet spectroscopic data are consistent with this conclusion [25]. With increase of the coordination number of phosphorus to four, the equivalence of the endocyclic PC (as well as

Table 3. Phospholes and phospholenes.

Compound	Ring conformation	Endocyclic bonds: bond type	Endocyclic bonds: bond length, Å	Exocyclic bonds: bond type	Exocyclic bonds: bond length, Å	Endocyclic valence angles: angle	Endocyclic valence angles: magnitude, deg	Exocyclic valence angles: angle	Exocyclic valence angles: magnitude, deg	Method	Refs.
 (IX)	envelope (weak)	$>P_c-C_c<$	1.783 (0.005)	$>P_c-\overset{\vert}{C}-$	1.858 (0.005)	CPC PCC	90.7 (0.2) 110.0 (0.4)	C_cPC PCC_{Ph}	106.0 (0.2) 116.4 (0.4)	X-ray	30
 (X)	ditto	ditto	1.822	$>P_c-C<$	1.822	—		C_cPC	105.3	ditto	31
 (XI)	envelope	$=P_c-C_c-$	1.835 (0.008)	$=P_c-Cl$ $-P_c=O$	2.040 (0.008) 1.440 (0.010)	CPC PCC	98.5 (1.5) 101.3 (1.5)	$CP=O$ $ClP=O$ CPCl	118.3 115.3(2.0) 101.3(1.0)	el.dif	32
 (XII)	envelope (methylene group closest to P atom displaced from plane of ring)	ditto $=P_c-C_c=$	1.830 (0.008) 1.791 (0.008)	$=P_c-Cl$ $-P_c=O$	2.057 (0.008) 1.451 (0.009)	CPC PCC $CP=C$	94.2 (1.0) 102.6 (calc.) 112.8 (1.0)	$C_cP=O$ $ClP=O$ $-C_cPCl$ $=C_cPCl$	117.5(3.0) 114.8(3.0) 105.6(2.0) 97.0(2.0)	ditto	33
 (XIII)	half chair	$=P_c-C_c-$ $=P_c-C<$	1.768 (0.009) 1.762 (0.009)	$=P_c-C-$ $-P_c=O$	1.864 (0.012) 1.471 (0.007)	CPC PCC $PC=C$	104.3 (0.4) 108.5 (0.6) 123.6 (0.6)	$-C_cP=O$ $CP=O$ $-C_cPC$ $=C_cPC$	113.8(0.4) 109.6(0.5) 110.2(0.5) 104.7(0.5)	X-ray	34

CC) bonds in phosphabenzene remains unaffected. Within the limits of experimental error, their length remains the same as for dicoordinate phosphorus and the endocyclic CPC angle increases only by 2–4°. However, the ring conformation deviates a little from planarity. Thus in compound (VI) the maximum displacement of a ring atom from the optimum plane reaches 0.055 Å. In compounds (VII) and (VIII), the displacement of the ring C atoms from the $C_{(3)}PC_{(5)}$ plane reaches up to 0.11 and 0.055 Å respectively. Although on passing from di- to tetra-coordinate phosphorus, the geometry of the phosphabenzene ring changes little, the problem of the aromaticity of the ring system in the latter case is more complex. This is particularly due to the ill-defined role of the *d* orbitals of phosphorus [26].

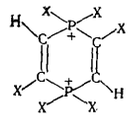
IV. PHOSPHOLES [(IX)–(X)] AND PHOSPHOLENES [(XI)–(XIII)]

According to microwave studies, the ring system of pyrrole, the nitrogen analogue of phosphole, is planar [27,28]. However, the first determinations of the structure of phosphole derivatives (Table 3) by X-ray diffraction showed that their five-membered ring with tricoordinate phosphorus and two C=C double bonds (1.350 Å) is non-planar. In particular, in compound (IX) the phosphorus atom deviates from the plane of the remaining ring atoms by 0.21 Å (the "envelope" conformation). The exocyclic $C_{(6)}$ atom is displaced relative to this plane in the direction opposite to that of the displacement of the phosphorus atom, i.e. it is, as it were, located in an equatorial position. According to one view [29], based on thermochemical data and semiempirical quantum-chemical calculations, the phosphole ring system may be aromatic. However, the barrier to the inversion of the phosphorus atom (16 kcal mole^{-1}), obtained from the NMR spectra of 1-isopropyl-2-methyl-5-phenylphosphole [35], is fairly high. The experimental structural parameters of phospholes do not indicate any significant delocalisation of electrons over the five-membered ring, although the $>P_c-C_c<$ bond in the ring is probably somewhat shorter and approaches the

length of the $=\overset{|}{P_c}-C_c\langle$ bond involving tetracoordinate phosphorus in phospholenes‡.

Phospholenes—phosphorus–carbon heterocycles with one double bond—also have non-planar conformations, the characteristics of which are determined, in particular, by the position of the double bond relative to the phosphorus atom. According to electron diffraction data, compound (XI) has the envelope conformation with displacement of the phosphorus atom from the plane of the ring. The $C_{(2)}PC_{(5)}/CCC$ dihedral angle in this structure is 13°. In compound (XII), the methylene group closest to the phosphorus atom is displaced from the P–C=C–C plane (dihedral angle 27°). In the condensed system (XIII), studied in the crystalline phase, the $C_{(4)}$, $C_{(5)}$, $C_{(6)}$, and P atoms are coplanar to within 0.05 Å, while the $C_{(2)}$ and $C_{(3)}$ atoms are 0.6 Å and 0.2 Å above and below this plane.

‡ On the basis of a combined spectroscopic study (infrared, ultraviolet, and NMR spectra)[36,37], it has been suggested that π electrons are delocalised in the six-membered PC system of the hexaphenyldiphosphoninocyclohexadiene cation.



However, X-ray diffraction data do not agree with the delocalisation hypothesis, at any rate in the analogous system with alkyl substituents[38]: $r(C{=}C)_c = 1.340(0.009)$ Å, $r(PC)_c = 1.788(0.008)$ Å, and $r(PC) = 1.793(0.003)$ Å, and the average valence angle of the phosphorus atom is 109.5 ± 0.5°; the average valence angle of the $\diagdown\!\!\diagup C=$ atoms is 120.0 ± 2.2°. The ring was found to be planar to within 0.003 Å.

V. SATURATED PHOSPHORUS–CARBON HETEROCYCLES [(XIV)–(XXIV)]

One of the most interesting saturated PC ring systems is ethylenephosphine (XIV)—a three-membered ring with tricoordinate phosphorus (Table 4). According to microwave data, the CPC endocyclic angle in this compound is only 47.4° ± 0.5°. This is the smallest valence angle of the phosphorus atom ever found. The length of the $\diagdown\!\!\diagup\overset{|}{P_c}-\overset{|}{C_c}-$ bonds is geater by 0.017 Å than in the open-chain analogue $HP(CH_3)_2$ (1.850 Å).[11]

According to X-ray diffraction data, in six-membered rings with tricoordinate phosphorus [compounds (XV) and (XVI)], the CPC endocyclic angle increases to about 98° and the $\diagdown\!\!\diagup\overset{|}{P_c}-\overset{|}{C_c}-$ bonds are shortened to the usual value of 1.84–1.85 Å. Both these rings have a non-planar conformation of the chair type with an axial location of the exocyclic phenyl substituent at the phosphorus atom despite the difference between the crystal fields in their macrostructures. The deviation of the ring atoms from the average plane diminishes somewhat at its phosphorus end.

Table 4. Saturated phosphorus–carbon heterocycles.

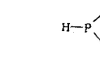
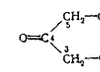
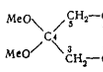
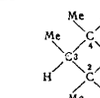
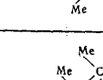
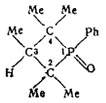
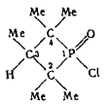
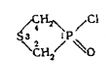
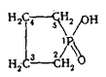
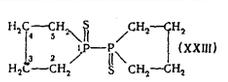
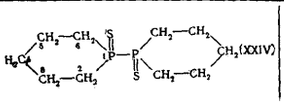
Compound	Ring conformation	Endocyclic bonds		Exocyclic bonds		Endocyclic valence angles		Exocyclic valence angles		Method	Refs.
		bond type	bond length, Å	bond type	bond length, Å	angle	magnitude, deg	angle	magnitude, deg		
 (XIV)	planar	$\diagdown P_c-\overset{\|}{C_c}-$	1.867 (0.005)	$\diagdown P_c-H$	1.428 (0.005)	CPC	47.4 (0.5)	CPH	95.2 (0.5)	microwave	39
 (XV)	chair	ditto	1.838 (0.005)		1.837 (0.005)	CPC PCC	98.2 (0.2) 116.5 (0.2)	C_cPC	102.9 (0.2)	X-ray	40
 (XVI)	ditto	»	1.855 (0.005)	ditto	1.854 (0.005)	PCP PCC	97.7 (0.2) 116.3 (0.2)	C_cPC	102.3 (0.2)	ditto	41
 (XVII)	non-planar	$=\overset{\|}{P_c}-\overset{\|}{C_c}-$	1.83 (0.02)	$=\overset{\|}{P_c}-O-$ $-\overset{\|}{P_c}=O$	1.54 (0.01) 1.48 (0.01)	CPC PCC	82.5 (0.5) 86.0 (0.6)		(106–121)	»	42
 (XVIII) (Me/P = O *cis*-form)	ditto	ditto	1.88 (0.02)	$=\overset{\|}{P_c}-C\diagup$ $-\overset{\|}{P_c}=O$	1.79 (0.01) 1.50 (0.02)	CPC PCC	84.9 (0.6) 86.7 (0.8)	$C_cP=O$ $C_{Ph}P=O$ C_cPC_{Ph}	120.0 (0.6) 110.0 (0.6) 111.4 (0.6)	»	43

Table 4 (continued).

Compound	Ring conformation	Endocyclic bonds: bond type	Endocyclic bonds: bond length, Å	Exocyclic bonds: bond type	Exocyclic bonds: bond length, Å	Endocyclic valence angles: angle	Endocyclic valence angles: magnitude, deg	Exocyclic valence angles: angle	Exocyclic valence angles: magnitude, deg	Method	Refs.
 (XIX) (Me/P = O *trans*-form)	non-planar	$=P_c-C_c-$	1.836 (0.004)	$=P_c-C$	1.809 (0.004)	CPC	81.3 (0.2)	$C_cP=O$	115.2 (0.2)	X-ray	44
				$-P_{II}=O$	1.494 (0.002)	PCC	87.1 (0.2)	$C_{Ph}P=O$	109.2 (0.2)		
								C_cPC_{Ph}	116.9 (0.2)		
 (XX)	ditto	ditto	1.84 (0.03)	$=P_c-Cl$	2.06 (0.01)	CPC	85.9 (1.4)	$C_cP=O$	122.0 (1.1)	ditto	45
				$-P_c=O$	1.48 (0.02)	PCC	84.2 (1.5)	ClP=O	110.1 (0.8)		
								C_cPCl	107.1 (0.9)		
 (XXI)	»	»	1.836 (0.015)	$=P_c-Cl$	2.032 (0.015)	CPC	86 (2)	$C_cP=O$	121	el. dif.	46
				$-P_c=O$	1.441 (0.010)			ClP=O	118 (3)		
								C_cPCl	103 (3)		
 (XXII)	half chair (twisted envelope)	»	1.786 (0.017)	$=P_c-O-$	1.567 (0.006)	CPC	94.8 (0.5)	CP=O	116 (mean)	X-ray	47
				$-P_c=O$	1.473 (0.01)	PCC	106.0 (1.5)	OP=O	113.4 (0.5)		
								CPO	107.4 (mean)		
 (XXIII)	non-planar	»	1.820 (0.007)	$=P_c-P_c=$	2.210 (0.004)	CPC	96.6 (0.3)	CP=S	117.6 (1.0)	ditto	48
				$-P_c=S$	1.950 (0.002)	PCC	105.0 (0.6)	PP=S	111.1 (1.0)		
								CPP	106.3 (1.0)		
 (XXIV)	ditto	»	1.810 (0.011)	$=P_c-P_c=$	2.21 (0.004)	CPC	101.8 (0.4)	CP=S	115.3 (0.4)	»	49
				$-P_c=S$	1.950 (0.004)	PCC	108.8 (0.8)	PP=S	112.7 (0.2)		
								CPP	105.2 (0.4)		

The distribution of torsion angles is as follows (in degrees):

	$PC_{(2)}C_{(3)}C_{(4)}$	$C_{(2)}C_{(3)}C_{(4)}C_{(5)}$	$C_{(3)}C_{(4)}C_{(5)}C_{(6)}$
in (XV)	−49.8	+53.0	−56.1
in (XVI)	−58.0	+62.4	−60.5

	$C_{(4)}C_{(5)}C_{(6)}P$	$C_{(5)}C_{(6)}PC_{(2)}$	$C_{(6)}PC_{(2)}C_{(3)}$
in (XV)	+56.3	−47.6	+44.3
in (XVI)	+56.1	−44.7	+45.5

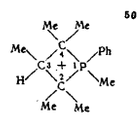
According to the NMR spectrum, in a solution of compound (XVI), one conformation also predominates, as has been suggested for the solid phase [41].

In saturated four-, five-, and six-membered rings with tetracoordinate phosphorus, the length of the $=P_c-C_c-$ bonds does not differ, within the limits of experimental error, from the values found for open-chain compounds. At the same time, the endocyclic CPC angles are determined by the ring size and increase from 82–86° in compounds (XVII)–(XXI) to 94.5–96.5° in compounds (XXII) and (XXIII) and to 102° in compound (XXIV). However, the last value is still less than the analogous angle in open-chain compounds (104–109°). [11] The ring conformations in these compounds are also non-planar. The displacement of the atoms from the optimal mean-square plane in the four-membered rings of (XVII)–(XXI) is 0.10–0.15 Å. The dihedral angles and other characteristics of the conformations of the rings§ are given in Table 5.

In compounds (XVIII)–(XX), the single methyl group at the $C_{(3)}$ atom is fixed in the equatorial position. Thus in these structures there is geometrical isomerism determined by the position of the exocyclic substituent at the P atom.

In the five-membered ring of (XXII), the P, $C_{(2)}$, $C_{(4)}$, and $C_{(5)}$ atoms are approximately in the same plane (the angle between the normals to the $PC_{(2)}C_{(5)}$ and $PC_{(5)}C_{(4)}$

§ In the cyclic cation



the $C_{(2)}PC_{(4)}/C_{(2)}C_{(3)}C_{(4)}$ dihedral angle is 24°. The remaining structural parameters have the following values: $r(PC)_c = 1.93(0.02)$ Å, $\angle(CPC)_c = 82.6°$, and $\angle(PCC)_c = 84.7°$. The methyl group at the $C_{(3)}$ atom is in the *cis*-position relative to the phenyl group.

planes is only 5°), from which only the $C_{(3)}$ atom deviates significantly. The torsion angles relative to the bonds in the ring have the following values starting from $PC_{(2)}$: 5°, 24°, 36°, 30°, and 14°¶.

Table 5.

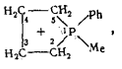
Compound	Dihedral angles, deg			Position of P=O bond	Position of CH_3 group at $C_{(3)}$ atom relative to P=O bond
	$C_{(2)}PC_{(4)}/C_{(2)}C_{(3)}C_{(4)}$	$PC_{(2)}C_{(3)}/PC_{(4)}C_{(3)}$	$C_{(2)}PC_{(4)}/XP{=}O$		
(XVII)	19.6				
(XVIII)	21.6	20.6	91.6	eq.	*cis-*
(XIX)	23.8	22.3	91.1	ax.	*trans-*
(XX)	26.4			aq.	*cis-*
(XXI)	10and35			mixture of isomers with ax. and eq. P=O bonds in proportions of 4 : 1	

VI. PHOSPHADIAZOLES [(XXV)–(XXVIII)], PHOSPHAOXADIAZOLES (XXIX), AND PHOSPHAOXAZOLES (XXX)

After phosphabenzenes, phosphadiazoles are the second class of compounds in which the existence of dicoordinate phosphorus was demonstrated (Table 6). The planarity of the five-membered ring system with dicoordinate phosphorus was studied by electron diffraction. The experimental geometrical parameters and the vibration, ultraviolet, and NMR spectroscopic data for compounds of this class [52,53,58] suggest that electrons are delocalised in the phosphadiazole rings of (XXV) and (XXVI) as in phosphabenzene derivatives.

The conformation of the five-membered rings with tricoordinate phosphorus in compounds (XXVII), (XXIX), and (XXX) is non-planar: the phosphorus atom is markedly displaced from the plane of the remaining four atoms (envelope conformation). According to electron diffraction data, the dihedral angles characterising the displacement of the phosphorus atom from the plane are respectively 28.8°, 20.0°, and 23.0°. The lengths of the endocyclic PO and PN bonds are normal for tricoordinate phosphorus [11]†. At the same time, it is striking that the endocyclic valence angle at the tricoordinate phosphorus atom is appreciably greater (by about 5°) than that at the dicoordinate phosphorus atom. The exocyclic PCl bonds in (XXVII), (XXIX), and (XXX) occupy axial positions. Their lengths (2.17–2.19 Å) are unusual for covalent bonds of tricoordinate phosphorus. They are significantly longer than in all the cases known previously (2.04–2.08 Å). [11]

¶ A fundamentally identical ring conformation was found in the cation [61]



where the torsion angles have the following values (also starting from $PC_{(2)}$): 5°, 26°, 40°, 36°, and 17°. The remaining parameters of this structure are as follows: $r(PC)_C$ = 1.765(0.02) Å, $r(PC_{Me})$ = 1.80(0.02) Å, $r(PC_{Ph})$ = 1.76(0.02) Å, $\angle(CPC)_C$ = 94.8(1.1)°, $\angle(PCC)_C$ = 101.1(1.7)°.

