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Phosphorus Rings, Clusters, Chains, and Layers

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Phosphorus compounds with P-P bonds (polyphosphides, phosphanes, and organophosphorus compounds) are considered as compounds formed by ions or radicals with a skeleton† consisting of phosphorus atoms linked covalently to one another; the structure of such skeletons depends little on the nature of the ions or radicals attached to them. The simplest structural elements of such skeletons have been isolated and the rules governing their combination into clusters, chains, layers, and cross-linked structures have been established. A classification is proposed and formulae are presented for homologous matrices of phosphorus skeletons and the wide variety of their structures is demonstrated. Certain aspects of the stereochemistry of polyphosphorus compounds are discussed. Its general features and the way it differs from the stereochemistry of organic compounds have been established. The considerable scope of the chemistry of polyphosphorus compounds is noted. The bibliography includes 47 references.

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I. INTRODUCTION

More than twenty years ago J.R.Van Wazer wrote in a foreward to his notable monograph of phosphorus chemistry "...there is a real need for a separate discipline just as there was a need for separating the chemistry of carbon compounds from the rest of chemistry. Instead of being merely a ragbag collection, the compounds of carbon are readily arranged into homologous series, and a small number of ground rules have proved sufficient to describe the relationships and interactions between these homologous series and between members of a given series. This state of affairs also seems to apply to the compounds of phosphorus... Furthermore, a system of ground rules, in some cases quite different from those of organic chemistry, appears to be emerging." (Van Wazer[1], p. 7).

The aim of the present review is to attempt to confirm the above words by analysing the characteristic features of the structure of skeletons consisting of two or more covalently linked phosphorus atoms in compounds of different classes: polyphosphides, phosphanes, and organophosphorus compounds. Analysis of structural data shows that the structure of the phosphorus skeletons in compounds of this kind depends little on the nature of the atoms or radicals joined to the skeleton.

Almost all the information about polyphosphorus compounds has been obtained in the last 15 years and nowadays this field of phosphorus chemistry is developing vigorously: it is therefore useful to examine critically and to arrange schematically the available literature data.

It is of interest to note that, despite the hypothesis of Krebs et al.[2] that many polyphosphides ($ZnPbP_{14}$, $HgPbP_{14}$) have a chain structure, and the available information concerning the complex allotropy of elemental phosphorus and about the existence of solid phosphorus hydrides and lower phosphorus oxides whose structure cannot be represented without assuming that phosphorus atoms are linked to one another, Van Wazer questioned the possibility of the existence of compounds involving a large number of covalently linked phosphorus atoms (Van Wazer[1], pp. 17, 123) and his view was shared by other workers[3,4].

More than 200 polyphosphorus compounds with skeletons comprising a finite (between 2 and 12) or an infinite number of phosphorus atoms are now known. On the other hand, the structures of only half of these compounds have been established, owing to the considerable difficulties of isolating and identifying the individual phases because of the slow attainment of equilibrium in the synthetic reactions, the simultaneous formation of a large number of different polyphosphorus compounds having similar physicochemical properties, and the tendency of the compounds to form amorphous or vitreous phases. However, even these experimental data are sufficient to demonstrate the exceptionally wide variety of the structures of phosphorus skeletons.

In this situation it is timely and useful to develop a classification and to determine the fundamental structural characteristics of the phosphorus skeletons. The first attempt at a classification of the compounds in terms of the structure of the phosphorus skeletons rather than the type of crystal lattice is due to Schnering[5], who achieved successful determinations of structures. However, his classification embraces only some of the polyphosphorus compounds (polyphosphides) and follows the relation between their structure and the structural elements of the lattices of white, red, and black phosphorus. We proposed a wider classification[6,7]; the present review is devoted to a detailed description of this classification and

† The absence of a generally accepted nomenclature in the description of compounds with element–element bonds (organic, cluster, and polymeric compounds of boron, sulphur, phosphorus, etc.) makes it difficult to choose names for groups comprising the atoms of an element joined together by chemical bonds and incorporated in a given compound as a polycation, a polyanion, or a neutral group. We decided to adopt the term "skeleton" for such groups, assuming that it will be understood unambiguously by specialists working in various fields of chemistry.

an examination of the fundamental characteristics of the structure of skeletons in the polyphosphorus compounds of different classes. The classification is based on: (a) quantum-chemical ideas about the configuration of valence orbitals and the length of bonds formed by atomic phosphorus as the structural element of the phosphorus skeletons (Van Wazer, p. 3); (b) the analysis of ~100 structures of different polyphosphorus compounds, invoking data for the structures of phosphorus compounds with bivalent electronegative elements incorporating $\rangle P-E-P\langle$ groups (where E = O, S, Se, or Te) having the same structures as some of the phosphorus skeletons; (c) certain stereochemical ideas in organic chemistry[8]. We shall now formulate the fundamental characteristics defining the structure of phosphorus skeletons.

1. The P–P bond is formed predominantly by p electrons, so that the phosphorus atoms involved in the formation of such bonds are formally tervalent‡. The σ-linked phosphorus atoms are separated by a distance of 2.17–2.30 Å, approximately equal to twice the covalent radius of phosphorus. A decrease of this distance indicates a certain amount of multiple bond character. However, such shortening of the bond is not characteristic of phosphorus and in the present review skeletons with bonds of this kind are not considered at all§. The valance angles of tervalent phosphorus are usually intermediate between 90° and 109°29′, corresponding to the p^3 and sp^3 states; in the P_3 group the valence angle is 60° ("bent" bonds).

2. The skeleton of a polyphosphorus compound can incorporate phosphorus atoms linked by a single bond with one, two, or three adjoining phosphorus atoms. We shall henceforth refer to such atoms as singly-linked ($\rangle P-P\langle$), doubly-linked ($\rangle P-\underset{|}{P}-P\langle$), and triply-linked ($\rangle P-\underset{|}{\underset{P}{P}}-P\langle$).[5] If the numbers of these atoms are designated by l, m, and n respectively, then a skeleton consisting of x phosphorus atoms and having y free bonds is described by the formula $P_x^y = (P'_l P''_m P'''_n)^{(2l+m)}$.

