PHOSPHONITRILIC DERIVATIVES AND RELATED COMPOUNDS

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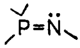
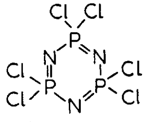
The essential structural characteristic of phosphonitrilic derivatives is the formally unsaturated repeating unit (I) which occurs in a large number of cyclic and linear molecules. The best-known phosphonitrilic compound is the trimeric chloride (II), which was discovered by Liebig[1] in an attempt to prepare the amides of phosphoric acid, though the correct empirical and molecular formulae were not established till later.[2] Stokes[3] showed that the series $(NPCl_2)_n$ extended at least as far as the heptamer, and suggested cyclic formulae which have been confirmed in many ways. The method of preparation of the chlorides has since been improved, and related procedures have been used for alkyl-, aryl-, and bromo-phosphonitriles. Substitution reactions, especially of the trimeric chloride, have been explored in detail, and have raised interesting questions of positional, geometrical, and configurational isomerism. In the fluoride series, cyclic structures persist up to at least $(NPF_2)_{17}$, rivalling the organic macrocyclic compounds in size, though not yet in detailed chemistry. The polymerisation of the phosphonitrilic halides has also been studied, rubber-like solids of high thermal stability being obtained; both thermal and chemical stability are sensitive to substitution. The physical and chemical properties of phosphonitrilic derivatives depend on their electronic structures. Theoretical studies show that although such structures as (II) are formally the same as the Kekulé structures of benzene, there is an essential difference, because *d*-orbitals are necessarily involved in the formation of double bonds between quinquevalent phosphorus and nitrogen. The valency problem is more complicated than in carbon compounds because of the wider variety of *d*-orbitals and the different symmetries of *p*- and *d*-orbitals. The theoretical work is, however, sufficiently advanced for useful comparisons to be made with experiment for both phosphonitrilics and for other series in which $p\pi$–$d\pi$ bonds make some contribution to the structure, notably siloxanes, polyphosphates, and thiazyl compounds.

(I)





(II)

Among a number of reviews,[4] that by Haber[4a] is valuable for its infor-

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[1] Liebig, *Annalen*, 1834, **11**, 139.

[2] Gerhardt, *Compt. rend.*, 1846, **22**, 858; Gladstone and Holmes, *J.*, 1864, **17**, 225.

[3] Stokes, *Amer. Chem. J.*, 1897, **19**, 782.

[4] (*a*) Haber, "Inorganic Polymers", *Chem. Soc. Special Publ.* No. 15, London, 1961, p. 115; (*b*) Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247; (*c*) Schmulbach, "Progress in Inorganic Chemistry," Interscience, New York, 1962, Vol. 4, p. 275; (*d*) Audrieth, Steinman, and Toy, *Chem. Rev.*, 1943, **32**, 109; (*e*) Paddock and Searle, "Advances in Inorganic Chemistry and Radiochemistry," Academic Press, New York, 1959, Vol. 1, p. 347; (*f*) Gribova and Ban-Yuań, *Russ. Chem. Rev.*, 1961, **30**, 1.

mation on recently-developed preparative methods, and the most recent, by Shaw, Fitzsimmons, and B. C. Smith,[4b] and by Schmulbach,[4c] for their extensive coverage of the literature and their detailed numerical information. All three contain references to other reviews.

The chemistry of phosphonitrilic derivatives is extensive, and, perhaps for that reason, is often considered in isolation, though many of the relevant ideas are applicable to the chemistry of other systems. Our object here, therefore, is to outline the main preparative methods of phosphonitrilic chemistry, to discuss the theoretical concepts and their experimental basis, and to illustrate the application of the ideas to other properties of phosphonitrilic derivatives and to groups of related compounds of silicon, phosphorus, and sulphur.

Preparative Methods

Formation of the P=N Grouping.—The simplest compounds containing the phosphonitrilic grouping (I) are the phosphinimines $R_3P{:}NR'$, in which R, R′ may be alkyl, aryl, or halogen. They can be synthesised by the reaction of organic azides with tertiary phosphines;[5]

$$R_3P + R'N_3 \rightarrow R_3P{\cdot}N_3R' \rightarrow R_3P{:}NR' + N_2 \qquad (1)$$

The rate of reaction of a series of aromatic azides $R'N_3$ with triphenylphosphine[6] increases in the order $R'{=}p\text{-}Me_2N{\cdot}C_6H_4$, C_6H_5, $p\text{-}NO_2{\cdot}C_6H_4$, suggesting that the reaction involves nucleophilic attack of the phosphine on nitrogen.

Another method depends on the decomposition of the conjugate acids of phosphinimines, the aminophosphonium ions $[R_3P{\cdot}NHR']^+$. The salts can be prepared (*a*) by the reaction of chloramine,[7] methylchloramine[7b] or hydroxylamine-*o*-sulphonic acid[7a,8] with triphenylphosphine,

$$Ph_3P + ClNH_2 \rightarrow [Ph_3P{\cdot}NH_2]^+Cl^- \qquad (2)$$

or (*b*) from the reaction of triphenylphosphine dihalides with ammonia or primary aliphatic or aromatic amines.[9]

$$Ph_3PBr_2 + 2RNH_2 \rightarrow [Ph_3P{\cdot}NHR]^+ + RNH_3^+ + 2Br^- \qquad (3)$$

They can also be obtained by the interaction of triphenylphosphine with hydrazoic acid[5b]

$$Ph_3P + 2HN_3 \rightarrow [Ph_3P{\cdot}NH_2]^+N_3^- + N_2. \qquad (4)$$

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[5] (*a*) Staudinger and Meyer, *Helv. Chim. Acta*, 1919, **2**, 635; (*b*) Staudinger and Hauser, *ibid.*, 1921, **4**, 861.

[6] Horner and Gross, *Annalen*, 1955, **591**, 117.

[7] (*a*) Appel, *Angew. Chem.*, 1959, **71**, 374; (*b*) Sisler, Sarkis, Ahuja, Drago, and N. L. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 2982; (*c*) Appel and Hauss, *Chem. Ber.*, 1960, **93**, 405; (*d*) Sisler, Ahuja, and N. L. Smith, *J. Org. Chem.*, 1961, **26**, 1819.

[8] Appel, Büchner, and Guth, *Annalen*, 1958, **53**, 618.

[9] Horner and Oediger, *Annalen*, 1959, **627**, 142.

Aminophosphonium salts are comparatively stable in water, and the anions can be exchanged readily.[7b,8] The *N*-aryl salts can be deprotonated with triethylamine[9]

$$[R_3P{\cdot}NHAr]^+ + Et_3N \rightarrow R_3P{:}NAr + [Et_3NH]^+ \qquad (5)$$

but the analogous formation of triphenylphosphinimine itself requires such stronger bases as sodamide in liquid ammonia[7c,10] or magnesium hydride.[7d]

The P–N bond in phosphinimines is polar in the sense $P^+–N^-$. Those formed from tertiary aryl phosphines and Chloramine-T take up water if the aryl group carries electron-withdrawing substituents;[11] the product can be formulated either as an aminophosphonium hydroxide or a derivative of quinquecovalent phosphorus.

$$Ph_3P{\cdot}N{\cdot}SO_2{\cdot}C_6H_4{\cdot}CH_3 + H_2O \rightarrow Ph_3P(OH){\cdot}NH{\cdot}SO_2{\cdot}C_6H_4{\cdot}CH_3 \qquad (6)$$

Triphenylphosphinimine itself re-forms aminophosphonium salts with both hydrogen halides[5b,12] and alkyl halides,[12] and, like the iso-electronic phosphine oxides R_3PO and methylene-phosphoranes $R_3P{:}CH_2$, it forms complexes with ions of the transition metals,[13] *e.g.*, $(PH_3P{\cdot}NH)_2CoCl_2$. Triphenylphosphinimine reacts with halogens to give *N*-halogeno-phosphinimines,[12,14]

$$2Ph_3P{:}NH + Br_2 \rightarrow Ph_3P{:}NBr + [Ph_3P{\cdot}NH_2]^+Br^- \qquad (7)$$

and *N*-bromotriphenylphosphinimine, analogously to chloramine, reacts[12] with triphenylphosphine

$$Ph_3P{:}NBr + Ph_3P \rightarrow [Ph_3P{:}N{:}PPh_3]^+Br^- \qquad (8)$$

The same product is obtained by the reaction of triphenylphosphine dibromide with triphenylphosphinimine

$$Ph_3PBr_2 + 2Ph_3P{:}NH \rightarrow [Ph_3P{:}N{:}PPh_3]^+Br^- + [Ph_3P{\cdot}NH_2]^+Br^- \qquad (9)$$

In the last reaction, the formation of a linear P–N–P system is limited to a triatomic species by the phenyl groups. If, however, the phosphorus atom carries, *e.g.*, a chlorine atom, which is stable as an anion, the condensation process can continue, with the formation of polymeric phosphinimines, better known as phosphonitrilic derivatives.* The general methods for the preparation of phosphinimines are therefore also appropriate for phosphonitriles. Linear phosphonitriles have also been prepared by the action of, *e.g.*, phosphorus trichloride on tetrasulphur tetranitride, a reaction

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* Another system of nomenclature, which recognises the unsaturation of the P–N grouping has been proposed.[4b] Linear and cyclic phosphonitriles are consistently named phosphazenes, with appropriate prefixes.

[10] Appel and Hauss, *Angew. Chem.*, 1959, **71**, 626.

[11] Mann and Chaplin, *J.*, 1937, 527.

[12] Appel and Hauss, *Z. anorg. Chem.*, 1961, **311**, 290.

[13] Appel and Schaaf, *Z. Naturforsch.*, 1961, **16**b, 405.

[14] Appel, Hauss, and Buchler, *Z. Naturforsch.*, 1961, **16**b, 405.

without a parallel in the phosphinimine series (see Ref. 4*a* for details).

The use of azides in the preparation of phosphonitriles is comparatively recent.[4a] The general reaction is

$$R_2PX + MN_3 \rightarrow 1/n\,(NPR_2)_n + N_2 + MX \qquad (10)$$

in which X is a halogen and M is an alkali metal, preferably lithium. In published examples, R = Br, Ph, Cl[15] or CF_3;[16] the substituents on the phosphorus atom need not be identical, and the method is probably widely applicable. The product in each case is predominantly highly polymeric, though the first related compound of arsenic, $(NAsPh_2)_4$ is prepared in this way,[17] and is probably cyclic.

Phosphonitrilic derivatives are more commonly prepared by the ammonolysis of the pentahalides of phosphorus or their substituted derivatives, the most familiar of such reactions being that between phosphorus pentachloride and ammonium chloride,[3] usually carried out in an inert solvent, such as tetrachloroethane.[18]

The simple equation

$$PCl_5 + NH_4Cl \rightarrow 1/n\,(NPCl_2)_n + 4HCl \qquad (11)$$

conceals some complexity; according to conditions, either cyclic or linear products can predominate.[19,20]

The covalent form of phosphorus pentachloride in solution is in equilibrium[21] with the ions $PCl_4^+ + PCl_6^-$, and derived ionic intermediates are important in its reaction with ammonium chloride. In tetrachloroethane, the electrical conductivity of the solution increases, by a factor of about 5000, to a maximum near half-reaction,[22] when the average composition of the dissolved reaction mixture is $NPCl_2{\cdot}PCl_5$. At this stage, only traces of cyclic polymers are present in the solution. During the completion of the reaction, the conductivity falls continuously, with the conversion of the ionic intermediates to the cyclic chlorides. The first half of the reaction (only) is accelerated by the use of highly polar solvents, such as nitrobenzene, which facilitate charge separation.

The first reaction scheme to be suggested[19] involved the formation of ammonium hexachlorophosphate and its dehydrochlorination to *P*-trichlorophosphinimine

$$NH_4Cl + PCl_5 \rightarrow NH_4PCl_6 \xrightarrow{-2HCl} NH_2{\cdot}PCl_4 \xrightarrow{-HCl} NH{:}PCl_3 \qquad (12)$$

followed by successive reactions with phosphorus pentachloride and

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[15] Herring, *Chem. and Ind.*, 1960, 717.

[16] Tesi, Haber, and Douglas, *Proc. Chem. Soc.*, 1960, 219.

[17] Reichle, *Tetrahedron Letters*, 1962, 51.

[18] Schenck and Römer, *Chem. Ber.*, 1924, **57***B*, 1343.

[19] Proctor, Thesis, London, 1958.

[20] Lund, Paddock, Proctor, and Searle, *J.*, 1960, 2542.

[21] Payne, *J.*, 1953, 1052.

[22] Unpublished work from laboratories of Messrs. Albright and Wilson; Paddock, 135th Nat. Meeting, A.C.S., Boston, 1959.

ammonium chloride. The characteristic products of the reaction are then expected to be the linear derivatives $PCl_4(NPCl_2)_nCl$ and $H(NPCl_2)_nCl$, the cyclic chlorides being formed from the latter compounds by intramolecular elimination of hydrogen chloride. Both types of linear derivative have been isolated.[20,23]

Recent work on the intermediates has shown that they are mainly ionic, their chemistry following naturally from that of the phosphinimines discussed above. The (indirect) evidence for the participation of ammonium hexachlorophosphate has been summarised elsewhere.[4a] While aminotetrachlorophosphorane $NH_2{\cdot}PCl_4$, the immediate precursor of trichlorophosphinimine, is no doubt too reactive to be isolated, the analogous compound $NH_2{\cdot}P(CF_3)_2Cl_2$ is formed by chlorination of $NH_2{\cdot}P(CF_3)_2$ in chloroform at -30°C, and decomposes on warming to room temperature, to give a mixture of the previously unknown trimeric and tetrameric derivatives $[NP(CF_3)_2]_{3,4}$, together with some high polymer.[24] Hexa-(perfluoropropyl)triphosphonitrile has been obtained in high yield by a similar reaction.[24] Another amino-phosphorane, $NH_2{\cdot}PPh_2Cl_2$, is formed by the reaction of chloramine with chlorodiphenylphosphine, and can be dehydrochlorinated[25] to the tetrameric diphenylphosphonitrile $[NPPh_2]_4$. It is therefore likely that the formation of cyclic phosphonitriles in ammonolysis reactions depends on the decomposition of compounds $NH_2{\cdot}PR_2Cl_2$ ($R = Cl, Br, CF_3$, alkyl, aryl), perhaps predominantly as amino-phosphonium salts $[NH_2{\cdot}PR_2Cl]^+Cl^-$, as suggested for the reaction of the phenyl derivative.[25]

The evidence for the phosphinimine $NH{:}PCl_3$ is again indirect, but strong. Phosphorus pentachloride reacts with both amides[26] and primary amines[27,28] to give compounds of general formula $RN{:}PCl_3$, which are often dimeric. In polar solvents at low temperatures, phosphorus pentachloride and ammonium chloride react[29] to give a compound P_3NCl_{12}, proved to have the structure $[PCl_3{:}N{:}PCl_3]^+PCl_6^-$ (cf. eqns. 8, 9) by its nuclear magnetic resonance spectrum (N.M.R.), the suggested reaction path[30] involving nucleophilic attack of $NH{:}PCl_3$ on PCl_4^+

$$PCl_4^+PCl_6^- + NH{:}PCl_3 \rightarrow [PCl_3{:}N{:}PCl_3]^+PCl_6^- + HCl \qquad (13)$$

At 150°C, this salt reacts with more $NH{:}PCl_3$ to give[31] another cation,

$$[PCl_3(NPCl_2)Cl]^+ + NH{:}PCl_3 \rightarrow [PCl_3(NPCl_2)_2Cl]^+ + HCl \qquad (14)$$

[23] Becke-Goehring and Koch, *Chem. Ber.*, 1959, **92**, 1188.

[24] Tesi and Douglas, *J. Amer. Chem. Soc.*, 1962, **84**, 549.

[25] Sisler, Ahuja, and N. L. Smith, *Inorg. Chem.*, 1962, **1**, 84.

[26] Kirsanov, *Khim. i Prim. Fos. Akad. Nauk S.S.S.R. Trudy* 1-oi *Konferents*, 1955, 99 (Publ. 1957); *Chem. Abs.*, 1958, **52**, 251.

[27] Zhmurova and Kirsanov, *J. Appl. Chem.* (*U.S.S.R.*) 1960, **30**, 3044; *Chem. Abs.*, 1961, **55**, 17551.

[28] Chapman, Holmes, Paddock, and Searle, *J.*, 1961, 1825.

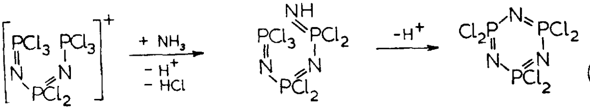
[29] Becke-Goehring and Lehr, *Chem. Ber.*, 1961, **94**, 1591.

[30] Becke-Goehring and Fluck, *Angew. Chem.*, 1962, **74**, 382.