† Anomalous PN bond lengths were found by X-ray diffraction in the structure of the cation $Cl_4P(NCH_3)_2C^+Cl$—a planar four-membered ring system with hexacoordinate phosphorus [59]. The lengths of both PN bonds—axial (1.91 ± 0.04 Å) and equatorial (1.85 ± 0.06 Å)—are significantly greater than the sum of the covalent radii after correction for heteropolarity (1.75 Å). This can also be said of the exocyclic PCl bonds (2.15 ± 0.02 Å and 2.09 ± 0.02 Å) found in this structure.

VII. PHOSPHONITRILES [(XXXI)–(LXI)]

Phosphonitriles are cyclic structures comprising a variable number of formally unsaturated $-\underset{|}{\overset{|}{P}}{=}N-$ units formed by tetracoordinate quinquevalent phosphorus and dicoordinate tervalent nitrogen. Nevertheless there is no alternation of single and multiple bonds in phosphonitriles (Table 7).

1. Phosphonitriles with Identical Substituents at the Phosphorus Atoms [(XXXI)–(L)]‡

When the substituents at all the phosphorus atoms are the same, the PN bonds in the ring have the same length, which however is much smaller, particularly in more complex rings, when the number of ring units $n > 4$, than the $=\underset{|}{\overset{|}{P}}-N\langle$ (1.60–1.71 Å) and even $-\underset{|}{\overset{|}{P}}{=}N-$ (up to 1.64 Å) bond lengths in acyclic structures [11]. The length of the PN endocyclic bonds is significantly influenced by the substituents at the phosphorus atom. Whereas in the trimers this effect is relatively small [the average r(PN) remains within the limits 1.58 ± 0.02 Å], in the octafluorotetramer (XLIII) r(PN) = 1.507 Å and in the decachloropentamer (XLVII) r(PN) = 1.521 Å, which is far outside the range of the other values. Although the endocyclic valence angles of the phosphorus atom vary in these structures comparatively little (117–123°), these changes are also related to the properties of the substituents. A large NPN angle is obtained when the substituents are halogen atoms. The range of variation of the PNP angles is much greater (120–149°). A gradual increase in the PNP angles takes place with increase of ring size up to hexamers, but subsequently the angles appear to decrease. A systematic effect of the properties of exocyclic substituents on the PNP angles could not be discovered.

It is interesting that the ratio of the ranges of variation of the NPN and PNP angles in phosphonitriles is the reverse of the ratio of the ranges of variation of the BPB and PBP angles in phosphinoborines (see above).

The conformations of the phosphonitrile ring systems bear a definite relation to the number of PN units. The trimers (XXXI)–(XXXVIII) have planar or almost planar ring conformations, the average endocyclic angle being always close to 120°. As a rule, the deviations from the ideal symmetry D_{3h} are minimal: the displacement of the ring atoms from the plane usually does not exceed 0.07 Å. More pronounced distortions were found in only two cases. In compound (XXXII), five ring atoms lie in one plane, while one of the N atoms is displaced from it by 0.15 Å. In (XXXIII), two nitrogen atoms are displaced from the plane of the remaining ring atoms in opposite directions

‡ Symmetrical phosphonitriles with non-geminal substituents [compounds (XLI), (XLV), and (XLVI)] are also included here.

Table 6. Phosphadiazoles, phosphaoxadiazoles, and phosphaoxazoles.

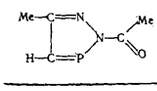
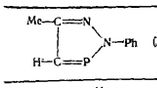
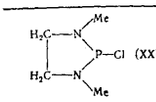
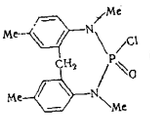
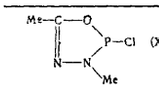
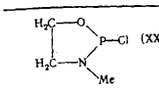
Compound	Ring conformation	Endocyclic bonds: bond type	Endocyclic bonds: bond length, Å	Exocyclic bonds: bond type	Exocyclic bonds: bond length, Å	Endocyclic valence angles: angle	Endocyclic valence angles: magnitude, deg	Exocyclic valence angles: angle	Exocyclic valence angles: magnitude, deg	Method	Refs.
 (XXV)	planar	$=P_c-N_c<$ $-P_c=C_c<$	1.68 (0.01) 1.75 (0.01)	—		NPC PNN	89.0 (1.5) 115.0 (2.5)	—		el. dif.	52
 (XXVI)	ditto	$=P_c-N_c<$ $-P_c=C_c<$	1.65 (0.03) 1.75 (0.03)	—		NPC PNN	92 110 (assumed)	—		ditto	53
 (XXVII)	envelope	$>P_c-N_c<$	1.68 (assumed)	$>P_c-Cl$	2.19 (0.02)	NPN PNC CCN	89.3 113.7 (1.0) 106.2 (1.5)	NPCl	102 (2)	»	54
 (XXVIII)	non-planar	$=P_c-N_c<$	1.644 (0.006)	$=P_c-Cl$ $-P_c=O$	2.069 (0.003) 1.492 (0.005)	NPN PNC	108.3 (0.3) 120.1 (mean)	NPCl NP=O ClP=O	103.0 (mean) 115.8 (mean) 109.2 (0.2)	X-ray	55
 (XXIX)	envelope	$>P_c-N_c<$ $>P_c-O_c-$	1.70 (0.015) 1.60 (0.015)	$>P_c-Cl$	2.170 (0.005)	NPO PNN POC	95 108 105.5	NPCl= =OPCl	101 (1)	el. dif.	56
 (XXX)	ditto	$>P_c-N_c<$ $>P_c-O_c-$	1.692 (0.013) 1.622 (0.013)	$>P_c-Cl$	2.174 (0.009)	NPO POC CCO=CCN PNC	93.9 115.6 107.8 (1.0) 112.7 (1.0)	NPCl OPCl	101.2 (1.5) 98.1 (1.5)	ditto	57

Table 7.

Compound	Ring conformation	Endocyclic bonds: bond type	Endocyclic bonds: bond length, Å	Exocyclic bonds: bond type	Exocyclic bonds: bond length, Å	Endocyclic valence angles: angle	Endocyclic valence angles: magnitude, deg	Exocyclic valence angles: angle	Exocyclic valence angles: magnitude, deg	Method	Refs.
A. Phosphonitriles with all substituents of the same type at the phosphorus atoms											
$(NPPh_2)_3$ (XXXI)	chair (weak)	$=P_c=N_c=$	1.597 (0.006)	$-P_c-C<$	1.804 (0.007)	NPN PNP	117.8 (0.4) 122.1 (0.3)	CPC NPC	103.8 (0.3) 108.6 (0.3)	X-ray	72
$[NP(-N=C=S)_2]_3$ (XXXII)	non-planar (weak)	ditto	1.58 (0.05)	$-P_c-N=$	1.63 (0.01)	NPN PNP	119 (3) 121 (4)	NPN N_cPN PNC N=C=S	100 (1) 109 (2) 152 (10) 175 (2)	ditto	73
$[NP(OPh)_2]_3$ (XXXIII)	non-planar (weak)	»	1.575 (0.002)	$-P_c-O-$	1.582 (0.002)	NPN PNP	117.3 (0.2) 121.9 (0.3)	OPO NPO POC	98.1 110.0 123.2	»	74
$[NP(OC_6H_4)_2]_3$ (XXXIV)	boat (weak)	»	1.572 (0.006)	$-P_c-O_c-$	1.584 (0.005)	NPN PNP	118.4 (0.25) 121.0 (0.25)	$(OPO)_c$ NPO $(POC)_c$	102.7 (0.25) 108.6 (0.25) 120.0 (0.4)	»	75
$(NPO_2C_6H_4)_3$ (XXXV)	planar	»	1.576 (0.002)	ditto	1.598	NPN PNP	119 122	$(OPO)_c$ NPO	97 107.0	»	76
$(NPF_2)_3$ (XXXVIa)	ditto	»	1.586 (0.013)	$-P_c-F$	1.548 (0.013)	NPN=PNP	120.0 (assume)	FPF	98.8 (3.0)	el. dif	77
$(NPF_2)_3$ (XXXVIb)	»	»	1.560 (0.012)	ditto	1.521 (0.012)	NPN PNP	119.4 (0.9) 120.3 (0.9)	FPF NPF	99.1 (0.7) 109.0 (0.6)	X-ray	78
$(NPCl_2)_3$ (XXXVIIa)	chair (weak)	»	1.582 (0.005)	$-P_c-Cl$	2.006 (0.003)	NPN=PNP	119.7 (0.2) (mean)	ClPCl	101.5 (1.5)	el. dif	79

Table 7 (continued).

Compound	Ring conformation	Endocyclic bonds		Endocyclic bonds		Endocyclic valence angles		Endocyclic valence angles		Method	Refs.
		bond type	bond length, Å	bond type	bond length, Å	angle	magnitude, deg	angle	magnitude, deg		
$(NPCl_2)_3$ (XXXVIIb)	chair (weak)		1.581 (0.003)		1.993 (0.002)	NPN PNP	118.4 (0.2) 121.4 (0.3)	ClPCl NPCl	101.4 (0.1) 108.9 (0.3)	X-ray	80
$(NPBr_2)_3$ (XXXIII)	ditto	ditto	1.576 (0.008)		2.162 (0.004)	NPN PNP	118.5 (0.6) 121.4 (0.6)	BrPBr NPBr	102.1 (0.1) 108.8 (0.5)	ditto	81
$(NPMe_2)_4$ (XXXIX)	saddle	»	1.596 (0.005)		1.805 (0.008)	NPN PNP	119.8 (0.3) 131.9 (0.3)	CPC NPC	104.1 (0.3) 108.0 (mean)	»	82
$[NP(NMe_2)_2]_4$ (XL)	ditto	»	1.578 (0.01)		1.679 (0.01)	NPN PNP	120.1 (0.5) 133.0 (0.6)	NPN PNC CNC N_cPN	103.8 (0.5) 119.1 (mean) 116.0 (1.0) 108 (mean))	»	83
$N_4P_4Ph_4(NHMe)_4^*$ (XLI)	chair	»	1.59 (0.01)	 	1.81 (0.01) 1.68 (0.01)	NPN PNP	120 (mean) 128 (mean)	CPN PNC	106.0 (0.5) 120 (0.5)	»	84
$[NP(OMe)_2]_4$ (XLII)	saddle	»	1.570 (0.01)		1.581 (0.01)	NPN PNP	121.0 (0.6) 132.2 (0.7)	OPO POC NPO	105.5 (0.5) 121.0 (0.9) 107.4 (0.5)	»	85
$(NPF_2)_4$ (XLIII)	planar	»	1.507 (0.017)		1.514 (0.015)	NPN PNP	122.7 (1.0) 147.2 (1.4)	FPF NPF	99.9 (1.0) 108.0 (1.0)	»	86
$(NPCl_2)_4$ (XLIVa) (*K*-form)	boat	»	1.570 (0.01)		1.989 (0.004)	NPN PNP	121.2 (0.5) 131.3 (0.6)	ClPCl ClPN	102.8 (0.2) 108 (mean)	»	87
$(NPCl_2)_4$ (XLIVb) (*T*-form)	chair	ditto	1.559 (0.012)	ditto	1.992 (0.004)	NPN PNP	120.5 (0.7) 135.6 (mean)	ClPCl ClPN	103.1 (0.2) 108 (mean)	»	88
$N_4P_4Ph_4Cl_4^*$ (XLV) *trans*-isomer	chair	»	1.57 (mean)	 	1.79 (mean) 2.03 (mean)	NPN PNP	120 (mean) 135.5 (mean)	ClPC	104 (mean)	»	84
$N_4P_4Ph_4Cl_4^*$ (XLVI) *cis*- isomer	crown	»	1.573 (0.008)	 	1.783 (0.010) 2.042 (0.004)	NPN PNP	121.2 (0.5) 137.4 (0.5)	ClPC	103.0 (0.5)	»	89
$(NPCl_2)_5$ (XLVII)	nearly planar	»	1.521 (0.02)	ditto	1.961 (0.01)	NPN PNP	118.3 (1.0) 148.6 (1.5)	ClPCl ClPN	102.2 (0.5) 108.7 (mean))	»	90
$[NP(NMe_2)_2]_6$ (XLVIII)	boat	»	1.563 (0.01)		1.669 (0.01)	NPN PNP	120.0 (0.5) 147.5 (0.7)	NPN PNC CNC N_cPN	102.9 (0.5) 120.1 (0.8) 113.0 (1.0) 108.2 (mean)	»	91
$[NP(OMe)_2]_8$ (XLIX)	consists of two plane and parallel segments	»	1.561 (0.005)		1.576 (0.005)	NPN PNP	116.7 (mean) 136.7 (mean)	OPO POC N_cPO	101.3 (mean) 120.6 (0.4) 109.4 (mean)	»	92
$(NCPl_2)_\infty$ (L)	plane fibres	»	1.60			NPN PNP	119 127			»	93
B. Phosphonitriles with substituents of different types at the phosphorus atoms											
$N_3P_3Ph_2F_4$ (LI)	boat (weak)	»	1.539 (0.005) 1.558 (0.004) 1.618 (0.005)	 	1.79 (0.01) 1.526 (0.005)	NPN PNP	115.5 (0.3) 120.6 (0.3) 120.5 (0.2)	CPC NPC FPF NPF	107.9 (0.3) 108.4 (0.3) 96.9 (0.2) 109.4 (0.3)	»	94
$N_3P_3Ph_2Cl_4$ (LII)	chair (weak)	»	1.555 (0.005) 1.578 (0.005) 1.615 (0.005)	 	1.788 (0.006) 1.998 (0.002)	NPN PNP	115.2 (0.3) 119.7 (0.3) 119.2 (0.3) 122.0 (0.3)	CPC ClPCl	104.4 (0.3) 100.3 (0.1)	»	95

Table 7 (continued).

Compound	Ring conformation	Endocyclic bonds: bond type	Endocyclic bonds: bond length, Å	Exocyclic bonds: bond type	Exocyclic bonds: bond length, Å	Endocyclic valence angles: angle	Endocyclic valence angles: magnitude, deg	Exocyclic valence angles: angle	Exocyclic valence angles: magnitude, deg	Method	Refs.
$N_3P_3Ph_4Cl_2$ (LIII)	boat (weak)		1.556 (0.009) 1.578 (0.008) 1.609 (0.008)	 	1.792 (0.011) 2.017 (0.005)	NPN PNP	115.5 (0.4) 120.7 (0.5) 121.1 (0.5) 124.9 (0.5)	CPC ClPCl	104.4 (0.5) 98.5 (0.2)	X-ray	96
$N_3P_3Cl_5F$ (LIV)	planar	ditto	1.563 (0.007)		1.963 (0.005) (mean)	NPN PNP	118.5 (0.5) 121.9 (0.4)	HalPHal NPHal	100.5 (0.2) 108.9 (0.4)	ditto	97
$N_4P_4Me_2F_6$ (LV)	saddle	»	1.487 (0.006) 1.532 (0.006) 1.470 (0.006) 1.584 (0.006)	 	1.481 (0.009) 1.794 (0.008)	NPN PNP	125.4 (0.5) 116.9 (0.5) 145.0 (0.5)	FPF CPC FPN CPN	93.7 (0.5) 105.7 (0.6) 107.9 (0.5) 108.4 (0.4)	»	98
$N_4P_4Me_4F_4$ (LVI)	saddle	»	1.53 (0.01) 1.59 (0.01)	 	1.52 (0.01) 1.81 (0.01)	NPN PNP	125.9 (0.9) 117.5 (0.5) 134.6 (0.7)	FPF CPC FPN CPN	96.7 (1.2) 106.9 (0.7) 108 (mean) 108 (mean)	»	99
C. Diphosphatriazines and phosphatriazines											
$NPCl_2(NSOCl)_2$ (LVII)	chair	»	1.585 (0.013)		1.957 (0.006)	NPN PNS	115.3 (0.7) 122.5 (0.8)	ClPCl NPCl	104.4 (0.3) 109.2 (0.5)	»	100
$(NPPh_2)_2NCMe$ (LVIII)	twisted boat	»	1.597 (0.003) 1.620 (0.003)		1.801 (0.002)	PNP PNP PNC	116.5 (0.2) 115.4 (0.2) 119.9 (0.2)	CPC NPC	105.4 (0.2) 108.5 (mean)	»	101
$(NPPh_2)_2NCNMe_2$ (LIX)	ditto	»	1.597 (0.002) 1.608 (0.002)	ditto	1.802 (0.002)	NPN PNP PNC	117.1 (0.1) 115.4 (0.1) 120.9 (0.1)	CPC NPC	104.1 (0.1) 108.1 (mean)	»	102
D. Structures complicated by additional covalent bonds at the nitrogen atom											
$[(NPMe_2)_4H]CuCl_3$ (LX)	boat	»	1.56 (0.02) 1.60 (0.02) 1.63 (0.02) 1.67 (0.02)		1.78 (0.03)	NPN PNP	115 (1.5) 113 (1.5) 129 (mean)	CNC	106.6 (mean)	»	103
$N_7P_6Cl_9$ (LXI)	condensed non-planar structure	 	1.572 (0.007) 1.559 (0.007) 1.723 (0.006)		1.980 (0.004) 2.004 (0.004)	N=P=N N—P=N PNP	116.9 110.7 125.5	ClPCl NPCl NPN	101.6 (0.1) 109.3 (0.3) 113.1 (0.4)	»	104

*Each ring phosphorus atom has two different substituents.

by 0.13 and 0.17 Å. Since most of the investigations were made by X-ray diffraction on crystalline materials, the deviations from the planar conformation are frequently accounted for by intermolecular interactions. This view appears to be confirmed by the vibration spectra of solutions of (XXXII) [60] and also the spectra of the tetrafluoro- and hexachloro-compounds in solutions and in liquid and gaseous phases [61,62], which agree with the D_{3h} symmetry. When the substituents at the phosphorus atoms are very bulky, the distortion of the planar conformation can also be a consequence of intramolecular steric interactions. The almost planar ring conformation in trimers and also the equivalence of the endocyclic PN bonds are sometimes quoted as evidence in support of the aromaticity of the $(R_2PN)_3$ system [63].