3. The fundamental structural elements of the phosphorus skeletons are simple chains of finite or infinite length and rings incorporating 3–6 or more atoms. If the frequency of such structural elements in various phosphorus compounds is adopted as a measure of their stability, then the rings should be more stable than the chains with the same number of atoms and among rings those which are five- and six-membered should be the most stable[1,9,10,12,13].

4. Simple chains and rings can play the role of independent phosphorus skeletons in polyphosphorus compounds or can be condensed into more complex skeletons having finite or infinite dimensions.

5. Phosphorus skeletons with infinite dimensions can be constructed by the regular or irregular condensation of structural elements. In the first case the skeletons present in crystalline phosphorus compounds or in crystalline allotropic modifications of elemental phosphorus are formed. In the second case the products are the skeletons of vitreous or amorphous phosphorus-containing phases.

A structural classification of the phosphorus skeletons in various polyphosphorus compounds is presented in the Table. The structures of the phosphorus skeletons presented in the text are illustrated by graph schemes. To facilitate the comparison of various layer or cyclic structures, the distances between neighbouring phosphorus atoms in certain schemes, which are not linked to one another, are represented by the same lengths as those between covalently linked phosphorus atoms. The filled, open, and half-filled circles in the schemes illustrate respectively triply-, doubly-, singly-linked phosphorus atoms. In analysing the structures of phosphorus skeletons having infinite dimensions, we shall confine ourselves to regular structures. The structures are described in terms of arbitrarily selected basic groups, whose repetition by translation or 180° rotation makes it possible to construct the entire structure; the basic groups in the graph scheme are enclosed by dashed lines.

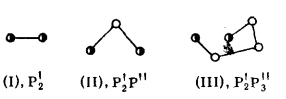
The characteristics of the structures of the phosphorus skeletons of each type are discussed below.

II. "ISLAND" STRUCTURES

We shall assign to "island" structures phosphorus skeletons having finite dimensions: simple chains, rings, clusters, and skeletons formed by the condensation of these simplest elements.

Simple Chains

The successive linking of phosphorus atoms can lead to the formation of unbranched ($P'_2P''_m$) or branched ($P'_{n+2}P''_m.P'''_n$) chains. Simple chains are described by the homologous formula $P_x^{(x+2)}$. It is satisfied by certain phosphanes[14,15] and organic derivatives of di-, tri-, and tetraphosphanes (Mellor[9], p. 912, Baudler et al.[12], and Baudler and Koch[13]). Skeletons comprising two phosphorus atoms [structure (I)] are present in certain phosphorus sulphides (Van Wazer[1], p. 294), in tetraphosphorus trithiodi-iodide[16], in a series of mono- and di-phosphides (Corbridge[10], pp. 17, 18, 62), and certain phosphorus acids (Mellor[9], p. 597). P_3^5 and P_5^7 chains have been found in lanthanum diphosphide[19] [(II) and (III)]:



Rings

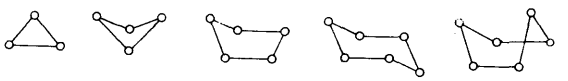
Rings consisting only of doubly-linked phosphorus atoms are described by the formula $P_m^n = P_x^x$ [structures (IV) to (VIII)]. According to the phosphorus stereochemistry, when $m > 3$ the rings are bent. The analogy between

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‡ Skeletons comprising linked quinquevalent phosphorus are less characteristic. They are involved in the structures of the molecules of certain phosphorus acids, for example $H_4P_2O_6$, $H_5P_3O_8$, $H_6P_4O_{10}$, and $H_6P_6O_{12}$, and their salts (Mellor[9], p. 598), as well as the compound $(PO)_4(PPh)_6$ (Corbridge[10], p. 422).

§ The structures of the polyphosphides K_4P_6 and Pb_4P_6 contain planar six-membered P_6^{4-} rings in which the distance between the phosphorus atoms is 2.15 Å, indicating the presence of a non-localised π bond between phosphorus atoms[11].

phosphorus and non-aromatic carbon rings suggests that a six-membered phosphorus ring can exist in the "chair" and "boat" forms [structures (VII) and (VIII)], the former being energetically preferable (Corbridge[10], p. 383):



(IV), P_3^{II} (V), P_4^{II} (VI), P_5^{II} (VII), P_6^{II} (VIII), P_6^{II}

Classification of types of phosphorus skeletons.

