Preparation and Donor Properties of the Cyclic Methylphosphazenes

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The cyclic methylphosphazenes $(NPMe_2)_{3-5}$ form simple salts such as $N_3P_3Me_6.HCl$, $N_4P_4Me_8.2HClO_4$, and $N_5P_5Me_{10}H_2CuCl_4.H_2O$, and complexes such as $N_4P_4Me_8.2HgCl_2$, $N_4P_4Me_8.4AgNO_3$ and $N_4P_4Me_8.HCl.CuCl_2$. All three phosphazenes form quaternary salts $N_nP_nMe_{2n}.RI$ (n = 3—5; R = Me or Et) with alkyl iodides. The iodide can be exchanged for other anions such as Cl^- or HgI_3^-; the tetramer forms a dipositive cation in $N_4P_4Me_9HZn(NCS)_4$. The phosphorus *d*-orbitals are less electronegative than they are in the halogenophosphazenes, the ring bonds are consequently weakened, and π-charge is concentrated on nitrogen. The molecular structures of $N_4P_4Me_8H^+$, $N_4P_4Me_9^+$, and $N_5P_5Me_{10}H_2^{2+}$ show that localisation of two electrons by an acceptor induces substantial bond length inequalities, with patterns expected for the perturbation of an otherwise delocalised π-system. The methylphosphazenes begin to absorb strongly near 190 nm, the band being attributable to a ring transition. Its large energy shows that the electronegativities of the phosphorus and nitrogen orbitals are appreciably different, and, as a consequence, methylphosphazenes make no significant use of antibonding orbitals in complexes with transition metals.

THE properties of the cyclic phosphazenes $(NPX_2)_n$ vary with the nature of the substituent X, and, from a theoretical point of view, the variation can be expected to depend on the characteristics of the highest occupied orbitals, which are of the π-type. The concept of a delocalised π-system in these molecules, and its treatment by simple HMO methods, has been found to be satisfactory for the interpretation not only of ionisation potentials,[1] but also, for example, of relative reaction rates [2] and orientation patterns.[3] The π-electron distribution is expected to depend on the size of the *d*-orbitals,[4] which are contracted to the maximum extent (in a neutral molecule) by fluorine, and π-electron effects are consequently most pronounced in the fluorophosphazenes $(NPF_2)_n$.[1,5] Less electronegative substituents both lengthen and weaken the ring bonds, and diminish the effect of ring size on ionisation potential; relative orbital electronegativity is perhaps the most significant single variable affecting the properties of phosphazenes. The study of alkylphosphazenes is of special interest in assessing its importance, because the substituent is comparatively electropositive, and some degree of electron localisation is to be expected. Methylphosphazenes do indeed act as donors to metal carbonyls [6,7] and metal ions,[8,9] but some characteristic π-electron effects remain. Fully alkylated phosphazenes have previously been prepared by the chloramination of dialkylchlorophosphazenes,[10] by the ammonolysis of dialkyltrichlorophosphazenes, either with [11,12] or without [6] a solvent, and by the alkylation of fluorophosphazenes,[3] but yields are not always high. Experimental detail is here added to that given in preliminary reports.[11,13]

The simple structures of the ^1H and ^{31}P n.m.r. spectra

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of $(NPMe_2)_{3-5}$ (Table 1), which are consistent with the attachment of two equivalent methyl groups to each phosphorus atom, themselves all equivalent, show that the molecules are cyclic. Confirmation for $N_4P_4Me_8$ is provided by the determination of its crystal structure,[14] which is discussed below. The vibrational spectra show features characteristic of the attachment of two methyl groups to phosphorus, specifically a doublet in the i.r. spectra corresponding to $\delta_s(CH_3)$ at 1290/1300 cm^{-1}, and another $[\delta_{as}(CH_3)]$ at 1413/1424 cm^{-1} in $N_3P_3Me_6$. The highest frequency component is split further to 1422/1430 in $N_4P_4Me_8$ and $N_5P_5Me_{10}$. Table 1 also shows how the frequency of the intense ν_{as}(PNP) band varies with ring size, and, by comparison with similar information on the fluorides and chlorides, with ligand electronegativity. The Table also includes the base strengths of the three methylphosphazenes and details of their u.v. spectra.