In the crystalline phase, the tetrameric phosphonitriles (XXXIX)–(XLVI) have significantly non-planar rings with the exception of the octafluoro-compound (XLIII), the conformation of which in the crystalline phase shows only a slight deviation from the D_{4h} symmetry. The displacement of the phosphorus atoms from the mean plane [83] varies as a function of substituents up to 0.35 Å and that of the nitrogen atom is almost constant (0.47–0.54 Å) in such structures, with the exception of (XLIII).

One should note that the vibration spectra of the octafluoro-compound in the gaseous and liquid phases [62] were interpreted on the basis of a lower symmetry (probably C_{2h}) than those of the crystalline phase ($\sim D_{4h}$). The authors [62] believe that this is an indication of a high flexibility of the phosphonitrile ring.

The importance of the role of steric interactions in the determination of the conformations of the tetrameric rings is confirmed by the existence of configurational isomers in the crystalline phase. The first known example (the octachloro-compound) has two polymorphic forms (XLIVa) and (XLIVb) with similar bond lengths and valence angles: the K-form (boat, symmetry close to S_4) and the T-form (chair, symmetry close to C_{2h}). The conformation of the

ring of (XLIV) is evidently different in the liquid and gaseous phases. The vibration spectra of the octachloro-compound in the vapour and liquid phases and in two solid modifications are interpreted according to latest data on the basis of the molecular symmetries D_{4h}, D_{2h}, S_4, and C_{2h} respectively[64], although previously the spectra of the gaseous phase were interpreted on the basis of a lower symmetry[62].

Yet another example of configurational isomerism is provided by a structure with symmetrical non-geminal substituents at the phosphorus atoms: $N_4P_4(C_6H_5)_4Cl_4$. Two crystalline modifications, (XLV) and (XLVI), are known; their molecules differ not only by the ring from (chair, close to C_{2h} symmetry, and crown with distortions resulting in a lowering to C_{2v} symmetry instead of C_{4v} symmetry) but also by the mutual orientation of the substituents at the phosphorus atoms. Whereas in (XLV) the chlorine atoms as well as the C_6H_5 groups are located alternately above and below the ring (the *trans*-isomer), in (XLVI) all the chlorine atoms lie on one side of the ring (the *cis*-isomer). Since (XLV) and (XLVI) are geometrical isomers, the differences between their ring forms are most probably due to steric factors.

Despite the fact that the ring conformations of the tetramers are mainly non-planar, a common feature of phosphonitriles is believed to be a tendency to assume a planar ring conformation. This tendency competes with steric influences of different types.

Analysis of the vibration spectra of solutions and of the liquid and gaseous phases[61,62] suggested a planar ring conformation (symmetry close to D_{5h}) of the decafluoro-pentamer and a lower, probably C_{5v}, symmetry (crown conformation) for the decachloro-pentamer. X-Ray diffraction showed that in the decachloro-pentamer (XLVII) the ring conformation is also very nearly planar: the displacement of the atoms from the plane are not more than 0.2 Å). In the case of D_{5h} symmetry, a planar ten-membered ring would require an increase of the nitrogen valence angles to about 170° (since the endocyclic phosphorus angles usually differ little from 120°). The actual planar conformation (symmetry C_{2v}) is achieved owing to the formation by two nitrogen atoms of angles directed inwards into the ring ("re-entrant" angles). As a result, the average angle of the nitrogen atom decreases to 148°. The vibration spectra of the decabromo-pentamer[65] indicate a distortion of the ring conformation with a consequent change from D_{5h} symmetry probably to a C_{2v} structure, of the type observed for the chloro-derivative. The ring system of the octamer (XLIX) consists of two symmetrical six-membered segments located in parallel planes and joined to one another via PN units. The planarity of each segment (the average deviation of the atoms from the plane is about 0.12 Å) is ensured, as in compound (XLVII), by re-entrant nitrogen atoms. The deviation of the ring atoms from the common plane is also small (0.26 Å).

A nearly planar distribution of PN bonds was found by X-ray diffraction in the structure of the high-polymer (L). This is not inconsistent with infrared spectroscopic data[66]. According to X-ray diffraction, the $[NPF_2]_\infty$ fibres also have a planar chain structure[67]. In this case two molecular conformers were found.

However, the hexamer (XLVIII) has a highly puckered ring. The displacement of the phosphorus atoms from the average plane is 0.56 Å and that of the nitrogen atoms is 0.39 Å. This is regarded as a consequence of the steric interactions of the substituents at the phosphorus atoms—$N(CH_3)_2$ groups.

2. Phosphonitriles with Different Substituents at the Nitrogen Atoms [(LI)–(LVI)]

The different exocyclic substituents at the phosphorus atoms result in the inequality of the PN bond lengths and the analogous angles in the ring. The length of the PN bond in each PNP segment depends in general on substituents at the two extreme phosphorus atoms. For example, r(PN) on the side of halogen atoms is somewhat shorter than on the side of hydrocarbon groups. This is clearly illustrated by the results of an X-ray diffraction study of trimers (in Å): (LI) (1.558 for $=PF_2-N=PF_2$; 1.539 and 1.618 for $=PF_2-N=PPh_2=$); (LII) (1.578 for $=PCl_2-N=PCl_2=$; 1.555 and 1.615 for $=PCl_2-N=PPh_2=$); (LIII) (1.556 and 1.609 for $=PPh_2-N=PPh_2=$; 1.578 for $=PCl_2-N=PPh_2=$). Similar relations were found also for the tetramers (LV) and (LVI).

An increase of the relative number of halogen substituents leads to a systematic decrease of the average PN bond length in the ring, although in the chloro-derivatives these changes are in general within the limits of experimental error; we have (in Å):

1.597 in $N_3P_3Ph_6$ (XXXI) → 1.581 in $N_3P_3Cl_2Ph_4$ (LIII) → 1.583 in $N_3P_3Cl_4Ph_2$ (LII) → 1.581 in $N_3P_3Cl_6$ (XXXVII).

However, in the fluoro-derivatives the changes are fairly explicit:

1.597 in $N_3P_3Ph_6$ (XXXI) → 1.572 in $N_3P_3F_4Ph_2$ (LI) → 1.560 in $N_3P_3F_6$ (XXXVI);

1.596 in $N_4P_4Me_8$ (XXXIX) → 1.560 in $N_4P_4F_4Me_4$ (LVI) → 1.518 in $N_4P_4F_6Me_2$ (LV) → 1.507 in $N_4P_4F_8$ (XLIII).

The conformations of the trimeric rings are nearly planar, as in the case discussed above. In compound (LII) the maximum deviation of the ring atoms from the average plane does not exceed 0.078 Å. In (LI) five P and N atoms are located approximately in one plane and the sixth atom (phosphorus), linked to two phenyl groups, is displaced from this plane by 0.20 Å. The opposite N atom is displaced from the plane of the remaining four atoms by 0.06 Å. This form of the ring may be regarded as a weak boat type of conformation. A similar conformation was found in compound (LIII).

The six-membered ring is closest to planarity in compound (LIV), where the maximum deviation of the P and N atoms from the plane is only 0.011 Å.

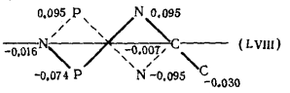
In the tetramer (LVI), the N atoms deviate from the plane of the phosphorus atoms by 0.48 Å. In (LV) the deviation is much less (0.15 Å). In this case, there is a correlation between the increase of the number of F atoms and the tendency towards the formation of a planar ring.

3. Diphosphatriazines and Phosphatriazines [(LVII)–(LIX)]

The six-membered diphosphatriazine rings N_3P_2C are intermediate between the planar triazine structures N_3C_3 and the trimeric phosphonitriles, which, apart from the hexafluoro-compounds, have incompletely planar ring conformations.

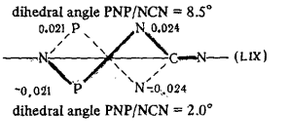
The replacement of one of the phosphorus atoms in the trimer by a carbon atom $=C\langle$ results, according to X-ray diffraction data, in a lengthening of the PN(C) bonds in the ring compared with the PN(P) bonds, to 1.620 Å in (LVIII) and to 1.608 Å in (LIX). Moreover, the endocyclic NPN and PNP angles are smaller than the corresponding angles

in the trimeric phosphonitriles. The ring conformations in both molecules were found to be non-planar, although X-ray diffraction study of the $(NPMe_2)_2NCNMe_2$ structure led to the opposite conclusion [68]. In the methyl derivative (LVIII), the displacement of the ring atoms from the average plane reaches 0.1 Å. In the amino-derivative (LIX), the degree of puckering of the ring is significantly smaller (the displacement of the atoms from the average plane is up to 0.024 Å). However, this difference has little influence on the geometrical ring parameters.



(LVIII)

dihedral angle PNP/NCN = 8.5°



(LIX)

dihedral angle PNP/NCN = 2.0°

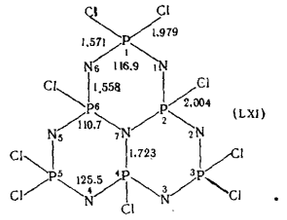
The ring in compound (LVII) also has a non-planar conformation of the chair type which is somewhat distorted owing, it is believed, to intermolecular interactions in the crystalline phase.

4. Structures Complicated by Additional Covalent Bonds at the N Atoms [(LX) and (LXI)]

In compound (LX), the proton and the $CuCl_3$ group are linked covalently to the N atoms at the opposite ends of the eight-membered ring which thus become tricoordinate§. This causes a significant increase in the length of the nearest PN endocyclic bonds. PN bonds of different lengths are located in the ring symmetrically in pairs, the effect of the proton on their length being more pronounced than that of the $CuCl_3$ group: the respective lengths are 1.67, 1.56, 1.60, and 1.63 Å. The valence angles of the P atoms differ significantly from those in the initial compound (XXXIX): the average NPN angle is 114° against 119.8° in the initial compound and the exocyclic CPC angle is 106.6° against 104°. In the absence of factors distorting their symmetry, the endocyclic NPN angles do not differ significantly from 120° in any of the phosphonitrile structures and the exocyclic XPX angles as a rule do not exceed 104°.

The conformation of the ring in compound (LX) is non-planar boat. As in other tetrameric structures (see above), the displacement of the N atoms from the average plane is somewhat greater than that of the P atoms (0.55 and 0.48 Å).

In the condensed cyclic structure of (LXI), the geometrical parameters of the central fragment with a tricoordinate central N atom are of special interest. The average length of the three PN bonds formed by this atom is 1.723 Å, i.e. greater than the average length of the exocyclic PN bonds in phosphonitriles and also of the endocyclic bonds in cyclophosphazanes with tetracoordinate phosphorus (see below). The central N atom is almost coplanar with the neighbouring P atoms (its deviation from their plane amounts to only 0.04 Å), while in the last two cases the N atoms have less planar bond configurations. The increase of the PN bond length with retention of a nearly planar configuration of the N bonds was noted also in the review of the molecular structures of acyclic phosphorus compounds [11].



(LXI)

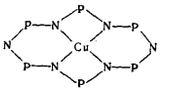
The three penta-atomic segments in compound (LXI) (without the $N_{(7)}$ atom) are almost planar (the average deviation is 0.06 Å) but on the whole the molecule is non-planar; the average dihedral angle of the type $N_{(1)}P_{(2)}N_{(2)}/P_{(2)}P_{(4)}P_{(6)}$ is 49°.

---

§ In contrast to compound (LX), the complex $[(NPMe_2)_4H^+]_2CoCl_4^{2-}$ has an ionic structure [69]. In each of the two cyclic cations, the only perturbing factor is the proton linked to one of the N atoms. It is interesting to note that the rings have different conformations. One of them has the same boat conformation as (LX), the displacement of the N atoms from the average plane being greater than that of the P atoms (0.59 and 0.40 Å). The other has a conformation of the saddle type, where the P atoms are in one plane to within 0.02 Å and the N atoms are located alternately above and below this plane at a distance of about 0.61 Å. Despite this, the variation of the PN bond length in the two rings is the same: the average length of each pair of bonds is independent of the conformation. Starting with the protonated N atom, the longest of the PN bonds is followed by the shortest bond, after which a long bond is followed by a shorter bond: 1.695, 1.538, 1.614, and 1.582 (±0.015) Å. The remaining parameters are close to those found for compound (LX).

In the trimeric cation $N_3P_3Cl_2(iso\text{-}C_3H_7NH)_4H^+$, [70] the protonation of the ring also has an appreciable influence on the endocyclic bonds and angles. The variation of the PN bond in the ring, starting with the protonated N atom, is as follows: 1.666, 1.583, and 1.558 (±0.005) Å. The shortest bond is near the PCl_2 group, i.e. the differences between the substituents at the P atoms also affect the ring parameters. The lengths of the exocyclic bonds are $r(PN) = 1.609(5)$ and $r(PCl) = 2.000(3)$ Å. The ring has a distorted boat conformation with deviations of the N and P atoms from the average plane up to 0.09 Å.

In the hexameric cyclic cation $[N_6P_6(NMe)_2]_{12}CuCl^+$, [71] the copper atom is linked covalently to four ring N atoms as well as to the Cl atom (overall symmetry $\sim C_2$). As a result there are two types of PN bonds in the ring system



with di- and tri-coordinate N atoms: bond lengths of 1.55 and 1.62 (±0.02) Å. The average endocyclic N and P angles are reduced, compared with those found in the initial structure of (XLVIII), to 133.6(1.3)° and 107.5(1.1)° against 147.5° and 120.0°.

Table 8. Cyclophosphazanes.

Compound	Ring conformation	Endocyclic bonds		Exocyclic bonds		Endocyclic valence angles		Exocyclic valence angles		Method	Refs.
		bond type	bond length, Å	bond type	bond length, Å	angle	magnitude, deg	angle	magnitude, deg		
$[ClP(=S)NMe]_2$ (LXII)	planar	$=P_c(-N_c)<$	1.67	$=P_c-Cl$	1.93	NPN	84.0	NPCl=NP= =S	114.7	X-ray	118
				$-P_c=S$	1.93	PNP	96.0	ClP=S	111.5		
$[MeOP(=O)NMe]_3$ (LXIII)	twisted boat	ditto	1.664 (0.011)	$=P_c-O-$	1.564 (0.011)	NPN	105.2(0.6)	NP=O OP=O	113.5 (0.7) 116.1 (0.7)	ditto	119
				$-P_c=O$	1.453 (0.012)	PNP	121.7(0.6)	OPN POC	103.7 (0.7) 119.3 (1.0)		
$(F_3PNMe)_2$ (LXIV)	planar	$(P_cN_c)_a$	1.735	$(P_cF)_a$	1.605	NPN	77.9	F_aPN_e	99.1	el. dif.	120
								F_aPF_e	88.5		
		$(P_cN_c)_e$	1.595	$(P_cF)_e$	1.570	PNP	102.1	N_aPN_e	92.0		
								F_aPF_e	103.9		
								N_ePF_e	127.5		
$(PhF_2PNMe)_2$ (LXV)	ditto	$(P_cN_c)_a$	1.78 (0.02)	$(P_cF)_a$	1.62 (0.02)	NPN	80.6	F_aPN_e	92.5	X-ray	121
								F_aPF_e	87.0		
		$(P_cN_c)_e$	1.64 (0.02)	$(P_cF)_e$	1.57 (0.02)	PNP	99.4	F_aPC_e	91.8		
				$(P_cC)_e$	1.79 (0.02)			N_aPF_e	91.7		
								N_aPC_e	97.9		
								N_ePF_e	128		
								N_ePC_e	122		
								F_ePC_e	109		
$(Cl_3PNMe)_2$ (LXVIa)	»	$(P_cN_c)_a$	1.769 (0.007)	$(P_cCl)_a$	2.133 (0.003)	NPN	80.5 (0.4)	Cl_ePCl_e	110 (0.2)	ditto	122
		$(P_cN_c)_e$	1.635 (0.007)	$(P_cCl)_e$	2.026 (0.004)	PNP	99.5 (0.4)	Cl_aPN_e	124.8 (0.3)		
								X_aPX_e	90.2–94.5		
$(Cl_3PNMe)_2$ (LXVIb)	»	$(P_cN_c)_a$	1.776 (0.01)	$(P_cCl)_a$	2.152 (0.005)	NPN	81.7 (0.5)	Cl_aPN_e	93.8 (0.4)	»	123
		$(P_cN_c)_e$	1.629 (0.01)	$(P_cCl)_e$	2.020 (0.005)	PNP	98.3 (0.5)	Cl_aPCl_e	90.5 (0.3)		
								N_aPCl_e	92.0 (0.4)		
								Cl_ePCl_e	109.8 (0.3)		
								N_ePCl_e	124.9 (0.4)		
$P_5Cl_5(NMe)_6$ (LXVII)	»	$(P_cN_c)_a$	1.74 (mean)	$(P_cCl)_a$	2.16	NPN	80.6			»	124
		$(P_cN_c)_e$	1.66 (mean)	$(P_cCl)_e$	2.05 2.10	PNP	99.4				

*The subscripts a and e correspond to the axial and equatorial bonds in the trigonal bipyramidal structure.