[31] Becke-Goehring, Fluck, and Lehr, *Z. Naturforsch.*, 1962, **17b**, 126.

which is found in solution as its hexachlorophosphate. The latter compound had been recognised earlier[32] by its empirical formula P_2NCl_7, and thought to have the structure $PCl_4^+NPCl_3^-$; the structure given above is required by its electrical conductivity, its apparent molecular weight, and, especially, by its nuclear magnetic resonance spectrum. Both these new cations can be regarded as generalised chlorophosphonium ions. Their hexachlorophosphates are more completely dissociated than the analogous phosphorus pentachloride, mainly because of the large size of the ions, and possibly because of some resonance stabilisation. A similar mode of ionisation has been proposed to account for the reactions of triaryl phosphite dihalides.[33]

Further condensation with $NH{:}PCl_3$ can take place, and the linear polymers which have been formulated[20] as $(NPCl_2)_nPCl_5$ should perhaps be regarded as $[PCl_3(NPCl_2)_{2n}Cl]^+PCl_6^-$, consistent with their high dielectric constants and insolubility in non-polar media. Ring-closure, on the other hand, now becomes a competitive process (III), and depends on the reaction of the polynuclear cations with either ammonia or ammonium chloride, with a simultaneous decrease in conductivity.



(III)

A similar scheme can be written for the higher cyclic polymers, which are normally formed in decreasing amount with increasing ring size. If the chains are long enough, chain growth predominates over cyclisation, ammonolysis of a typical mixture of higher linear polymers $(NPCl_2)_n{\cdot}PCl_5$, ($n{\sim}17$) giving a rubber-like high polymer.[20]

All the processes considered involve the elimination of hydrogen chloride, and it is likely that removal of the chloride ion is aided by partial transfer to phosphorus of lone-pair electrons from neighbouring nitrogen atoms. The cyclisation of phosphonitriles can be compared with the formation of *B*-chloroborazoles from amines and boron trichloride. In the latter reaction, part of the driving-force is the delocalisation energy of the trimeric product, the release of a chloride ion from boron being aided by the partial charge-transfer in the intermediates $RNH_2{\cdot}BCl_3$ and $RNH{\cdot}BCl_2$. It is also catalysed by some transition metals and their chlorides.[34] Similarly, the ammonolysis of phosphorus pentachloride is catalysed by metal chlorides with acceptor properties.[35] Some (*e.g.*, $MgCl_2$, $MnCl_2$) increase the rate of cyclisation; others, like $AlCl_3$, accelerate the earlier stages of

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[32] (*a*) Groeneveld, Visser, and Seuter, *J. Inorg. Nuclear Chem.*, 1958, **8**, 245; (*b*) Glemser and Wyszomirski, *Naturwiss.*, 1961, **48**, 25.

[33] Rydon, "Phosphoric Esters and Related Compounds," Chem. Soc. Special Publ., No. 8, London, 1957, p. 61.

[34] Emeléus and Videla, *Proc. Chem. Soc.*, 1957, 288.

[35] Paddock and Searle, B.P. 905,315/1962.

the reaction, but remain attached to the chain,* probably as end-groups in such structures as $AlCl_2(NPCl_2)_nCl$.

Phosphonitrilic chloride chains can be terminated with the elements of other acid chlorides, by direct addition,[32a,36] by the reaction of hydroxylamine hydrochloride with phosphorus pentachloride,[37] and in other ways.[38] The compound $PCl_3{:}N{\cdot}POCl_2$ has been isolated,[37,38] and its structure proved from its nuclear magnetic resonance spectrum.[39]

Cyclic phosphonitrilic bromides[40] $(NPBr_2)_{3,4}$ and chloridebromides[41] $N_3P_3Cl_xBr_{6-x}$ have been prepared similarly, but less is known about the intermediate stages. An orange crystalline compound[40c] $NPBr_2{\cdot}PBr_5$ gives the cyclic trimeric and tetrameric bromides on further treatment with ammonium bromide; its structure is unknown. Alkyl- and aryl-phosphonitriles have been prepared by the ammonolysis of Me_2PCl_3,[42] Et_2PCl_3,[43,44] Ph_2PCl_3,[44,45] $PhPCl_4$[46] and $PhPBr_4$.[47] Removal of the elements of the hydrogen halide from the intermediates in these reactions is more difficult than in the preparation of the chlorides, the base strength being increased by the organic groups. Cyclisation of alkyl-phosphonitriles requires either heat[43] or, like *N*-trialkyl-*B*-trichloroborazoles,[48] the use of a tertiary base.[42] It is possible[4b] that $(NPEt_2)_3,HCl$, reported as linear,[44] is in fact the hydrochloride of the cyclic molecule. A crystalline compound[44,45b] $N_3P_2H_4Ph_4Cl$ (IV), prepared by the reaction of Ph_2PCl_3 with liquid ammonia, gives mainly the cyclic tetramer $[NPPh_2]_4$ on pyrolysis. The structural formulae that have been suggested for (IV) all involve covalently bound chlorine; it is also possible that it may be a salt $[NH_2{\cdot}PPh_2{:}N{\cdot}PPh_2{\cdot}NH_2]^+Cl^-$, like many other phosphonitrilic intermediates.

In most of the above compounds, each phosphorus atom is symmetrically and similarly substituted. If each phosphorus atom is similarly, but

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* For a fuller account of the interaction of metallic halides with phosphonitrilic chlorides, which includes information from publications with a restricted circulation, see Ref. 4*c*.

[36] Paddock, *Can. P.*, 575,069/1959.

[37] Barth-Wehrenalp and Kowalski, Abstracts, 135th Nat. Meeting of Amer. Chem. Soc., Boston, 1959; Kahler, U.S.P. 2,925,320/1960.

[38] Becke-Goehring, Mann, and Euler, *Chem. Ber.*, 1961, **94**, 193; Becke-Goehring, Debo, Fluck, and Goetze, *Chem. Ber.*, 1961, **94**, 1383.

[39] Fluck, *Chem. Ber.*, 1961, **94**, 1388.

[40] (*a*) Besson, *Compt. rend.*, 1892, **114**, 1479; (*b*) Bode, *Z. anorg. Chem.*, 1944, 252, 113; (*c*) John and Moeller, *J. Amer. Chem. Soc.*, 1960, **82**, 2647; (*d*) Bean and Shaw, *Chem. and Ind.*, 1960, 1189; (*e*) John and Moeller, *J. Inorg. Nuclear Chem.*, 1961, **22**, 199.

[41] Rice, Daasch, Holden, and Kohn, *J. Inorg. Nuclear Chem.*, 1958, **5**, 190.

[42] Searle, *Proc. Chem. Soc.*, 1959, 7.

[43] Bilbo, *Z. Naturforsch.*, 1960, **15**b, 330.

[44] Korshak, Gribova, Artamanova, and Bushmarina, *Vysokomol, Soedeninya*, 1960, **2**, 377.

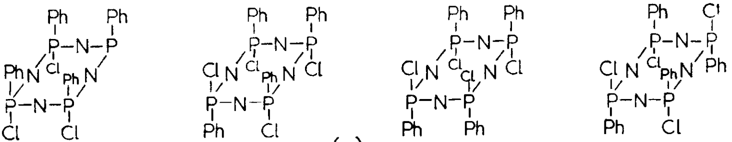
[45] (*a*) Haber, Herring, and Lawton, *J. Amer. Chem. Soc.*, 1958, **80**, 2116; (*b*) Bezman and Smalley, *Chem. and Ind.*, 1960, 839.

[46] (*a*) Shaw and Stratton, *Chem. and Ind.*, 1959, 52; (*b*) *J.*, 1962, 5004; (*c*) Humiec and Bezman, *J. Amer. Chem. Soc.*, 1961, **83**, 2210.

[47] Moeller and Nannelli, *Inorg. Chem.*, 1962, **1**, 721.

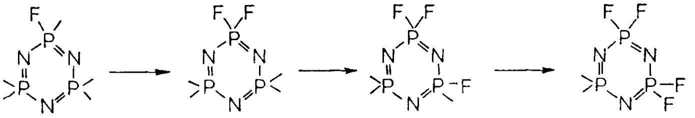
[48] Turner and Warne, *Chem. and Ind.*, 1958, 526.

unsymmetrically substituted, and the rings are (statistically) planar, two geometrically isomeric molecules $(NPXY)_3$, and four $(NPXY)_4$ are possible, as for cyclopropane and cyclobutane derivatives. Both isomers are known for the trimeric phenyl-chloro-[46c] and phenyl-bromo-phosphonitriles,[47] and three of the possible four tetrameric phenyl-chloro-phosphonitriles (V) have been obtained,[46b] and many derivatives of them prepared. Their configurations have not been determined. The possibility of configurational isomerism, arising from non-planarity of the ring, will be discussed later.



(V)

Substitution Reactions.—Among phosphonitrilic compounds obtained by direct synthesis, the chlorides are the most readily obtained, and most other derivatives have been made from them, and especially from the trimeric chloride. The majority of the reactions appear to be nucleophilic displacements. The orientation pattern depends on a number of factors, but especially on whether the entering group decreases or increases the electron density at phosphorus. The first type of reaction is exemplified by the fluorination of the trimeric chloride with potassium fluorosulphite[49] (VI). (For clarity, only the substituting groups are shown in VI, IX, X, XI).



The orientation of the substituents has been established by infrared and NMR spectroscopy;[49] geminal substitution takes place almost exclusively. One of two trimeric fluoride-chlorides described earlier[50] does not fall into this pattern, redistribution reactions evidently occurring at high temperatures. Sodium mercaptides react readily with trimeric phosphonitrilic chloride,[51] especially in polar solvents, and here, too, geminal substitution has been proved by NMR spectroscopy.[52] By contrast, substitution by amines increases the electron density at phosphorus, important contributions being made[53] by such resonance structures as (VII). As will be seen later, the ability of phosphorus to accept

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[49] (*a*) Chapman, Paine, Searle, D. R. Smith, and White, *J.*, 1961, 1768; (*b*) Allen, Barnard, J. Emsley, Paddock, and White, *Chem. and Ind.*, 1963, 952; (*c*) Heffernan and White, *J.*, 1961, 1382.

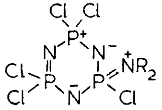
[50] Schmitz-Dumont and Braschos, *Z. anorg. Chem.*, 1940, **243**, 113.

[51] A. P. Carroll and Shaw, *Chem. and Ind.*, 1962, 1908.

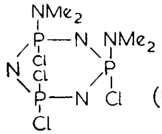
[52] Boden, J. W. Emsley, Feeney, and Sutcliffe, *Chem. and Ind.*, 1962, 1909.

[53] Becke-Goehring, John, and Fluck, *Z. anorg. Chem.*, 1959, **302**, 103.

electrons has important consequences; its effect here is that successive amination tends to take place on different atoms (VIII; R represents

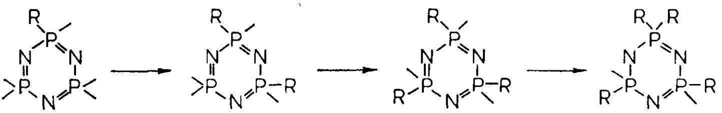


(VII)



(IX)

an amine residue), the increasing difficulty of substitution being attributed partly to electronic[53] and partly (especially for bulky amines) to steric

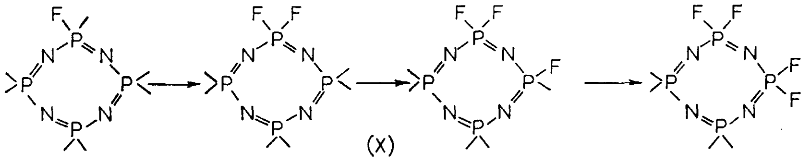


(VIII)

factors.[54] The orientation of the substituents has been established both spectroscopically[53,54] and by the preparation of isomers.[53] It has recently been shown[55] that in the bis-dimethylamido-derivative (IX) prepared from the trimeric chloride and dimethylamine, both substituents are on the same side of the ring.

Geminal substitution by amines also occurs. It has been suggested for aromatic amines,[53,56] and established for partial substitution by ethyleneimine.[57] The fully substituted derivative had been described earlier.[58] For other amines, information is less detailed. Piperidine,[59] morpholine,[60] and pyrrolidine[61] each give a series of compounds $N_3P_3Cl_nR_{6-n}$ ($n = 0$—5). Two isomers have been obtained for each of the bis-, tris-, and tetrakis-pyrrolidides, but it is not known whether these compounds are *cis*- and *trans*-isomers, or whether geminal substitution takes place to some extent.

Similar behaviour is found in the tetrameric series. Successive substitution of chlorine by fluorine takes place geminally, followed by attack at a neighbouring phosphorus atom[49b] (X). Other tetrameric fluoride-chlorides $N_4P_4F_4Cl_4$ and $N_4P_4F_6Cl_2$ are known,[62] in which the orientation-pattern



(X)

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[54] Ray and Shaw, *J.*, 1961, 872.

[55] Bezman and Ford, *Chem. and Ind.*, 1963, 163.

[56] Bode, Bütow and Lienau, *Chem. Ber.*, 1948, **81**, 547.

[57] Kobayashi, Chasin, and Clapp, *Inorg. Chem.*, 1963, **2**, 212.

[58] Rätz and Grundmann, U.S.P. 2,858,306/1958.

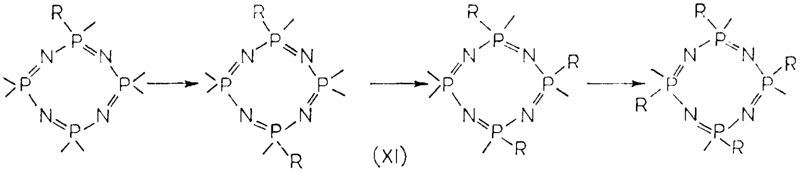
[59] Kropacheva, Mukhina, Kashnikova, and Parshina, *Zhur. obschei. Khim.*, 1961, **31**, 1036.

[60] Kropacheva and Kashnikova, *Zhur. obschei Khim.*, 1962, **32**, 521.

[61] Kropacheva and Kashnikova, *Zhur. obschei Khim.*, 1962, **32**, 652.

[62] Schmitz-Dumont and Külkens, *Z. anorg. Chem.*, 1938, **238**, 198.

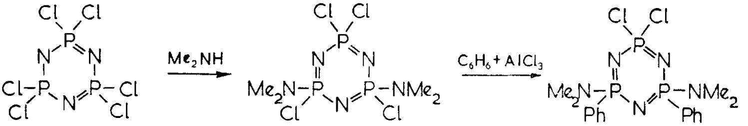
must be different; since they were produced by the reaction of lead fluoride and the trimeric chloride at a high temperature, rearrangement of the primary products is likely to have occurred. Successive substitution by amines takes place preferentially at remote phosphorus atoms (XI), bis-[63] and tetrakis-[64] amido-derivatives having been isolated.



(XI)

In both series, the orientations have again been proved by the structure of the NMR spectra involving the isotope phosphorus-31; *e.g.*, the bis-amido derivatives show a pair of triplets of equal intensity (excluding successive substitution at the 1:3 positions) and in the tetra-substituted products the environments of all the phosphorus atoms are identical.[63,64] Other tetrameric amido-chloro-compounds have been described.[65]

Partially-substituted derivatives of known orientation have also been made by the Friedel–Crafts reaction, and by reaction of the halides with organometallic compounds. The trimeric chloride with benzene and aluminium chloride gives[66] the geminally-substituted diphenyl-tetrachloride $N_3P_3Ph_2Cl_4$, which reacts further with amines.[67] As would be expected, successive phenylation of a partially aminated trimer occurs preferentially at the aminated positions[55] (XII).



(XII)

The main product of the reaction of the trimeric chloride with phenylmagnesium bromide[66] was found to be a halogen-containing derivative, which gave a linear compound $Ph(PPh_2N)_3H{\cdot}HClO_4$ on treatment with alcoholic silver perchlorate. Small yields of the cyclic hexaphenyl triphosphonitrile have also been reported.[68] Trimethyltrichlorotriphosphonitrile has been obtained[69] indirectly by the following series of reactions (XIII) which establishes the orientation. The trimeric fluoride reacts with organolithium derivatives,[70] and a series of phenyl-fluoro compounds

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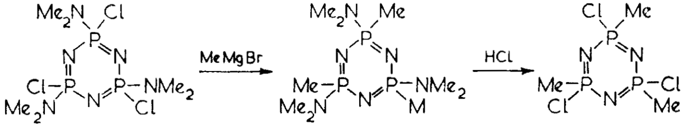
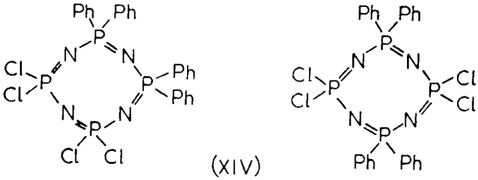
[63] John, Moeller, and Audrieth, *J. Amer. Chem. Soc.*, 1960, **82**, 5616.
[64] John, Moeller, and Audrieth, *J. Amer. Chem. Soc.*, 1961, **83**, 2608.
[65] de Ficquelmont, *Ann. Chim. (France)*, 1939, (11), **12**, 214.
[66] Bode and Bach, *Chem. Ber.*, 1942, **75**, 215.
[67] Becke-Goehring and John, *Z. anorg. Chem.*, 1960, **304**, 126.
[68] Rosset, *Bull. Soc. chim. France*, 1925, **37**, 518; Ramain, Runavot and Schneebeli, *J. Chim. phys.*, 1959, **56**, 659.
[69] Tesi and Slota, *Proc. Chem. Soc.*, 1960, 404.
[70] Moeller and Tsang, *Chem. and Ind.*, 1962, 361.

$N_3P_3F_nPh_{6-n}$ (n = 1—5) has been obtained; their orientations are unknown.