TABLE 1

N.m.r. parameters,[a] P–N stretching frequency, base strength, and u.v. absorption of methylphosphazenes

		$N_3P_3Me_6$	$N_4P_4Me_8$	$N_5P_5Me_{10}$
τ (J_{PH}/Hz)	CCl_4	8·70 (14·0) [b]	8·66 (12·0)	8·62 (12·4)
	D_2O	8·47 (12·0) [c]	8·53 (12·0) [d]	8·43 (12·0)
δ_P	D_2O	80·6	86·2 [e]	92·9
ν_{as}(PNP)/cm^{-1} [f]		1185 [g]	1222 [h]	1255 [i]
	pK_{BH^+} [m]	5·03	5·72	6·69 [n]
ε/l cm^{-1} mol^{-1} [p]	190 nm	6170	5740	11,800
	195	3420	4220	7140
	200	1840 (700) [q]	3040 (650) [q]	4920 (340)

[a] Dilute solutions. Reference $SiMe_4$, external (D_2O) or internal (CCl_4). Phosphorus shifts, p.p.m., relative to external P_4O_6. [b] $^4J_{PH}$ 1·2 Hz. [c] In sufficiently acid solution ($H^+/N_3P_3Me_6 > 3$) the spectrum consists of two doublets, 1 : 2, τ 7·80, J_{PH} 15·0 Hz; τ 8·20, J_{PH} 14·0 Hz, corresponding to $N_3P_3Me_6H_2^{2+}$. [d] Doublet structure persists on acidification, but the shift reaches a limit at $H^+/N_4P_4Me_8 = 2$, corresponding to $N_4P_4Me_8H_2^{2+}$; τ 8·17, J_{PH} 11·5 Hz. [e] 98·7 p.p.m. in CCl_4. [f] Dilute solutions in CCl_4. [g] $N_3P_3Cl_6$ 1218 [j], $N_3P_3F_6$ 1305 [k]. [h] $N_4P_4Cl_8$ 1315 [j], $N_4P_4F_8$ 1425/1445 [k]; in $N_4P_4Me_8,4H_2O$, ν_{as}(PNP) 1170 cm^{-1}. [i] $N_5P_5Cl_{10}$ 1367 [l], $N_5P_5F_{10}$ 1437 [l]. [j] L. W. Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403. [k] H. J. Becher and F. Seel, *Z. anorg. Chem.*, 1960, **305**, 148. [l] E. Steger and G. Mildner, *Z. Naturforsch.*, 1961, **166**, 836. [m] $\pm 0·01$. [n] $pK_{BH_2^{2+}}$ 3·97. [p] Aqueous solutions, 1—2·5 × 10^{-4}M. [q] Values in parentheses obtained with 1 equivalent of HCl. Possible small increase in the extinction coefficient of $N_3P_3Me_6$ on the addition of a second equivalent of HCl. Extinction coefficients of acidified solutions obtained at shorter wavelengths were considered to be unreliable, because of the intense charge transfer band of the Cl^- ion.

The methylphosphazenes form such simple salts as the hydrochloride, the perchlorate, and iodomercurates containing either the HgI_3^- or the HgI_4^{2-} ion. The trimer is normally a monoacidic and the tetramer and pentamer are diacidic bases. All three compounds form mono-quaternary salts with alkyl iodides. The structures of the methiodides, deduced from their n.m.r. spectra, are shown in Figure 1, which includes information on chemical shifts and coupling constants. The two methyl groups attached to a particular phosphorus atom are not differentiated magnetically, but, in view of the crystal structure determinations referred to below, the implied planarity of the $(PN)_{4,5}$ rings is evidently attained statistically. As expected, the infrared spectra of the methylphosphazenium iodides show the features expected from an N-methyl group, which are (1) the appearance of ν(CN) at 1065—1075 cm^{-1}, (2) additional $\delta(CH_3)$ bands near 1420 cm^{-1}, and (3) an additional $\rho(CH_3)$ band near 980 cm^{-1}. The chlorides and other salts were obtained from the iodides by ion exchange, and several complexes with metal salts were prepared. Crystal structures of $N_4P_4Me_8$,[14] of $N_4P_4Me_8HCuCl_3$,[9] of $(N_4P_4Me_8H)_2CoCl_4$,[15] of $N_4P_4Me_9Cr(CO)_5I$[16] and of $N_5P_5Me_{10}H_2CuCl_4,H_2O$[17] have been determined. The chemical, spectroscopic, and structural properties of the different types of molecule are interpreted with the help of a simple theoretical model.