VIII. CYCLOPHOSPHAZANES [(LXII)–(LXVII)]

In contrast to phosphonitriles, the phosphazane ring systems contain tricoordinate nitrogen and are saturated. Among compounds of this class, the structures with tetra- and penta-coordinate phosphorus have been investigated (Table 8).

In the first case, there are X-ray diffraction data for the dimer (LXII) and the trimer (LXIII)¶. The endocyclic PN bonds in each molecule are equivalent. Their average length (1.67 Å) is greater by about 0.1 Å than in phosphonitriles, where the terminal PN bonds have the same length only in structures complicated by additional bonds formed by the N atoms (see above). This length is comparable to that of single PN bonds formed by tetracoordinate phosphorus in acyclic structures (1.60–1.71 Å).[11] The configuration of the bonds involving the nitrogen atom is planar.

It is also striking that the endocyclic angles of the phosphorus atom in compound (LXIII) (105.2°) are significantly

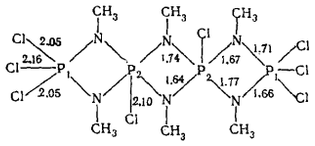
¶ In addition there are data for the structures of the cyclic phosphazane anions $(HNPO_2)_n^{n-}$, where $n = 3$ or 4. These structures differ from those of the non-ionised phosphazanes by the fact that their exocyclic PO bonds are equivalent. It has been shown by X-ray diffraction[105–107] that the endocyclic PN bonds in phosphazane anions are also equivalent (1.66–1.68 Å). The endocyclic angles NPN (104.5° in the trimer[105] and 107–108° in the tetramers[106,107]) are much smaller than in phosphonitriles.

The six-membered ring of the trimer has C_{3v} symmetry (chair conformation), which is confirmed by the vibration spectra of the crystalline structures and solutions[108,109]. The conformational isomerism of eight-membered rings is extremely interesting. X-Ray diffraction data[106,107] and the vibration spectra of the crystalline structures[110,111] showed that the tetrameric anions have conformations of the chair (C_{2h}), boat (S_4), and saddle (D_{2d}) types, the difference between the conformations not affecting the geometrical parameters. The non-planarity of the ring in the tetrameric phosphazane anions is probably greater than in the tetrameric phosphonitriles. In one of the structures with the boat conformation[106], the displacement of the phosphorus atoms from the mean plane[83] is $\Delta P = 0.42$ Å and that of nitrogen atoms $\Delta N = 0.71$ Å, which is greater than in the tetrameric phosphonitriles (see above).

smaller than the exocyclic OP=O angles (116.1°), while in phosphonitriles the opposite relation obtains between the endocyclic NPN angles (115–122°) and the exocyclic XPX angles (97–108°). The ring system of the dimer (LXII) is planar. However, in the molecule of the trimer (LXIII) the ring has a non-planar boat conformation with a symmetry approaching C_s. The N and P atoms located at the opposite ends of the molecule are displaced from the plane of the remaining four ring atoms by about 0.54 Å. Two of the exocyclic MeO groups are located on one side of the ring and the third is on the other. The study of the dipole moments of the dimers with tetracoordinate phosphorus showed that there is a possibility of geometrical (*cis–trans*) isomerism, depending on the relative positions of the exocyclic substituents at the P atom [112].

In dimeric cyclophosphazanes with pentacoordinate phosphorus [compound (LXIV–(LXVII)], the immediate environment of each phosphorus atom gives rise to a distorted trigonal bipyramid. According to X-ray diffraction and electron diffraction data, the endocyclic PN bonds are not equivalent: one of the N atoms is axial and the other is equatorial. The equatorial PN bonds (~1.63 Å) are shorter than the PN bonds in phosphazanes with tetracoordinate phosphorus. The average length of the axial PN bonds (1.74–1.78 Å) is somewhat greater than the sum of the covalent radii corrected for heteropolarity by the Shoemaker–Stevenson method (1.75 Å). The configuration of the bonds involving the N atoms is planar. It is interesting to note that the empirical rule according to which the axial positions in the trigonal bipyramidal structure of substituted fluorophosphoranes should contain F atoms does not hold for the fluoro-derivatives (LXIV) and (LXV). [113,114]

The conformation of the four-membered ring in the dimers with pentacoordinate phosphorus is planar. This is confirmed for (LXIV) by the vibration spectra of solutions [115,116] and also of the liquid and vapour phases [117]. It is striking that the endocyclic NPN angle is smaller than the PNP angle. The condensed structure of (LXVII) contains three planar four-membered rings. The interatomic distances and the angles around $P_{(1)}$ are largely consistent with those found in (LXVI). The trigonal bipyramid around $P_{(2)}$ is distorted much more, since the $P_{(2)}$ atom is involved simultaneously in two rings.



(LXVII)

IX. CYCLIC PHOSPHITES [(LXVIII)–(LXXI)] AND PHOSPHATES [(LXXII)–(LXXXIV)]

In cyclic phosphites, the PO bond length is greater and the OPO bond angles are smaller than the corresponding ring parameters of cyclic phosphates (Table 9), as in the open-chain compounds [11].

However, in the cyclic structures, the geometrical parameters depend on the dimensions of the ring system. In the five-membered rings of (LXVIII)–(LXX) and (LXXII)–(LXXIV), the endocyclic OPO and POC angles

Table 9. Cyclic phosphites and phosphates.

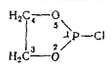
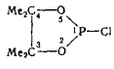
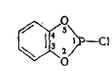
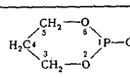
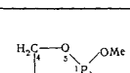
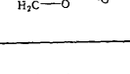
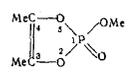
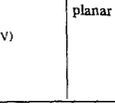
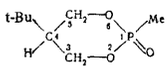
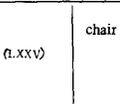
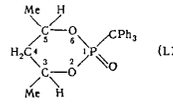
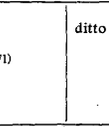
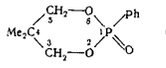
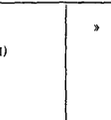
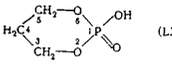
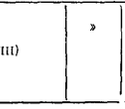
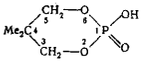
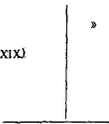
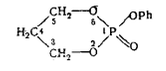
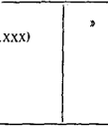
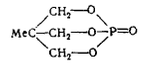
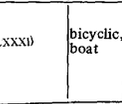
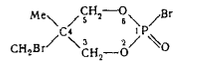
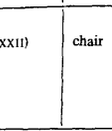
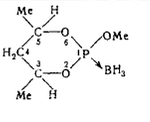
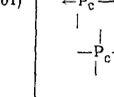
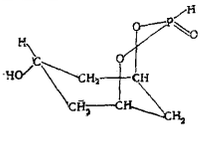
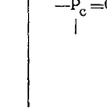
Compound	Ring conformation	Endocyclic bonds		Exocyclic bonds		Endocyclic valence angles		Exocyclic valence angles		Method	Refs.
		bond type	bond length, Å	bond type	bond length, Å	angle	magnitude, deg	angle	magnitude, deg		
 (LXVIII)	envelope	$>P_c-O_c-$	1.631(0.007)	$>P_c-Cl$	2.105 (0.007)	OPO POC	95.7 110.6	OPCl	99.6(0.5)	el. dif	125
 (LXIX)	half-chair	ditto	1.630(0.01)	ditto	2.093 (0.009)	OPO POC	95.9(2.0) 112.0	ditto	103.2 (0.6)	ditto	126
 (LXX)	envelope	»	1.65(0.03)	»	2.106 (0.008)	OPO POC	99.0(1.0) 104.6(1.0)	»	101.6(2.0)	»	127
 (LXXI)	chair	»	1.63 (assumed)	»	2.128 (0.008)	OPO POC	102.6(3.0) 120.1(1.0)	»	100.8(1.8)	»	128
 (LXXII)	envelope (distorted)		1.585(0.01)		1.54(0.01) 1.45(0.01)	OPO POC	98.1(0.5) 113.4(0.8)	POC $O_cP=O$ OP=O O_cPO	119.7(1.1) 116.5(0.8) 108.6(0.9) 108.3 ((mean)	X-ray	129, 130
 (LXXIII)	half chair	ditto	1.58(0.01)		1.56(0.01) 1.44(0.01)	OPO POC	98.4(0.5) 112.1(0.8)	POC $O_cP=O$ OP=O O_cPO	123.4(0.9) 116.6(0.6) 112.6(0.6) 105.6(0.7)	ditto	131

Table 9 (continued).

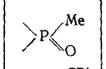
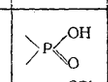
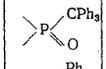
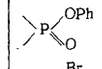
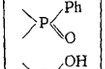
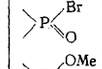
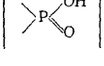
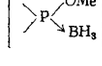
Compound	Ring conformation	Endocyclic bonds: bond type	Endocyclic bonds: bond length, Å	Exocyclic bonds: bond type	Exocyclic bonds: bond length, Å	Endocyclic valence angles: angle	Endocyclic valence angles: magnitude, deg	Exocyclic valence angles: angle	Exocyclic valence angles: magnitude, deg	Method	Refs.
 (LXXIV)	planar		1.58(0.02)		1.53(0.02) 1.38(0.03)	OPO POC	98.5(0.6) 108.0(1.5)	POC $O_cP{=}O$ $OP{=}O$ O_cPO	122.9(0.9) 116.2(0.7) 109.5(0.8) 107.9(0.7)	X-ray	132
 (LXXV)	chair	»	1.57(0.01)		1.81(0.03) 1.48(0.01)	OPO POC	104.4(0.4) 120.0(0.8)	$C_cP{=}O$ $CP{=}O$ O_cPC	113.1(0.5) 108.7(0.5) 108.7(0.5)	ditto	133
 (LXXVI)	ditto	»	1.579(0.015)		1.860 (0.025) 1.469 (0.021)	OPO POC	104.6(0.8) 127.7(1.2)	$O_cP{=}O$ $CP{=}O$ O_cPC	113.2(1.1) 113.1(1.1) 106.0(0.9)	»	134
 (LXXVII)	»	»	1.55(0.02)		1.82(0.02) 1.47(0.02)	OPO POC	106.2(0.8) 119.9(1.5)	$O_cP{=}O$ $CP{=}O$ O_cPC	112.5(0.9) 111.7(0.9) 107.2(0.9)	»	135
 (LXXVIII)	»	ditto	1.57(0.03)		1.55(0.03) 1.51(0.03)	OPO POC	104.6(0.5) 118.9(1.1)	$O_cP{=}O$ $OP{=}O$ O_cPO	110.2(0.6) 116.6(0.7) 107.3(0.7)	»	136
 (LXXIX)	»	»	1.581(0.012)		1.542 (0.011) 1.457 (0.014)	OPO POC	106.1(0.8) 116.0(1.2)	$O_cP{=}O$ $OP{=}O$ O_cPO	111.3(0.8) 117.8(0.8) 104.7 (mean)	»	137
 (LXXX)	»	»	1.565(0.01)		1.59(0.01) 1.48(0.01)	OPO POC	106.6(0.6) 117.6(0.9)	POC $O_cP{=}O$ $OP{=}O$ O_cPO	121.3(0.9) 114 114 104.5	»	138
 (LXXXI)	bicyclic, boat	»	1.57(0.02)		1.46(0.02)	OPO POC	103.7(0.6) 115.2(1.1)	$O_cP{=}O$	115.0(1.1)	»	139
 (LXXXII)	chair	»	1.555(0.013)		2.171 (0.06) 1.443 (0.016)	OPO POC	104.9(0.7) 120.5(1.2)	$O_cP{=}O$ $BrP{=}O$ O_cPBr	115.0(1.0) 111.5(0.7) 104.8(0.5)	»	140
 (LXXXIII)	»		1.562(0.01)		1.562 (0.01) 1.879 (0.017)	OPO POC	105.1(0.6) 119.3(0.9)	O_cPB OPB O_cPO POC	113.6(0.7) 115.5(0.7) 104 (mean) 119.9(1.1)	»	141
 (LXXXIV)	boat		1.550(0.005)		1.430 (0.006)	OPO POC	107.5(0.2) 121.7(0.4)	$O_cP{=}O$	114.5 (0.3)	»	142

are significantly smaller (by 5–10°) than in the open-chain analogues. Conversely, the magnitude of the exocyclic OPO and POC angles in (LXXII)–(LXXIV) is characteristic also of acyclic esters. The six-membered rings of (LXXI) and (LXXV)–(LXXXIV) are very similar to the acyclic structures as regards the parameters under consideration. It is also noteworthy that the exocyclic PCl bonds in cyclic phosphites are significantly longer than in the PCl_3 or $MeOPCl_2$ molecules (by 0.05–0.08 Å),[11] but not to the same extent as in the oxaphosphadiazole,

etc. structures discussed above. The length of the PBr bond in the six-membered cyclic phosphate is greater by 0.03 Å than in $POBr_3$.[11]

According to electron and X-ray diffraction data, cyclic phosphites and phosphates have as a rule non-planar ring conformations. The only exception is compound (LXXIV), where the five-membered ring with tetracoordinate phosphorus and one multiple bond was found to be planar. Five-membered cyclic phosphites have conformations of the envelope (with an axial exocyclic PCl bond) or twisted envelope (half-chair) types. The OPO/OCCO dihedral angle, characterising in the case of envelope conformation the displacement of the P atom from the plane of the remaining ring atoms, is 26° in (LXVIII) and 24.3° in (LXX). In non-planar five-membered cyclic phosphates, the dihedral angles $O_{(2)}PO_{(5)}/O_{(2)}C_{(3)}O_{(5)}$ and $O_{(2)}PO_{(5)}/O_{(2)}C_{(4)}O_{(5)}$ were found to be respectively 10.9° and 1.8° in (LXXII) (distorted enveloped conformation) and 12.2° and 12.1° in (LXXIII) (half-chair conformation). The only study so far of the six-membered cyclic phosphite (LXXI) showed that in the gas phase its ring has a chair conformation (with an axial exocyclic PCl bond). The chair conformation (with an equatorial P=O phosphoryl bond) is also most characteristic of six-membered cyclic phosphates in the crystalline phase. The phosphorus end of the ring in these compounds is more planar than the carbon end (Table 10).

Table 10.

Compound	Exocyclic substituents at P atom	Dihedral angles, deg		Compound	Exocyclic substituents at P atom	Dihedral angles, deg	
		$O_{(2)}PO_{(6)}/O_{(2)}C_{(3)}C_{(5)}O_{(6)}$	$C_{(3)}C_{(4)}C_{(5)}/O_{(2)}C_{(3)}C_{(5)}O_{(6)}$			$O_{(2)}PO_{(6)}/O_{(2)}C_{(3)}C_{(5)}O_{(6)}$	$C_{(3)}C_{(4)}C_{(5)}/O_{(2)}C_{(3)}C_{(5)}O_{(6)}$
(LXXV)		33.5	54.9	(LXXIX)		41.8	54.7
(LXXVI)		3.7	53.3	(LXXX)		36.5	53.1
(LXXVII)		32.6	51.2	(LXXXII)		36.7	52.5
(LXXVIII)		40.4	54.2	(LXXXIII)		38.3	54.0

The degree of smoothing of the conformation on the side of phosphate group is evidently determined by the nature of the exocyclic substituents at the phosphorus atom, since the $C_{(3)}C_{(4)}C_{(5)}/O_{(2)}C_{(3)}C_{(5)}O_{(6)}$ dihedral angle hardly changes on passing from one structure to the other. Boat conformations occur only in the bicyclic structures of (LXXXI) and (LXXXIV). Numerous studies dealing with the problems of conformational equilibrium and the geometrical isomerism and stereochemistry of cyclic phosphites[143-172] and phosphates[173-193] have been carried out by NMR, by determining the dipole moments, etc. However, as pointed out, in particular, by White et al.[166], the interpretation of the results of these studies is frequently ambiguous and contradictory. Further studies by structural methods are necessary for the solution of the above problems.