Structures of phosphorus skeletons	Homologous formula P_x^y	Polymorphic modifications of elemental phosphorus	Polyphosphorus compounds: phosphanes	poly-phosphides	organo-phosphorus compounds	other compounds	Compounds incorporating groups with similar structures and P–E–P linkages
"Island" structures							
Simple chains	$P'_{n+2}P''_m\cdot P'''_n=P_x^{x+2}$	—	P_xH_{x+2} (x=2—7)	CaP^*, LaP_2, MP_2(M=V, Nb, Ta, Mo, W, Fe, Ru, Os, Rh, Ni, Pt, Si), NiP_3^*, CoP_3^*	P_2R_4, P_3R_5, (R=Ph, Et, CF_3), $M_2P_4R_4$ (M=Li, Na, K; R=Et, Me)	$H_5P_3O_7$, $H_6P_4O_{10}$, $H_4P_2O_4$, $H_4P_2O_5$	$H_4P_2O_7$, $H_5P_3O_{10}$, $H_{n+2}P_nO_{3n+1}$
Rings	$P''_n=P_x^x$	—	P_xH_x (x=3—6)*	—	P_xPh_x (x=4—6) $P_x(CF_3)_x$ (x=4,5)	$(HPO_2)_6$	$(HPO_3)_3$, $(HPO_3)_4$, $H_4P_4O_{10}$
Clusters	$P''_mP'''_n=P_x^{x-n}$ (n-even)	P_4(gas, white phosphorus)	P_xH_{x-2} (x=4—8, 10)*, P_xH_{x-4} (x=6—9)*, P_xH_{x-6} (x=9, 10)*, P_xH_{x-8} (x=10—12)*,	Sr_3P_{14}, Ba_3P_{14}, Na_3P_{11},	$P_{10}Ph_6$, $P_{13}R_5^*$, $P_{14}R_4^*$, $P_7R_3^*$ (R=[$(CH_3)_3$·Si])	—	$P_4O_4S_6$, $P_4O_6S_4$, P_4S_x (x=3, 5, 7, 10), P_4O_x (x=6—11), $H_2P_4O_{11}$, $P_{10}Ph_6R_4$ (R=O, Sn, Ge, Si)
Condensed structures	—	—	$P_{12}H_4^*$, $P_xH_x^*$ (x=7,8)	—	—	—	$H_4P_4O_{12}$
Chain structures							
Simple chains	$P'_nP''_mP'''_n=P_1^1$	—	$P_xH_x^*$	LiP, NaP, tetragonal ZnP_2, monoclinic ZnP_2, PdP_2, monoclinic NiP_2, α-CdP_2, TiP_2, ZrP_2, HfP_2	—	—	—
Ring chains	$P''_\alpha P'''_{2(p+q)}$	—	—	MoP_4, CrP_4, MnP_4, BaP_3	—	—	—
Cluster chains	$P''_\alpha P'''_\beta$	P*(red, amorphous)	—	NaP_7, RbP_7, KP_{15}	—	—	—
Mixed chains	$P''_\alpha P'''_\beta$	—	—	$M'M''P_{14}$ (M'=Zn, Cd, Hg; M''=Pb, Sn)	—	—	—
Layer structures	$P''_\gamma P'''_{2t}$	P*(black, amorphous), P(black, orthorhombic)	—	CaP_3, SrP_3 CdP_4, MgP_4, CuP_2, AgP_2, MP_5(M=La, Ce, Nd, Sm, Gd)	—	—	P_4O^*, orthorhombic P_2O_5, orthorhombic-P_2O_5
Cross-linked structures							
Cross-linked "island" structures		—	—	—	—	—	—

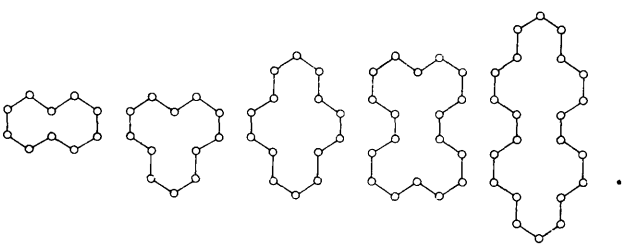
Table (contd.)

Structures of phosphorus skeletons	Homologous formula P_x^y	Polymorphic modifications of elemental phosphorus	Polyphosphorus compounds: phosphanes	poly-phosphides	organo-phosphorus compounds	other compounds	Compounds incorporating groups with similar structures and P–E–P linkages
Cross-linked chains	P''_{m-r-2s}	P(red, crystalline)	—	$LiP_5TlP_8\cdot LaP_7$	—	—	—
Cross-linked layers	$P'''_{n+2r+3s}$		—	—	—	—	—

Notation: l, m, and n represent the amounts of singly-, doubly-, and triply-linked phosphorus atoms in the skeleton respectively; t is the number of clusters and (or) rings joined together in the basic group; p and q are the numbers of P–P bonds and common edges necessary to construct the basic group; k is the number of atoms in the common sides in condensed clusters or rings; r and s are the numbers of $\rangle P-P-P\langle$ and $\rangle P-P\langle$ bridge bonds in the cross-linked skeletons; i are the indices of rings and clusters; j are indices of common sides or edges; $\alpha = \sum_{i=1}^{t} m_i - \sum_{j=1}^{q} k_j - 2(p+q)$;

$\beta = \sum_{i=1}^{t} n_i + 2(p+q)$; $\gamma = \frac{1}{2}\sum_{i=1}^{t} m_i - 3t$.

Five- and six-membered rings are the fundamental structural elements of the most stable clusters. We may note that cyclic chains and layers formed by the condensation of six-membered rings or derivatives of these rings comprising an even number of phosphorus atoms have been found in many polyphosphides [structures (IX)–(XIII)]. Rings with m = 4–6 are formed in organophosphorus compounds (Mellor[9], p. 913, and Corbridge[10], p. 383) and apparently in phosphanes having the composition P_XH_X (x = 3–6)¶ [15]:



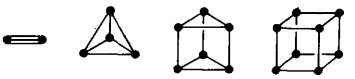
(IX), P_{10}^{II} (X), P_{12}^{II} (XI), P_{14}^{II} (XII), P_{16}^{II} (XIII), P_{22}^{II}

Clusters

The cluster structures consist of convex polyhedra the vertices of which contain triply-linked atoms and the faces are formed by rings comprising three–six phosphorus atoms. The number of faces in the cluster is determined by the number of triply-linked phosphorus atoms n and is equal to $\frac{1}{2}n + 2$. Consequently cluster structures may be made up of P_n''' skeletons, where n is even, consisting of

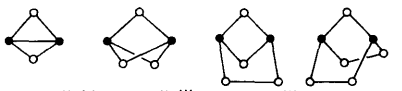
¶ The hypothesis[20] that the phosphanes P_XH_X have a chain structure is less probable. On this hypothesis, the phosphane P_3H_3 should have the structure $H_2P-P=PH$ and chains with a larger number of phosphorus atoms should be described by the formula $P'_2P'''_mP'''_2$.

an even number of triply-linked phosphorus atoms [structures (XIV)–(XVII)], the bonds between P‴ atoms being ruptured and doubly-linked phosphorus being added at the site of rupture. Each of the initial skeletons is the parent of an individual homologous series.