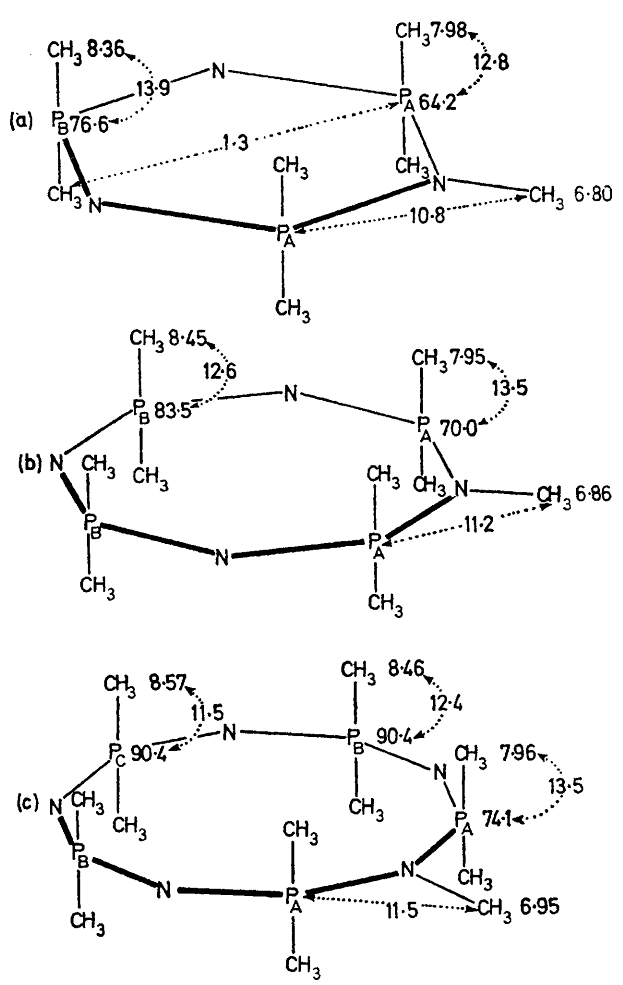

FIGURE 1 Chemical shifts of (a) $N_3P_3Me_7I$, (b) $N_4P_4Me_9I$, (c) $N_5P_5Me_{11}I$. ^1H: solutions in $CDCl_3$, internal reference tetramethylsilane. ^{31}P: solutions in D_2O, reference external P_4O_6. Individual shifts assigned by the use of selective decoupling

EXPERIMENTAL

Most n.m.r. spectra were obtained on a Varian HA100 instrument, using decoupling techniques, where appro-

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priate, developed by Dr. L. D. Hall and Mr. R. Burton (U.B.C.). The proton n.m.r. spectrum of $N_3P_3Me_7I$ in $CDCl_3$ (in which it is almost insoluble) was obtained on a Varian XL 100 instrument, using Fourier transform techniques. A Metropolitan Vickers MS9 mass spectrograph was used for the high resolution mass measurements, and a Perkin-Elmer model 457 instrument for the i.r. spectra. The u.v. spectra of solutions of the methylphosphazenes in deoxygenated water were measured on a Cary 16 spectrophotometer, the sample compartment being flushed with oxygen-free nitrogen. Base strength measurements were made by potentiometric titration of 10^{-4}M-aqueous solutions, using a Radiometer model 25 pH meter with expanded scale. p*K* Values were calculated at each of 20 points evenly spaced points within ± 2 pH units of the measured p*K*, and averaged. Microanalyses were carried out by Messrs. S. Greenfield, P. Borda, A. Bernhardt, and Dr. F Pascher.