(XIII)

Tetrameric phosphonitrilic chloride reacts with phenylmagnesium bromide to give two phenylated compounds $N_4P_4Ph_4Cl_4$, which, from a study of their decomposition products,[71] are formulated as position isomers (XIV). Two octaphenyl-derivatives $N_4P_4Ph_8$ (possibly configurational isomers) were obtained in the same work. Only the higher-melting compound was found in later investigations of the ammonolysis of diphenyltrichlorophosphorane,[45] and a repetition of the work, and a study of the structures of the two compounds, should give interesting results. An isomeric phenyl-chloro-compound $(NPPhCl)_4$ has been converted to the octaphenyl-derivative by phenylmagnesium bromide.[46b]



(XIV)

Fully-substituted trimeric and tetrameric amido-phosphonitriles, prepared by the action of ammonia or amines on the chlorides, are very numerous. A list of over 150 of them, which includes hydrazides and phenylhydrazides, is given in Ref. 4*b*. They will be referred to here only briefly; their properties will be considered later. The phosphonitrilamides[72] $[NP(NH_2)_2]_{3,4}$ are stable in water, and give adducts of the formula $[NP(NH_2)_2HAc]_{3,4}$ with acetic acid. On being heated, amorphous phosphams of empirical composition PN:NH are eventually formed,[72,73] their infrared spectra[74a,b,c] showing them to contain —P=N—P= and —P—NH—P— groups. Derivatives of primary amines decompose with elimination of part of the amine, substituted phosphams of empirical formula NP:NPh having been so obtained from the anilide $[NP(NHPh)_2]_3$. The reaction is reversible, suggesting that the trimeric ring structure is retained in the phospham.[75]

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[71] Bode and Thamer, *Chem. Ber.*, 1943, **76*B***, 121.

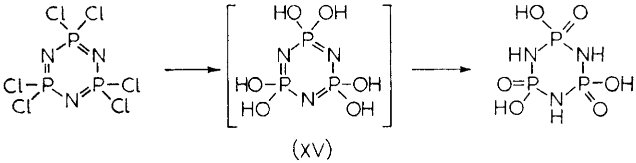
[72] Audrieth and Sowerby, *Chem. and Ind.*, 1959, 748; Sowerby and Audrieth, *Chem. Ber.*, 1961, **94**, 2670.

[73] de Ficquelmont, *Compt. rend.*, 1935, **200**, 1045.

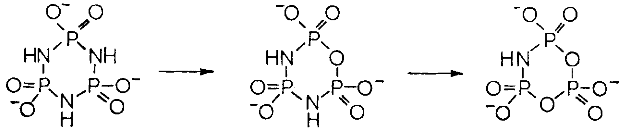
[74] (*a*) Steger, *Angew. Chem.*, 1957, **69**, 145; (*b*) *Chem. Ber.*, 1961, **94**, 266; (*c*) Steger and Lunkwitz, *Naturwiss.*, 1961, **48**, 522; (*d*) Pustinger, Cave, and Nielsen, *Spectrochim. Acta*, 1959, **11**, 909.

[75] Bode and Clausen, *Z. anorg. Chem.*, 1949, **258**, 99.

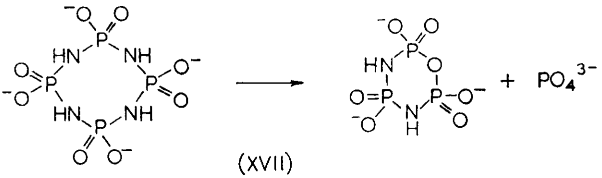
The phosphonitrilic halides are hydrolysed to the metaphosphimic acids, the reaction involving a tautomeric change (XV).[74d] The basicities of the trimeric and tetrameric acids are therefore three and four on normal neutralisation,[76] though all the hydrogen atoms are replaceable by silver.[76] *N*-Chloro-derivatives are formed by the reaction of the salts of the trimeric and tetrameric acids with sodium hypochlorite.[77] Further hydrolysis of trimetaphosphimate takes place,[78] imino-groups being replaced by oxygen atoms, apparently without opening of the ring (XVI). The cyclic trimetaphosphate is, however, often formed from linear phosphates, *e.g.*, from long-chain polyphosphates, even in the absence of water.[79] The marked preference for six-membered rings appears to be common to both series. The tetrametaphosphimate ion is degraded on hydrolysis first into an equimolar mixture of orthophosphate and di-imido-trimetaphosphate,[80] (XVII) the imino-groups then being replaced by oxygen atoms. Trimeric ring imidophosphates are also formed[81] on hydrolysis of the pentametaphosphimate ion $[NH{\cdot}PO_2^-]_5$.



(XV)



(XVI)



(XVII)

Phosphonitrilic esters of the type $[NP(OR)_2]_{3,4}$ (R = Me, Et, Pr^n, Bu^n) have been prepared from the corresponding chloride and either the

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[76] Stokes, *Amer. Chem. J.*, 1896, **18**, 629.

[77] Taylor, U.S.P. 2,796,321; 2,796,322 (1957).

[78] Narath, Lohman, and Quimby, *J. Amer. Chem, Soc.*, 1956, **78**, 4493.

[79] Thilo, "Advances in Inorganic Chemistry and Radiochemistry", Academic Press, New York, 1962, Vol. 4, p. 1.

[80] Pollard, Nickless, and Warrender, *J. Chromatog.*, 1962, **9**, 506.

[81] Pollard, Nickless, and Warrender, *J. Chromatog.*, 1962, **9**, 513.

alcohol (pyridine being used as an acceptor for hydrogen chloride)[82,83] or the alkali metal alkoxide.[83,84,85] The former method has been used in the preparation of nitroxyalkyl-esters,[86] and the latter for a series of fluoroalkyl phosphonitrilates of extreme thermal and chemical stability.[87] Aryl esters have been prepared by both methods;[83] a summary of earlier work, not yet published in the open literature, is given in Ref. 4*c*. Pseudo-halogen groups can also be introduced; the trimeric azide[88] $[NP(N_3)_2]_3$ and an amide-azide[89] $N_3P_3(NH_2)_4(N_3)_2$ have also been described, and a particularly rapid reaction takes place between potassium thiocyanate and the trimeric and tetrameric chlorides in acetone,[90] with formation of the corresponding isothiocyanates, $N_3P_3(NCS)_6$ and $N_4P_4(NCS)_8$.

The foregoing reactions have concerned the trimeric and tetrameric phosphonitrilic chlorides almost exclusively. The only series of larger ring compounds so far investigated is that of the fluorides. The trimeric and tetrameric fluorides were first prepared by the action of KSO_2F on the chlorides,[91] and have also been obtained by the fluorination of a phosphorus nitride.[92] Subsequent work has shown that a mixture of potassium fluoride and sulphur dioxide is also effective,[93,94] and the larger-ring compounds in the range $(NPF_2)_{5-17}$ have been similarly prepared from the chlorides.[94] Acetonitrile[95] and nitrobenzene[96] are also suitable media for the reaction with simple fluorides, which is catalysed by water and hydrogen fluoride.[96] The properties of the fluorides and other phosphonitrilic derivatives are considered below in relation to their electronic structures.

Electronic and Molecular Structure

By using the preparative methods described above, a broad range of substituent groups can now be attached to the 6- and 8-membered phosphonitrilic rings. The properties of the derivatives so obtained are diverse.

The chlorides (except the heptamer) are crystalline solids, easily soluble in organic media and in sulphuric acid. They undergo hydrolysis, and other

[82] Yokoyama, *J. Chem. Soc. Japan*, 1959, **80**, 1192.

[83] Fitzsimmons and Shaw, *Chem. and Ind.*, 1961, 109.

[84] Dishon, *J. Amer. Chem. Soc.*, 1949, **71**, 2251.

[85] Rätz and Hess, *Chem. Ber.*, 1951, **84**, 889.

[86] Chang and Matuszko, *Chem. and Ind.*, 1962, 410.

[87] (*a*) Rätz and Grundmann, U.S.P. 2,876,247; 2,876,248/1959; (*b*) Rätz, Schroeder, Ulrich, Kober, and Grundmann, *J. Amer. Chem. Soc.*, 1962, **84**, 551; (*c*) Mao, Dresdner, and Young, *J. Inorg. Nuclear Chem.*, 1962, **24**, 53.

[88] Grundmann and Rätz, *Z. Naturforsch.*, 1955, **10**b, 116.

[89] Chang and Matuszko, *J. Amer. Chem. Soc.*, 1960, **82**, 5756.

[90] Otto and Audrieth, *J. Amer. Chem. Soc.*, 1958, **80**, 5894; Tesi, Otto, Sherif, and Audrieth, *J. Amer. Chem. Soc.*, 1960, **82**, 528.

[91] (*a*) Seel and Langer, *Angew. Chem.*, 1956, **68**, 461; (*b*) *Z. anorg. Chem.*, 1958, **295**, 316.

[92] Mao, Dresdner, and Young, *J. Amer. Chem. Soc.*, 1959, **81**, 1020.

[93] Haber and Uenishi, *Chem. and Eng. Data Ser.*, 1958, **3**, 323.

[94] Chapman, Paddock, Paine, Searle, and D. R. Smith, *J.*, 1960, 3608.

[95] Tullock and Coffman, *J. Org. Chem.*, 1960, **25**, 2016.

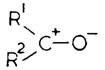
[96] Moeller, John, and Tsang, *Chem. and Ind.*, 1961, 347.

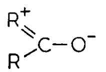
substitution reactions, comparatively slowly. The fluorides are all volatile, and, except for the trimer and tetramer, are mobile liquids which resemble fluorocarbons in their behaviour as solvents. The alkyl derivatives are soluble in water, as are many amido-phosphonitriles, which are fairly strong bases. Aryl-, aryloxy-, and especially fluoro-alkyl- and fluoro-alkoxy-phosphonitriles are stable both to high temperatures and to chemical attack. The halides and isothiocyanates have been polymerised thermally, the rubber-like polymers being easily hydrolysed in damp air. Because of its variety within a uniform structural scheme, phosphonitrilic chemistry forms a good basis for assessing theories of bonding which are applicable to second-row elements generally.

The formulae have so far been written as if single and double bonds alternated in the ring, though in fact in all the structures determined so far the ring bonds are equal in length within experimental error. To a first approximation, a system of π-electrons, which is at least partly delocalised, is formed by overlap of alternate $3d\pi$-orbitals (on phosphorus) and $2p\pi$-orbitals (on nitrogen). Some of the properties of this system follow from the nature of the *localised* $p\pi$–$d\pi$ bond. We shall consider them first, by comparing the properties of phosphoryl and carbonyl bonds, and shall afterwards discuss phosphorus–nitrogen compounds, in which the bonding shows additional features due to delocalisation.

Comparison of Phosphoryl and Carbonyl Groups.—The important differences between the phosphoryl and carbonyl groups arise from the *d*-orbitals in the phosphorus atom. The characteristic properties of carbonyl compounds, as compared with saturated compounds, depend on the increased electronegativity of the carbon atom, by reason of the increased *s*-component of the σ-bonds, and the transmission of the inductive effect of the more electronegative oxygen atom by the polarisable π-system. On balance, the carbon acquires acceptor properties, and the other substituents interact with the carbonyl group to an extent dependent on their electronegativities and their abilities to conjugate with it, either directly or by the release of electrons to carbon.[97]

Carbonyl compounds can be regarded formally as polar compounds (XVIII), the three groups donating electrons competitively into the $2p\pi$-orbital of carbon, conjugation with the ligands[98] being expressed by such structures as (XIX). The effect of the electronegativity of the ligand can be seen by comparing carbonyl fluoride and acetone (Table 1); substitution of fluorine for methyl shortens and strengthens the carbonyl bond. In methyl acetate, conjugation (as above) ensures that the total


(XVIII)


(XIX)

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[97] Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, New York, 1953.

[98] Hartwell, Richards, and Thompson, *J.*, 1948, 1436.

TABLE 1. *Properties of carbonyl compounds*

Compound	$L(C{=}O)$ (Å)[a]	$\nu(C{=}O)$ (cm.$^{-1}$)[b]	$E(C{=}O)$ (kcal.)[c]
Me_2CO	1·22[d]	1742[h]	179[k]
F_2CO	1·17[e]	1928[i]	185[l]
$MeCO_2Me$	1·22[f]	1774[h]	197[m]
$MeC(O)NH_2$	1·21[g]	1710[j]	199[n]

[a] L(X–Y) stands for the length of the bond X–Y. [b] Determined in vapour phase. [c] Obtained by subtracting average bond energy terms [Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958 (2nd edn.)] from the total atomisation energy. The references give the heats of formation. [d] Allen, Bowen, Sutton, and Bastiansen, *Trans. Faraday Soc.*, 1952, **48**, 991. [e] Brown and Livingston, *J. Amer. Chem. Soc.*, 1952, **74**, 6084. [f] O'Gorman, Shand, and Schomaker, *J. Amer. Chem. Soc.*, 1950, **72**, 4222. [g] Kimura and Aoki, *Bull. Chem. Soc. Japan*, 1953, **26**, 429. [h] Hartwell, Richards, and Thompson, *J.*, 1948, 1436. [i] Nielsen, Burke, Woltz, and Jones, *J. Chem. Phys.*, 1952, **20**, 596. [j] Estimated from the value obtained in dilute solution (Richards and Thompson, *J.*, 1947, 1248). [k] Miles and Hunt, *J. Phys. Chem.*, 1941, **45**, 1346. [l] Patrick, "Advances in Fluorine Chemistry", Butterworths, London, 1961, Vol. 2, p. 1, based on heat of hydrolysis (von Wartenburg and Riteris, *Z. anorg. Chem.*, 1949, **258**, 356). [m] Green, *Quart. Rev.*, 1961, **15**, 125; Landolt–Bornstein, 4 Teil Kalorische Zustandgrössen, Springer-Verlag, 1961. [n] Selected Values of Chemical Thermodynamic Properties, Circ. 500, Nat. Bur. Stand., Washington, 1952.

bond energy remains high, partly at the expense of the carbonyl bond itself. In acetamide, the contrast between $\nu(C{=}O)$ and the increase in total atomisation energy, here artificially concentrated in $E(C{=}O)$, is still greater, nitrogen being the better donor atom. L(C–O) and L(C–N) are also reduced, by 0·07Å and 0·11Å respectively,[99,100] from the accepted values for single bonds.[101] Such electron-releasing groups also make the carbonyl carbon atom less electrophilic; the increase in activation energy (9 kcal./mole) for the hydrolysis of ethyl chloroformate,[102] as compared with acetyl chloride,[103] is attributed to conjugation of the ester oxygen atom with the carbonyl group.[104]

The differences between phosphoryl and carbonyl compounds arise because of the increased size of the phosphorus atom and the different sizes, symmetries, and numbers of available 2*p*- and 3*d*-orbitals. Overlap schemes for $p\pi$–$p\pi$ and $p\pi$–$d\pi$ bonds are shown in Fig. 1. Because of the large size of the phosphorus atom, overlap takes place in a comparatively weak nuclear field, so that $p\pi$–$d\pi$ bonds are weaker than their $p\pi$–$p\pi$ counterparts.[105] Their polarity is accentuated by the shape of the *d*-orbital, which tends to concentrate charge close to the oxygen atom. If the three other groups attached to phosphorus are identical, the molecule has 3-fold symmetry, and the π-system is doubly degenerate. It now includes another pair of orbitals like that in Fig. 1*b* but in a plane rotated by 90°

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[99] O'Gorman, Shand, and Schomaker, *J. Amer. Chem. Soc.*, 1950, **72**, 4222.

[100] Kimura and Aoki, *Bull. Chem. Soc. Japan*, 1953, **26**, 429.

[101] "Interatomic Distances", *Chem. Soc. Special Publ.* No. 11, 1958, pp. 516, 517.

[102] Bohme and Schurhoff, *Chem. Ber.*, 1951, **84**, 28.

[103] Zimmerman and Ching Yuan, *J. Amer. Chem. Soc.*, 1955, **77**, 332.

[104] Hudson and Keay, *J.*, 1960, 1859.