(XIV), $P_2^{'''}$ (XV), $P_4^{'''}$ (XVI), $P_6^{'''}$ (XVII), $P_8^{'''}$

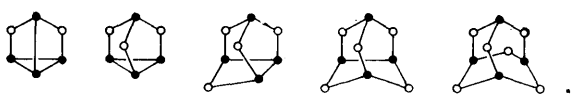
The homologous series originating from the $P_2^{'''}$ skeleton (XIV) is described by the formula $P_m^{''}P_2^{'''} = P_X^{X-2}$ [(XVIII) to (XXI)]. The phosphanes P_XH_{X-2} ($x = 4-8$, 10) satisfy this formula[14].



(XVIII), $P_2^{''}P_2^{'''}$ (XIX), $P_3^{''}P_2^{'''}$ (XX), $P_4^{''}P_2^{'''}$ (XXI), $P_5^{''}P_2^{'''}$

In polyphosphides and organophosphorus compounds clusters of this series have not been found in a free form, but the $P_5^{''}P_2^{'''}$ cluster ("boat" configuration whose raised ends are linked by the seventh phosphorus atom) (XXI) is the fundamental structural element in the lattice of crystalline red phosphorus[21] and many polyphosphides[5,22,23].

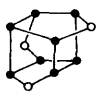
Clusters based on the tetrahedral molecule $P_4^{'''}$ (XV) are described by the formula $P_m^{''}P_X^{'''} = P_X^{X-4}$ [structures (XXII)–(XXIV)]:



(XXII), $P_2^{''}P_4^{'''}$ (XXIII), $P_3^{''}P_4^{'''}$ (XXIV), $P_4^{''}P_4^{'''}$ (XXV), $P_5^{''}P_4^{'''}$ (XXVI), $P_6^{''}P_4^{'''}$

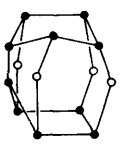
This formula is satisfied by the phosphanes P_6H_2, P_8H_4, P_9H_5, and P_7H_3. The P_7^{3-} cluster (XXIII) has been found in the polyphosphides Ba_3P_{14} and Sr_3P_{14}. We may note that these clusters have the same structures as phosphorus sulphides and oxides.

The homologous series of the P_X^{X-6} and P_X^{X-8} clusters may be constructed similarly on the basis of the trigonal prism $P_6^{'''}$ (XVI) and cube $P_8^{'''}$ (XVII). The formulae of these series are satisfied by the phosphanes P_9H_3, $P_{10}H_4$, $P_{10}H_2$, $P_{11}H_3$, and $P_{12}H_4$.[14] A representative of the homologous series based on the cube is present in the lattice of the polyphosphide Na_3P_{11} (XXVII)[24] and probably in the compound $[(CH_3)Si]_5P_{13}$.[25]



(XXVII), $P_3^{''}P_6^{'''}$

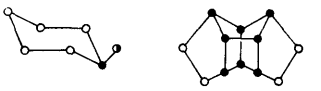
One can imagine clusters consisting of more than eight triply-linked phosphorus atoms which give rise to the homologous series P_X^{X-10}, P_X^{X-12}, etc. For example, the P_{14}^4 cluster in the compound $[(CH_3)Si]_4P_{14}$[25] may be obtained from the $P_{10}^{'''}$ cluster, which consists of a pentagonal prism. The cluster constructed in this way should be represented by formula (XXVIII):



(XXVIII), $P_4^{''}P_{10}^{'''}$

Condensed Structures

Rings containing more than seven phosphorus atoms have not been detected in the structures investigated. The P_8H_8 and P_9H_9 phosphanes have been reported[14,15]. They can be made up of eight- or nine-membered rings, but the formula P_X^X is also satisfied by phosphorus structures (XXIX) having the composition $P_n^{'}P_m^{''}P_n^{''}$ and formed by the addition of singly-linked phosphorus atoms to rings:



(XXIX), $P^{'}P_5^{''}P^{'''}$ (XXX), $P_4^{''}P_8^{'''}$

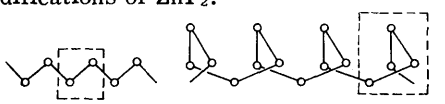
An example of the condensed "island" structure is also the P_{12}^4 cluster (XXX) obtained from two clusters (XXI) when the latter are joined via their common edge and a P–P bond. This cluster is the structural element of the phosphorus skeletons in the crystal lattice of red phosphorus[21] and many polyphosphides[5,22,23].

III. CHAIN STRUCTURES

Chain structures are formed when single phosphorus atoms (simple chains), rings (ring chains), and clusters (cluster chains) are joined together to form infinitely long chains. Ordered chains have been found in the crystal lattices of many polyphosphides[5] and in the structure of crystalline red phosphorus[21].

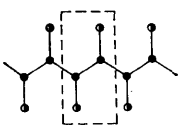
Simple Chains

The consecutive combination of phosphorus atoms can lead to the formation of zigzag or helicoidal chains described by the formula P_X^X (Schnering[5] and Corbridge[10], p.40). Zigzag chains (XXXI) are present in the crystal lattices of titanium, hafnium, zirconium, and palladium diphosphides (Corbridge[10], p.40), helicoidal chains (XXXII) have been found in the LiP,[26] NaP,[26] and α-CdP_2[27] lattices and in the lattices of the tetragonal and monoclinic modifications of ZnP_2.[28,29]



(XXXI), $P_2^{''}$ (XXXII), $P_4^{''}$

One may postulate the formation of branched phosphorus chains having the general formula $P_n^{'}P_m^{''}P_n^{'''} = P_1^1$, for example, with $m = 0$ and $n = 1$ as in structure (XXXIII):

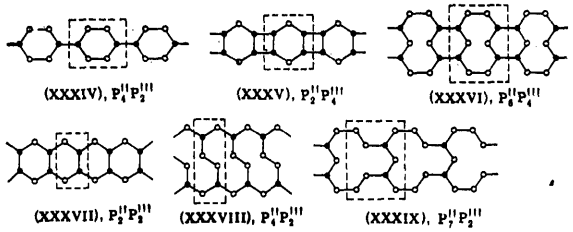


(XXXIII), $P_2^{'}P_2^{'''}$

Multiring Chains

When identical or different rings are joined together in an ordered or non-ordered manner, multiring chains may be formed. Such chains are either independent structural elements or form part of more complex phosphorus structures.