Hexamethylcyclotriphosphazene and Octamethylcyclotetraphosphazene.—Dimethyltrichlorophosphorane (37·6 g, 0·22 mol) and ammonium chloride (15·0 g, 0·28 mol) in 250 ml *sym*-tetrachloroethane were heated under reflux until evolution of hydrogen chloride (0·64 mol, 71%) had almost ceased (2 h), and the solvent evaporated off. An i.r. spectrum of the solid product (obtained in a later experiment) showed it to contain the hydrochlorides of the cyclic compounds. The product was further heated for 7 h under reflux with chloroform (250 ml) and triethylamine (40 ml). The excess of ammonium chloride was filtered off and the solvent evaporated. The methylcyclophosphazenes (12·3 g, 73%) were extracted from the residual triethylamine hydrochloride with light petroleum. The individual compounds $(NPMe_2)_{3,4}$, in the approximate molar ratio 1 : 3, were separated by fractional crystallisation from light petroleum. The trimeric derivative $N_3P_3Me_6$ was obtained as nodular triclinic crystals,[18] m.p. 195—196° [Found: C, 31·9; H, 8·0; N, 18·6%; *M*(ebull., benzene) 226. $C_6H_{18}N_3P_3$ requires C, 32·0; H, 8·0; N, 18·7%, *M*, 225]. The tetrameric derivative $N_4P_4Me_8$ crystallised as tetragonal prisms, m.p. 163—164° (Found: C, 32·1; H, 8·1; N, 18·5%; *M*, 301. $C_8H_{24}N_4P_4$ requires *M*, 300). Both compounds are soluble in all common organic solvents, and in water, in which their molecular weights are the same as in benzene. Octamethylcyclotetraphosphazene crystallises from organic solvents containing a little water as mica-like plates of the tetrahydrate $N_4P_4Me_8,4H_2O$ (Found: C, 26·0; H, 8·7; N, 15·1; P, 33·2. $C_8H_{32}N_4O_4P_4$ requires C, 25·8; H, 8·7; N, 15·05; P, 33·3%). The i.r. spectrum of the crystals showed the ν_s,ν_{as}(OH) bands of water at 3260, 3270 cm^{-1}, and δ(OH) as a pair of lines at 1656 and 1680 cm^{-1}. The crystals were orthorhombic,[18] $a = 31{\cdot}47$, $b = 17{\cdot}78$, $c = 7{\cdot}38$ Å, space group F_{dd2} (No. 43), $Z = 8$. D_m 1·216, D_c 1·197 g ml^{-1}. They decomposed into their components above 78°. Hydrolysis of the aqueous solutions of both $N_3P_3Me_6$ and $N_4P_4Me_8$ took place on boiling the solutions, slowly when neutral, more rapidly (with the eventual formation of dimethylphosphinic acid) when acidified.

Decamethylcyclopentaphosphazene.[13]— Decafluorocyclopentaphosphazene (11·8 g, 31·5 mmol) in ether (50 ml) was cooled to −20° and added dropwise to methyl-lithium (0·325 mol) in ether (200 ml) at −35°. After completion of the reaction (40 h) at −35°, the solvent was removed and the residual solid (largely insoluble) extracted with light petroleum. Thin layer chromatography of the extract (2·8 g) on alumina showed the presence of two minor constituents and a major one; the latter was purified by repeated crystallisation from light petroleum (35°) at −10° and repeated vacuum sublimation to give 2·6 g (19·5%) of decamethylcyclopentaphosphazene, m.p. 64—65° (Found: C, 32·0; H, 8·1; N, 18·6%; *M*, 373·119. $C_{10}H_{30}N_5P_5$ requires *M*, 375·118).