[105] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

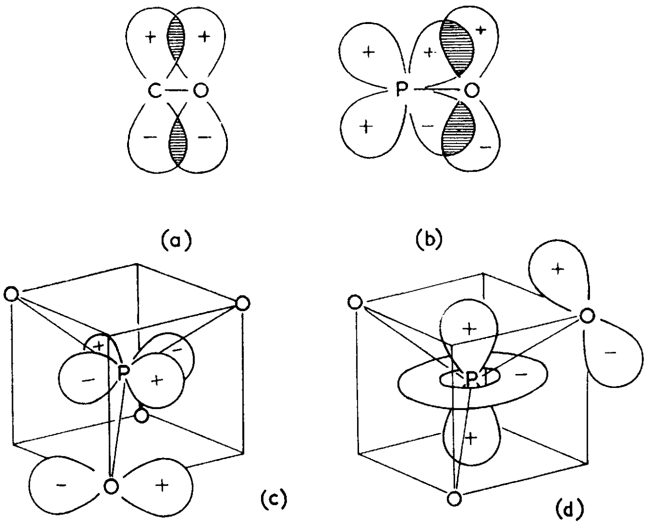

Fig. 1. *Overlap schemes (a) for* $p\pi$–$p\pi$ *bond in* $>C{=}O$; *(b)* $p\pi$–$d\pi$ *bond in* $\geqslant P{=}O$; *(c) and (d),* π *and* π' *bonds in* PO_4^{3-}.

about the bond axis. If the ligands can release electrons to phosphorus, they can participate in the double π-system; in the limit of regular tetrahedral symmetry, as in the PO_4^{3-} ion, the two π-systems, sometimes distinguished as π and π', become equal and equally shared among the four ligands. In the orientation of axes shown in Fig. 1(*c*,*d*) they are formed from the $d\gamma$ pair, the $d_{x^2-y^2}$ and d_{z^2} orbitals.[106,107] (The $d\epsilon$ triplet interacts less strongly.) The availability of this strongly π-bonding pair of orbitals leads to two differences from $p\pi$–$p\pi$ systems: the central atom becomes more electrophilic, and conjugation does not depend on planarity.[107]

The extent of conjugation in phosphoryl compounds is still controversial. The ultraviolet spectra of phenylphosphonates suggest only slight interaction of the phenyl groups with the phosphoryl group,[108] though this is very much increased if the ligands are strong donors, such as *N*-alkylpyrryl (conjugation is even then not as strong as in carbonyl compounds).[109] Conjugation is, however, indicated by nuclear quadrupole resonance measurements, [110] and [111] by the reduction in $\nu(P{=}O)$ in the series $POCl_3$ (1305 cm.$^{-1}$), $POCl_2NMe_2$ (1268 cm.$^{-1}$) and $POCl(NMe_2)_2$ (1241 cm.$^{-1}$). Quantitative information is given in Table 2 for a series of compounds R_3PO. If we take $\nu(P{=}O)$ as a measure of the strength of the phosphoryl

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[106] Cruickshank, *J.*, 1961, 5486.

[107] Jaffé, *J. Phys. Chem.*, 1954, **58**, 185.

[108] Jaffé and Freedman, *J. Amer. Chem. Soc.*, 1952, **74**, 1069; Jaffé, *J. Chem. Phys.*, 1954, **22**, 1430.

[109] Griffin and Polsky, *J. Org. Chem.*, 1961, **26**, 4772.

[110] Lucken and Whitehead, *J.*, 1961, 2459.

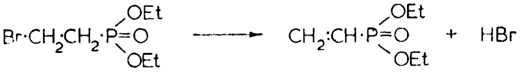
[111] Harvey and Mayhood, *Canad. J. Chem.*, 1955, **33**, 1552.

TABLE 2. *Properties of phosphoryl compounds*

R	Br	Cl	F	OEt	NEt_2	Ph	Me
$\nu(P{=}O)$[a] (cm.$^{-1}$)	1261[b]	1290[c]	1395[d]	1272[e]	1212[f]	1195[g]	1170[h]
$D(P{=}O)$ (kcal./mole)	119[i]	122[i]	130[j]	151[k]	156[l]	128[m]	139[n]

[a] Dilute solution. [b] Gerding and van Driel, *Rec. Trav. chim.*, 1942, **61**, 419. [c] Cabannes and Rousset, *Ann. Physique*, 1933, (10), **19**, 229. [d] Delwaulle and François, Compt. rend., 1948, **226**, 894. [e] Average value (Bellamy and Beecher, *J.*, 1952, 475). [f] In $PO(NMe_2)_3$ (Paddock, unpublished work). [g] Cotton, Barnes, and Bannister, *J.*, 1960, 2199. [h] Daasch and Smith, *J. Chem. Phys.*, 1959, **19**, 22. [i] Charnley and Skinner, *J.*, 1953, 450. [j] Ebel and Bretscher, *Helv. Chim. Acta*, 1929, **12**, 450. [k] Chernick and Skinner, *J.*, 1956, 1401. [l] Kearney, quoted by Claydon and Mortimer, *J.*, 1962, 3212. [m] Bedford and Mortimer, *J.*, 1960, 1622. [n] Claydon, Fowell, and Mortimer, *J.*, 1960, 3284.

bond, it can be seen that, among the halides, the phosphoryl bond strength and the total additional bond energy (over PR_3) increase together with the electronegativity of the halogen. $D(P{=}O)$ in fact contains both σ- and π-components in all the bonds, but an approximation to the total π-energy can be obtained by subtracting E(P–O), here taken as 92 kcal./mole.[112] It is noticeable that, even in phosphoryl fluoride, the (approximate) π-energy (38 kcal./mole) is very much less than in carbonyl compounds, where it is 80-90 kcal. In triethyl phosphate (58 kcal.) and in trisdiethylamidophosphine oxide (64 kcal.) the total π-energies are very much higher, even though the phosphoryl bond itself is somewhat weaker, and are consistent with strong interaction of the oxygen and nitrogen lone pairs with the phosphorus centre. The detailed allocation of energy in such compounds has been considered by McCoubrey and his co-workers.[112] Some conjugation of the phenyl groups in triphenylphosphine oxide is also suggested, and the combination of an especially low value of $\nu(P{=}O)$ with a high π-energy (47 kcal.) in trimethylphosphine oxide is noteworthy. Similar values of $D(P{=}O)$ are found for other trialkyl phosphine oxides.[113] The importance of $p\pi$–$d\pi$ interaction between phosphorus and carbon, at least in the transition state, is confirmed by the rapid exchange of the protons in the tetramethylphosphonium ion with heavy water [114] and by the easy elimination of hydrogen bromide from β-bromoethylphosphonates.[115] (Eqn. 15). Stabilisation of carbanions by $p\pi$–$d\pi$ bonding is



$$Br{\cdot}CH_2CH_2{\cdot}P(OEt)_2{=}O \longrightarrow CH_2{:}CH{\cdot}P(OEt)_2{=}O + HBr \qquad (15)$$

well known,[116] and perhaps occurs because it does not involve a large shift of electron density towards the d-centre.

Conjugation of the phosphoryl group with electron-releasing substituents also lengthens the phosphoryl bond and increases its polarity, and

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[112] S. B. Hartley, W. S. Holmes, Jacques, Mole, and McCoubrey, *Quart. Rev.*, 1963, **17**, 204.

[113] Chernick and Skinner, *J.*, 1956, 1401.

[114] Doering and Hoffmann, *J. Amer. Chem. Soc.*, 1955, **77**, 521.

[115] Ford-Moore and Williams, *J.*, 1947, 1465.

[116] Henbest, *Ann. Reports*, 1956, **53**, 137.

hence its donor properties. Phosphate esters, unlike most carbonate esters, are readily soluble in water,[117] and dialkylphosphinic acids $R_2P(O)OH$ have basic properties,[118] forming hydrochlorides which are presumably dialkylphosphonium salts $[R_2P(OH)_2]^+Cl^-$. The phosphorus centre also is affected. Displacement reactions of phosphinyl chlorides $R_2P(O)Cl$ obey the same (second-order) rate law as those of acyl halides,[119] and for both types of compound the increase in activation energy accompanying the introduction of electron-releasing substituents is attributed to stabilisation of the ground state by conjugation.[104] As a result of the enhanced acceptor properties, however, the phosphorus compounds are more sensitive to substitutional change.[117] Phosphoryl compounds therefore resemble their carbonyl analogues qualitatively, but effects due to polarity and polarisability are more strongly marked with them. The combination of electrophilic character with competitive donation from the ligands into a double $p\pi$–$d\pi$ system is important for other series of compounds, and especially for phosphorus–nitrogen compounds.

The P=N Bond in Phosphinimines.—The simplest compounds containing the P=N bond are the phosphinimines $R_3P{:}NR'$, which may be expected to resemble phosphoryl compounds. The limited thermochemical evidence suggests that the total π-energy is strongly dependent on the nature of the attached groups. In the singly-bonded compound trisdiethylamidophosphine $P(NEt_2)_3$, $E(P–N) = 66{\cdot}8$ kcal.,[120] and in the two phosphinimines $Ph_3P{:}NEt$ and $Me_3P{:}NEt$, $E(P=N)$ is 98·4 kcal. and 69·7 kcal. respectively.[121,122] The large difference between these two figures is in the opposite sense to that between corresponding phosphoryl compounds. The P=N bond in phosphinimines is highly polar, a typical reaction (16) being that with ketones to give ketimines.[56] Similarly, phosphinimines $R'N{:}PR_3$ are dimeric if the strength of the parent amine is great enough.[27] Dimerisation

$$R_2CO + R'N{:}PR_3 \rightarrow R'N{:}CR_2 + R_3PO \qquad (16)$$

also requires the substituents at phosphorus to be electron-withdrawing groups; $Ph_3P{:}NEt$ is monomeric, whereas $Cl_3P{:}NMe$ and a number of other compounds in which the phosphorus atom carries such groups as P=O or P=S are dimeric.[123] Dimeric *N*-methyltrichlorophosphinimine has been investigated more closely than the other molecules, its vibrational spectra showing the presence of a four-membered, planar, P_2N_2 ring.[28] The conditions for dimerisation are precisely those for development of such structures as (XX), and there is spectroscopic evidence for the partial delocalisation of the nitrogen lone pairs. In addition, the average value of

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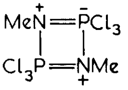
[117] G. S. Hartley, Ref. 33, p. 33.
[118] Crofts and Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3379.
[119] Dostrovsky and Halmann, *J.*, 1953, 502, 508, 511, 516; 1956, 1004.
[120] Fowell and Mortimer, *J.*, 1959, 2913.
[121] Mortimer, *Pure and Appl. Chem.*, 1961, **2**, 71.
[122] Claydon, Fowell, and Mortimer, *J.*, 1960, 3284.
[123] Trippett, *J.*, 1962, 4731.

E(P–N) (74·3 kcal.)[124] is greater than that of a single bond. It is surprising that trimeric molecules are not formed preferentially, since increased



(XX)

stability should result both from the attainment of the natural valency angles, and from the accompanying increased π-electron energy. A four-membered silazane ring presents a similar problem;[125] it is possible that in both compounds steric interactions would be greater in the larger rings.

Bonding in Cyclic Phosphonitriles.—The structural effect of variations in π-bonding is better understood in the cyclic phosphonitrilic derivatives $(NPX_2)_n$. It is possible to regard these compounds as constructed from linked tetrahedra, and the π-bonds in them as formed by linking the orbitals of the double π-system of the individual units. This model has been developed especially by Cruickshank;[106] the sharing of π-orbitals gives an acceptable picture of the bond-lengths and angles in many compounds of tetra-co-ordinated silicon, phosphorus, and sulphur, and the double π-system is expected to make an important contribution to the bonding in phosphonitrilic compounds too. The more detailed knowledge of these compounds, however, makes a deeper analysis necessary.

Formally, the new features arise because of the lower molecular site symmetry of the phosphorus atom, which is now at most C_{2v} rather than T_d, so that the two strongly π-bonding orbitals are no longer degenerate with each other.[126] It is now convenient to use a co-ordinate system in which the z-axis is perpendicular to the local NPN plane (which for symmetry D_{nh} is the plane of the molecule), so recognising the importance of overlap with the $2p\pi(p_z)$ orbital on nitrogen. The orientation of the five d-orbitals in the co-ordinate system employed is shown in Fig. 2. The π-system in the ring is now composed of the two phosphorus orbitals d_{xz} and d_{yz}, and the π'-system of d_{xy} and $d_{x^2-y^2}$; each system in a non-planar molecule overlaps both $2p_z$ and an s–p_y hybrid at nitrogen. Exocyclic π-bonding also has two components, using respectively d_{z^2} and the pair d_{xz}, d_{yz}, but it is at present less profitable to distinguish between them.* The reality of the difference even here can, however, be seen in structure of the tetrameric dimethylamide (see below). Conjugation between the ring and the exocyclic π-systems will still occur, especially with electron-releasing ligands, but because of the greater deviation from regular tetrahedral geometry, it is likely to be less important than in phosphoryl compounds.

* *Notation:*—In a planar molecule, the π'-orbitals lie in the plane of the molecule, and might well be labelled σ'. In general, however, the relevant molecules are non-planar, so that the reference plane is not defined. The notation used recognises that both π- and π'-orbitals change sign on rotation by 180° about the local bond axis.

[124] Fowell and Mortimer, *Chem. and Ind.*, 1960, 444.

[125] Wheatley, *J.*, 1962, 1721.

[126] Craig and Paddock, *J.*, 1962, 4118.

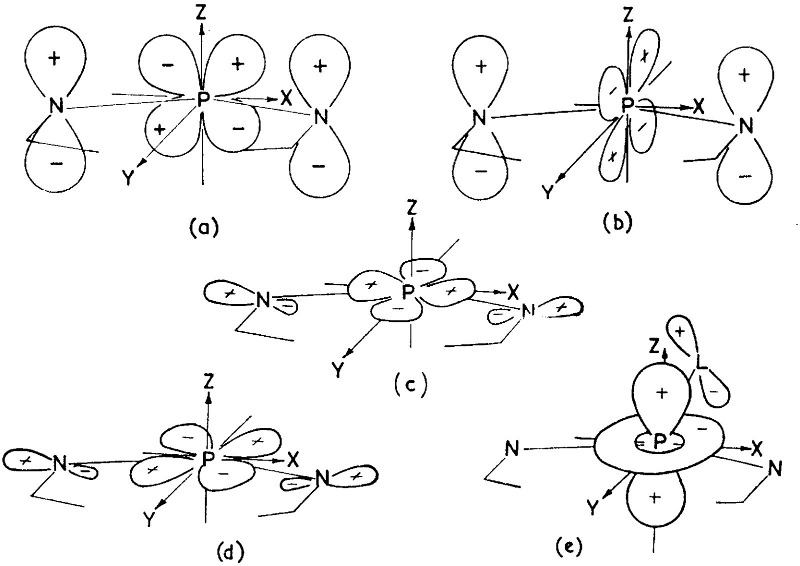


FIG. 2. *Overlap schemes for π-bonding of (a)* d_{xz}, *(b)* d_{yz} *with* p_z; *(c) π′-bonding of* $d_{x^2-y^2}$ *and (d)* d_{xy} *with an s-*p_y *hybrid; (e) π-bonding of* d_{z^2} *with ligand p-orbital.*

Of the two possible types of interaction within the ring[106,126] (π and π′), most attention has been devoted to the π-system.[127,128] The two *d*π-components are not required to be equal by symmetry, and it is likely that d_{xz} is more strongly involved than d_{yz}. If it is, a delocalised π-system is formed, of a different type from that in benzene, because the interactions of the d_{xz}-orbital with the 2*p*π orbitals on either side are of opposite sign (Fig. 2*a*, *b*). The essential results of a simple molecular-orbital treatment[127] are that (1) for unequal electronegativities of the π-orbitals, any even number of electrons forms a closed shell, and (2) for a given difference of electronegativity, π-electron energies (per electron) increase steadily with ring size. Fig. 3 shows π-electron energies as a function of ring size for *p*π–*p*π and for *p*π–*d*π systems. On this basis it is not to be expected that trimeric and tetrameric phosphonitrilic derivatives will differ as much as do benzene and cyclo-octatetraene, and indeed the separate series of phosphonitrilic halides, $(NPCl_2)_n$ and $(NPF_2)_n$ have comparable properties among themselves. The effect of increased mixing-in of the d_{yz}-orbital is to reduce the expected differences between successive members of these series. In the limit of equal contributions,[128] the π-system is resolved into a series of 3-centre P–N–P "islands" (Fig. 4).

The secondary π′-bonds in the ring are formed, in planar molecules, by

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[127] (*a*) Craig and Paddock, *Nature*, 1958, **181**, 1052; (*b*) Craig, *Chem. Soc. Special Publ.* No. 12, 1958, p. 343; (*c*) *J.*, 1959, 997; (*d*) "Kekulé Symposium on Theoretical Organic Chemistry", Butterworths, London, 1959, p. 20.

[128] Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.

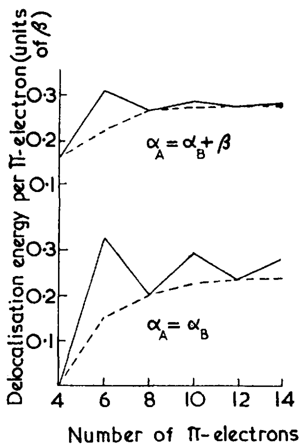

FIG. 3. *Delocalisation energies in planar* (AB)$_n$ *systems. Upper diagram; Coulomb integrals differing by* β*: lower diagram, equal Coulomb parameters. Full lines refer to* $p\pi$-$p\pi$ *and broken lines to* $p\pi$–d_{xz}. (Reproduced with permission from Craig, *J.*, 1959, 997.)

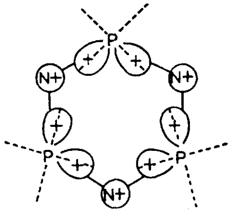

FIG. 4. *Orbital overlap scheme for* 3*-centre* P–N–P *bonds. The two d-orbitals at phosphorus, here seen in plan, are formed by taking the sum and difference of* d_{xz}, d_{yz} (*Fig.* 14), *and make angles of* 45° *with them.*

overlap of the $d\pi'$-orbitals with s–p_y hybrids on nitrogen, and, as the shape departs from planarity, increasingly with the p_z-orbital. Release of electrons to phosphorus is important, competitively from the ligands and from the lone pairs on the ring nitrogen atoms,[129] and in the latter case contributes predominantly to the π'-system. The two $d\pi'$ orbitals, however, differ in their interactions with p_y (Fig. 2*c*,*d*); $d_{x^2-y^2}$, which according to overlap calculations should be the more strongly involved, interacts (like a p-orbital) with the same sign on its two sides, and, to the extent that it is used, should impose a minor alteration on the $p\pi$–$d\pi$ energies shown in Fig. 3.