On forming chains, the rings can be joined by one [as in (XXXIV)] or two [as in (XXXV) and (XXXVI)] bonds or by a common side [as in (XXXVII)–(XXXIX)]:



(XXXIV), $P_4''P_2'''$ (XXXV), $P_2''P_4'''$ (XXXVI), $P_6''P_4'''$

(XXXVII), $P_2''P_3'''$ (XXXVIII), $P_4''P_4'''$ (XXXIX), $P_7''P_2'''$

On formation of each bond between the rings, two doubly-linked phosphorus atoms become triply-linked. In order to form a common side, it is necessary to remove k atoms from two rings; the common side then consists of two triply-linked and $k-2$ doubly-linked phosphorus atoms. In the general case the basic group of such an infinite ordered chain, made up of t rings, is described by the formula $P_x^{x-2(p+q)}$, where $x = \sum_{i=1}^{t} m_i - \sum_{j=1}^{q} k_j$, m_i is the number of phosphorus atoms in each initial ring, p the number of new P–P bonds formed when the rings are linked to one another, and q the number of common sides, each of which contain k_j phosphorus atoms.

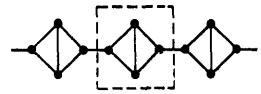
The most typical should be the simplest cases where the chain is made up of identical rings, linked to one another in the same manner. In this case $i = 1$ and, for singly-linked rings ($p = 1$, $q = 0$), we obtain the homologous formula P_x^{x-2} ($x = m$); for doubly-linked rings ($p = 2$, $q = 0$), we have the formula P_x^{x-4} ($x = m$); for rings linked by a common side ($p = 0$, $q = 1$), we have the formula P_x^{x-2} ($x = m - k$). Infinite chains made up of singly-linked six-membered rings in the chair form (XXXIV) are the structural elements of the BaP_3 crystal lattice [30]. The multiring chains (XXXVII) are components of the phosphorus structure in lithium polyphosphide LiP_5. [31]

Cluster Chains

Like rings, clusters can be joined together to form chains via one or two P–P bonds or by the formation of common edges. The linking of clusters by three P–P bonds or by the formation of a common face is unlikely in view of steric hindrance. There is also a possibility that clusters are linked together with formation of both a P–P bond and a common edge [as in (XXX)]. The basic group in an infinite ordered cluster chain consisting of t clusters $P_{m_i}''P_{n_i}'''$, joined by p P–P bonds, and forming q common sides is described by the formula P_x^y, where

$$x = \sum_i (m_i + n_i) - \sum_{j=1}^{q} k_j, \quad y = \sum_i m_i - 2(p+q) - \sum_{j=1}^{q} k_j.$$

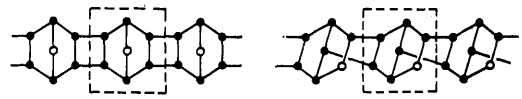
In order that the clusters can be connected to form chains, they must contain at least two doubly-linked phosphorus atoms [see (XVIII)–(XXVIII)]. The basic group of a chain consisting of identical clusters $P_m''P_n'''$, linked to one another by a single P–P bond, is described by the formula $P_{m+n}^{m-2} = P_x^{x-n-2}$. Such a chain (XL), obtained by joining together singly-linked clusters (XVIII), can be seen in the structure of amorphous red phosphorus proposed by Pauling and Simonetta [32].



(XL), P_4'''

Clusters joined together by two bonds should have at least four doubly-linked phosphorus atoms. The clusters (XX), (XXI), (XXII), and (XXX) may be of this kind. The formula of the basic group of the chain consisting of identical clusters is $P_{m+n}^{m-4} = P_x^{x-n-4}$.

Structures (XLI) and (XLII) consist of chains comprising the $P_5''P_2'''$ cluster (XXI):



(XLI), $P''P_6'''$ (XLII), $P''P_6'''$

Such chains occur in the crystal lattices of the polyphosphides RbP_7 (XLI) and LiP_7, NaP_7 (XLII). [5,31]

Clusters joined together with formation of common sides must have at least two edges containing not less than two P'' atoms. This condition is satisfied only by clusters (XXI) and (XXX). Evidently these clusters are in fact the most convenient structural elements of the cluster chains. The structures of crystalline red phosphorus (XLIII) [21] and a number of polyphosphides, for example KP_{15}^{33} (XLIV), are constructed on their basis:



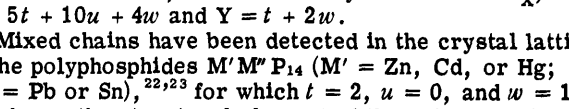
(XLIII), $P_2''P_{16}'''$ (XLIV), $P''P_{14}'''$

If the chain is formed from t clusters of type (XXI) by joining together the latter with formation of p new P–P bonds and q common sides, the formula of the basic group becomes $P_{7t-2q}^{5t-2p-4q} = P_x^{x-2(p+t+q)}$ (for example, in the KP_{15} structure we have $t = 3$, $p = 1$, and $q = 3$).