X. CYCLIC OXYPHOSPHORANES [(LXXXV)–(LXXXVII)]

1. Characteristics of the Geometrical Structure

Cyclic oxyphosphoranes are a new class of compounds in which a pentacoordinate phosphorus atom is located at the centre of a distorted trigonal bipyramid. The distortion may be due to the presence of a ring system and of different substituents at the phosphorus atom.

In compound (LXXXV), which was investigated by X-ray diffraction, two ester groups in the axial and equatorial positions are linked to a five-membered ring. Two tendencies (Table 11) may be noted: (1) the length of the axial bonds is greater than that of the equatorial bonds, as in other trigonal bipyramidal structures; (2) the PO bonds in the five-membered ring are much longer than the corresponding exocyclic bonds (by 0.05 Å for the equatorial bonds and by 0.1 Å for the axial bonds). The OPO angle in this ring (89.3° ± 0.3°) is smaller than in five-membered cyclic phosphates and phosphites and corresponds to the angle between the axial and equatorial bonds. The POC endocyclic bonds are smaller than the exocyclic bonds and close to the analogous angles in the five-membered cyclic phosphites and phosphates.

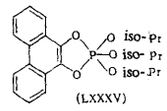
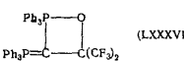
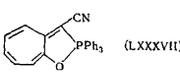
In contrast to compound (LXXXV), in compounds (LXXXVI) and (LXXXVII) the phosphorus atom can be regarded as the centre of a trigonal bipyramid only by convention. The endocyclic axial PO bonds in the last two compounds are significantly longer than in (LXXXV) (by 0.25 and 0.6 Å respectively). On the other hand, the endocyclic PC bonds, which are formally equatorial in the trigonal bipyramid, are unusually short. In the four-membered ring of (LXXXVI), this bond (1.76 ± 0.02 Å) is of the same length as the exocyclic P=C bond (1.75 ± 0.02 Å) within the limits of experimental error. The investigators who studied the structure of (LXXXVI) suggest a delocalisation of electrons in the P=C=P system and explain thereby the stability of the ring. It is noteworthy that the CPO angle in the ring is only 71.3° ± 1.0°, which is smaller by 10° than in four-membered phosphorus–carbon heterocycles, while the POC angle is 94.1° ± 1.0°. In the five-membered ring of (LXXXVII), the equatorial PC bond is even shorter (1.70 Å) than in (LXXXVI). The ring conformations in the above structures are planar to within 0.07–0.10 Å.

2. Pseudorotation

The study of the NMR spectra of oxyphosphoranes with four-, five-, and six-membered rings[198-208] showed that, as in acyclic fluorophosphoranes[11], they undergo an intramolecular rearrangement which is usually described as "pseudorotation". This process involves a deformation of the valence angles and as a result two axial groups of the trigonal bipyramid move to the equatorial positions and correspondingly two equatorial groups move to the axial positions. This mechanism was proposed by Berry[209]. However, it is noteworthy that Berry's mechanism does not always provide a sufficiently complete explanation of the characteristics of the spectra[202,207]. The possible mechanisms of pseudorotation are also discussed in other reports[210-215].

It is assumed that in ring structures pseudorotation is hindered by two principal factors characterised by the polarity[216] and strain rules[217,218]. According to the former, alkyl groups occupy preferentially equatorial

Table 11. Cyclo-oxyphosphoranes*.

Compound	Ring conformation	Endocyclic bonds: bond type	Endocyclic bonds: bond length, Å	Exocyclic bonds: bond type	Exocyclic bonds: bond length, Å	Endocyclic valence angles: angle	Endocyclic valence angles: magnitude, deg	Exocyclic valence angles: angle	Exocyclic valence angles: magnitude, deg	Method	Refs.
 (LXXXV)	planar	$(P_cO_c)_a$ $(P_cO_c)_e$	1.752 (0.007) 1.633 (0.007)	$(P_cO)_a$ $(P_cO)_e$	1.638 (0.006) 1.581 (0.008)	O_aPO_e PO_aC PO_eC	89.3 (0.3) 111.9 (0.6) 114.2 (0.6)	PO_aC PO_eC	121.8 (0.6) 128.7 (mean) distortion of trigonal bipyramid within the limits of experimental error	X-ray	194, 195
 (LXXXVI)	ditto	$(P_cO_c)_a$ $(P_cO_c)_e$	2.01 (0.02) 1.76 (0.02)	$(P_cC)_{av}$ $C_c{=}P$	1.848 (0.02) 1.745 (0.02)	O_aPC_e PO_aC PC_eC	71.3 (1.0) 94.1 (1.0) 98.5 (1.0)	C_aPO C_ePO C_aPC_e C_ePC_e	172.4 (0.8) 86.1 (mean) 99.3 (mean) 106.8 (0.9) 122.6 (mean)	ditto	196
 (LXXXVII)	»	$(P_cO_c)_a$ $(P_cC_c)_e$	2.36 1.70	$(P_cC)_a$ $(P_cC)_e$	1.83 1.775			C_aPO C_aPC C_ePC_e	177.8 102.6 (mean) 112 116 119	»	197

*The subscripts a and e correspond to axial and equatorial bonds in the trigonal-bipyramidal structure.

positions, while O atoms occupy preferentially axial positions. According to the second rule, the pentacoordinate phosphorus atom is bound to the adjacent ring atoms mainly via one axial and one equatorial bond. This reduces ring strain to a minimum, as a result of which the angle between the axial and the equatorial bonds involving the phosphorus atom is smaller than, for example, that between two equatorial bonds. Pseudorotation requires an energy sufficient to overcome the barrier due to one of these factors or to both at the same time. According to the available data, the potential barrier caused by the polarity rule in alkoxyphosphoranes containing at least one PO bond in a five-membered ring is 10–17 kcal mole^{-1}.[203] The barrier due to the strain rule has been estimated as higher—up to 22 kcal mole^{-1}.[203] In such structures at a temperature ≤140°C, an axial–equatorial arrangement of the ring is greatly preferred[202,203]. In alkoxyphosphoranes with a four-membered phosphetane ring (i.e. having only PC bonds in the ring), an axial–equatorial arrangement of the ring is also preferred, at least at a temperature ≤30°C.[207] The barrier to the transition of the ring to a diequatorial arrangement is estimated in this case as 20 kcal mole^{-1}.[204] Six-membered rings with two oxygen atoms linked to a phosphorus atom can assume a diequatorial arrangement[208]. It is interesting that in the $C_5H_{10}PF_3$ molecule, containing a six-membered phosphorus–carbon ring, there is no pseudorotation at room temperature and the ring assumes a diequatorial arrangement[216].

XI. CYCLIC POLYPHOSPHATES [(LXXXVIII)–(LXXXIX)] AND PHOSPHORUS OXIDES [(XC)–(XCVI)]

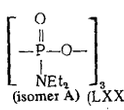
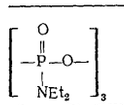
The cyclic skeletons of the molecules of these compounds consist of alternating P and O atoms. Among the unionised polyphosphates, only two geometrical isomers of the trimeric diethylamide of metaphosphoric acid, (LXXXVIII) and (LXXXIX), have been investigated. In the first of these, the six-membered ring has the chair conformation, two atoms (phosphorus and oxygen) deviating from the plane of the remaining four by +0.61 and −0.53 Å. Overall, the molecule has the ~C_{3v} symmetry: all three endocyclic P=O bonds lie on one side of the ring (axial bonds) and all three PN bonds are on the other side (equatorial bonds). In the second structure the ring has an unusual conformation: three oxygen atoms and two phosphorus atoms lie approximately in one plane (to within 0.1 Å) and the third phosphorus atom deviates from this plane by 0.54 Å. Two PN bonds are located on one side of the ring and the third on the other. The PO bonds in the ring were found to have the same length (Table 12)†, which however is greater by about 0.05 Å than the length of the analogous bonds in six-membered cyclic phosphates and also in acyclic structures[11]. On the other hand, the OPO endocyclic angles were found to be somewhat smaller than in cyclic phosphates. The configuration of the bonds involving the exocyclic N atoms is almost planar in both structures.

Phosphorus oxides form three-dimensional polycyclic structures. In the simplest of these (the trioxide P_4O_6), tervalent phosphorus atoms are located at the vertices of a tetrahedron and O atoms form bridging bonds along the edges of the tetrahedron. The pentoxide molecules P_4O_{10} consist, as it were, of a P_4O_6 nucleus and four terminal oxygen atoms completing the tetrahedron around each

† Until recently, X-ray diffraction data could not yield an unambiguous answer concerning the identity or non-identity of the PO endocyclic bond lengths in trimeric and tetrameric cyclic polyphosphate anions[4,219]. The identity of the bond lengths has now been demonstrated. In the $Na_3P_3O_9$ crystal structure, the $P_3O_9^{3-}$ anions (the chair conformation) have the following geometrical parameters[220]: $r(P_c{-}O_c) = 1.615(0.004)$ Å, $r(-P_c{=}O) = 1.484(0.004)$ Å, ∠POP = 126.9(0.2)°, and ∠OPO = 101.1(0.3)°.

In the $(NH_4)_4P_4O_{12}$ structure, these parameters for the $P_4O_{12}^{4-}$ anion (the chair conformation) have the following values[221]: 1.607(0.004) Å, 1.479(0.004) Å, 131.2(0.0)°, and two different OPO angles—98.7(0.02)° and 104.5(0.2)°.

Table 12. Cyclic polyphosphates and phosphorus oxides*.

Compound	Ring conformation	Endocyclic bonds		Exocyclic bonds		Endocyclic valence angles		Exocyclic valence angles		Method	Refs.
		bond type	bond length, Å	bond type	bond length, Å	angle	magnitude, deg	angle	magnitude, deg		
 (isomer A) (LXXXVIII)	chair		1.62 (0.03)		1.44 (0.03) 1.67 (0.04)	OPO POP	104 (2) 124 (2)	OP=O NP=O NPO PNC CNC	115 (2) 116 (2) 102 (2) 121 (3) 117 (3)	X-ray	222
 (isomer B) (LXXXIX)	non-planar	ditto	1.62 (0.02)		1.49 (0.02) 1.62 (0.02)	OPO POP	102 (0.5) 132 (1)	OP=O NP=O NPO PNC CNC	112 (1) 117 (1) 104 (1) 121 (3) 115 (3)	ditto	223
$(P_2O_5)_\infty$ (XC)	three dimensional network of rings formed by six PO_4 tetrahedra	»	1.56 (0.015)		1.49 (0.015)	OPO POP	103 145	OP=O	116	»	224
P_4O_{10} (XCI a)*	tricyclic structure	»	1.58 (mean)	ditto	1.43 (mean)	OPO POP	101 124	ditto	117	»	225
$P_4O_6S_4$ (XCII a)	ditto	»	1.61 (0.02)		1.862 (0.02)	OPO POP	100.8 (0.9) 124.5 (0.6)	OP-S	117.2 (0.8)	»	226
$P_4O_8S_4$ (XCII b)	»	»	[1.85 (0.02)]	ditto	1.85 (0.02)	OPO POP	101.5 (1.0) 123.5 (1.0)	ditto	116.5 (1.0)	el.dif.	227

*See also Table 13.

Table 13. Bond lengths and valence angles in phosphorus oxides.

Compound	Bond lengths, Å*					Valence angles, deg*							Method	Refs.
	$P^{III}-OP^{III}$	$P^{III}-OP^{V}$	$P^{V}-OP^{III}$	$P^{V}-OP^{V}$	$P^{V}=O$	$P^{III}OP^{III}$	$P^{III}OP^{V}$	$P^{V}OP^{V}$	$OP^{III}O$	$OP^{V}O$	(P^{III}) OP=O	(P^{V}) OP=O		
P_4O_6 (XCI II)	1.638 (0.003)	—	—	—	—	126.4 (0.7)	—	—	99.8 (0.8)	—	—	—	el. dif.	228
P_4O_7 (XCIV)	1.637	1.67	1.59	—	1.424	128	125	—	99.5	105	117	—	estimate	228
P_4O_8 (XCV)	1.633 (0.014)	1.668 (0.014)	1.556** 1.596 (0.014)	1.596 (0.014)	1.414 (0.014)	130.1 (0.9)	124.4 (0.9)	121.2 (0.9)	98.0 (mean)	104 (mean)	115.6 (1.0)	113.6 (0.8)	X-ray	228
P_4O_9 (XCVI)	—	1.661 (0.014)	1.605 (0.014)	1.590 (0.014)	1.418 (0.014)	—	126.8 (0.7)	122.8 (0.7)	96.7 (0.7)	102 (mean)	118.8 (0.7)	114.6 (0.7)	X-ray	229
P_4O_{10} (XCI b)	—	—	—	1.604 (0.004)	1.429 (0.004)	—	—	123.5 (0.7)	—	101.6 (0.8)	—	116.5 (0.3)	el. dif.	229
Weighted mean values	1.637 (0.004)	1.666 (0.008)	1.586 (0.010)	1.598 (0.004)	1.424 (0.004)	128.0 (0.6)	125.3 (0.5)	122.6 (0.5)	98.4 (0.8)	103.0 (0.8)	117.0 (0.5)	115.3 (0.3)	—	—

*The symbols P^{III} and P^{V} denote tervalent and quinquevalent phosphorus respectively.
**Beagley et al.[228] believe that the length 1.556 Å is due to an unusual error in the X-ray diffraction data.

quinquevalent phosphorus atom. The remaining oxides differ from these by the number of terminal oxygen atoms (and correspondingly by the number of tervalent and quinquevalent phosphorus atoms). The replacement of P=O by P=S bonds in $P_4O_6S_4$ leaves the overall structure the same as before.

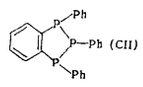
Table 13, which we took from Stosick[227], lists the bond lengths and the valence angles of all the phosphorus oxides. The $P^{III}-O$ bridging bonds are not the same for both types of oxygen atoms (the difference is 0.029 ± 0.009 Å). This is evidence that the intermediate oxides P_4O_7, P_4O_8, and P_4O_9 cannot be regarded as comprising simply fragments of the terminal members of the series (P_4O_6 and P_4O_{10}).

The $P^{III}-O$ bridging bonds are longer than the $P^{V}-O$ bonds and the corresponding bonds in the acyclic structures (1.60 Å).[11]

XII. CYCLIC POLYPHOSPHINES AND ELEMENTAL PHOSPHORUS

An interesting feature of the PP bond in acyclic structures is the low sensitivity of its length to changes in the valence state of the phosphorus atom and in the nature of the attached groups (2.18–2.22 Å).[11] In the ring systems

Table 14. Cyclic polyphosphines and elemental phosphorus.

Compound	Ring conformation	Endocyclic bonds		Exocyclic bonds		Endocyclic valence angles		Exocyclic valence angles		Method	Refs.
		bond type	bond length, Å	bond type	bond length, Å	angle	magnitude, deg	angle	magnitude, deg		
$(PCF_3)_4$ (XCVII)	non-planar	$>P_c-P_c<$	2.213 (0.005)	$>P_c-C-$	1.867 (0.014)	PPP	84.7	PPC	97.8	X-ray	230,231
$(PC_6H_{11})_4$ (XCVIII)	ditto	ditto	2.224 (0.002)	ditto	1.874 (0.002)	ditto	85.5 (0.06)	ditto	102.7 (0.2)	ditto	232
$(PC_6F_5)_4$ (XCIX)	»	»	2.236 (0.002)	$>P_c-C<$	1.838 (0.003)	»	85.24 (0.04)	»	101.05 (0.1)	»	233
$(PCF_3)_5$ (C)	envelope	»	2.223 (0.017)	$>P_c-C-$	1.906 (0.020)	»	101.3 (mean)	»	97.6 (mean)	»	234,235
$(PPh)_5$ (CI)	ditto	»	2.217 (0.006)	$=P_c-C<$	1.843 (0.01)	»	100 (mean)	»	102	»	236
 (CII)	planar bicyclic ring system	»	2.209 (0.003)	ditto	1.825 (0.01)	» PPC PCC	97.3 (0.1) 99.7 (0.2) 120.5 (mean)	»	101.8 (mean)	»	237
$(PPh)_6$ (CII)	chair	»	2.235 (0.005)	»	1.843 (0.01)	PPP	95.0 (0.5)	»	98.5 (0.5)	»	238,239
P_4 (vapour)(CIV)	tricyclic structure (tetrahedron)	»	2.21 (0.02)	—		ditto	60	—		el. dif.	240
Black orthorhombic phosphorus $(P_6)_\infty$ (CV)	chair	»	2.234 (mean)	—		»	100	—		X-ray	241
Violet phosphorus (eight-, nine-membered groups) (CVI)	non-planar	»	2.219 (0.01)	—		»	101.0 (0.3)	—		ditto	242

considered (Table 14), the length of the $>P-P<$ bond is apparently somewhat greater, although the range of its variation remains fairly narrow (2.21–2.24 Å)‡. Within the limits of each structure the PP bonds are almost equal. The valence angles of the phosphorus atoms vary with the complexity of the ring.