However the electrons are distributed between the π- and π'-systems, the multiple bond system is highly polarisable, and the different distributions of electrons in differently-substituted molecules have important effects on their physical and chemical properties. In the next sections we shall discuss the structural, spectroscopic, and thermochemical evidence on electron distri-

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[129] Shustorovich, *Zhur. strukt. Khim.*, 1962, 3, 218.

bution, and shall later show the applications to other properties of phosphonitrilic derivatives and to other types of compound.

Structural Investigations.—The cyclic structures suggested by Stokes[3] for the phosphonitrilic chlorides, typically the trimer (II), have been amply confirmed by later work. Perhaps the clearest demonstration is provided by their NMR spectra using phosphorus-31, which show that the phosphorus atoms in any particular member of the series have identical environments.[20] A similar conclusion applies to the fluorides, up to at least $(PNF_2)_{11}$. The chemical shifts due to phosphorus-31 of some phosphonitrilic derivatives are shown in Fig. 5.

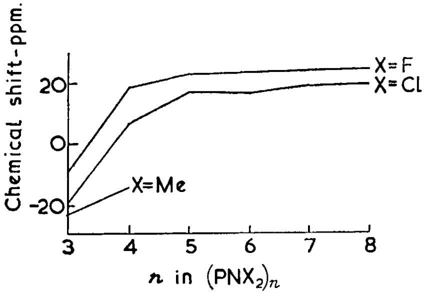

FIG. 5. ^{31}P *N.M.R. spectra of chloro-, fluoro- and methyl-phosphonitriles relative to* 85% H_3PO_4.
(R. F. M. White, quoted in Ref. 20, and unpublished work.) For $(NPBr_2)_{3,4}$ chemical shifts are + 49·5, + 71·8 p.p.m. (John and Moeller, *J. Inorg. Nuclera Chem.*, 1961, **22**, 199).

The molecular structures of seven phosphonitrilic derivatives are known. Details are given in Tables 3 and 4, which also contain information on corresponding phosphines and phosphine oxides. The lengths of the exocyclic bonds in the phosphonitrilic compounds [with the possible exception of $(NPBr_2)_3$] are very similar to those in the phosphoryl compounds, as expected. The ring angles at phosphorus are all close to 120°, and can be compared with 117°19′ for O=P—Cl in $POCl_3$.[130] They are slightly greater in the tetrameric molecules, especially in the halides, and are associated in these molecules with slightly decreased angles between the ligands. In the trimeric molecules, the ring angle at nitrogen hardly deviates from 120°, but in the 8-membered rings, with their greater geometrical freedom, it is appreciably increased, consistent with some delocalisation of the nitrogen lone pairs. Remarkably, the angle is the same in three of the molecules; in the fluoride, inductive effects are so great that the bond angle at nitrogen is increased to 147° and the ring becomes planar. The ring bond lengths in all the molecules are similar, and are appreciably shorter than the 1·78Å found[131] for *L*(P–N) in the phosphoramidate ion $[PO_3NH_3]^-$. Again the fluorides stand out; not only are their ring bond

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[130] Badgley and Livingston, *J. Amer. Chem. Soc.*, 1954, **76**, 261.
[131] Hobbs, Corbridge, and Raistrick, *Acta. Cryst.*, 1953, **6**, 621.

lengths shorter than those of the other compounds, but *L*(P–N) in the tetramer is significantly shorter than in the trimer. All these features are generally consistent with the existence of a π- (and π'-)system in the ring, the strength of which is controlled partly by the electronegativity of the ligands and partly by ring size. Stronger bonds are possible in the larger rings because of the improved orbital overlap, greater cyclic delocalisation, and because of the possibility of increased delocalisation of lone pairs on the nitrogen atom.[126]

TABLE 3. *Structural information on trimeric phosphonitrilic derivatives* $(NPR_2)_3$ *and related compounds*[a]

R		Br	Cl	F
L(P–R) (Å) in	R_3P	2·23	2·04	1·55
	R_3PO	2·06	1·99	1·52
	$(NPR_2)_3$	2·18	1·99	1·52
<RPR in	R_3P	100°	100°	104°
	R_3PO	108°	103·5°	102·5°
	$(NPR_2)_3$	103°	102°	99·5°
L(P=O) in (Å)	R_3PO	1·41	1·45	1·45
L(P=N) in (Å)	$(NPR_2)_3$	1·53	1·59	1·56
∠NPN	,,	117°	119·5°	119·5°
∠PNP	,,	123°	120·0°	120·5°

[a] References for the structures of individual compounds are: PBr_3, Gregg, Hampson, Jones, and Sutton, *Trans. Faraday Soc.*, 1937, **33**, 852, as revised by Lister and Sutton, *ibid.*, 1941, **37**, 393; PCl_3, Kisliuk and Townes, *J. Chem. Phys.*, 1950, **18**, 1109; PF_3, Gilliam, Edwards, and Gordy, *Phys. Rev.*, 1949, **75**, 1014; $POBr_3$, Secrist and Brockway, *J. Amer. Chem. Soc.*, 1944, **66**, 1941; $POCl_3$, Badgley and Livingston, *J. Amer. Chem. Soc.*, 1954, **76**, 261; POF_3, Williams, Sheridan, and Gordy, *J. Chem. Phys.*, 1953, **20**, 164; $(NPBr_2)_3$, de Santis, Giglio, and Ripamonti, *J. Inorg. Nuclear Chem.*, 1962, **24**, 469 (preliminary determination); $(NPCl_2)_3$, Pompa and Ripamonti, *Ricerca sci.*, 1959, **29**, 1516; Wilson and D. F. Carroll, *J.*, 1960, 2548; (an apparent inequality in *L*(P–N) in $(NPCl_2)_3$ (Giglio, *Ricerca sci.*, 1960, **30**, 721) may be due to the use of isotropic temperature factors); $(NPF_2)_3$, Dougill, *J.*, 1963, 3211. Equivalent bond lengths and angles are averaged in the phosphonitrilic molecules.

TABLE 4. *Structural information on tetrameric phosphonitrilic derivatives* $(NPR_2)_4$

R	NMe_2[a]	Me[b]	Cl[c]	F[d]
L(P–R) (Å)	1·68	1·80	1·99	1·51
L(P=N) (Å)	1·58	1·60	1·58	1·51
∠RPR	104°	104°	103°	100°
∠NPN	120°	120°	121°	122·5°
∠PNP	133°	132°	132°	147°

[a] Bullen, *J.*, 1962, 3193; [b] Dougill, *J.*, 1961, 5471; in Me_3P, *L*(P–C) = 1·85 Å, ∠CPC = 98·6° (Bartell and Brockway, *J. Chem. Phys.*, 1960, **32**, 512); in Me_3PO, *L*(P–C) = 1·81 Å, ∠CPC = 106°, *L*(P=O) = 1·48 Å [Wang, Forsvarets-Forskningsinstitutt (Norway) Intern. Rapport IR-K-225 (1960)]; [c] Hazekamp, Migchelsen, and Vos, *Acta Cryst.*, 1962, **15**, 539; [d] McGeachin and Tromans, *J.*, 1961, 4777.

The bond system is modified by electron release from the ligands in competition with release from the ring nitrogen atoms; ring vibration frequencies, reaction rates, the orientation of substituents, and molecular structures are all affected. The importance of electron release from exocyclic groups is shown in the structure of the tetrameric dimethylamide. The average exocyclic P–N bond length is 1·68Å, shorter than expected for a single bond as corrected for hybridisation changes (1·74Å), and comparable with *L*(P–N) in $(NH_2)_3P{\cdot}BH_3$ (1·65Å).[132] The average angle CNC angle (116°) is also greater than that[133] in trimethylamine (108°), the exocyclic groups being almost flat. Interaction of the dimethylamido-groups with the ring, although large, is limited by the mutual steric requirements of a pair attached to the same phosphorus atom. The one with its N-p_z orbital orientated most suitably for overlap with the strongly π-bonding P-d_{z^2} orbital has the slightly smaller exocyclic *L*(P–N) (1·671Å) and, more significantly, is the more nearly planar, the sum of the angles at nitrogen being 358·5°. The other dimethylamido-group is necessarily orientated so that its main *pπ–dπ* overlap takes place with the d_{xz} and d_{xy} orbitals, which interact less strongly, the former because it is already involved in the ring π-bonds. *L*(P–N) is therefore slightly greater (1·686Å) and the sum of the angles at nitrogen is smaller (349·5°), indicating decreased delocalisation of the lone pair on the ligand.

The structures are further differentiated by their configurations, which also show qualitatively the relative importance of π- and π′-bonding in different molecules. The trimeric halides are all close to planarity, the chloride and bromide being slightly distorted by lattice forces. As already discussed, the tetrameric fluoride also is planar, because the strong inductive influence of the fluorine atoms permits extensive delocalisation of the lone pairs on the nitrogen atoms, with consequent increase of the PNP bond angle. The other three molecules all have the same minimum symmetry S_4, but in the series $N_4P_4Cl_8$, $N_4P_4Me_8$, and $N_4P_4(NMe_2)_8$ tend increasingly towards the higher symmetry D_{2d}, the configuration of the phosphorus atoms becoming more nearly planar. It seems probable that the differences are due to differences in the compromise made between steric interactions and the inequality of π- and π′-bonding.[126]

The two *dπ*-orbitals, d_{xz} and d_{yz}, intersect in the *z*-axis, and the relative orientations of local *z*-axes on successive ring atoms gives a measure of the overlap of the N-*pπ* orbitals with the two *dπ*-orbitals or linear combinations of them.

Figs. 6—8 show stereographic projections of the three possible configurations of non-planar 8-membered rings $(NPX_2)_4$ which exhibit four-fold symmetry, the relative orientation of π-orbitals in them, and the steric relations between non-bonded groups. The first configuration (Fig. 6) is similar to that of cyclo-octatetraene, if all the displacements from the

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[132] Nordman, *Acta Cryst.*, 1960, **13**, 535.
[133] Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036.

plane of projection are assumed to be equal. The relative orientation of ocal z-axes (Fig. 6*a*) shows that π-interaction is strong between adjacent atoms on the same side of the plane, and weak otherwise, as found experimentally for cyclo-octatetraene,[134] In the second (saddle) configuration (Fig. 7) the four phosphorus atoms have been brought into a plane, so introducing two-fold axes and planes of symmetry, and increasing the symmetry to D_{2d}, necessarily equalising the interactions between successive π-orbitals. In the third (C_{4v}, crown) configuration (Fig. 8), the interactions are again all equal but are almost zero, the z-axes on adjacent atoms being nearly mutually perpendicular.

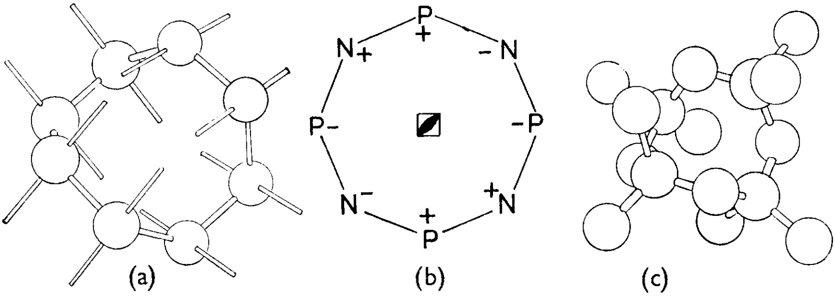

FIG. 6. *S_4 (tub) configuration; (a) orientation of z-axes, (b) stereographic projection (c) steric interactions.*

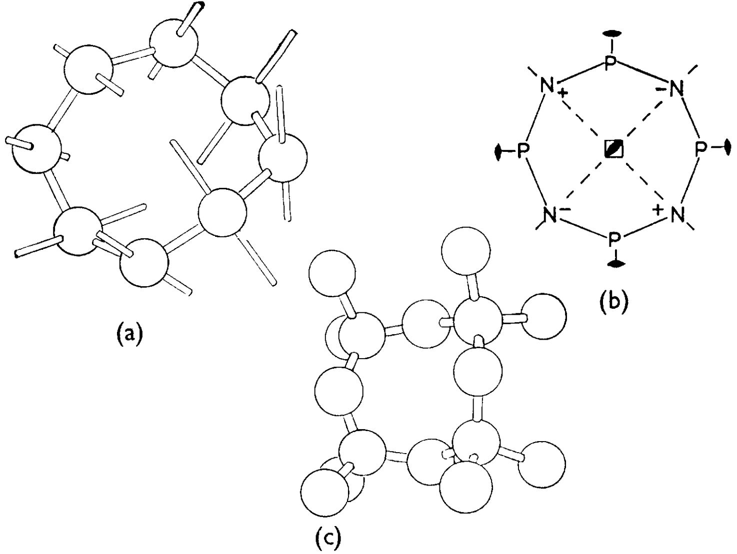

FIG. 7. *D_{2d} (saddle) configuration; (a) orientation of z-axes, (b) stereographic projection, (c) steric interactions.*

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[134] Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, 1957, **27**, 1311.

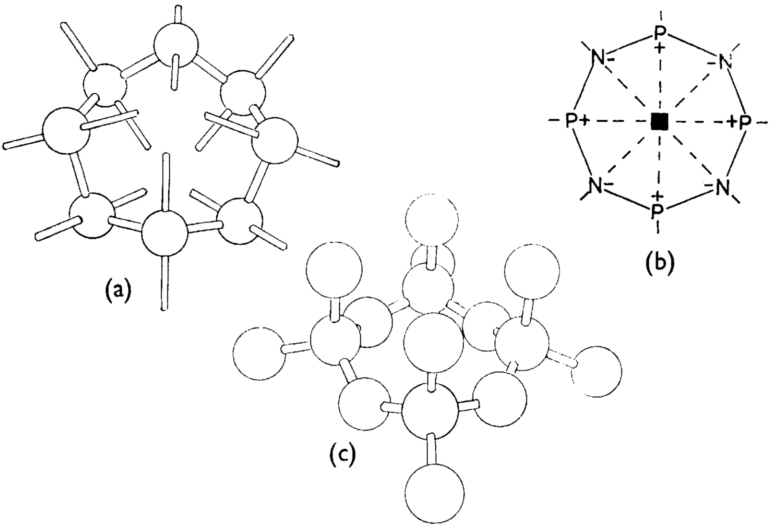

FIG. 8. *C_{4v} (crown) configuration; (a) orientation of z-axes, (b) stereographic projection, (c) steric interactions.*

There are two other important factors. First, we have to include π'-bonding, which uses *d*-orbitals with their density lobes concentrated in a plane perpendicular to that of the $d\pi$-orbitals, and is therefore strong where π-bonding is weak, and conversely; if π- and π'-contributions were equal, the bonds would have cylindrical symmetry. Secondly, the configurations differ in the importance of steric interactions. In the tub form (Fig. 6*c*) neighbouring PX_2 groups are staggered, whereas in the saddle and crown forms (Figs. 7*c*, 8*c*) the planes of symmetry bring them into the eclipsed position. The crown form combines the weakest π-bonds with the strongest repulsive interactions, and is not found in phosphonitrilic structures, though it is the preferred configuration when steric interactions on *adjacent* atoms need to be minimised, as in sulphur[135] S_8 and in the sulphur imides[136] $S_4(NH)_4$ and $S_6(NH)_2$. In the phosphonitrilic compounds, strengthening of the π-system by equalisation of the dihedral angles is offset by the repulsion between ligands on successive phosphorus atoms. For similar steric interactions, therefore, real configurations will approach the saddle form as π-bonding predominates over π'-bonding. The determined structures allow some assessment of the two types of contribution. Table 5 gives the displacements of the ring atoms from the mean molecular plane for the three non-planar tetrameric phosphonitrilic molecules; the ratio decreases as the symmetry D_{2d} is approached, and becomes zero in the limit.

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[135] Abrahams, *Acta Cryst.*, 1955, **8**, 661.

[136] Sass and Donohue, *Acta Cryst.*, 1958, **11**, 497; Weiss, *Z. anorg. Chem.*, 1960, **305**, 190.

TABLE 5. *Displacements of ring atoms from mean molecular plane*

	$(NPCl_2)_4$	$(NPMe_2)_4$	$[NP(NMe_2)_2]_4$
Displacements of Phosphorus (Å)	0·35	0·21	0·18
Displacements of Nitrogen (Å)	0·47	0·54	0·52
Ratio of Displacements P/N	0·75	0·39	0·35

From work on phosphoryl compounds described above, the ability to release electrons to phosphorus decreases in the order $Me_2N > CH_3 > Cl$. In the tetrameric dimethylamide, such electronic feed-back tends to prevent delocalisation of the lone pairs on the ring nitrogen atoms, so that π'-bonding is weak and the mismatch of dihedral angles small; in this molecule, we have the closest approach to pure π-bonding. Electron release is less from methyl and least from chlorine, so that π'-bonding increases, and the configuration, controlled more by steric interactions, departs increasingly from D_{2d} symmetry towards the S_4 structure in which the phosphorus and nitrogen atoms are equally displaced from the plane of projection (Fig. 6*b*).