Simple Salts.—Salts of $N_3P_3Me_6$ and $N_4P_4Me_8$ were prepared by standard methods. Dry hydrogen chloride was passed through a solution of $N_3P_3Me_6$ (0·480 g, 2·13 mmol) in CCl_4. The precipitated hydrochloride (0·536 g, 2·05 mmol) was filtered off and dried *in vacuo* (Found: HCl, 13·9. $C_6H_{19}ClN_3P_3$ requires HCl, 14·0%). The perchlorate was prepared by adding an excess of 60% perchloric acid to a concentrated solution of $N_3P_3Me_6$ (0·405 g, 1·8 mmol) in water. The white needles were filtered off, washed with a little methanol, and dried *in vacuo*, to give $N_3P_3Me_6,HClO_4$ (0·35 g, 1·1 mmol, 60%) (Found: $HClO_4$, 31·0. $C_6H_{19}ClN_3O_4P_3$ requires $HClO_4$, 30·9%). An iodomercurate was formed by adding a concentrated aqueous solution of K_2HgI_4 to a solution of $N_3P_3Me_6$ in water. The precipitate was filtered off and crystallised from nitromethane as pale yellow plates of $(N_3P_3Me_6H)_2HgI_4$, m.p. 206° (Found: C, 12·4; H, 3·1; I, 44·1; N, 7·1; P, 15·8. $C_{12}H_{38}I_4N_6P_6$ requires C, 12·4; H, 3·3; I, 44·7; N, 7·2; P, 16·0%).

Salts of $N_4P_4Me_8$ were prepared similarly, typically a dihydrochloride $N_4P_4Me_8,2HCl$ (Found: HCl, 19·3. $C_8H_{26}Cl_2N_4P_4$ requires HCl, 19·5%) and a diperchlorate $N_4P_4Me_8,2HClO_4$ (Found: $HClO_4$, 39·9. $C_8H_{26}Cl_2N_4O_8P_4$ requires $HClO_4$, 40·1%). An iodomercurate $(N_4P_4Me_8H_2)(HgI_3)_2$ was crystallised from nitromethane as pale yellow needles, m.p. 234° (Found: C, 6·5; H, 1·8; I, 52·2; N, 3·7; P, 8·3. $C_8H_{26}Hg_2I_6N_4P_4$ requires C, 6·6; H, 1·8; I, 52·0; N, 3·8; P, 8·5%). The pentameric methyl derivative gave a diperchlorate (Found: $HClO_4$, 34·7. $C_{10}H_{32}Cl_2N_5O_8P_5$ requires $HClO_4$, 34·9%). The i.r. spectra of the salts were generally similar to those of the parent phosphazene, with extensive band splitting. All showed broad weak bands above 3000 cm^{-1}, attributable to ν(N–H).

Quaternary Salts.[19]—Hexamethylcyclotriphosphazene (0·21 g, 0·94 mmol) was dissolved in methyl iodide and heated under reflux for 16 h. The white solid product was filtered off, washed with diethyl ether, and dried *in vacuo*, to give $N_3P_3Me_6,MeI$ (0·33 g, 0·90 mmol, 95%) (Found: C, 23·0; H, 5·6; I, 34·5; N, 11·35; P, 25·15. $C_7H_{21}IN_3P_3$ requires C, 22·9; H, 5·8; I, 34·6; N, 11·45; P, 25·3%). The ethiodide was prepared similarly (85%) (Found: C, 25·0; H, 6·0; I, 33·2; N, 11·0; P, 24·5. $C_8H_{23}IN_3P_3$ requires C, 25·1; H, 6·1; I, 33·3; N, 11·0; P, 24·4%). Octamethylcyclotetraphosphazene gave an 86% yield of $N_4P_4Me_8,MeI$ (Found: C, 24·5; H, 5·9; I, 28·8; N, 12·7; P, 27·9. $C_9H_{27}IN_4P_4$ requires C, 24·4; H, 6·1; I, 28·7; N, 12·7; P, 28·0%) and an 87% yield of $N_4P_4Me_8,EtI$ (Found: C, 26·3; H, 6·4; I, 27·8; N, 12·2; P, 27·1. $C_{10}H_{29}IN_4P_4$ requires C, 26·3; H, 6·4; I, 27·8; N, 12·3; P, 27·2%). The adduct $N_5P_5Me_{10},MeI$ (1·1 g, 80%) was prepared from decamethylcyclopentaphosphazene (1·0 g, 2·7 mmol) (Found: C, 25·5; H, 6·5; I, 24·4; N, 13·7. $C_{11}H_{33}IN_5P_5$ requires C, 25·5; H, 6·4; I, 24·6; N, 13·5%).