Mixed Chains

Infinite chains can also be formed by joining together clusters and rings. The formation of mixed chains from P_6^6 [(VII) and (VIII)] and the clusters P_7^5 (XXI) and P_{12}^4 (XXX), joined by their common sides, is most probable. The basic group, consisting of w rings P_6^6, t clusters P_7^5, and U clusters P_{12}^4, is described by the formula P_X^Y, where $x = 5t + 10u + 4w$ and $Y = t + 2w$.

Mixed chains have been detected in the crystal lattices of the polyphosphides $M'M''P_{14}$ (M' = Zn, Cd, or Hg; M'' = Pb or Sn), [22,23] for which $t = 2$, $u = 0$, and $w = 1$ and which are the structural element of the polyphosphide [34] TlP_5 ($t = 1$, $u = 0$, $w = 1$) [see (XLV) and (XLVI)]:

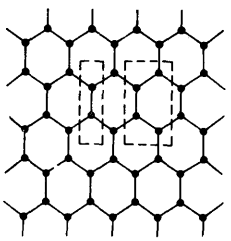


(XLV), $P_4''P_{10}'''$ (XLVI), $P_3''P_6'''$

IV. LAYER STRUCTURES

Regular layer structures can be made up by joining together ring chains via P–P bonds or by the formation of common sides. In the crystal lattice of black phosphorus and many polyphosphides layer structures based on the rings (VII) and (IX)–(XIII) have been detected[5,35]. The formation of layer structures from cluster chains is unlikely for steric reasons.

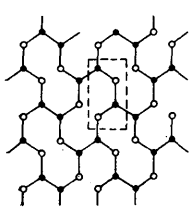
Suppose that a layer is made up of identical chains whose basic group is described by the formula $P''_mP'''_n$. If on formation of the layer two basic groups are joined by p bonds P–P and give rise to k common atoms of which j atoms are triply-linked, the formula of the basic group is P_x^y, where $x = m + n - k$ and $y = m - 2p - j$.



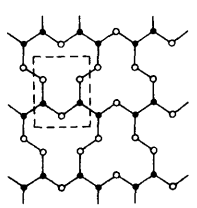
(XLVII), $P_2'''P_4'''$

For example, the structure of the layer in black phosphorus (XLVII) can be represented as a result of the linking of the chains (XXXVII) by P–P bonds (in this case $m = 2$, $n = 2$, $p = 1$, and $k = j = 0$) or by the formation of common sides ($m = 2$, $n = 2$, $p = 0$, $k = j = 2$). The same structure can be made up of the chains (XXXIV) by linking them via P–P bonds ($m = 4$, $n = 2$, $p = 2$, $k = j = 0$) or via common sides ($m = 4$, $n = 2$, $k = j = 4$).

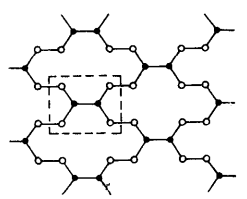
It is simpler to describe layer structures as a result of the joining together of rings of one or more types. It is readily seen that, when the layer is made up of identical rings P''_m, its basic group consists of $\frac{1}{2}(m - 2)$ phosphorus atoms, of which two are triply linked, i.e. the formula of the basic group is P_x^{x-2}, where $x = \frac{1}{2}(m - 2)$. Such layers can be made up only of rings with an even number of phosphorus atoms [the structures of black phosphorus (XLVII) and the polyphosphides CuP_2, AgP_2, CdP_4,[36] MgP_4 [37,38] (XLVIII), LnP_5 [39,40] (XLIX), and CaP_3 (L) [41]].



(XLVIII), $P_2''P_2'''$

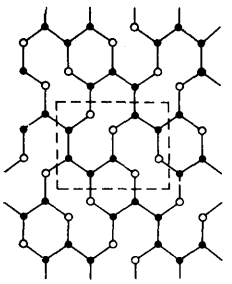


(XLIX), $P_3''P_2'''$

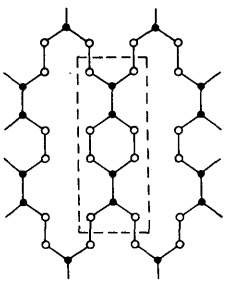


(L), $P_4''P_2'''$

If the layer consists of t rings of type P''_{m_i}, the basic group contains $x = \frac{1}{2}\sum_{i=1}^{t}(m_i - 2) = \frac{1}{2}\sum_{i=1}^{t} m_i - t$ phosphorus atoms, of which $2t$ are triply-linked. The formula of the basic group is P_x^{x-2t}. Examples of layers formed by the condensation of several rings are (LI) ($m_1 = 10$, $m_2 = 10$, $m_3 = 6$) and (LII) ($m_1 = 22$, $m_2 = 6$); the latter structure arises in the crystal lattice of the polyphosphide SrP_3.[40]



(LI), $P_4''P_6'''$



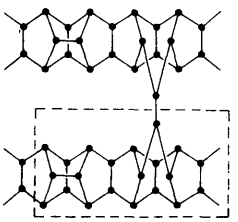
(LII), $P_8''P_4'''$

V. CROSS-LINKED STRUCTURES

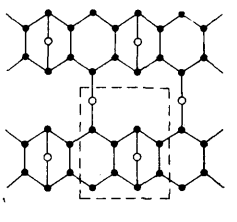
Elementary phosphorus skeletons can be joined together into more complex entities not only by simple connection but also by cross-linking via bridging doubly- or triply-linked phosphorus atoms. Cross-linked phosphorus structures have been found in the crystal lattices of red phosphorus[21] and certain polyphosphides[5,31,34].

The following variants of cross-linked structures may be postulated: chains, layers, and skeletal structures obtained by the cross-linking of rings or clusters; layers and skeletal structures formed from cross-linked chains; skeletal structures made up of cross-linked layers. However, only layer and skeletal structures obtained by the cross-linking of chains have been found in the crystals investigated hitherto.

