The dihydrate of the tetramer is particularly stable and is, in fact, the bishydroxonium salt of tetrametaphosphimic acid $[H_3O]_2^+[(NH)_4P_4O_6(OH)_2]^{2-}$ the anion of which has a boat configuration and is linked by short H bonds (246 pm) into a two-dimensional sheet (Fig. 12.29). The related salts $M_4^I[NHPO_2)_4].nH_2O$ show considerable variation in conformation of the tetrametaphosphimate anion, as do the 8-membered heterocyclic tetraphosphazenes $(NPX_2)_4$ (p. 537), e.g.

$[NH_4]_4[N_4H_4P_4O_8].2H_2O$ boat conformation

$K_4[N_4H_4P_4O_8].4H_2O$ chair conformation

$Cs_4[N_4H_4P_4O_8].6H_2O$ saddle conformation.

Figure 12.29   Schematic representation of the boat-shaped anion $[(NH)_4P_4O_6(OH)_2]^{2-}$ showing important dimensions and the positions of H bonds.

Applications. Many applications have been proposed for polyphosphazenes, particularly the non-cyclic polymers of high molecular weight, but those with the most desirable properties are extremely expensive and costs will have to drop considerably before they gain widespread use (cf. silicones, p. 365). The cheapest compounds are the chloro series $(NPCl_2)_n$ but these readily hydrolyse in moist air to polymetaphosphimic acids. Greater stability is displayed by amino, alkoxy, phenoxy and especially fluorinated derivatives, and these are attracting increasing interest as rigid plastics, elastomers, plastic films, extruded fibres and expanded foams.[160,170] Such materials (MW >500 000) are water-repellent, solvent-resistant, flame-resistant and flexible at low temperatures (Fig. 12.30). Possible applications are as fuel hoses, gaskets and O-ring seals for use in high-flying aircraft or for vehicles in Arctic climates. Their extraordinary dielectric strength makes them good candidates for metal coatings and wire insulation. Other applications of polyphosphazenes include their use to improve the high-temperature properties of phenolic resins and their use as composites with asbestos or glass for non-flammable insulating material. Some of the more reactive derivatives have been proposed as pesticides and even as ultra-high capacity fertilizers.

12.3.8 Organophosphorus compounds

A general treatment of the vast domain of organic compounds of phosphorus[171] falls outside the scope of this book though several important classes of compound have already been briefly mentioned, e.g. tertiary phosphine ligands (p. 494), alkoxyphosphines and their derivatives (p. 496), organophosphorus halides (p. 500), phosphate esters in life processes (p. 528) and organic derivatives of PN compounds (preceding section). There are also innumerable organic derivatives of the polycyclic polyphosphanes (p. 495),[67,70,172] and vast numbers of heterocyclic organophosphorus

[170] H. R. ALLCOCK, *Sci. Progr. Oxf.* **66**, 355–69 (1980).

[171] R. S. EDMONDSON (ed.) *Dictionary of Organophosphorus Compounds*, Chapman and Hall, New York, 1988, 1347 pp.

[172] G. FRITZ, H.-G. VON SCHERING *et al.*, *Z. anorg. allg. Chem.* **552**, 34–49 (1987); **584** 21–50, 51–70 (1990); **585**, 51–64 (1990); **595**, 67–94 (1991); and references cited therein.

Figure 12.30   Potential uses of polyphosphazenes: (a) A thin film of a poly(aminophosphazene); such materials are of interest for biomedical applications. (b) Fibres of poly[bis(trifluoroethoxy)phosphazene]; these fibres are water-repellant, resistant to hydrolysis or strong sunlight, and do not burn. (c) Cotton cloth treated with a poly(fluoroalkoxyphosphazene) showing the water repellancy conferred by the phosphazene. (d) Polyphosphazene elastomers are now being manufactured for use in fuel lines, gaskets, O-rings, shock absorbers, and carburettor components; they are impervious to oils and fuels, do not burn, and remain flexible at very low temperatures. Photographs by courtesy of H. R. Allcock (Pennsylvania State University) and the Firestone Tire and Rubber Company.