The adducts are all white crystalline solids, which are very soluble in polar solvents such as water or methanol,

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less so in chloroform, and insoluble in such non-polar solvents as benzene, carbon disulphide, and carbon tetrachloride. Silver iodide is precipitated quantitatively from their (conducting) aqueous solutions by silver nitrate, and they are therefore formulated as quaternary salts $(N_nP_nMe_{2n}R)^+I^-$ (R = Me or Et). They begin to decompose, without melting, near 200 °C. A sample of $N_5P_5Me_{11}I$ (0·8 g) was heated to 350 °C in an inert atmosphere; 0·17 g of a white solid was recovered from the dark product by extraction with light petroleum, and was found to consist principally of $N_3P_3Me_6$ and $N_4P_4Me_8$ in the ratio 5 : 1.

Other salts were prepared by standard methods. The chloride $N_4P_4Me_9Cl$ was obtained by passing an aqueous solution of the iodide through a column of Amberlite 1RA 400 resin loaded with chloride ion. The eluant was evaporated to give a white solid (Found: Cl^-, 10·0. $C_9H_{27}ClN_4P_4$ requires Cl^-, 10·1%). An iodomercurate $N_3P_3Me_7{}^+HgI_3{}^-$ was precipitated by the addition of a concentrated solution of K_2HgI_4 to a solution of $N_3P_3Me_7I$ (0·12 g, 0·33 mmol) in water. The pale yellow product (0·255 g, 94%) was filtered off, dried over calcium chloride *in vacuo*, and recrystallised from 90% ethanol as needles, m.p. 178° (Found: C, 10·1; H, 2·7; I, 46·5; N, 5·2; P, 11·3. $C_7H_{21}HgI_3N_3P_3$ requires C, 10·25; H, 2·6; I, 46·2; N, 5·1; P, 11·4%). The pale yellow crystalline compounds $N_3P_3Me_6EtHgI_3$ (m.p. 176°), $N_4P_4Me_9HgI_3$ (m.p. 144°), and $N_4P_4Me_8EtHgI_3$ (m.p. 123°) were obtained similarly. Isothiocyanatozincates were prepared by the addition of aqueous solutions of the quaternary iodides to acidified solutions containing zinc chloride and potassium thiocyanate. The white precipitate obtained from $N_3P_3Me_7I$ was recrystallised from water as $(N_3P_3Me_7)_2Zn(NCS)_4$, m.p. 144° (Found: C, 27·8; H, 5·3; N, 17·7; P, 21·3; S, 16·5; Zn, 8·4; NCS, 29·5. $C_{18}H_{42}N_{10}P_6S_4Zn$ requires C, 27·8; H, 5·4; N, 18·0; P, 23·9; S, 16·5; Zn, 8·4; NCS, 29·9%). Treated similarly, $N_4P_4Me_9I$ gave $N_4P_4Me_9HZn(NCS)_4$, m.p. 220° (Found: C, 25·0; H, 4·3; N, 18·3; P, 19·7; S, 20·9; Zn, 10·5; NCS, 37·6. $C_{13}H_{28}N_8P_4S_4Zn$ requires C, 25·4; H, 4·6; N, 18·2; P, 20·2; S, 20·9; Zn, 10·6; NCS, 37·7%). An attempt to prepare a corresponding hydrochloride of $N_4P_4Me_9I$ failed; the methyl iodide was displaced, and $N_4P_4Me_8,2HCl$, identified by its i.r. spectrum and by determination of the hydrogen chloride, was obtained instead. Aqueous solutions of the quaternary iodides gave precipitates with sodium tetraphenylborate, but no satisfactory solvent for recrystallisation could be found. No reaction took place, under the conditions used, between the methylphosphazenes and either methyl bromide or phenacyl bromide.