In the limit of equality, the total π-system exerts no control over molecular shape, and the existence of another configuration, chair-shaped and of symmetry C_{2h} (Fig. 9), in which steric repulsions are as small as in the tub configuration, opens the possibility of configurational isomerism. The first known example is the tetrameric phosphonitrilic chloride $(NPCl_2)_4$, in which the large mismatch of ring dihedral angles (Table 5) indicates a large relative π' component and therefore the highest probability (among known structures) of configurational inversion. This compound exists in two polymorphic forms, one of which (*K*) (for Ketelaar[137]) has already

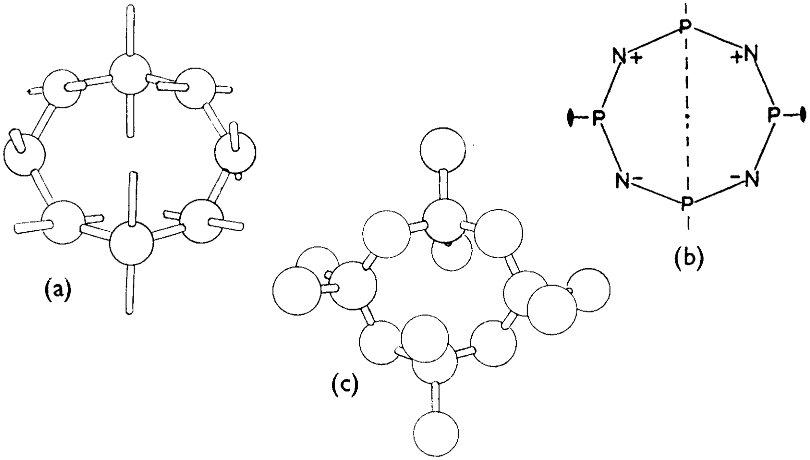

FIG. 9. C_2 *(chair) configuration;* (*a*) *orientation of z-axes,* (*b*) *stereographic projection,* (*c*) *steric interactions.*

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[137] Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081.

been described. The other (*T*; a label originally due to a mis-reading of 1 by the Reviewer) is required by space-group symmetry and packing considerations to be centrosymmetrical and therefore chair-shaped.[138] The detailed structure of *T*-$(NPCl_2)_4$ is at present being determined;[139] bond lengths and angles are unlikely to differ greatly from those in the K-form. While the nuclear quadrupole resonance spectrum of the trimeric[140] chloride is consistent with its crystal structure, having two pairs of lines of intensity 2:1, that of the tetrameric chloride[140] sometimes shows four lines of equal intensity, characteristic of the centrosymmetric *T*-form, historically the first indication of configurational isomerism.[141] At ordinary temperatures, the *T*-form is the more stable.

Configurational isomerism is also likely if the ligands are bulky enough, irrespective of the inequality of π- and π'-bonding. If this is large, however, the ring bonds would be expected to alternate in the S_4 configuration, and to be unequal in pairs in the C_{2h}-form. No example is yet known in the phosphonitrilic series, but, as will be seen later, thiazyl compounds and metaphosphates sometimes show inequalities in bond lengths which can be attributed to sterically forced variations in orbital overlap.

Possible bond-length variations in simple delocalised $p\pi$–$d\pi$-systems have been considered theoretically,[142] with interesting results. In cyclic aromatic hydrocarbons, with $4n + 2$ π-electrons, the π-electron energies decrease steadily to a limit with increasing ring size (Fig. 3). The energy of compression of the σ-bonds is therefore offset decreasingly by the π-energy as ring size is increased, and for a sufficiently big ring, localised $p\pi$–$p\pi$ bonds are more stable, and the skeletal bonds alternate in length.[143] In $p\pi$–$d\pi$-systems, on the other hand, π-electron energies *increase* to the same limit (Fig. 3) (for equal electronegativities) so that inequalities in bond lengths are to be expected for small rings only, and even then only if the electronegativity difference is small enough. Such conditions have not yet been found among phosphonitrilic compounds, but these investigations lend fresh point to a search for compounds $(PX_2{=}CH)_n$, in which the ring bonds might alternate.

Vibrational Spectra.—The complementary information derived from the Raman and infrared spectra of phosphonitrilic derivatives is less detailed than that given by direct structural determination, and is sometimes ambiguous. There are, for instance, some disagreements about individual

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[138] A. Wilson, unpublished work.

[139] A. J. Wagner, personal communication.

[140] Negita, *J. Sci. Hiroshima Univ.*, 1958, *A*21, 261, (*Chem. Abs.* 1958, **52**, 19468); Negita and Satou, *J. Chem. Phys.*, 1956, **24**, 621; *Bull Chem. Soc. Japan*, 1956, **29**, 426 (*Chem. Abs.* 1957, **51**, 12646). See also Torizuka, *J. Phys. Soc. Japan*, 1956, **11**, 84 (*Chem. Abs.* 1956, **50**, 9149).

[141] A. C. Chapman and A. Wilson, unpublished work.

[142] Davies, *Nature*, 1962, **194**, 82; Haigh and Salem, *Nature*, 1962, **196**, 1307; Davies, *Nature*, 1962, **196**, 1309.

[143] Longuet-Higgins and Salem, *Proc. Roy. Soc.*, 1959, *A*, **251**, 172.

assignments for the trimeric chloride[144–147] and fluoride,[146,148] though their vibrational spectra are both consistent with D_{3h} symmetry, which requires the ring bonds to be equal in length within each molecule. In solution and in the vapour phase,[94,146,148] the tetrameric fluoride is slightly distorted from the planar structure found in the crystal into a chair form of symmetry C_{2h}, the deviation from planarity depending on the solvent. The tetrameric chloride is less straightforward. Although its spectra in solution and in the vapour are very similar to those in the crystal (*K*-form), in which the molecule has the symmetry S_4, they are more nearly compatible with D_{4h},[145,149] D_{2d}[145] or other symmetries.[146] The symmetry D_{4h} has also been suggested[149] for the tetrameric bromide $(NPBr_2)_4$. Although no detailed crystal structure is available for comparison, the identity of space-groups of the tetrameric chloride and bromide and the close similarity of their cell-sizes[137,40b] suggests that the molecular symmetry of $(NPBr_2)_4$ is really S_4, a similar contradiction existing for both the chloride and the bromide. As a further difficulty, the vibrational spectra of *T*-$(NPCl_2)_4$ appear to be inconsistent with the presence of a centre of symmetry.[146] The higher chlorides and fluorides have been studied in less detail,[146,150] though the structure of the series of PF_2 symmetrical stretching bands in the fluorides $(NPF_2)_n$ provides a further proof of their cyclic nature.[94]

The most obvious feature of the infrared spectra of phosphonitrilic derivatives is a strong band at approximately 1200—1400 cm.$^{-1}$, usually known as the "P–N stretching frequency", and covering about the same range as $\nu(P{=}O)$ in phosphoryl compounds. It can be regarded as $\nu_{as}(P–N–P)$, but is strictly a degenerate ring-stretching vibration, with (if it is the first of the degenerate bands) an amplitude phase difference of $\delta = 2\pi/N$ between the vibrational motions of adjacent atoms, N being the number of atoms in the ring.* A simplified treatment, analogous to that of a zig-zag hydrocarbon chain, shows that if interaction with deformation is ignored, $\nu(P–N)$ should decrease with increase in ring size, as found for the chloride[20] and fluoride[94] series above $(NPX_2)_5$. The initial increase in frequency, between trimer and pentamer,[4,20,153] is probably due neither to the change in phase angle, nor, appreciably, to strengthening of the ring

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* For the use of δ in interpreting the spectra of polymeric chains, especially hydrocarbons, see Ref. 151. The application to cyclic molecules generally appears to have been made first by Parodi,[152] and to phosphonitrilic molecules by Chapman.[94]

[144] de Ficquelmont, Magat, and Ochs, *Compt. rend.*, 1939, **208**, 1960.

[145] Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403.

[146] Chapman and Paddock, *J.*, 1962, 635.

[147] Califano, *J. Inorg. Nuclear Chem.*, 1962, **24**, 483; Califano and Ripamonti, *ibid.*, p. 491.

[148] Becher and Seel, *Z. anorg. Chem.*, 1960, **305**, 148.

[149] Steger and Stahlberg, *Z. Naturforsch.*, 1962, **17b**, 780.

[150] Steger and Mildner, *Z. Naturforsch.*, 1961, **16b**, 836.

[151] Brown, Sheppard, and Simpson, *Discuss. Faraday Soc.*, 1950, **9**, 261; Deeds, Thesis, Ohio State University, 1951.

[152] Parodi, *Mem. des Sci. physiques*, 1944, **47**, 1 (73).

[153] Shaw, *Chem. and Ind.*, 1959, 54.

bonds; the same type of variation of ring-stretching frequency with ring size is found in the series of cyclic dimethylsiloxanes.[154]

For a particular ring size, ν(P–N) depends primarily on the electronegativity of the ligands. Some typical values are shown in Table 6. The value of ν (P–N) is also affected to an important extent by the donation of electrons to phosphorus by the exocyclic groups. In the dimethylamides, especially, electron release from the ligands limits the delocalisation of the lone pairs on the ring nitrogen atoms, and, analogously to the behaviour of phosphoramides,[111] depresses ν(P–N), even though the electronegativities of N and Cl are usually taken to be the same.

TABLE 6. *ν(P=N) in trimeric and tetrameric phosphonitrilic derivatives*

R	Me[a]	Ph[b]	Br[c]	NMe$_2$[d]	Cl[e]	OMe[d]	F[f]
$(NPR_2)_3$(cm.$^{-1}$)	1180	1190	1175	1195	1218	1275	1297–1305
$(NPR_2)_4$(cm.$^{-1}$)	1180	1213	1272–1280	1265	1315	1337	1435–1438

[a] Searle, *Proc. Chem. Soc.*, 1959, 7. [b] Bilbo, *Z. Naturforsch.*, 1960, **15**b, 330. [c] John and Moeller, *J. Inorg. Nuclear Chem.*, 1961, **22**, 199; Steger and Stahlberg, *Z.* Naturforsch., 1962, **17**b, 780. [d] Shaw, *Chem. and Ind.*, 1959, 54. [e] Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403. [f] Seel and Langer, *Z. anorg. Chem.*, 1958, **295**, 316; Chapman, Paddock, Paine, Searle, and D. R. Smith, *J.*, 1960, 3608.

The importance of steric effects on ν(P–N) has also been investigated. In both the trimeric[155] and the tetrameric[64] series the same trends are observed (Table 7). The relatively high frequencies exhibited by the compounds carrying the larger groups is attributed[155] to their greater difficulty in adopting the planar configuration of exocyclic nitrogen characteristic of appreciable electron release to phosphorus. In agreement with this interpretation, ν(P–N) is also high in the tetrameric dimethylamide (1265 cm.$^{-1}$), and, as we have seen, the complete development of exocyclic π-bonding in this molecule is prevented by steric interactions of the two dimethylamido-groups. ν(P–N) would probably be lower if both these groups were planar. It is also possible that ν(P–N) in the amino- and monomethylamino-derivatives is depressed by hydrogen-bonding of

TABLE 7. *ν(P=N) in trimeric and tetrameric alkylamino-phosphonitriles*[a]

R	NH$_2$	MeNH	EtNH	Pr^{n}NH	Bu^{n}NH	n-C$_5$H$_{11}$NH	n-C$_6$H$_{13}$NH
$(NPR_2)_3$ (cm.$^{-1}$)	1170	1175	—	1183	1195	1190	1192
$(NPR_2)_4$ (cm.$^{-1}$)	1240	1215	1262	1266	1260	1265	1265

[a] References are, for R=NH$_2$, Audrieth and Sowerby, *Chem. and Ind.*, 1959, 748; Sowerby and Audrieth, *Chem. Ber.*, 1961, **94**, 2670; for other trimers, Kokalis, John, Moeller, and Audrieth, *J. Inorg. Nuclear Chem.*, 1961, **19**, 191; other tetramers, John, Moeller, and Audrieth, *J. Amer. Chem. Soc.*, 1961, **83**, 2608.

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[154] Wright and Hunter, *J. Amer. Chem. Soc.*, 1947, **69**, 803; Richards and Thompson, *J.*, 1949, 124.

[155] Kokalis, John, Moeller, and Audrieth, *J. Inorg. Nuclear Chem.*, 1961, **19**, 191.

the ligands to the ring nitrogen atoms of other molecules. Such bonding would also be subject to steric interference, and its occurrence would be consistent with the insolubility of these compounds in organic media. The observed frequency shifts are rather smaller than those found for the protonation of the phosphoryl group.[156]

Thermochemistry.—The heats of formation of several phosphonitrilic derivatives have been determined (Table 8), and allow some estimate to be made of the total π-bond energies. The total bond energy exceeds the sum of nominal single bond energies by the amounts shown in the last row of the Table, the individual entries strictly including both σ- and π-components. They are useful quantities only to the extent that the single-bond energy terms are appropriate. E(P–N) is particularly suspect, because even tervalent phosphorus has acceptor properties (the dissociation energy of $PCl_3 \cdot NMe_3$ is 6·4 kcal./mole)[157] and the apparent value of E(P–N) in $P(NEt_2)_3$ may well include a contribution from partial lone-pair delocalisation, the P–N bonds having partial double-bond character. Although this does not affect a comparison between phosphonitrilic compounds, it is still impossible, on thermochemical grounds alone, to allocate the extra energy to individual bonds, or to distinguish σ- and π-contributions. From the values given, three tentative conclusions seem possible.

TABLE 8. *Thermochemistry of phosphonitrilic derivatives*[a]

	$(NPCl_2)_3$	$(NPCl_2)_4$	$(NPMe_2)_3$	$(NPPh_2)_4$	$[NP(OC_6H_{11})_2]_3$
$-\Delta H_f$ (Cryst.) (kcal./mole)	194·1 ± 0·7	259·2 ± 1·2	125·1 ± 2·7	−40·7 ± 11·5	582·0 ± 4·0
E(P–N) + E(P–X) (kcal.)[b]	152·3	152·7[d]	140·8	153·2	174·9[e]
ΔE(P–N) + ΔE(P–X) (kcal.)[c]	9·3	9·7[d]	12·4	18·9	16·1[e]

[a] Data for the chlorides are from S. B. Hartley, Paddock and Searle, *J.*, 1961, 430; for the other compounds, from Bedford and Mortimer, *J.*, 1960, 4649. [b] X refers to the first exocyclic atom. [c] Excess of measured E(P–N) + E(P–X) over sum of single-bond energy terms, taken to be: E(P–N) = 66·8, E(P–O) = 92·0, E(P–Cl) = 76·2, E(P–C) = 61·6 (Me_3P) and 67·5 (Ph_3P)kcal. See Ref. 112 for detailed sources. [d] Calculated from $\Delta H_f(NPCl_2)_3$ and measurements of the heats of polymerisation of $(NPCl_2)_{3,4}$ (Table 12). The use of $\Delta H_f(NPCl_2)_4$ gives values 0·2 kcal. lower. [e] Arithmetical error in source corrected.

(1) π-Electron energies are smaller in phosphonitrilic than in phosphoryl compounds, partly because nitrogen is less electronegative than oxygen, and partly because the overlap of the individual orbitals is less effective. In phosphonitrilic chlorides, it is of the order of 6-10 kcal./bond. (2) The difference between the trimeric and tetrameric chlorides is real, and dis-

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[156] Zingaro and White, *J. Inorg. Nuclear Chem.*, 1960, **12**, 315.
[157] R. R. Holmes, *J. Phys. Chem.*, 1960, **64**, 1295.

tinguishes $p\pi-d\pi$ from $p\pi-p\pi$ systems. Comparison of their heats of combustion shows that the average ring-bond energy in cyclo-octatetraene[158] is 5·5 kcal. less than in benzene.[159] In the phosphonitrilic series, the ring bonds are stronger in the 8-membered ring, as expected theoretically,[127] though there is no doubt that increased lone-pair delocalisation in the larger molecule accounts for part of the difference. (3) It is noteworthy that the additional bond energy is appreciably greater in the methyl- and phenyl-phosphonitriles than in the chlorides, in spite of the lower electronegativity of carbon suggesting that here (surprisingly), as in phosphoryl compounds, there is some electron-release to phosphorus.

It is clear from the foregoing paragraphs that the mutual interaction of the groups attached to phosphorus is too great for the concept of "resonance energy" as a distinguishable contribution to the total heat of formation to be of much use in phosphonitrilic chemistry, and other methods of organising the information have been developed.[112] There is another important difference between doubly-bonded phosphorus and carbon. In organic compounds, the change from saturation to a double-bonded system is accompanied by a change in σ-hybridisation from sp^3 to sp^2, whereas in the change from (*e.g.*) PCl_3 to $POCl_3$ the change in σ-hybridisation is likely to be smaller, so that the π-bond energy is offset by a greater σ-compression energy than in carbon compounds.[112] In phosphorus compounds, therefore, $\sigma-\pi$ interaction may be very important, and the high compression-energy of an sp^3 σ-bond may explain why a $p\pi-d\pi$ bond may be both short and apparently weak.[160]

Chemical Properties of Phosphonitrilic Derivatives

Delocalisation.— As we have seen, the bond system in phosphonitrilic derivatives is composed of two parts (π and π') in both the ring and the ligands. The structural investigations allow a qualitative relative estimate of those two major contributions, but do not distinguish, for instance, between the d_{xz} and d_{yz} components of π-bonding, which are in general unequal. The relative heats of formation of $(NPCl_2)_{3,4}$ are compatible with the results of the simple theory, in which d_{xz} is dominant, but a part of the difference may arise from the greater contribution from delocalisation of the lone pairs on the nitrogen atom in the eight-membered ring. Thermochemical evidence alone does not therefore fix the relative, importance of d_{xz} and d_{yz}, or the extent of π-delocalisation, which depends on it.