compounds.[173,174] Within the general realm of organic compounds of phosphorus it is convenient to distinguish organophosphorus compounds as a particular group, i.e. those which contain one or more direct P–C bond. In such compounds the coordination number of P can be 1, 2, 3, 4, 5 or 6 (p. 484). Examples of coordination number 1 were initially restricted to the relatively unstable compounds HCP, FCP and MeCP (cf. HCN, FCN and MeCN). HC≡P was first made in 1961 by subjecting PH$_3$ gas at 40 mmHg pressure to a low-intensity rotating arc struck between graphite electrodes;[175] it is a colourless, reactive gas, stable only below its triple point of −124° (30 mmHg). Monomeric HCP slowly polymerizes at −130° (more rapidly at −78°) to a black solid, and adds 2HCl at −110° to give MePCl$_2$ as the sole product. Both monomer and polymer are pyrophoric in air even at room temperature. More recently[176] MeCP was made by pyrolysing MeCH$_2$PCl$_2$ at 930° in a low-pressure flow reactor and trapping the products at −78°. Dramatic stabilization of a phospha-alkyne has been achieved by η^2-complexation to a metal centre:[177]

$$\text{Bu}^t\text{C}{\equiv}\text{P} + [\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2] \xrightarrow[\text{room temp}]{\text{C}_6\text{H}_6} \text{C}_2\text{H}_4$$

$$+ [\text{Pt}(\eta^2\text{-Bu}^t\text{CP})(\text{PPh}_3)_2].\text{C}_6\text{H}_6$$

The translucent, cream-coloured benzene solvate was characterized by single-crystal X-ray analysis and by ^{31}P nmr spectroscopy. The first free phospha-alkyne stable to polymerization was Bu^{t}C≡P,[178] and its chemistry has been extensively investigated.[179,180] The similarly bulky ArC≡P (Ar = 2,4,6,-Bu$^t_3$C$_6$H$_2$) has been studied by X-ray crystallography[182] and the C–P distance found to be 152 pm, similar to the short C–P distance of 154 pm deduced from the microwave spectrum of HCP and MeCP. The most studied reactions of phospha-alkynes are cyclo-additions to give organo-P heterocycles,[179−181] and reactions with nucleophiles to give phospha-alkenes and 1,3-diphosphabutadienes.[182]

As with coordination number 1, the first 2-coordinate P compound also appeared in 1961:[183] Me$_3$P=PCF$_3$ was made as a white solid by cleaving cyclo-[P(CF$_3$)]$_4$ or 5 with PMe$_3$; it is stable at low temperatures but readily dissociates into the starting materials above room temperature. More stable is the bent 2-coordinate phosphocation occurring in the orange salt[184]

The aromatic heterocycle phosphabenzene C$_5$H$_5$P (analogous to pyridine) was reported in 1971,[185] some years after its triphenyl derivative 2,4,6-Ph$_3$C$_5$H$_2$P. See also HP=CH$_2$[29] and [P(CN)$_2$]$^{-}$[30] (p. 484). The burgeoning field of heterocyclic phosphorus compounds featuring

[173] E. FLUCK and B. NEUMÜLLER, in H. W. ROESKY (ed.), *Rings, Clusters and Polymers of Main Group and Transition Metals*, Elsevier, Amsterdam, 1989, pp. 193–5.

[174] A. SCHMIDPETER and K. KARAGHIOSOFF, in H. W. ROESKY (ed.), *Rings, Clusters and Polymers of Main Group and Transition Metals*, Elsevier, Amsterdam, 1989, pp. 307–43.

[175] T. E. GIER, *J. Am. Chem. Soc.* **83**, 1769–70 (1961).

[176] N. P. C. WESTWOOD, H. W. KROTO, J. F. NIXON and N. P. C. SIMMONS, *J. Chem. Soc., Dalton Trans.*, 1405–8 (1979).