Complexes.—(a) *Mercuric chloride*. The white precipitate formed on mixing hot solutions of $N_4P_4Me_8$ and $HgCl_2$ in benzene was filtered off, washed with hot benzene, dried *in vacuo*, and recrystallised from water as $N_4P_4Me_8,2HgCl_2$, m.p. 234° (Found: C, 11·6; H, 2·7; Cl, 16·7; P, 14·7. $C_8H_{24}Cl_4Hg_2N_4P_4$ requires C, 11·4; H, 2·9; Cl, 16·8; P, 14·7%).

(b) *Silver nitrate*. The white precipitate slowly formed by mixing concentrated aqueous solutions of $N_4P_4Me_8$ and $AgNO_3$ was recrystallised from water as $N_4P_4Me_8$, $4AgNO_3$, dec. 260° (Found: C, 10·0; H, 2·4; Ag, 44·1; N, 11·5; P, 12·61. $C_8H_{24}Ag_4N_8O_{12}P_4$ requires C, 9·8; H, 2·5; Ag, 44·0; N, 11·4; P, 12·7%). Another complex $N_4P_4Me_8,2AgCO_2CF_3$ (dec. 210°) was prepared by mixing solutions of the components in benzene (Found: C, 19·2; H, 3·0; Ag, 29·1; F, 15·0; N, 7·6; P, 17·0. $C_{12}H_{24}Ag_2F_6N_4O_4P_4$ requires C, 19·4; H, 3·3; Ag, 29·1; F, 15·4; N, 7·6; P, 16·7%).

(c) *Copper*(II) *chloride*. The anhydrous salt was prepared by heating a suspension of $CuCl_2,2H_2O$ in ethyl methyl ketone. A concentrated solution of $N_4P_4Me_8$ in the same solvent was added to it, filtered, and the solvent allowed to evaporate. The yellow crystals of $N_4P_4Me_8HCuCl_3$ were dried *in vacuo*, m.p. 226° (Found: C, 20·7; H, 5·5; Cl, 22·2; N, 11·9; P, 26·4. $C_8H_{25}Cl_3CuN_4P_4$ requires C, 20·4; H, 5·4; Cl, 22·6; N, 4·9; P, 26·4%). In another experiment, a solution of $CuCl_2$ in ethyl methyl ketone was added dropwise to $N_5P_5Me_{10}$ (1·4 g, 3·7 mmol) in the same solvent until precipitation was complete. The yellow precipitate of $N_5P_5Me_{10}H_2CuCl_4,H_2O$ was filtered off and recrystallised from acetonitrile (Found: C, 19·8; H, 5·8; Cl, 23·7; N, 11·5; P, 25·2. $C_{10}H_{34}Cl_4CuN_5OP_5$ requires C, 20·0; H, 5·7; Cl, 23·6; N, 11·7; P, 25·8%).

(d) *Cobalt*(II) *chloride*. Concentrated solutions of cobalt(II) chloride and of octamethylcyclotetraphosphazene in ethyl methyl ketone were mixed, the initial precipitate filtered off, and the solvent evaporated. The composition of the product was indefinite, but in the presence of a little hydrogen chloride, pale blue crystals of $(N_4P_4Me_8H)_2CoCl_4$ were obtained (Found: C, 23·8; H, 6·4; Cl, 17·8; N, 13·8; P, 30·8. $C_{16}H_{50}Cl_4CoN_8P_8$ requires C, 23·9; H, 6·3; Cl, 17·7; N, 14·0; P, 30·9%).

DISCUSSION

The properties of methylphosphazenes, compared to those of derivatives with more electronegative substituents, depend on the fact that the methyl group is electron releasing relative to, for example, fluorine or chlorine. Determinations of the ionisation potentials of phosphazenes show that σ- and π-bonding are sufficiently distinct to be treated separately,[1] and it is to be expected that ligand electronegativity will have a smaller effect on the σ-bonds, formed mainly from *s*- and *p*-orbitals, than on the π-bonds, which depend on the sensitivity of *d*-orbitals to their electrical environment. Variation in properties is therefore likely to depend mainly on the π-electron distribution.