Nor is other evidence decisive. The ultraviolet spectrum of a $p\pi-d\pi$ delocalised system is not expected to resemble those of benzene derivatives, because the top occupied and the bottom occupied π-levels in phosphonitrilic compounds are expected to be non-degenerate (and a transition

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[158] Springall and White, *Trans. Faraday Soc.*, 1954, **50**, 815.
[159] Prosen, Gilmont, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 65.
[160] J. C. McCoubrey, personal communication.

between them is in any case forbidden by symmetry). The spectra of the chlorides[20,161] have absorption maxima below 1850Å (but see also Krause[162]), and those of the fluorides occur at 1494 ± 5 Å for $(NPF_2)_3$ and at 1475 ± 5 Å for $(NPF_2)_4$, $\log_{10} \epsilon_{\max.} > 4$ in both cases. For $(NPBr_2)_3$, $\lambda_{\max.} = 2015$ Å, $\log_{10} \epsilon = 4{\cdot}44$, and in sulphuric acid $\lambda_{\max.} = 1930$ Å, $\log_{10} \epsilon = 4{\cdot}24$.[163] For $(NPCl_2)_3$, the interpolated value of $\lambda_{\max,}$ is 1755 Å. It is likely that the bands in all three halides are due to the same type of transition, the insensitivity to protonation, especially, suggesting excitation of halogen lone pairs.[20,161,163] A ring π–π^* transition is not ruled out,[161] though the chemical effects of ultraviolet radiation are to promote replacement of the chlorine atoms by organic groups without breaking the ring bonds.[164]

Two phosphonitrilic derivatives are magnetically anisotropic in the same sense as benzene.[165,166] The σ-anisotropy has to be estimated, and the residual ring current in $(NPCl_2)_3$, small because of the large electronegativity difference between consecutive atoms, is paramagnetic, as expected for a $p\pi$–$d\pi$ system. The result, however, is not a conclusive demonstration of cyclic delocalisation, the evidence for which consists of numerous suggestive indications from molecular structure and other physical properties rather than of assignable quantitative data. In the following sections we shall illustrate the consequences of the concepts developed above in relation to typical chemical properties of phosphonitrilic derivatives, avoiding as far as possible invoking cyclic delocalisation. It is often sufficient to regard the primary π-system as supplemented by competitive donation to phosphorus by the ring nitrogen and the ligands, the balance being influenced by inductive, conjugative, and, in some cases, steric effects.

Base Strength.—The phosphonitrilic chlorides are very weak bases. The trimer forms a complex with nitrogen dioxide,[167] and adds three molecules of sulphur trioxide[168] to give $(NPCl_2)_3,3SO_3$. The trimeric chloride also takes up two molecules of aluminium chloride,[66] but does not react with a number of transition-metal halides.[169] All the chlorides take up protons in sulphuric acid (Table 9). Electron release to phosphorus, especially by amino-groups increases the base strength considerably. In nitrobenzene, the amidophosphonitriles are stronger bases than the parent amine.[170] The relative strengths are reversed in water, because of the greater stabilisa-

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[161] Foster, Mayor, Warsop, and Walsh, *Chem. and Ind.*, 1960, 1445.
[162] Krause, *Z. Elektrochem.*, 1955, **59**, 1004.
[163] Lakatos, Hess, Holly, and Horvath, *Naturwiss.*, 1962, **21**, 493.
[164] Dishon and Hirshberg, *J. Polymer Sci.*, 1949, **4**, 75.
[165] Craig, Heffernan, Mason, and Paddock, *J.*, 1961, 1376.
[166] Bullen, *J.*, 1962, 3193.
[167] Besson and Rosset, *Compt. rend.*, 1906, **143**, 37.
[168] Goehring, Hohenschutz and Appel, *Z. Naturforsch.*, 1954, **9**b, 678.
[169] Lakatos, Bohus, and Hess, *Magyar Kem. Folyóirat*, 1961, **67**, 374.
[170] Ray and Shaw, *Chem. and Ind.*, 1961, 1173.

TABLE 9. *Number of protons taken up by the phosphonitrilic chlorides* $(NPCl_2)_n$ *in 100% sulphuric acid*[a]

n	3	4	5	6	7	8
No. of protons (cryoscopic)	1·2	2·0	2·0	2·0	2·3	2·8
No. of protons (conductimetric)	1·14	1·72	2·20	2·63	2·20	2·60

[a] D. R. Smith, unpublished work. The reason for the discrepant results for the hexameric chloride is unknown.

tion of the aminium ion by hydrogen-bonding,[171] and relative base strengths in nitrobenzene[172] are therefore a better measure of proton-accepting capacity. The conclusion[170] that protonation takes place on the ring, rather than at exocyclic positions, is supported[172a] by measurements of pK_a for the addition of a second proton to trimeric amido-derivatives.* The general interpretation is that charge is drained from exocyclic to ring nitrogen atoms *via* π-bonding between the nitrogen lone pairs and the phosphorus *d*-orbitals.[172a] There are other points of interest. The trimeric and tetrameric ethylphosphonitriles are also quite strongly basic (Table 10), like the trialkylphosphine oxides. It is also possible that the induction coefficients used[173] for correlating the strengths of substituted fatty acids are also applicable here, but with a greatly increased transmission coefficient, as a result of the polarisability of the π-system. The relative strengths of the trimeric and tetrameric compounds are also interesting. The electron density at nitrogen should be smaller in the latter compounds because of increased lone-pair delocalisation, and this is reflected in the Table in weaker basicities for the tetrameric molecules in which R = Cl, NH_2, or NHMe. The reversal in the other cases quoted may be a result of differential steric hindrance of solvation, reducing especially the base strength of the more

TABLE 10. *Base strengths of trimeric and tetrameric phosphonitrilic derivatives*[a]

	Cl	NH_2	NHMe	NMe_2	Et	Ph	OEt
p$K_a(NPR_2)_3$	$-8{\cdot}2^b$	7·65	8·8	7·6	6·4	1·5	0·20
p$K_a(NPR_2)_4$	$-8{\cdot}6^b$	7·55	8·2	8·3	7·6	2·2	0·60

[a] Feakins, Last, and Shaw, *Chem. and Ind.*, 1962, 510, Feakins, Last, Neemuchwala, and Shaw, *Chem. and Ind.*, 1963, 164, except for chlorides. Determined in nitrobenzene, except for R=NH_2, determined in water. [b] D. R. Smith, unpublished work.

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* For later work on base properties and the formation of molecular addition compounds, see Moeller and Kokalis, *J. Inorg. Nuclear Chem.*, 1963, **25**, 875; Das, Shaw, B. C. Smith, Last, and Wells, *Chem. and Ind.*, 1963, 866.

[171] Trotman-Dickenson, *J.*, 1949, 1293.

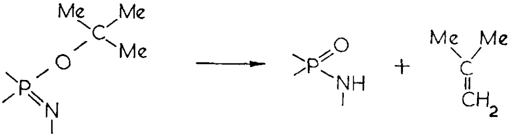
[172] (*a*) Feakins, Last, and Shaw, *Chem. and Ind.*, 1962, 510; (*b*) Feakins, Last, Neemuchwala, and Shaw, *Chem. and Ind.*, 1963, 164.

[173] Branch and Calvin, "The Theory of Organic Chemistry", Prentice-Hall, New York, 1941.

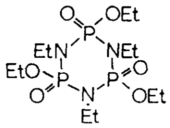
hindered trimer molecules, as proposed for the protonation of 2,6-di-t-butylpyridine.[174]

Molecular Rearrangements.—Electron release from exocyclic groups leaves them relatively electrophilic. Polymeric phosphonitrilic chloride with sodium t-butoxide gives isobutene,[23] presumably by nucleophilic attack of a ring nitrogen atom on a methyl group (XXI), and the partial rearrangement of a methyl ester (XXII) has been attributed to the electrophilic behaviour of the methyl groups. Complete rearrangements in the same sense, comparable to others in the triazine series,[46] have been achieved[175] for both trimeric and tetrameric alkyl esters. *N*-Ethyl esters of the same type have been prepared by the action of ethyl iodide on the silver salts of the acids;[176] they have singly-bonded structures (XXIII) and form stable hydrochlorides.

(XXI)



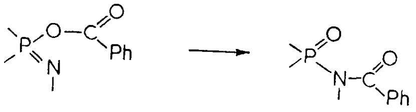
(XXII)



(XXIII)

The reaction of trimeric phosphonitrilic chloride with sodium benzoate leads to a more deep-seated rearrangement,[177] the first-formed normal benzoate apparently undergoing a tautomeric change to an *N*-benzoyl compound (XXIV). Benzoic anhydride is eliminated in a reaction with a third molecule of sodium benzoate, the final products being benzonitrile and a metaphosphate. Salts of other organic acids are also effective.[170,87c] Nitriles are also formed in a Wittig-like reaction, by the decomposition[26] of *N*-acyl-trichlorophosphinimines.

(XXIV)



$$Cl_3P{:}N{\cdot}C(O)R \rightarrow Cl_3PO + RCN \qquad (17)$$

Rates of Substitution Reactions.—The kinetics of the hydrolysis of phosphoryl halides are uniformly bimolecular,[104,119] and optical inversion, characteristics of rear-face attack at a tetrahedral centre, has been demon-

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[174] Gold, in "Progress in Stereochemistry," Butterworths, London, 1962, Vol. 3, p. 169.

[175] Fitzsimmons and Shaw, *Proc. Chem. Soc.*, 1961, 258.

[176] Rätz and Hess, *Chem. Ber.*, 1951, **84**, 889.

[177] Bezman and Reed, *J. Amer. Chem. Soc.*, 1960, **82**, 2167.

strated[178] for the analogous reaction (18). The phosphorus atoms in

$$R_1R_2P(O)OMe^* + MeO^- \rightarrow R_1R_2P(O)OMe + Me^*O^- \qquad (18)$$

phosphonitrilic compounds would be expected to be similarly electrophilic, and the orientational effects referred to earlier do not suggest any important difference in mechanism. Kinetic information is given in Table 11.

TABLE 11. *Kinetics of substitution reactions of phosphoryl and phosphonitrilic derivatives*

Compound	Reagent	Solvent	Temp.	Kinetic parameters		Ref.
				E(kcal./mole)	$\log_{10}A$	
$Et_2P(O)Cl$	H_2O	Acetone	various	7·3	5·5	*a*
$(MeO)EtP(O)Cl$	,,	,,	,,	8·4	5·3	,,
$(MeO)_2(P(O)Cl$	,,	,,	,,	10·6	5·3	,,
$(NPCl_2)_3$	Cl^-	Acetonitrile	0—35°	18·3	12·1	*b*
$(NPCl_2)_4$	,,	,,	,,	16·3	12·0	,,
$(NPCl_2)_5$	,,	,,	,,	17·0	11·9	,,
$(NPCl_2)_6$	,,	,,	,,	16·3	11·2	,,
$(NPCl_2)_3$	Aniline	Ethanol–benzene	34·5°	$k_2 = 1{\cdot}48 \times 10^{-3}$ l.mole^{-1}sec^{-1}		*c*
,,	Ethanol	,, ,,	,,	$k_2 = 0{\cdot}01 \times 10^{-3}$ l.mole.$^{-1}$sec.$^{-1}$		,,
,,	Piperidine	Toluene	0°	$k_2 = 2{\cdot}2 \times 10^{-3}$ l.mole.$^{-1}$sec.$^{-1}$		*d*
				$k_3 = 1{\cdot}7$ l.^{2}mole^{-2}sec.$^{-1}$		,,
,,	,,	Catalysis by tri-n-butylamine		$k_3 = 1{\cdot}4 \times 10^{-2}$ l.^{2} mole^{-2}sec.$^{-1}$		

[a] Hudson and Keay, *J.*, 1960, 1859. [b] Sowerby, personal communication. [c] Bailey and Parker, *Chem. and Ind.*, 1962, 1823. [d] Capon, Hills, and Shaw, *Proc. Chem. Soc.*, 1962, 390.

The rate of the bimolecular reaction of trimeric phosphonitrilic chloride with bases increases in the order ethanol<aniline<piperidine<chloride ion. The smallness of the discrimination between ethanol and aniline,[179] as compared with the similar reaction of picryl chloride, shows that bond-breaking is more important in the transition state in the phosphonitrile. This finding is supported[179] by the unreactivity of the trimeric fluoride to nucleophilic attack.[91b] On the other hand, the importance of a pentacoordinated complex in the transition state is suggested by the reaction of the trimeric chloride with trimethylamine, in which methyl chloride is eliminated,[180] and, especially, by the strong catalysis of its reaction with piperidine by tri-n-butylamine and by piperidine itself.[181] The two results are not incompatible. Hudson and Keay[104] have pointed out that the transition-state structures in acylation and phosphylation are different,

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[178] Green and Hudson, *Proc. Chem. Soc.*, 1962, 307.

[179] Bailey and Parker, *Chem. and Ind.*, 1962, 1823.

[180] Burg and Caron, *J. Amer. Chem. Soc.*, 1959, **81**, 836.

[181] Capon, Hills, and Shaw, *Proc. Chem. Soc.*, 1962, 390.

being based respectively on sp^3 and sp^3d hybrids, bond-breaking being more important in the latter case, and a similar argument would apply to comparative substitution in the aromatic and phosphonitrilic series.

The participating *d*-orbital may come from either the π' or the π set. Bailey and Parker suggest the former (d_{xy}), reaction involving the flank attack established for the hydrolysis of a silyl hydride.[182] Alternatively, if d_{yz} is used, the reaction should proceed by inversion.

In this connection, Sowerby's results (Table 11) on the exchange of radioactive chloride ion with a series of phosphonitrilic chlorides are interesting. Electron density at phosphorus is expected to increase with increase in ring size (*a*) because of the increased π-delocalisation energy and (*b*) because of increased delocalisation of electrons of nitrogen. The NMR evidence (Fig. 7) is in agreement with this. Further, on the basis of the crystal structure determination,[183] steric hindrance (by a chlorine atom on an adjacent phosphorus atom) to rear-face attack is greater in the tetrameric than in the trimeric chloride. On all counts, the reactivity of the tetramer should be the less, and yet general experience, now reinforced by a preliminary estimate of relative rates[181] and the determination of activation energies (Table 11) shows that it is usually greater. Similar difficulties exist for the hypothesis of flank attack. Although steric effects no longer favour the trimer, a decrease in activation energy from trimer to tetramer is difficult to understand.

The explanation is probably that the reactions do proceed *via* inversion, the sp^3d transition state involving deformation of the ring, reactivity being dependent on ring flexibility. We have already seen that the near-equality of π- and π'-bonding in $(NPCl_2)_4$ allows an easy conversion between tub (S_4) and chair (C_{2h}) configurations, access of a reagent to the phosphorus centre being particularly easy in the latter case. This concept adds a dynamic steric effect to the static effects already suggested[54] to account for the slowness of successive substitution by bulky amines.*

Molecular flexibility, induced especially by electronegative ligands, arises from delocalisation of electrons on nitrogen, and is of two types. Resistance to angular deformation is decreased, so that increase of angle at nitrogen is expected to be accompanied by decrease of deformation constant. Also, insofar as the local ring configuration approximates to planarity, the delocalised electrons tend to occupy the π'-orbitals of phosphorus, so reducing the inequality of π- and π'-bonding and, with it, the torsional rigidity of the P–N bond. In the trimeric molecules, in which delocalisation of nitrogen electrons and π'-bonding are restricted geometrically, deformability is least, and the activation energy for displacement reactions greatest.

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* Steric effects of the type discussed above have been recognised by Moeller and Kokalis (*J. Inorg. Nuclear Chem.*, 1963, **25**, 1397) in the relative rates of aminolysis of trimeric and tetrameric phosphonitrilic fluorides, chlorides and bromides.

[182] Sommer, Bennett, Campbell, and Weyenberg, *J. Amer. Chem. Soc.*, 1957, **79**, 3295.

[183] Hazekamp, Migchelsen, and Vos, *Acta Cryst.*, 1962, **15**, 539.