[177] J. C. T. R. BURKETT-ST. LAURENT, P. B. HITCHCOCK, H. W. KROTO and J. F. NIXON, *J. Chem. Soc., Chem. Commun.*, 1141–3 (1981).

[178] G. BECKER, G. GRESSER and W. UHL, *Z. Naturforsch., Teil B* **36**, 16 (1981).

[179] J. F. NIXON, *Chem. Rev.* **88**, 1327–62 (1988).

[180] M. REGITZ, *Chem. Rev.* **90**, 191–213 (1990). See also M. REGITZ and O. J. SCHERER, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Georg Thieme Verlag, Stuttgart, (1990).

[181] R. BARTSCH and J. F. NIXON, *Polyhedron*, **8**, 2407 (1989).

[182] A. M. ARIF, A. F. BARRON, A. H. COWLEY and S. W. HALL, *J. Chem. Soc., Chem. Commun.*, 171–2 (1988).

[183] A. BURG and W. MAHLER, *J. Am. Chem. Soc.* **83**, 2388–9 (1961).

[184] K. DIMROTH and P. HOFFMANN, *Chem. Ber.* **99**, 1325–31 (1966); R. ALLMANN, *Chem. Ber.* **99**, 1332–40 (1966).

[185] A. J. ASHE, *J. Am. Chem. Soc.* **93**, 3293–5 (1971).

2-coordinate and 3-coordinate P has been fully reviewed,[173,174] as has the equally active field of phospha-alkenes $\left(-P{=}C\!\!\!\diagdown\right)$ and diphosphenes $(-P{=}P-)$.[179,180,186,187]

The most common coordination numbers for organophosphorus compounds are 3 and 4 as represented by tertiary phosphines and their complexes, and quaternary cations such as $[PMe_4]^+$ and $[PPh_4]^+$. Also of great significance are the 4-coordinate P ylides† $R_3P{=}CH_2$; indeed, few papers have created so much activity as the report by G. Wittig and G. Geissler in 1953 that methylene triphenylphosphorane reacts with benzophenone to give Ph_3PO and 1,1-diphenylethylene in excellent yield.[188]

$$Ph_3P{=}CH_2 + Ph_2CO \longrightarrow Ph_3PO + Ph_2C{=}CH_2$$

The ylide $Ph_3P{=}CH_2$ can readily be made by deprotonating a quaternary phosphonium halide with *n*-butyllithium and many such ylides are now known:

$$[Ph_3PCH_3]^+Br^- \xrightarrow{\text{LiBu}^n} Ph_3P{=}CH_2$$
$$+ LiBr + Bu^nH$$

$$[PMe_4]^+Br^- + NaNH_2 \xrightarrow{\text{thf/0°}} Me_3P{=}CH_2$$
$$+ NaBr + NH_3$$

The enormous scope of the Wittig reaction and its variants in affording a smooth, high-yield synthesis of $C{=}C$ double bonds, etc., has been amply delineated by the work of Wittig

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[186] R. APPEL, F. KNOLL and I. RUPPERT, *Angew. Chem. Int. Edn. Engl.* **20**, 731–44 (1981).

[187] N. C. NORMAN, *Polyhedron* **12**, 2431–6 (1993).

† An ylide can be defined as a compound in which a carbanion is attached directly to a heteroatom carrying a high degree of positive charge:

Thus $Ph_3P{=}CH_2$ is triphenylphosphonium methylide (see pp. 274–304 of reference 2, or textbooks of organic chemistry for a fuller treatment of the Wittig reaction).

[188] G. WITTIG and G. GEISSLER, *Annalen* **580**, 44–57 (1953).