The cross-linked chains (XLVI) form phosphorus layers in the crystal lattice of TlP_5 [34] (LIII). In the structure of crystalline red phosphorus the chains (XLIII) are linked by bridges comprising a pair of P''' atoms [see (LIV)] with formation of a double layer:

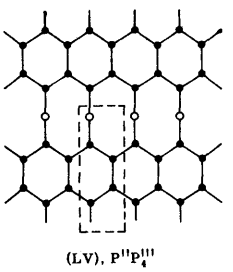


(LIII), P_{21}'''



(LIV), P_2'', P_8'''

The cross-linking of the chains leads to the formation of skeletal structures made up of phosphorus atoms in the crystal lattices of LiP_5 [31] and LaP_7.[42] The projection of the former onto the plane in which the parallel chains are located is of the form



(LV), $P''P_4'''$

The formation of a skeleton in these structures is due to the fact that the bridging phosphorus atoms link together chains located in different planes.

In cross-linking by bridging doubly linked phosphorus atoms $\rangle P-P-P\langle$ two doubly linked phosphorus atoms become triply-linked for each cross-linked bond and a further doubly-linked atom is added. Therefore, if the basic group which was described by the formula $P''_mP'''_n$. before cross-linking is joined to another similar group by r bridge bonds, the formula of the basic group in the cross-linked structure is $P''_{m-r}P'''_{n+2r} = P^y_x$, where $x = m+n+r$ and $y = m-r$. For example, when chains (XXXVII) of the type $P''_2P'''_2$ are cross-linked by bridge bonds (one bond per basic group), we have $m = 2$, $n = 2$, and $r = 1$, i.e. the formula of the basic group in the cross-linked structure is $P''P'''_4 = P^1_5$ (LV).

In cross-linking by triply linked atoms $\rangle P-P\langle$ each bridging atom is connected to two doubly-linked atoms, converting them into triply-linked atoms. The formula of the basic group after cross-linking is therefore $P''_{m-2s}P'''_{n+3s}$, where s is the number of bridge bonds. For example, cross-linking of the chains P^1_{20} (XLIII) yields the cross-linked structure (LIV) with the basic group P'''_{21}.

VI. CONCLUSION

Using the procedures described above, it is possible to construct a very large number of phosphorus skeletons, including some which have not been considered in this review. It therefore becomes possible to predict the structures of skeletons in polyphosphorus compounds of known composition. As an example, the Appendix presents the development of various procedures for the construction of phosphorus skeletons having the composition P^1_2, the most accurate of which (from our point of view) are then selected. Such phosphorus skeletons should be present in the phosphorus hydride $(P_2H)_x$ and in the polyphosphides having the general formula MP_{2n} (n is the valence of the metal).

Since the same formula corresponds to a whole series of structures, additional information about the properties of the compound is required for an unambiguous selection [6]. Consider an example. The preparation of the solid phosphorus hydride $(PH)_x$ has been reported [9]. Since this compound is resistant to acids and alkalis and decomposes *in vacuo* only at 400°C, it is logical to suppose that it has a polymeric structure. The formula P^1_1 is satisfied only by simple chains and rings, so that one can claim that the phosphorus hydride $(PH)_x$ contains either infinite branched or unbranched phosphorus chains or structures made up of condensed rings formed by a large number of phosphorus atoms, as happens in catenanes [43]; the first hypothesis appears to be more likely.

A greater abundance of comparatively simple skeletons consisting of a small number of structural elements is to be expected for binary compounds of phosphorus with electropositive elements or radicals. The skeletons in polyphosphorus compounds with several different elements or radicals, particularly when these are characterised by different valences, should have a more complex structure.

The ability of phosphorus to form different structures corresponding to the same formula of the basic group reflects the unusual isomerism of phosphorus skeletons. On the basis of this property, one may postulate the possibility of the polymorphism of many polyphosphorus compounds, which may be caused only by changes in the packing of atoms in the unit cell without an alteration of the structure of the phosphorus skeleton (tetragonal [28] and monoclinic [29] modifications of ZnP_2) or may be a consequence of a change in the skeleton [elemental phosphorus and cubic (Corbridge [10], p. 429) and monoclinic [44] modifications of NiP_2].

In the present review we confined ourselves to an examination of regular chain, layer, and three-dimensional structures which are usually present in the crystalline phases. If a statistical distribution of the initial elements in infinite phosphorus structure is postulated, one may investigate different variants of the structures of amorphous and vitreous phases, which are common in the chemistry of phosphorus.

The principles of the construction of phosphorus skeletons described are applicable, as shown above, also to the construction of neutral phosphorus structures consisting solely of triply-linked phosphorus atoms. This makes it possible to build up the probable configurations of polymorphic modifications of elemental phosphorus which have not yet been investigated and which have been mentioned in a number of publications [9,10].

On the basis of the wide variety of structures of phosphorus skeletons, one may postulate the existence of a very large number of different polyphosphorus compounds, since experience gained in the development of chemistry indicates a high reliability of the predictions of the structures of compounds on the basis of the classical theory of valence [45]. In terms of this ability to form polyatomic compounds, phosphorus is inferior only to carbon and possibly to boron [46]. In fact, if the element–element bond energy and the number of covalent bonds are adopted as criteria of the ability to form polyatomic compounds, then, among elements forming more than two bonds, carbon, boron, and phosphorus give rise to the most stable bonds. The smaller number of polyphosphorus compounds compared with carbon compounds is caused both by the tervalence of phosphorus (in contrast to the quadrivalence of carbon) and the smaller energy of the P–P covalent bond (53 kcal mole^{-1}) compared with the energy of the aliphatic C–C bond (83 kcal mole^{-1}). [47] The lower electronegativity of phosphorus and the presence of a lone electron pair and of vacant 3*d* orbitals in a three-coordinated phosphorus atom lead to a greater reactivity of phosphorus compounds compared with the analogous carbon compounds, which creates definite experimental difficulties.