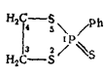
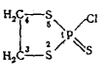
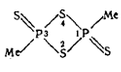
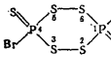
The conformation of the cyclic polyphosphines investigated in the crystal phase is as a rule non-planar. The only exception is compound (CII), where the average torsion angle is only 5° within the limits of the bicyclic ring system. The tetramers (XCVII)–(XCIX) have the molecular symmetry ~D_{2d} with equatorial orientation of the exocyclic substituents. Their PPPP torsion angles are respectively 34°, 31.4°, and 32.2°. The Raman spectra of liquid cyclic polyphosphines $(PR)_4$ have also been interpreted in terms of D_{2d} symmetry [243]. In the pentamers (C) and (CI), the PPPP torsion angles vary in the ranges 18–58° and 2–61° (the envelope conformation), the average in both structures being 38°. In these molecules, the exocyclic substituents at the two adjacent phosphorus atoms lie on one side of the ring, since, in contrast to the tetramers, a regular alternation of the directions in which the substituents are oriented relative to the average plane is in this case impossible. The ring system of the hexamer (CIII) has a chair conformation characterised by an average torsion angle of 84° with equatorial orientation of the exocyclic phenyl groups.

The possibility that the cyclicpolyphosphine ring systems $(PR)_n$ ($n = 4$, 5, or 6) are aromatic was discussed recently [7,29,244]. This hypothesis arose in connection with certain characteristics of the ultraviolet spectra of these compounds [245,246]. One must emphasise that there are no grounds for such a conclusion from the standpointof the structure of cyclic polyphosphines. In particular the absence of electron delocalisation is indicated by the invariance of the PP bond lengths.

The tetrahedral molecules of elemental phosphorus (CIV) in the vapour phase may be regarded as a tricyclic phosphine. The valence angles of the phosphorus atoms are in this case only 60°. It has been suggested that white (crystalline) phosphorus has a similar structure [247,248]. Red phosphorus is formed from white phosphorus when one of the bonds in the tetrahedra is cleaved and the tetrahedra are joined together to form chains or rings [249]. This hypothesis is consistent with the variation spectra of amorphous red phosphorus [250], which agrees best with a polymeric structure consisting of puckered four-membered rings with the D_{2d} (or C_{2v}) symmetry which is the same as (or similar to) the symmetry of the molecules of tetrameric cyclicpolyphosphines (XCVII)–(XCIX). None of the crystalline modifications of red phosphorus, the existence of which has been demonstrated by X-ray diffraction [251], has been subjected to a detailed structural analysis. The different modifications of black phosphorus (CV) and (CVI) contain more complex rings as repeating structural units.

‡ Anomalous $>P-P<$ (2.26–2.33 Å) bond lengths were found in the crystal structures of phosphorus sulphides and selenides (see below).

Table 15. Cyclic phosphonothioates, phosphorohalidothioates, polyphosphonothioates, and polyphosphorohalidothioates.

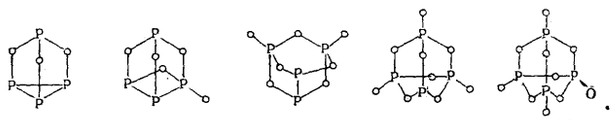
Compound	Ring conformation	Endocyclic bonds		Exocyclic bonds		Endocyclic valence angles		Exocyclic valence angles		Method	Refs.
		bond type	bond length, Å	bond type	bond length, Å	angle	magnitude, deg	angle	magnitude, deg		
 (CVII)	envelope»		2.087 (0.002)		1.801 (0.006)	SPS	98.5 (0.1)	$S_cP{=}S$	115.1 (0.1)	X-ray	252
					1.936 (0.002)	PSC	99.4 (0.4)	CP=S S_cPC	113.9 (0.2) 106.4 (0.2)		
 (CVIII)	half-chair	ditto	2.051 (0.005)		2.059 (0.004)	SPS	100.5 (0.2)	$S_cP{=}S$	117.3 (0.2)	ditto	253
					1.940 (0.005)	PSC	96.1 (0.5)	ClP=S S_cPCl	111.4 (0.2) 104.5		
 (CIX)	Planar	»	2.141 (0.006)		1.830 (0.015)	SPS	94.54 (0.22)	$S_cP{=}S$	116.56 (0.18)	»	254, 255
					1.945 (0.005)	PSP	85.46 (0.23)	CP=S S_cPC	113.54 (0.51) 106.81 (0.18)	–	
 (CX)	boat	»	2.10 (0.02)		2.07 (0.02)	SPS	106			»	256
					1.98 (0.02)	PSS	100				

XIII. CYCLIC PHOSPHONOTHIOATES (CVII), PHOSPHOROHALIDOTHIOATES (CVIII), POLYPHOSPHONOTHIOATES (CIX), AND POLYPHOSPHOROHALIDOTHIOATES (CX)

The length of the $=\overset{|}{P}-S-$ endocyclic bonds in five-membered phosphonothioates and phosphorohalidothioates (Table 15) has been shown by the first studies of these structures in the crystalline phase not to differ from that in the acyclic structures (2.07–2.09 Å) within the limits of error [11]. The SPS endocyclic angles are similar to the OPO angles in five-membered cyclic phosphates (98–99°) (see above), but the PSC angles are significantly smaller than the POC angles. The conformations of five-membered rings in phosphonothioates and phosphorohalidothioates are non-planar, as for cyclic phosphates. In structure (CVII), the phosphorus and sulphur atoms deviate from the mean-square plane by 0.15 Å in the opposite directions (the envelope conformation); in structure (CVIII) the deviations of the ring atoms from the best plane are −0.194 Å for P, 0.299 Å for $S_{(2)}$, −0.336 Å for $C_{(3)}$, 0.161 Å for $C_{(4)}$, and 0.071 Å for $S_{(5)}$ (the conformation is close to that of the half-chair form). The conformation of the four-membered ring of the polyphosphonothioate (CIX) is planar (C_{2h} symmetry), like that found for the diphosphazane molecule with tetracoordinate phosphorus [compound (LXII)]. The six-membered ring in compound (CX) has a boat conformation with a PSSP torsion angle of 86°.

XIV. PHOSPHORUS SULPHIDES [(CXI)–(CXVII)] AND SELENIDES [(CXVIII)–(CXX)]

Phosphorus sulphides and selenides (Table 16) consist of large polycyclic molecules P_4S_n or P_4Se_n (n = 3, 5, 7, 9, or 10):



(CXI, CXVIII) (C_{3v}) (CXIV, CXX) (C_1) (CXV *a* and *b*) (C_s) (CXVI) (C_s) (CXVII) (C_{3v})

In contrast to phosphorus oxides, among phosphorus sulphides and selenides there are structures without symmetry elements. The isomeric di-iodo-derivatives resemble closely this series of compounds:



The polycyclic systems contain three-, four-, five-, and six-membered rings. The conformation of the four-membered rings in (CXIV) and (CXX) is close to that of the rings of tetrameric cyclic polyphosphines (see above). The five-membered rings in each of the sulphides [except (CXVI) and (CXVII)] and selenides show a considerable geometrical similarity to the rings of the five-membered polyphosphines (C) and (CI) (the envelope conformation).

Table 16. Phosphorus sulphides and selenides.

Compound	Endocyclic PE bonds (E = S, Se)					Exocyclic bonds, Å	Endocyclic valence angles (E = S, Se, or P)					Exocyclic bonds		Method	Refs.
	$P^{III}-EP^{III}$	$P^{III}-EP^{V}$	$P^{V}-EP^{III}$	$P^{V}-EP^{V}$	$P^{III}-P^{III}$		$EP^{III}E$	$EP^{V}E$	$P^{III}EP^{III}$	$P^{III}EP^{V}$	$P^{V}EP^{V}$	angle	magnitude, deg		
P_4S_3 (CXI a)	2.090 (0.005)	—	—	—	2.235 (0.005)	—	60** 99.4 103.1	—	103.0	—	—		—	X-ray	257
P_4S_3 (CXI b)	2.17 (0.02)	—	—	—	2.21 (0.02)	—	—	—	105(3)		—		—	el. dif.	258
α-$P_4S_3I_2$ (CXII)	2.10 (0.04)	—	—	—	2.20 (0.04)	2.48(0.03) (>P_c—I)	102—105	—	104		—	PPI SPI	98 104	X-ray	259
β-$P_4S_3I_2$ (CXIII)	2.095 (0.016) 2.13 (0.01)	—	—	—	2.21 (0.01)	2.471(0.008) (>P_c—I)	101.6 (0.3)	—	99.6(0.3) 106(0.3)		—	PPI SPI	94.5(0.2) 103.0(0.4)	ditto	260
P_4S_5 (CXIV)	2.11 (mean)	2.14 (mean)	2.085 (0.01)	—	2.26 (0.01) 2.24 (P^V—P^{III})	1.94 (0.01) 	85** 102.5 (mean)	89.6*** 108.4	103.8 (mean)	88.7*** 103.4	—	PP=S SP=S	125.5 112 (mean)	»	261, 262
α-P_4S_7 (CXV a)	—	2.108 (0.007)	2.079 (0.007)	2.114 (0.007)	2.326 (0.007)	1.918(0.007) 	103.5 (mean)	107 (mean)	—	102.4	110.1	SP=S	112 (mean)	»	262, 263
β-P_4S_7 (CXV b)	—	2.11 (0.045)	2.07 (0.04)	2.12 (0.04)	2.26 (0.02)	1.89(0.045) 	103 (mean)	107 (mean)	—	102.5	110	SP=S	112	»	264
P_4S_9 (CXVI)	—	2.11 (0.01)	2.12 (0.01)	2.12 (0.01)	—	1.93 (0.01)	108.4	109.6	—	110.8	108.7	SP=S	109.3	»	265
P_4S_{10} (CXVII)	—	—	—	2.097 (0.015)	—	1.908(0.015) 	—	109.3 (0.7)	—	—	109.8 (0.7)	SP=S	109.6(0.7)	»	262, 263
P_4Se_3 (CXVIII)	2.24 (0.03)	—	—	—	2.25 (0.03)	—	60** 100 105	—	100	—	—	—	—	»	266
β-$P_4Se_3I_2$ (CXIX)	2.25 (0.04)	—	—	—	2.22 (0.03)	2.47 (0.02) (>P_c—I)	102.7 (1.2)	—	97.1(1.5) 103.6(1.1)	—	—	PPI SePI	94.6(1.0) 101.4(0.8)	»	267
P_4Se_5 (CXX)	2.25 (mean)	2.285 (mean)	2.245 (0.015)	—	2.294 (0.019) 2.237 (0.016) (P^V—P^{III})	2.123(0.013) 	86.5(0.5)*** 103.2 (mean)	89.6(0.6)*** 109.3 (mean)	102 (mean)	85.4(0.4)*** 99.7(0.4)	—	PP=Se SeP=Se	121.9(0.6) 112 (mean)	»	268

*The symbols P^{III} and P^{V} denote tervalent and quinquevalent phosphorus respectively.
**In a tervalent (three-membered?) ring.
***In a quadrivalent (four-membered?) ring.

The six-membered rings in compounds (CXVI) and (CXVII), which include tri- and tetra-coordinate phosphorus, have a chair conformation—the same as in (CIII) and (CV). In the molecules of the di-iodides (CXII), (CXIII), and (CXIX), two five-membered rings are joined by a common PXP fragment.

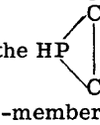
In turn, the remaining endocyclic bonds form a common six-membered ring in the boat form with the following endocyclic angles:

(CXII)	(CXIII)	(CXIX)
PPS 91° (mean)	PPP 96.5±0.5° SPS 103.2±0.5°	PPP 97.8±1.5° SePSe 103.6±1.3°

It is interesting that the PPP bonds considered are much smaller than in the six-membered rings of black phosphorus (102°). As already noted, the PP bonds in the sulphides and selenides are significantly longer in many cases than the usual bond. The lengths of the PS(PSe) bonds are on average little different from those found in the acyclic compounds[11]. The difference between the bonds of tervalent and quinquevalent phosphorus are not as pronounced as in the oxides. On the other hand, in certain structures [for example, in (CXIV) and (CXX)] the lengths of the single PS and PSe bonds are different, the differences reaching about 0.1 Å.

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The above discussion of the molecular structures of cyclic organophosphorus compounds shows that their geometrical structures have certain definitely unusual features.

In small rings with $n = 3-5$ atoms, the valence angles involving the phosphorus atom are apparently largely determined by the dimensions of the ring system. The smallest of the known valence angles of the phosphorus atom—the CPC angle in the  molecule—is only 47.4°. In four- and five-membered rings, the valence angles of the phosphorus atoms are still significantly

smaller than the analogous angles in the acyclic structures. In small rings, the single phosphorus–element bonds are as a rule longer than the bonds in the acyclic structures.

In the case of six-membered rings (excluding, of course, phosphonitriles and similar formally unsaturated structures), there is usually considerable similarity with acyclic structures as regards the above parameters. The main reason for such differences is frequently believed to be the existence of ring strain in small ring systems. However, an appreciable increase in the length of PO bridge bonds occurs also in six-membered rings in the structure of phosphorus oxides.

The effect of exocyclic substituents on the geometrical parameters of the ring system is shown, in particular, in phosphonitriles, where the inhomogeneity of these substituents leads to different lengths of endocyclic bonds and a decrease of the symmetry of the ring system.

It is as a rule impossible to establish significant differences between the parameters of endocyclic bonds and those of acyclic compounds. However, the length of the PCl bonds in phosphadiazoles (2.17–2.19 Å for tricoordinate phosphorus and 2.07 Å for tetracoordinate phosphorus) is much greater (by up to 0.20 Å) than in other phosphorus compounds. In most of the structures investigated, the PCl bonds are shorter than the sum of the covalent radii (2.09 Å). This factor was interpreted as an increase in the multiplicity of the PCl bonds. The greater length of the PCl bond found in phosphadiazoles compared with the sum of the covalent radii gives rise to new theoretical problems.

Ring structures with pentacoordinate phosphorus (cyclophosphazanes) constitute the first case to which the empirical rule of the preferential axial location of fluorine atoms in the trigonal-bipyramidal environment of the phosphorus atom is inapplicable.

The simplest cyclic systems (three-membered systems) do not present any conformational problems, since in such cases only planar structures are possible. Examination of the complete set of the available data shows that in more complex rings the conformation is non-planar when tricoordinate phosphorus is present. The only exception is the five-membered ring in compound (CII), where the average torsion angle is only 5°. Planar conformations are apparently characteristic of ring systems containing di- and penta-coordinate phosphorus. Structures containing tetracoordinate phosphorus can have both planar and non-planar conformations. The non-planarity of the phosphole ring merits particular attention. It implies the non-planarity of ethylene systems, which is difficult to expect in view of the high barrier to rotation about the C=C bond.

It is believed that the ring conformations are due to the operation of forces associated with angular deformations and torsional interactions in relation to bonds. Thus the replacement of hydrogen atoms linked to terminal carbon atoms in five-membered cyclic phosphites and phosphates by methyl groups leads to an increase of torsional interactions and a change in conformation from envelope to half-chair. On the other hand, the envelope conformation is difficult to expect for a ring of this type on the basis of the hypothesis concerning the twisting moments about different bonds, since in this case there is an eclipsed configuration relative to the C–C bond, although it is known that the barrier to rotation relative to this bond is greater than that relative to the C–O and P–O bonds.

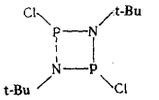
The axial disposition of the P–Cl bonds in the molecules of five- and six-membered ring phosphites and phosphates may be regarded as analogous to the *gauche*-conformation of such bonds about the P–O bonds in the acyclic derivatives.

The valence angles involving the exocyclic N and O atoms are appreciably greater, as in the acyclic compounds, than the values found in trimethylamine and in methyl ether: the nitrogen atom has a planar bond configuration and the POC valence angles are about 120°, exceeding the COC valence angle by 10°.

On the whole, analysis of the structures investigated makes it possible so far to elucidate only the general trends, which require further confirmation and refinement. The inadequacy of the available data is caused not only by the small number of studies but to a greater extent by the insufficient accuracy of their results.

ADDENDUM

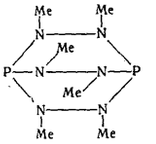
The structure of the dimeric molecule of a cyclophosphazane (CXXI) with tricoordinate phosphorus was investigated for the first time by Muir and Nixon[269]. It was shown by X-ray diffraction that the four-membered ring of this molecule is slightly non-planar: the P and N atoms are alternately 0.045 Å above and below the average plane (a dihedral angle of 6°). Both Cl atoms linked to the P atoms occupy equatorial positions, i.e. they are located on the same side of the ring as the N atoms. However, the substituents at the N atoms are not equivalent in this respect: one of them is in the *cis*-position relative to the Cl atoms and the other in the *trans*-position:



(CXXI).

The molecule of compound (CXXI) has the following geometrical parameters: $r(>P_c-Cl) = 2.105(0.009)$ Å; $r(>P_c-N_c<) = 1.689(0.005)$ Å; ∠NPN = 82.5(0.3)°; ∠PNP = 97.3(0.4)°; ∠NPCl = 103.3(0.4)°; ∠PNC = 129.5° (on average). Evidently the bond lengths and valence angles in the ring are very close to the values of the corresponding parameters for the dimeric molecule of a cyclophosphazane with tetracoordinate phosphorus (LXII). However, the PCl bond length in (CXXI) is much greater. A correction for thermal motion increases the length of this bond to 2.149(0.009)Å.