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and others and culminated in the award of the 1979 Nobel Prize for Chemistry (jointly with H. C. Brown for hydroboration, p. 166). The reaction of P ylides with many inorganic compounds has also led to some fascinating new chemistry.[189] The curious yellow compound $Ph_3P{=}C{=}PPh_3$ should also be noted:[190] unlike allene, $H_2C{=}C{=}CH_2$, which has a linear central carbon atom, the molecules are bent and the structure is strikingly unusual in having 2 crystallographically independent molecules in the unit cell which have substantially differing bond angles, 130.1° and 143.8°. The short $P{=}C$ distances (163 pm as compared with 183.5 pm for $P{-}C(Ph)$) suggest double bonding, but the nonlinear $P{=}C{=}P$ unit and especially the two values of the angle, are hard to rationalize (cf. the isoelectronic cation $[Ph_3P{=}N{=}PPh_3]^+$ which has various angles in different compounds).

Pentaorgano derivatives of P are rare. The first to be made (by G. Wittig and M. Rieber in 1948) was PPh_5:

$$Ph_3PO \xrightarrow[\text{(2) HCl}]{\text{(1) LiPh}} [PPh_4]^+Cl^- \xrightarrow{\text{HI}}$$
$$[PPh_4]^+I^- \xrightarrow{\text{LiPh}} PPh_5 \text{ (d. 124°)}$$

Unlike $SbPh_5$ (which has a square-pyramidal structure p. 598), PPh_5 adopts a trigonal bipyramidal coordination with the axial $P{-}C$ distances (199 pm) being appreciably longer than the equatorial $P{-}C$ distances (185 pm). More recently (1976) $P(CF_3)_3Me_2$ and $P(CF_3)_2Me_3$ were obtained by methylating the corresponding chlorides with $PbMe_4$. There are also many examples of 5-coordinate P in which not all the directly bonded atoms are carbon. One such is the dioxaphenylspiro-phosphorane shown in Fig. 12.31; the local symmetry about P is essentially square pyramidal, and the factors which affect the choice between this geometry and trigonal bipyramidal is a topic of active

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[189] H. SCHMIDBAUR, *Acc. Chem. Res.* **8**, 62–70 (1975).

[190] A. T. VINCENT and P. J. WHEATLEY, *J. Chem. Soc. (D), Chem. Commun.*, 592 (1971).

Figure 12.31   Schematic representation of the molecular structure of [P(C₃HMe₅)(O₂C₂H₄)Ph] showing the rectangular-based pyramidal disposition of the 5 atoms bonded to P; the P atom is 44 pm above the C_2O_2 plane.

current interest.[39,191] It should also be noted that the compounds, Ph_3PBr_2 and Ph_3PI_2, which might have been thought to involve 5-coordinate P, feature instead 4-coordinate P and an unusual end-on bonding of the dihalogen moiety, i.e. $Ph_3P-Br-Br$,[192] and Ph_3P-I-I.[193]

The corresponding interhalogen adducts Ph_3PIX (X = Cl, Br) appear to be 4-coordinate but ionic, i.e. $[Ph_3PI]^+X^-$.[194]

Many organophosphorus compounds are highly toxic and frequently lethal. They have been actively developed for herbicides, pesticides and more sinister purposes such as nerve gases which disorient, harass, paralyse or kill.[9]

[191] W. ALTHOFF,   R. O. DAY,   R. K. BROWN   and R. R. HOLMES, *Inorg. Chem.* **17**, 3265–70 (1978); see also the immediately following two papers, pp. 3270–6 and 3276–85.
[192] N. BRICKLEBANK,   S. M. GODFREY,   A. G. MACKIE, C. A. MCAULIFFE and R. G. PRITCHARD, *J. Chem. Soc., Chem. Commun.*, 355–6 (1992).
[193] S. M. GODFREY,   D. G. KELLY,   C. S. MCAULIFFE, A. G. MACKIE, R. G. PRITCHARD and S. M. WATSON, *J. Chem. Soc., Chem. Commun.*, 1163–4 (1991).

[194] K. B. DILLON and J. LINCOLN, *Polyhedron*, **8**, 1445–6 (1989).