Homologous series are common in organic chemistry, while in the chemistry of polyphosphorus compounds homologous matrices, consisting of families of homologous series, are abundant. It may turn out that some of the homologous series are represented by a small number of members or even only one member, but one can also encounter skeletons with a similar structure belonging to different homologous series but described by the common formula of the homologous matrix.

The extremely wide variety of structures of polymeric phosphorus molecules noted above, compared with carbon, is associated with the different structures of the two elements.

Rigid tetrahedral sp^3 bonds with a high deformation energy and valence angles differing little from tetrahedral values are characteristic of saturated carbon compounds.

On the other hand, the pyramidal p^5 phosphorus bonds are readily deformed†, which leads to the wide variety of the existing phosphorus skeletons. The tervalence of the phosphorus atom is responsible for the relatively greater abundance of clusters and cluster structures than in the case of carbon. Thus the role of the cluster (XXI) in building up the phosphorus chains has already been noted. The stability of such a cluster is due to the fact that the valence angle in the P–P–P linkage is ~100°. For carbon, which has a greater valence angle, the formation of this type of cluster involves the appearance of strained bonds and carbon compounds involving such a cluster are not typical, although they do exist[8].

The above analysis of the structure of phosphorus skeletons in various polyphosphorus compounds demonstrated, as might have been expected, the existence of homologous series and homologous matrices for the description of which it is sufficient to have a small number of fundamental rules, which in certain cases differ from the rules of organic chemistry. This emphasises yet again the characteristic features of the chemistry of phosphorus and the desirability of separating it as an individual chemical discipline with its own rules governing the description of compounds and the reactions involving them and an individual approach to problems of the specific synthesis of such compounds‡.

VII. APPENDIX (DETERMINATION OF THE STRUCTURES OF P_2^1 PHOSPHORUS SKELETONS)

The P_2^1 phosphorus skeleton is described by the formula $P_l'P_m''P_n'''$ in which $m = n - 3l$. The most typical skeletons do not contain singly-linked phosphorus atoms ($l = 0$) and correspond to the condition $m = n$. We shall confine ourselves to an examination of "island", chain, and layer structures formed by such skeletons.

"Island" Structures

Only $P_2''P_2'''$ (XVIII), $P_4''P_4'''$ (XXIV), $P_6''P_6'''$, etc. clusters as well as condensed structures for which $m = n$ satisfy the formula P_2^1. Since $m = \sum_{i=1}^{t} m_i - \sum_{j=1}^{q} k_j - 2(p+q)$ and $n = \sum_{i=1}^{t} n_i + 2(p+q)$, the relation between the parameters characterising such structures is defined by the equation $\sum_{i=1}^{t} (m_i - n_i) - \sum_{j=1}^{q} k_j = 4(p+q)$. For example, when the condensed cluster is formed from two identical clusters linked by a single P–P bond, we have $t = 2$, $k = 0$, $p = 1$, $q = 0$, and $m_1 - n_1 = 2$. Consequently $P_4''P_2'''$, $P_6''P_4'''$, etc. clusters can be combined into an "island" structure in the way described.

The formation of the following "island" structures is most probable: the $P_4''P_4'''$ cluster all sides of which consist of five-membered rings or the cluster (XXIV) whose sides consist of two five-membered rings, one six-membered ring, and one four-membered ring.

Among condensed structures, the formation of the $P_6''P_6'''$ cluster, obtained when two $P_5''P_2'''$ (XXI) clusters combine with establishment of a common side comprising two atoms, is most probable.

Chain Structures

Multiring, cluster, or mixed chains can correspond to the formula P_2^1. The condition $m = n$ for multiring chains may be formulated as follows: $\sum_{i=1}^{t} m_i - \sum_{j=1}^{q} k_j = 4(p+q)$. For chains made up of identical rings ($t = 1$), this formula assumes the form $m_1 - k_1 = 4(p+q)$. Consequently a singly-linked chain ($p = 1$, $q = 0$, $k = 0$) consists of four-membered rings; a doubly-linked chain ($p = 2$, $q = 0$, $k = 0$) consists of eight-membered rings; a chain formed by the linking together of rings consisting of m_1 phosphorus atoms and involving the establishment of a common side comprising k_1 atoms ($p = 0$, $q = 0$) is described by the formula $m_1 = k_1 + 4$. If $k_1 = 2$ and $m_1 = 6$, we obtain the chain (XXXVII). Chains with $k_1 > 2$ are unlikely for steric reasons.

Cluster and mixed P_2^1 chains are described by the equation $\sum_{i=1}^{t} (m_i - n_i) - \sum_{j=1}^{q} k_j = 4(p+q)$. Analysis shows that the formation of such chains with a simple structure is impossible.

Layer Structures

The condition $m = n$ assumes the following form for layers whose basic group consist of t rings: $m_1 - k_1 = 4(p+q)$. The layer formed by the condensation of identical rings should therefore incorporate P_{10}'' rings (XLVIII). The layer obtained by the condensation of P_{m_1}'' and P_{m_2}'' rings of different kinds must satisfy the condition $m_1 + m_2 = 20$, i.e. it can be formed only for $m_1 = 6$ (VII) and $m_2 = 14$ (XI).

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† In the structure of crystalline red phosphorus the valence angles between bonds vary from 84.5° to 115.9° and the distance between linked phosphorus atoms varies from 2178 to 2.299 Å,[22] although the average valence angle (101°) and the P–P distance (2.22 Å) are close to the optimum values observed in the structure of the most stable modification—black phosphorus[27].

‡ See also the recently published review by H.G. Schnering (in "Homoatomic Ring Chain Macromolecules of Main-group Elements", Elsevier, Amsterdam, 1977) in which new structural data, not included in this review, are presented.

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