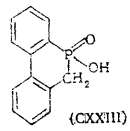
According to an X-ray diffraction study[270], the fundamental geometrical parameters of the bicyclic molecule of (CXXII) have the following values: $r(>P_c-N_c<) =$ 1.68(0.03) Å; ∠NPN = 100(3)°; ∠PNN = 117(4)°; the sum of the valence angles of the nitrogen atom α_N = 345(2)°. The PNNP chain in (CXXII) was found to be planar to within 0.06(0.02) Å.



(CXXII).

Two X-ray diffraction studies of cyclic structures with tetracoordinate phosphorus, carried out at the beginning of the 1960's but not mentioned in earlier reviews, are of interest. In one of

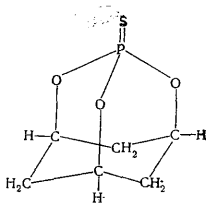
these investigations [271], it was found that in the molecule of compound (CXXIII) the P atom and the C atom of the methylene group are located in the planes of the closest benzene rings, the angle between these planes being 22°.



(CXXIII)

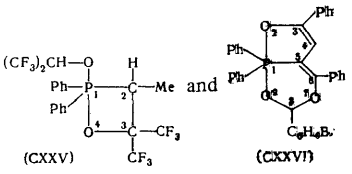
The geometrical parameters of the phosphorus fragment in (CXXIII) are are follows: $r(=P_c-C_c<) = 1.80$ Å; $r(=P_c-C_c-) = 1.79$ Å; $r(-P_c=O)_1 = 1.47$ Å; $r(-P_c=O)_2 = 1.57$ Å; $\angle OP{=}O = 115°$; $\angle CPO = 107°$; $\angle CP{=}O = 114°$; $\angle(CPC)_c = 101°$.

In the second of the above two investigations [272], the following parameters were found for the (CXXIV) molecule: $r(-P_c=S) = 1.90(0.01)$ Å; $r(=P_c-O_c-) = 1.58(0.002)$ Å; $\angle OP{=}S = 113.7(0.9)°$; $\angle OPO = 104.7(1.1)°$; $POC = 113.3(1.7)°$. All three oxygen atoms in the (CXXIV) molecule occupy axial positions in relation to the cyclohexane ring.



(CXXIV)

A further two X-ray diffraction studies have been made on the structure of the cyclicoxyphosphoranes (CXXV) and (CXXVI):



(CXXV) (CXXVI)

In both molecules the oxygen atoms occupy axial positions. In (CXXV), [237] the P atom is in the centre of a distorted trigonal bipyramid with a four-membered ring in the axial-equatorial plane. The ring is non-planar but has a relatively small $C_{(2)}PO_{(4)}/C_{(2)}C_{(3)}O_{(4)} = 11°$ dihedral angle, which corresponds to a displacement of the atoms from the average ring plane by not more than 0.06 Å. The (CXXV) molecule has the following fundamental geometrical parameters: $r(P_cO_c)_a = 1.79(0.01)$ Å; $r(P_cO)_a = 1.71(0.01)$ Å; $r(P_cC_c)_e = 1.83(0.02)$ Å; $r(P_cC)_e = 1.79$ Å (mean); $C_{(2)}PO_{(4)} = 75.5(0.6)°$; $\angle PO_{(4)}C_{(3)} = 94.8(1.0)°$; $\angle PC_{(2)}C_{(3)} = 94.8(1.0)°$.

In the (CXXVI) molecule [274], the P atom is in the centre of an almost regular trigonal bipyramid. Both rings occupy axial-equatorial positions. The five-membered ring is planar, with the parameters $r(P_cO_c)_a = 1.786(0.006)$ Å; $r(P_cC_c)_e = 1.815(0.006)$ Å; $\angle OPC = 87.3(0.2)°$; $\angle POC = 113.8(0.2)°$.

The non-planar six-membered ring has the following parameters: $r(P_cO_c)_a = 1.737(0.006)$ Å; $\angle OPC = 92.7(0.2)°$; $\angle POC = 113.3(0.2)°$.

REFERENCES

1. V. M. Tatevskii, "Khimicheskoe Stroenie Uglevodorodov i Zakonomernosti v ikh Fiziko-khimicheskikh Svoistvakh" (Chemical Structures of Hydrocarbons and Regularities in Their Physicochemical Properties), Izd. Moskov. Gos. Univ., Moscow, 1953.
2. V. M. Tatevskii, Dokl. Akad. Nauk SSSR, 101, 515, 901 (1955).
3. V. M. Tatevskii and V. P. Spiridonov, Vestnik Moskov. Gos. Univ., Ser. Khim., 4, 3 (1962).
4. D. E. Corbridge, M. S. Pearson, and C. Walling, "Topics in Phosphorus Chemistry", Interscience Publ., New York, London, Sydney, 1966, Vol. 3, pp. 57–394.
5. M. J. Gallagher and I. D. Jenkins, "Topics in Stereochemistry", Interscience Publ., New York, London, Sydney, Toronto, 1968, Vol. 3.
6. A. H. Cowley, J. Chem. Educ., 41, 530 (1964).
7. A. H. Cowley, Chem. Rev., 65, 617 (1965).
8. R. A. Shaw, B. W. Fitzsimmons, and B. S. Smith, Chem. Rev., 62, 247 (1962).
9. N. L. Paddock, Quart. Rev., 18, 168 (1964).
10. A. F. Grapov, N. N. Mel'nikov, and L. V. Razvodovskaya, Uspekhi Khim., 39, 39 (1970) [Russ. Chem. Rev., No. 1 (1970)].
11. L. S. Khaikin and L. V. Vilkov, Uspekhi Khim., 40, 2174 (1971) [Russ. Chem. Rev., No. 12 (1971)].
12. L. Pauling, "Nature of the Chemical Bond" (Translated into Russian), GONTI, Khim. Lit, Moscow, 1947.
13. G. J. Bullen and P. R. Mallinson, Chem. Comm., 132 (1969).
14. W. C. Hamilton, Acta Cryst., 8, 199 (1955).
15. P. Goldstein, Ph. D. Dissertation, Princeton University, 1964.
16. P. Goldstein and R. A. Jacobson, J. Amer. Chem. Soc., 84, 2457 (1962).
17. K. Dimroth and P. Horrmann, Chem. Ber., 99, 1325 (1966).
18. R. Allmann, Chem. Ber., 99, 1332 (1966).
19. I. Kawada and R. Allmann, Angew. Chem., 80, 40 (1968).
20. J. C. J. Bart and J. J. Daly, J. Chem. Soc. (A), 567 (1970).
21. W. Fischer, E. Hellner, A. Chatzidakis, and K. Dimroth, Tetrahedron Letters, 6227 (1968).
22. J. J. Daly, J. Chem. Soc. (A), 1832 (1970).
23. U. Thewalt, Angew. Chem., 81, 783 (1969).
24. U. Thewald and C. E. Bugg, Acta Cryst., 28B, 871 (1972).
25. G. Markl, Angew. Chem., 78, 907 (1966).
26. R. Vilceann, A. Balint, and Z. Simon, Nature, 217, 61 (1966).
27. B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Andersen, J. Chem. Phys., 24, 720 (1956).
28. L. Nygaard, J. T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen, and G. O. Sorensen, J. Mol. Struct., 3, 491 (1969).
29. R. F. Hudson, "Organic Chemistry" Vol. 6, "Structure and Mechanism in Organophosphorus Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1967, pp. 43–47.

30. P. Goggon, J. P. Engel, A. T. McPhail, and L. D. Quin, J. Amer. Chem. Soc., 92, 5779 (1970).
31. W. P. Ozbirn, R. A. Jacobson, and J. C. Clerdy, Chem. Comm., 1062 (1971).
32. V. A. Naumov and V. N. Semashko, Zhur. Strukt. Khim., 11, 979 (1970).
33. V. A. Naumov and V. N. Semashko, Dokl. Akad. Nauk SSSR, 193, 348 (1970).
34. M. ul-Haque, J. Chem. Soc. (B), 711 (1970).
35. W. Egan, R. Tang, G. Zon, and K. Mislow, J. Amer. Chem. Soc., 92, 1442 (1970).
36. A. M. Aguiar, K. C. Hansen, and G. S. Reddy, J. Amer. Chem. Soc., 89, 3067 (1967).
37. A. M. Aguiar and K. C. Hansen, J. Amer. Chem. Soc., 89, 4235 (1967).
38. R. L. R. Towns, R. Majeste, J. N. Brown, and L. M. Trefonas, J. Heterocyclic Chem., 7, 835 (1970).
39. M. T. Bowers, R. A. Beaudet, H. Goldwhite, and R. Tang, J. Amer. Chem. Soc., 91, 17 (1969).
40. A. T. McPhail, J. J. Breen, and L. D. Quin, J. Amer. Chem. Soc., 93, 2574 (1971).
41. A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, and L. D. Quin, Chem. Comm., 1020 (1971).
42. D. D. Swank and C. N. Caughlan, Chem. Comm., 1051 (1968).
43. M. ul-Haque, J. Chem. Soc. (B), 938 (1970).
44. M. ul-Haque, J. Chem. Soc. (B), 117 (1971).
45. M. ul-Haque, J. Chem. Soc. (B), 934 (1970).
46. V. A. Naumov and V. N. Semashko, Dokl. Akad. Nauk SSSR, 200, 882 (1971).
47. F. Alver and H. M. Kjoge, Acta Chem. Scand., 23, 1101 (1969).
48. J. D. Lee and G. W. Goodacre, Acta Cryst., 25B, 2127 (1969).
49. J. D. Lee and G. W. Goodacre, Acta Cryst., 26B, 507 (1970).
50. C. Moret and L. M. Trefonas, J. Amer. Chem. Soc., 91, 2255 (1969).
51. E. Alver and B. H. Holtedahl, Acta Chem. Scand., 21, 356 (1967).
52. L. V. Vilkov, L. S. Khaikin, A. F. Vasil'ev, N. P. Ignatova, N. N. Mel'nikov, V. V. Negrebetskii, and N. I. Shvetsov-Shilovskii, Dokl. Akad. Nauk SSSR, 197, 1081 (1971).
53. A. F. Vasil'ev, L. V. Vilkov, N. P. Ignatova, N. N. Mel'nikov, V. V. Negrebetskii, N. I. Shvetsov-Shilovskii, and L. S. Khaikin, Dokl. Akad. Nauk SSSR, 183, 95 (1968).
54. V. A. Naumov, N. A. Gulyaeva, and M. A. Pudovik, Dokl. Akad. Nauk SSSR, 203, 590 (1972).
55. T. S. Cameron, J. Chem. Soc., Perkin Trans., 591 (1972).
56. L. V. Vilkov, L. S. Khaikin, A. F. Vasil'ev, T. A. Italinskaya, N. N. Mel'nikov, V. V. Negrebetskii, and N. I. Shvetsov-Shilovskii, Dokl. Akad. Nauk SSSR, 187, 1293 (1969).
57. V. A. Naumov and M. A. Pudovik, Dokl. Akad. Nauk SSSR, 203, 351 (1972).
58. V. V. Negrebetskii, N. P. Ignatova, N. I. Shvetsov-Shilovskii, and N. N. Mel'nikov, Zhur. Strukt. Khim., 11, 633 (1970).
59. M. L. Ziegler and J. Weiss, Angew. Chem., 81, 430 (1969).
60. R. Stahlberg and E. Steger, Spectrochim. Acta, 23A, 2185 (1967).
61. E. Steger and G. Mildner, Z. Naturforsch., 16B, 836 (1961).
62. A. C. Chapman and N. L. Paddock, J. Chem. Soc., 635 (1962).
63. D. P. Craig, J. Chem. Soc., 997 (1959); 430 (1961).
64. I. C. Hisatsune, Spectrochim. Acta, 25A, 301 (1969).
65. G. E. Coxon and D. B. Sowerby, Spectrochim. Acta, 24A, 2145 (1968).
66. T. R. Manley and D. A. Williams, Polymer, 10, 307 (1969).
67. H. R. Allcock, G. F. Konopski, R. L. Kugel, and E. G. Stroh, Chem. Comm., 985 (1970).
68. U. Klement and A. Schmidpeter, Z. Naturforsch., 23B, 1610 (1968).
69. J. Trotter and S. H. Whitlow, J. Chem. Soc. (A), 460 (1970).
70. N. V. Mani and A. J. Wagner, Acta Cryst., 27B, 51 (1971).
71. W. C. Marsh and J. Trotter, J. Chem. Soc. (A), 1482 (1971).
72. F. R. Ahmed, P. Singh, and W. H. Barnes, Acta Cryst., 25B, 316 (1969).
73. J. B. Faught, T. Moeller, and I. C. Paul, Inorg. Chem., 9, 1656 (1970).
74. W. C. Marsh and J. Trotter, J. Chem. Soc. (A), 169 (1971).
75. H. R. Allcock, M. T. Stein, and J. A. Stanko, J. Amer. Chem. Soc., 93, 3173 (1971).
76. L. A. Siegel and J. H. van den Hende, J. Chem. Soc. (A), 817 (1967).
77. M. I. Davis and J. W. Paul, J. Mol. Struct., 9, 476 (1971).
78. A. W. Dougill, J. Chem. Soc., 3211 (1963).
79. M. I. Davis and J. W. Paul, J. Mol. Struct., 12, 249 (1972).
80. G. J. Bullen, J. Chem. Soc. (A), 1450 (1971).
81. H. Zoer and A. J. Wagner, Acta Cryst., 26B, 1812 (1970).
82. M. W. Dougill, J. Chem. Soc., 5471 (1961).
83. G. J. Bullen, J. Chem. Soc., 3192 (1962).
84. G. J. Bullen, P. R. Mallinson, and A. H. Burr, Chem. Comm., 691 (1969).
85. G. B. Ansell and G. J. Bullen, J. Chem. Soc. (A), 2498 (1971).
86. H. McD. McGeachin and F. R. Tromans, J. Chem. Soc., 4777 (1961).
87. R. Hazekamp, T. Migchelsen, and A. Vos, Acta Cryst., 15, 539 (1962).
88. A. J. Wagner and A. Vos. Acta Cryst., 24B, 707 (1968).
89. G. J. Bullen and P. A. Tucker, Chem. Comm., 1185 (1970).
90. A. W. Schlueter and R. A. Jacobson, J. Chem. Soc. (A), 2317 (1969).
91. A. J. Wagner and A. Vos, Acta Cryst., 24B, 1423 (1968).
92. N. L. Paddock, J. Trotter, and S. H. Whitlow, J. Chem. Soc. (A), 2227 (1968).
93. E. Giglio, F. Pompa, and A. Ripamonti, J. Polymer Sci., 59, 293 (1962).
94. C. W. Allen, J. B. Faught, T. Moeller, and I. C. Paul, Inorg. Chem., 8, 1719 (1969).
95. N. V. Mani, F. R. Ahmed, and W. H. Barnes, Acta Cryst., 19, 693 (1965).
96. N. V. Mani, F. R. Ahmed, and W. H. Barnes, Acta Cryst., 21, 375 (1966).
97. R. Olthof, Acta Cryst., 25B, 2040 (1969).
98. W. C. Marsh and J. Trotter, J. Chem. Soc. (A), 573 (1971).
99. W. C. Marsh and J. Trotter, J. Chem. Soc. (A), 569 (1971).
100. J. C. van den Grampel and A. Vos, Acta Cryst., 25B, 651 (1969).