There are no direct measurements of deformation or torsional constants. The small dipole moments of cyclic phosphonitrilic halides[162,184] prevent a measurement of molecular relaxation time from dielectric absorption measurements,[184] though, to take the extreme case, the infrared spectra of the fluorides and the absence of configurational isomerism[94,146] both suggest that the life-time of any particular configuration is short. Activation volumes for viscous flow are small and even less dependent on ring size[94] than for the cyclic dimethylsiloxanes.[185]

Polymerisation.—The extent of lone-pair delocalisation also has an important effect on polymerisability. It is well known[3] that the cyclic chlorides polymerise on heating to about 300° to a solid with the mechanical properties of natural rubber,[186] though if the material is pure enough, polymerisation is extremely slow.[187] The fluorides[91a] and bromides[40c,d] also polymerise, as do the isothiocyanates,[90] at a much lower temperature (150°). The kinetics of the polymerisation of the trimeric chloride have been investigated by several authors.[188] The trimeric chloride polymerises more rapidly than the tetramer,[188c] the rate being proportional to the concentration of trimer. The reaction is catalysed by metals and by oxygen-containing organic compounds, benzoic acid being especially effective. It seems likely that the mechanism is the same in each case, and it has been suggested[188e] that a chloride ion is first detached, propagation occurring by the attack of a linear species $P_3N_3Cl_5^+$ on the cyclic trimer. A similar ionisation has been proposed[189] to account for the semiconductivity of the trimeric chloride. Radicals appear to play only a small part in polymerisation, which results neither from high-energy electrons[190] nor from γ-radiation,[191] though 50kv X-rays are more effective, especially just below the melting point.[192] Some molecular chlorine is released from the trimeric chloride, and a little nitrogen from larger-ring compounds.[190] Irradiation of trimeric phosphonitrilic chloride in solution in butanol by high-energy electrons causes esterification, without appreciable increase in degree of polymerisation.[193] Graft copolymers have been prepared by irradiation of the phosphonitrilic chloride polymer together with styrene,[194] the product having a reduced susceptibility to hydrolysis.

[184] Corfield, *J.*, 1962, 4258.

[185] Gee, *Proc. Chem. Soc.*, 1957, 111.

[186] Meyer, Lotmar, and Pankow, *Helv. Chim. Acta*, 1936, **19**, 930.

[187] Colclough, personal communication.

[188] (*a*) Patat and Kollinsky, *Makromol. Chem.*, 1951, **6**, 292; (*b*) Patat and Frömbling, *Monatsh.*, 1955, **86**, 718; (*c*) Patat and Derst, *Angew. Chem.*, 1959, **71**, 105; (*d*) Konecny and Douglas, *J. Polymer Sci.*, 1959, **36**, 195; (*e*) Konecny, Douglas, and Gray, *J. Polymer Sci.*, 1960, **42**, 383.

[189] Eley and Willis, *J.*, 1963, 1534.

[190] Spindler and Vale, *Makromol. Chem.*, 1961, **43**, 232.

[191] Manley, *Nature*, 1959, **184**, 899.

[192] Caglioti, Cordischi, and Mele, *Nature*, 1962, **195**, 491.

[193] Spitzyn, Afanasieva, Rikaev, Kolli, and Glazunov, *Doklady Akad. Nauk S.S.S.R.* 1960, **131**, 1106.

[194] Spindler and Vale, *Makromol. Chem.*, 1961, **43**, 237.

The difference (1·7 kcal./mole) between the energies of activation for polymerisation[195] (24·3 kcal./mole) and depolymerisation[188c] (26·0 kcal./mole) agrees with a direct determination of the heat of polymerisation of the trimeric chloride by differential thermal analysis[196] (Table 12). Depolymerisation of polyphosphonitrilic chloride begins at about 350°C,

TABLE 12. *Heats of polymerisation of phosphonitrilic chlorides*

	$(NPCl_2)_3$	$(NPCl_2)_4$	$(NPCl_2)_5$	$(NPCl_2)_6$
$-\Delta H_{lc}$ $1/n$ $(NPCl_2)_n$ (kcal./mole)	0·46	0·22	0·16	0·04

and an equilibrium between the cyclic molecules is believed to be set up at 600°C, though no quantitative information is available.[197] The molecular weights of different samples of polyphosphonitrilic chloride have been estimated in many ways. Typical values are $3{\cdot}7 \times 10^4$ (from elastic constants)[198] and $31{\cdot}7 \times 10^4$ (from light-scattering measurements).[199] The polymer has a helical structure,[186] which a recent structure determination[200] shows to be nearly flat (Fig. 10). Intramolecular steric interactions between PCl_2 groups are much reduced as compared with the tetrameric chloride, so that the small excess of π- over π′-bonding is sufficient to bring the chain close to planarity, the torsion angles about N–P and P–N bonds being alternatively 14° and 156°, a mismatch of 10°. The high polymer is much more reactive to water and other nucleophiles than the cyclic polymers, presumably because of its open structure and ease of deformation. The initial rate of hydrolysis in aqueous acetone is of the first-order with respect to the polymer,[201] the rate constant at 25°C being $(5{\cdot}48 \pm 0{\cdot}28) \times 10^{-3}$ min.$^{-1}$

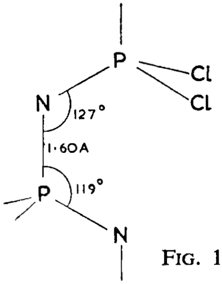

FIG. 10

It is striking that, apart from the isothiocyanates, which may polymerise through the ligands, the only phosphonitrilic derivatives to polymerise

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[195] Gimblett, *Polymer*, 1960, **1**, 418.
[196] Jacques, unpublished work.
[197] Schmitz-Dumont, *Angew. Chem.*, 1939, **52**, 498; *Z. Elektrochem.*, 1939, **45**, 651.
[198] Specker, *Z. anorg. Chem.*, 1950, **263**, 133; *Angew. Chem.*, 1953, **65**, 299.
[199] Knoesel, Parrod, and Benoit, *Compt. rend.*, 1960, **251**, 2944.
[200] Giglio, Pompa, and Ripamonti, *J. Polymer Sci.*, 1962, **59**, 293.
[201] Gimblett, *Trans. Faraday Soc.*, 1960, **56**, 528.

on heating are the halides. This may result from the strong inductive influence of the halogens, an appreciable part of the heat of polymerisation of (especially) the trimeric molecules coming from the opening of the ring angle at nitrogen and delocalisation of its lone pair. Less electronegative ligands, and especially electron-releasing groups, tend to prevent delocalisation of electrons from nitrogen, and reduce the difference between units in the trimer and the high polymer, so that the heat of polymerisation may be inadequate to compensate for the loss of translational entropy. High polymers prepared at low temperatures (*e.g.*, by the azide method) may therefore be thermodynamically unstable, even with high bond energies, and may depend on kinetic factors to ensure stability at moderate temperatures. Similar views have been expressed by Burg.[202]

Applications to Other Molecules

The importance of $p\pi$–$d\pi$ bonding in other compounds of silicon, phosphorus, and sulphur has often been pointed out, and the structural evidence for a double π-system in many of them, both linear and cyclic, has been reviewed by Cruickshank.[106]

Compounds of sulphur and nitrogen include many with formally alternating double and single bonds, which are in this respect analogous to phosphonitrilic compounds. The results of three recent structure determinations are shown in Fig. 11. In both trithiazyl chloride and α-sulphanuric chloride all the ring bonds are equal in length, consistent with at

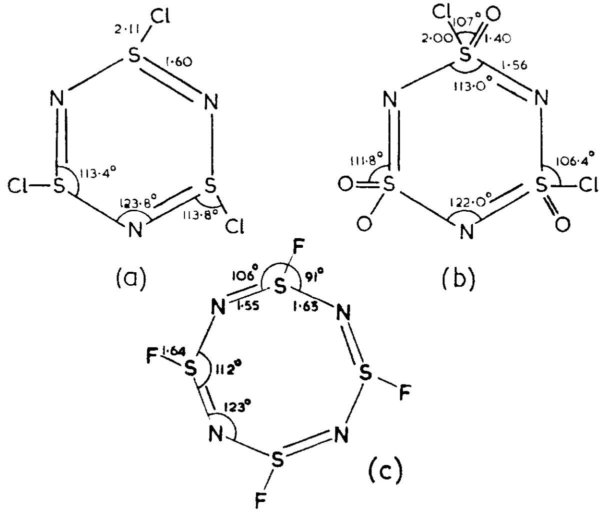

FIG. 11. *Structures of* (*a*) *trithiazyl chloride,*[a] (*b*) α*-sulphanuric chloride,*[a,b] *and* (*c*) *tetrathiazyl fluoride.*[c]
[a] Wiegers and Vos, *Proc. Chem. Soc.*, 1962, 387; [b] Bannister and Hazell, *Proc. Chem. Soc.*, 1962, 282; [c] Wiegers and Vos, *Acta Cryst.*, 1961, **14**, 562.

[202] Burg, *J. Chem. Educ.*, 1960, **37**, 482.

least partial cyclic delocalisation, and are shorter in the latter molecule; an oxygen atom doubly-bonded to sulphur or phosphorus is especially effective in polarising *d*-orbitals.[203] The ring angle at sulphur is kept small in the thiazyl compound by the lone pair on sulphur, which also prevents delocalisation of the nitrogen lone pair, and in α-sulphanuric chloride by the concentration of electrons in the exocyclic double bonds. Here, too, the angle at nitrogen is small, perhaps because the environment of sulphur is nearly regular tetrahedral, and the $d\epsilon$ orbitals which would be used by the electrons delocalised from nitrogen are only weakly π-bonding.[106] The ring is therefore non-planar, with symmetry close to C_{3v}. In tetrathiazyl fluoride, the local geometry at both sulphur and nitrogen is very similar to that in the first two compounds, but the symmetry of the configuration (S_4), while minimising repulsive interactions, also ensures that π-interactions, and consequently bond lengths, alternate round the ring; the difference from (*e.g.*) tetraphosphonitrilic chloride may arise because the lone pair on sulphur prevents delocalisation of the lone pairs on nitrogen.[126]

In other molecules, notably polyphosphates and siloxanes, development of π-character in the skeletal bonds requires delocalisation of lone pairs, is therefore weaker, and is more sensitive to extramolecular influences. The trimetaphosphate anion is chair-shaped, its symmetry being close to C_{3v} (Fig. 12). The tetrametaphosphate ion in the monoclinic form of $Na_4P_4O_{12}$, $4H_2O$ is chair-shaped, nearly C_{2h}, a symmetry required by the space-group for ammonium tetrametaphosphate.[204] Like the tub, the chair configuration is well adapted to minimising exocyclic repulsive interactions, here of PO_2^- groups, but its symmetry is too low for equalisation of π-interactions round the ring (Fig. 9), so that the bond lengths are unequal in pairs[126] (Fig. 12).

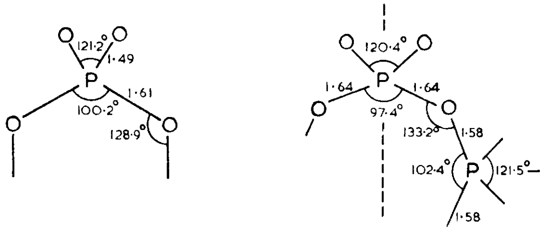

FIG. 12. *Structures of the anions in* $LiK_2P_3O_9,H_2O^a$ *and in monoclinic* $Na_4P_4O_{12},4H_2O.^b$
[a] Eanes and Ondik, *Acta Cryst.*, 1962, **15**, 1280; [b]Ondik, Block and MacGillavry, *Acta Cryst.*, 1961, **14**, 555.

In a second (triclinic) modification of $Na_4P_4O_{12},4H_2O$, in which the anion is similarly chair-shaped, the ring bonds are more nearly equal.[205] While the reason for the difference is still unexplained, it is known that the

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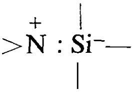
[203] K. A. R. Mitchell, Thesis, Univ. of London, 1963.
[204] Romers, Ketelaar, and MacGillavry, *Acta Cryst.*, 1951, **4**, 114.
[205] H. M. Ondik, personal communication.

more highly charged cupric and magnesium ions cause an inversion to the D_{2d} symmetry characteristic of stronger π-bonding,[206] and it is possible that a change of cation arrangement in the sodium tetrametaphosphates may alter the π/π' ratio without change of configuration.

A description of the bonds in metaphosphates in these terms is still incomplete, however, because it does not account for the instability of a polyphosphate chain as compared with trimetaphosphate at ordinary temperatures.[79] The high polymer is stable only above the melting point of trimetaphosphate, and must therefore be formed from it endothermically, contrary to expectation for simple $p\pi$–$d\pi$ bonding. The ring angle at phosphorus in the trimetaphosphate ion, however, is smaller than in phosphonitrilic structures, so permitting some delocalisation of the lone pairs on the ring oxygen atoms, and more effective use of the $d_{x^2-y^2}$ orbital, with a pattern of π-electron energies like $p\pi$–$p\pi$ interaction (Fig. 3). Such interaction would stabilise, especially, the six-membered ring.

There is extensive stereochemical evidence for $p\pi$–$d\pi$ contributions to the bonding in simple compounds in which silicon is bound to a more electronegative element carrying lone pairs; the planarity and low basicity of trisilylamine[207] and the linearity of silyl isothiocyanate[208] are well known, each being consistent with some contribution from forms like (XXV). Similarly, ∠SiNC is large (130 ± 5°) in $Me_3SiNHMe$.[209] Comparative values of bond angles are given in Table 13. The possible tendency towards an expansion of the central valency angle, from propane to dimethyl ether, as a result of increased bond polarity, is counteracted by the increased repulsion from the unshared pairs on the central atom.[210]



$$>\overset{+}{N} : \overset{|}{\underset{|}{Si}}{}^{-}\text{—}$$

(XXV)

TABLE 13. *Bond angles and force constants in some compounds of carbon and silicon*

	$MeCH_2Me$	$MeNHMe$	$MeOMe$
∠CXC[a]	111·5°	111°	111°
	$Me_3SiCH_2SiMe_3$	$Me_3SiNHSiMe_3$	$Me_3SiOSiMe_3$
∠SiXSi[b]	120°	131°	150°
$\frac{\text{Deformation const. SiXSi}}{\text{Stretching const. Si–X}}$	0·051	0·031	0·021

[a] From Ref. 101. [b] Bond angles and force constants estimated from vibrational spectra (Kriegsmann, *Z. Elektrochem.*, 1957, **61**, 1088). Owing to the simplicity of the assumed force field, the results for the silicon compounds are approximate only.

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[206] Steger and Simon, *Z. anorg. Chem.*, 1958, **294**, 1; Steger, *ibid.*, p. 146.

[207] Hedberg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491.

[208] Jenkins, Kewley, and Sugden, *Proc. Chem. Soc.*, 1960, 220.

[209] Roper and Wilkins, *Trans. Faraday Soc.*, 1962, **58**, 1686.

[210] Dickens and Linnett, *Quart. Rev.*, 1957, **11**, 291; Gillespie and Nyholm, *ibid.*, p. 339; Gillespie, *J. Amer. Chem. Soc.*, 1960, **82**, 5978.

Partial delocalisation of the lone pairs into the acceptor orbitals of silicon decreases the deformation constant and increases the bond repulsion, especially because the asymmetry of the $p\pi$–$d\pi$ bond (Fig. 1b) concentrates electron density near the central atom. The effect of relative electronegativity on bond angles in ring and chain molecules[211] in which Si, P, S alternate with C, N, or O is therefore indirect, and it is possible to understand on this basis why E(Si–O) in hexamethylcyclotrisiloxane $(Me_2SiO)_3$ is hardly larger (108 kcal.)[212] than would be expected for a single bond, even though [213]$\angle$SiOSi = 136°, indicating appreciable lone-pair delocalisation. It is also understandable that this angle increases[214] in the centrosymmetrical octamethylcyclotetrasiloxane to an average of 142·5° without the attachment of electronegative ligands, and that the increase is accompanied by an increased bond strength [$\Delta H_{\text{pol.}}(Me_2SiO)_3 = -3{\cdot}5$ kcal./mole;[215] $\Delta H_{\text{pol.}}(Me_2SiO)_4 \sim 0$[216]] and a decreased base strength.[217]

Because of the tendency of the oxygen atom to localise the π-bonding pairs close to itself, these effects, which are similar to those found in a comparison of trimeric and tetrameric phosphonitrilic derivatives, are probably better regarded as due to lower steric strain in the larger molecules; certainly the comparative thermochemistry[218] and base strengths[217] of cyclic and linear siloxanes are consistent with this view, the weakness of π-bonding in $(Me_2SiO)_4$ being confirmed by the small average ring angle at silicon (109°).[214] Although they have the same origin, and their qualitative effects are similar, π-bonding and steric strain are distinct, the balance between them depending on relative electronegativity. In silicates, as in phosphates, the nature of the cation has important effects on the distribution of π-electrons.[219]

These examples show that the concepts of d-orbital interaction developed especially in connection with phosphonitrilic chemistry are relevant to other compounds of silicon, phosphorus, and sulphur, and often show up their chemistry in a new light. There is a useful gain in coherence that leads to an indication of areas of new experiment, especially in those cases where the relation between structure and reactions is still imperfectly understood.

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[211] Liebau, *Acta Cryst.*, 1961, **14**, 1103.
[212] Tanaka, Takahashi, Okawara, and Watase, *Bull. Chem. Soc., Japan*, 1955, **28**, 15.
[213] Peyronel, *Atti. Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1954, **16**, 231.
[214] Steinfink, Post, and Fankuchen, *Acta Cryst.*, 1955, **8**, 420.
[215] Piccoli, Haberland, and Merker, *J. Amer. Chem. Soc.*, 1960, **82**, 1883.
[216] A. J. Barry, personal communication.
[217] West, Whatley, and Lake, *J. Amer. Chem. Soc.*, 1961, **83**, 761.
[218] Tanaka, *Bull. Chem. Soc. Japan*, 1960, **33**, 282.
[219] Noll, *Angew. Chem. Int. Edn.*, 1963, **2**, 73.