101. F.R.Ahmed and D.R.Pollard, Acta Cryst., 27B, 163 (1971).
102. D.R.Pollard and F.R.Ahmed, Acta Cryst., 27B, 172 (1971).
103. J.Trotter and S.H.Whitlow, J.Chem.Soc.(A), 455 (1970).
104. W.Harrison and J.Trotter, J.Chem.Soc., Dalton Trans., 623 (1972).
105. R.Olthof, T.Migchelsen, and A.Vos, Acta Cryst., 19, 596 (1965).
106. T.Migchelsen, R.Olthof, and A.Vos, Acta Cryst., 19, 603 (1965).
107. B.Berking and D.Mootz, Acta Cryst., 24B, 740 (1971).
108. J.V.Pustinger, W.T.Cave, and M.L.Nielsen, Spectrochim.Acta, 15, 909 (1959).
109. K.Lunkwitz and E.Steger, Spectrochim.Acta, 23A, 2593 (1967).
110. E.Steger and K.Lunkwitz, J.Mol.Struct., 3, 67 (1969).
111. E.Steger and K.Lunkwitz, Z.anorg.Chem., 313, 262 (1961).
112. V.A.Grazhan, A.F.Grapov, A.V.Razvodovskaya, and N.N.Mel'nikov, Zhur.Obshch.Khim., 39, 1501 (1969).
113. E.L.Muetterties, W.Mahler, and R.Schmutzler, Inorg.Chem., 2, 613 (1963).
114. E.L.Muetterties, W.Mahler, K.J.Packer, and R.Schmutzler, Inorg.Chem., 3, 1298 (1964).
115. A.J.Downs, Chem.Comm., 628 (1967).
116. A.C.Chapman, W.S.Holms, N.L.Paddock, and H.T.J.Searle, J.Chem.Soc., 1825 (1961).
117. M.P.Yagupsky, Inorg.Chem., 6, 1770 (1967).
118. J.Wiess and G.Hartmann, Z.Naturforsh., 21B, 891 (1966).
119. G.B.Ansell and G.J.Bullen, J.Chem.Soc.(A), 3026 (1968).
120. A.Almeningen, B.Andersen, and E.E.Astrup, Acta Chem.Scand., 23, 2179 (1969).
121. J.W.Cox and E.R.Corey, Chem.Comm., 123 (1967).
122. L.G.Hoard and R.A.Jacobson, J.Chem.Soc.(A), 1203 (1966).
123. H.Hess and D.Forst, Z.anorg.Chem., 342, 240 (1966).
124. J.Weiss and G.Hartmann, Z.anorg.Chem., 351, 152 (1967).
125. V.A.Naumov, N.M.Zaripov, and V.G.Dashevskii, Dokl.Akad.Nauk SSSR, 188, 1062 (1969).
126. V.A.Naumov and N.M.Zaripov, Zhur.Strukt.Khim., 11, 1108 (1970).
127. B.A.Arbuzov, V.A.Naumov, S.A.Shaidullin, and E.G.Mukmenev, Dokl.Akad.Nauk SSSR, 204, 859 (1972).
128. V.A.Naumov and N.M.Zaripov, Zhur.Strukt.Khim., 13, 768 (1972).
129. T.A.Steitz and W.N.Lipscomb, J.Amer.Chem.Soc., 87, 2488 (1965).
130. Y.-Y.H.Chiu and W.N.Lipscomb, J.Amer.Chem.Soc., 91, 4150 (1969).
131. M.G.Newton, J.R.Cox, and J.A.Bertrand, J.Amer.Chem.Soc., 88, 1503 (1966).
132. D.Swank, C.N.Caughlan, F.Ramirez, O.P.Madan, and C.P.Smith, J.Amer.Chem.Soc., 89, 6503 (1967).
133. M.ul-Haque, C.N.Caughlan, J.H.Hargis, and W.G.Bentrude, J.Chem.Soc.(A), 1786 (1970).
134. M.G.B.Drew and J.Rodgers, Acta Cryst., 28B, 924 (1972).
135. R.C.G.Killean, J.L.Lawrence, and I.M.Magennis, Acta Cryst., 27B, 189 (1971).
136. M.ul-Haque, C.N.Caughlan, and W.L.Moats, J.Org.Chem., 35, 1446 (1970).
137. W.Murayama and M.Kainosho, Bull.Chem.Soc.Japan, 42, 1819 (1969).
138. H.J.Giess, Rec.Trav.chim., 86, 362 (1967).
139. D.M.Nimrod, D.R.Fitzwater, and J.G.Verkade, J.Amer.Chem.Soc., 90, 2780 (1968).
140. T.A.Beineke, Acta Cryst., 25B, 413 (1969).
141. J.Rodgers, D.W.White, and J.G.Verkade, J.Chem.Soc.(A), 77 (1971).
142. D.M.Nimrod, Inorg.Chim.Acta, 2, 149 (1968).
143. L.D.Quin and H.E.Shook, Tetrahedron Letters, 2193 (1965).
144. B.Fontal and H.Goldwhite, Tetrahedron, 22, 3275 (1966).
145. R.H.Cox, M.G.Newton, and B.S.Campbell, J.Amer.Chem.Soc., 93, 528 (1971).
146. D.Gagnaire, J.B.Robert, and J.Verrier, Bull.Soc.chim.France, 3719 (1966).
147. P.Haake, J.P.McNeal, and E.J.Goldsmith, J.Amer.Chem.Soc., 90, 715 (1968).
148. R.F.M.White, J.Mol.Struct., 6, 75 (1970).
149. J.G.Verkade, R.W.King, and C.W.Heitsch, Inorg.Chem., 3, 884 (1964).
150. D.Z.Denney and D.B.Denney, J.Amer.Chem.Soc., 88, 1830 (1966).
151. G.Aksnes, R.Eriksen, and K.Mellingen, Acta Chem.Scand., 21, 1028 (1967).
152. D.Gagnaire, J.B.Robert, and J.Verrier, Bull.Soc.chim.France, 2240 (1967).
153. A.V.Bogatskii, A.A.Kolesnik, Yu.Yu.Samitov, and T.D.Butova, Zhur.Obshch.Khim., 37, 1048 (1967).
154. J.H.Hargis and W.G.Bentrude, Tetrahedron Letters, 5365 (1968).
155. D.Gagnaire, J.B.Robert, and J.Verrier, Bull.Soc.chim.France, 2392 (1968).
156. D.W.White, G.K.McEwen, and J.G.Verkade, Tetrahedron Letters, 5369 (1968).
157. F.R.Farmer, Diss.Abs., 28B, 2767 (1968).
158. J.P.Albrand, D.Gagnaire, J.B.Robert, and M.Haemers, Bull.Soc.chim.France, 3496 (1969).
159. C.Bodkin and J.P.Simpson, Chem.Comm., 829 (1969).
160. W.G.Bentrude, J.H.Hargis, and P.E.Rusek, Chem.Comm., 296 (1969).
161. R.S.Edmundson, Tetrahedron Letters, 1905 (1969).
162. M.Mikolajczyk, Chem.Comm., 1221 (1969).
163. M.Mikolajczyk and H.M.Schiebel, Angew.Chem., Int.Ed., 8, 511 (1969).
164. J.H.Finley and D.B.Denney, J.Amer.Chem.Soc., 92, 362 (1970).
165. W.G.Bentrude and J.H.Hargis, J.Amer.Chem.Soc., 92, 7136 (1970).
166. D.W.White, R.D.Bertrand, G.K.McEwen, and J.G.Verkade, J.Amer.Chem.Soc., 92, 7125 (1970).
167. W.G.Bentrude and K.C.Yee, Tetrahedron Letters, 3999 (1970).
168. B.A.Arbuzov and R.P.Arshinova, Dokl.Akad.Nauk SSSR, 195, 835 (1970).
169. C.L.Bodkin and P.Simpson, J.Chem.Soc.(B), 1136 (1971).
170. W.G.Bentrude, K.C.Yee, R.D.Bertrand, and D.M.Grant, J.Amer.Chem.Soc., 93, 797 (1971).
171. E.E.Nifant'ev, A.A.Borisenko, I.S.Nasonovskii, and E.I.Margosov, Dokl.Akad.Nauk SSSR, 196, 121 (1971).

172. K. Bergesen and P. Albriktsen, Acta Chem. Scand., 25, 2257 (1971).
173. L. D. Quin, J. P. Gratz, and R. E. Montgomery, Tetrahedron Letters, 2187 (1965).
174. K. Bergesen, Acta Chem. Scand., 21, 578 (1967).
175. W. S. Wadsworth, J. Org. Chem., 32, 1603 (1967).
176. K. D. Bartle, R. S. Edmundson, and D. W. Jones, Tetrahedron, 23, 1701 (1967).
177. R. S. Edmundson and E. W. Mitchell, J. Chem. Soc. (C), 2091 (1968).
178. L. D. Hall and R. B. Malcolm, Chem. Ind. (London), 92 (1968).
179. K. Bergesen, Acta Chem. Scand., 22, 1366 (1968).
180. W. G. Bentrude and J. H. Hargis, Chem. Comm., 1113 (1969).
181. M. Kainosho and T. Shimozawa, Tetrahedron Letters, 865 (1969).
182. J. P. Majoral and J. Navech, Compt. rend., 268C, 2117 (1969).
183. J. P. Majoral, R. Kraemer, J. Devillers, and J. Navech, Bull. Soc. chim. France, 3917 (1970).
184. K. Bergesen, Acta Chem. Scand., 24, 1122 (1970).
185. K. Bergesen and A. Berge, Acta Chem. Scand., 24, 1844 (1970).
186. K. Bergesen, Acta Chem. Scand., 24, 2019 (1970).
187. A. R. Katritzky and M. R. Nesbit, J. Chem. Soc. (B), 140 (1970).
188. J. P. Majoral and J. Navech, Bull. Soc. chim. France, 95 (1971).
189. J. P. Majoral and J. Navech, Bull. Soc. chim. France, 1331 (1971).
190. B. Z. Arbuzov, R. P. Arshinova, and V. M. Zoroastrova, Dokl. Akad. Nauk SSSR, 199, 1061 (1971).
191. K. Bergesen and T. Vikane, Acta Chem. Scand., 25, 1147 (1971).
192. D. W. White, G. K. McEven, R. D. Bertrand, and J. G. Verkade, J. Chem. Soc. (B), 1454 (1971).
193. K. C. Yee and W. G. Bentrude, Tetrahedron Letters, 2775 (1971).
194. W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, J. Amer. Chem. Soc., 89, 2268 (1967).
195. R. D. Spratley, W. C. Hamilton, and J. Ladell, J. Amer. Chem. Soc., 89, 2272 (1967).
196. G. Chioccola and J. J. Daly, J. Chem. Soc. (A), 568 (1968).
197. I. Kawamoto, T. Hata, Y. Kishida, and O. Tamura, Tetrahedron Letters, 2417 (1971).
198. D. Gorenstein and F. H. Westheimer, J. Amer. Chem. Soc., 89, 2762 (1967).
199. F. Ramirez, J. E. Pilot, O. P. Madan, and C. P. Smith, J. Amer. Chem. Soc., 90, 1275, 3299 (1968).
200. F. Ramirez, C. P. Smith, and J. F. Pilot, J. Amer. Chem. Soc., 90, 6728 (1968).
201. F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, J. Org. Chem., 33, 3787 (1968).
202. D. Gorenstein and F. H. Westheimer, J. Amer. Chem. Soc., 92, 634 (1970).
203. D. Gorenstein, J. Amer. Chem. Soc., 92, 644 (1970).
204. R. E. Duff, R. K. Oram, and S. Trippett, Chem. Comm., 1011 (1971).
205. J. R. Corfield, N. J. De'Ath, and S. Trippett, Chem. Comm., 1502 (1970).
206. P. Haake, R. D. Cook, T. Koizumi, P. S. Ossip, W. Schwartz, and D. A. Tyssel, J. Amer. Chem. Soc., 92, 3828 (1970).
207. D. Z. Denney, D. W. White, and D. B. Denney, J. Amer. Chem. Soc., 93, 2066 (1971).
208. B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, J. Amer. Chem. Soc., 93, 4004 (1971).
209. R. S. Berry, J. Chem. Phys., 32, 933 (1960).
210. R. R. Holms and R. M. Deiters, J. Amer. Chem. Soc., 90, 5021 (1968).
211. E. L. Muetterties, J. Amer. Chem. Soc., 91, 4115 (1969).
212. F. H. Westheimer, Acc. Chem. Res., 1, 70 (1968).
213. F. Ramirez, Acc. Chem. Res., 1, 168 (1968).
214. K. Mislow, Acc. Chem. Res., 3, 321 (1970).
215. G. M. Whitesides and H. L. Mitchell, J. Amer. Chem. Soc., 91, 5384 (1969).
216. E. L. Muetterties, W. Mahler, and R. Schmutzler, Inorg. Chem., 2, 613 (1963).
217. P. C. Haake and F. H. Westheimer, J. Amer. Chem. Soc., 83, 1102 (1961).
218. D. A. Usher, E. A. Dennis, and F. H. Westheimer, J. Amer. Chem. Soc., 87, 2320 (1965).
219. D. W. J. Cruickshank, J. Chem. Soc., 5486 (1961).
220. H. M. Ondik, Acta Cryst., 18, 226 (1965).
221. D. A. Koster and A. J. Wagner, J. Chem. Soc. (A), 435 (1970).
222. V. I. Andrianov, N. G. Bokii, V. V. Cherepinskii-Malov, B. L. Tarnopol'skii, and Yu. T. Struchkov, Zhur. Strukt. Khim., 10, 865 (1969).
223. V. D. Cherepinskii-Malov, A. I. Gusev, I. A. Nuretdinov, and Yu. T. Struchkov, Zhur. Strukt. Khim., 12, 126 (1971).
224. D. W. J. Cruickshank, Acta Cryst., 17, 679 (1964).
225. D. W. J. Cruickshank, Acta Cryst., 17, 677 (1964).
226. F. C. Mijlhoff, J. Portheine, and C. Komers, Rec. Trav. chim., 86, 257 (1967).
227. A. J. Stosick, J. Amer. Chem. Soc., 61, 1130 (1939).
228. B. Beagley, D. W. J. Cruickshank, T. C. Hewitt, and K. H. Jost, Trans. Faraday Soc., 65, 1219 (1969).
229. B. Beagley, D. W. J. Cruickshank, and T. G. Hewitt, Trans. Faraday Soc., 63, 836 (1967).
230. G. J. Palenik and J. Donohue, Acta Cryst., 15, 564 (1962).
231. J. Donohue, Acta Cryst., 15, 708 (1962).
232. J. C. J. Bart, Acta Cryst., 25B, 762 (1969).
233. F. Sanz and J. J. Daly, J. Chem. Soc. (A), 1083 (1971).
234. C. J. Spencer and W. N. Lipscomb, Acta Cryst., 14, 250 (1961).
235. C. J. Spencer, F. G. Simpson, and W. N. Lipscomb, Acta Cryst., 15, 509 (1962).
236. J. J. Daly, J. Chem. Soc., 6147 (1964).
237. J. J. Daly, J. Chem. Soc. (A), 1020 (1966).
238. J. J. Daly, J. Chem. Soc., 4789 (1965).
239. J. J. Daly, J. Chem. Soc. (A), 428 (1966).
240. L. R. Maxwell, V. M. Mosley, and S. B. Hendricks, J. Chem. Phys., 3, 698 (1935).
241. A. Brown and S. Rudquist, Acta Cryst., 19, 684 (1965).
242. Von H. Thurn and H. Krebs, Acta Cryst., 25B, 125 (1969).
243. R. L. Amster, N. B. Colthup, and W. A. Henderson, Spectrochim. Acta, 19, 1841 (1963).
244. A. H. Cowley and R. P. Pinnell, "Topics in Phosphorus Chemistry", Interscience Publ., New York, 1967, Vol. 4.
245. W. Mahler and A. B. Burg, J. Amer. Chem. Soc., 79, 251 (1957); 80, 2462 (1958).
246. W. A. Henderson, M. Epstein, and F. S. Seichter, J. Amer. Chem. Soc., 85, 2462 (1963).
247. H. S. Gutowsky and C. J. Hoffman, J. Amer. Chem. Soc., 72, 575 (1950).

248. H. J. Bernstein and J. Powling, J. Chem. Phys., 18, 1083 (1950).
249. L. Pauling and M. Simonetta, J. Chem. Phys., 20, 29 (1952).
250. J. R. Durig and J. M. Casper, J. Mol. Str., 5, 351 (1970).
251. M. Grayson and E. J. Griffith, "Topics in Phosphorus Chemistry", Interscience Publ., New York, 1966, Vol. 3.
252. J. D. Lee and G. W. Goodacre, Acta Cryst., 27B, 1841 (1971).
253. J. D. Lee and G. W. Goodacre, Acta Cryst., 27B, 1055 (1971).
254. P. J. Wheatley, J. Chem. Soc., 300 (1962).
255. J. J. Daly, J. Chem. Soc., 4065 (1964).
256. F. W. B. Einstein, B. R. Penfold, and Q. T. Tapsell, Inorg. Chem., 4, 186 (1965).
257. Y. C. Leung, J. Waser, S. Van Houten, A. Vos, G. A. Wiegers, and E. H. Wiebenga, Acta Cryst., 10, 574 (1957).
258. P. A. Akishin, N. G. Rambidi, and Yu. S. Ezhov, Zhur. Neorg. Khim., 5, 747 (1960) [Russ. J. Inorg. Chem., No. 3 (1960)].
259. D. A. Wright and B. R. Penfold, Acta Cryst., 12, 455 (1959).
260. G. W. Hunt and A. W. Cordes, Inorg. Chem., 10, 1935 (1971).
261. S. Van Houten and E. H. Wiebenga, Acta Cryst., 10, 156 (1957).
262. A. Vos, R. Olthof, F. Van Bolhuis, and R. Botterweg, Acta Cryst., 19, 864 (1965).
263. A. Vos and E. H. Wiebenga, Acta Cryst., 8, 217 (1955).
264. D. T. Dixon, F. W. B. Einstein, and B. R. Penfold, Acta Cryst., 18, 221 (1965).
265. W. Hilmer, Acta Cryst., 25B, 1229 (1969).
266. E. Kewlen and A. Vos, Acta Cryst., 12, 323 (1959).
267. G. J. Penney and G. M. Sheldrick, Acta Cryst., 26B, 2092 (1970).
268. G. J. Penney and G. M. Sheldrick, J. Chem. Soc. (A), 245 (1971).
269. K. W. Muir and J. F. Nixon, Chem. Comm., 1405 (1971).
270. W. van Doorne, G. W. Hunt, P. W. Perry, and A. W. Cordes, Inorg. Chem., 10, 2591 (1971).
271. P. J. Wheatley, J. Chem. Soc., 3733 (1962).
272. P. Andersen and K. E. Hjortaas, Acta Chem. Scand., 14, 829 (1960).
273. M. ul-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, J. Amer. Chem. Soc., 93, 5229 (1971).
274. D. D. Swank, C. N. Caughlan, F. Ramirez, and J. F. Pilot, J. Amer. Chem. Soc., 93, 5236 (1971).

Faculty of Chemistry,
Lomonosov Moscow State
University