The expansion of the *d*-orbitals by a comparatively electropositive substituent is equivalent to a reduction in orbital electronegativity, and is expected to lead to a decrease in bond order. As in most homogeneously-substituted phosphazenes, the PN bonds in $N_4P_4Me_8$ are equal in length,[14] but are longer [1·596(5) Å] than those in $N_4P_4F_8$ [1·507(16) Å] [20] or in $N_4P_4Cl_8$ [mean 1·565(7) Å].[21] Similarly, the PN stretching frequencies (Table 1) of the methyl derivatives are lower than those of the chloride or fluoride of the same ring size, and the inference that the ring bonds in $N_3P_3Me_6$ are weaker than those in $N_3P_3Cl_6$ is supported thermochemically.[22] In an investigation of the partial methylation of octafluorocyclotetraphosphazene,[3] it was found that the progressive lengthening of the ring bonds with increased methylation was accompanied by a decrease

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in the bond angle at nitrogen, suggesting progressive localisation of electrons on nitrogen. The consequent development of significant donor properties, correlated with a reduction in bond strength, is an important part of the chemistry of the methylphosphazenes, and is discussed below.

A simple (Hückel) m.o. treatment provides further detail, by showing that bond order and π-electron density (and other properties) depend differently on relative orbital electronegativity, introduced conveniently through the parameter $\rho = (\alpha_N - \alpha_P)/\beta$, where α_N, α_P are Coulomb parameters, and β is the resonance integral, assumed (since only typical results are required) to be independent of molecular geometry. For a homomorphic [23] π-system based on a 6-membered ring, Figure 2 shows how (*a*) excess π-charge on nitrogen (*i.e.* charge in excess of the $q = 1{\cdot}0$ characteristic of equielectronegative orbitals), (*b*) two-electron localisation energy, (*c*) bond order, and (*d*) diamagnetic susceptibility, depend on ρ. It is clear that a large fraction of the maximum bond order is retained even in circumstances which concentrate most of the π-charge on nitrogen; alternatively (from the point of view of 'lone-pair delocalisation'), if two electrons are thought of as initially localised on each nitrogen atom, 80% of the maximum bond order is attained with only 19% delocalisation ($\rho = 2$), rising to 93% with 31% lone-pair delocalisation at $\rho = 1$. For relative electronegativities of a likely order, significant cyclic delocalisation and moderate π-bond orders are consequently to be expected in conjunction with π charges substantially on nitrogen, a result confirmed qualitatively by the crystal structure of $N_4P_4Me_8$ and the base strengths (Table 1).

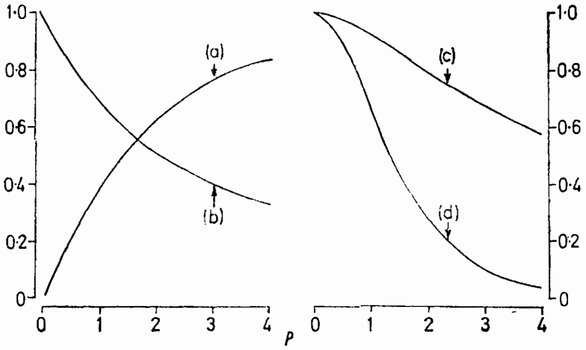

FIGURE 2 Typical π-m.o. quantities of a homomorphic $(PN)_3$ ring, as a function of the relative electronegativity parameter $\rho = (\alpha_N - \alpha_P)/\beta$, all relative to equielectronegative P and N orbitals ($\rho = 0$). (a) Excess π-charge on N, (b) 2-electron localisation energy, (c) bond order, (d) diamagnetic susceptibility

Figure 2d shows that diamagnetic susceptibility falls off very rapidly with increasing ρ, and it is not surprising that the proton shifts in the neutral phosphazenes (Table 1) are insignificantly different from those in phosphines ($PhPMe_2$, τ 8·62) [24] or phosphine oxides [$RP(O)Me_2$, τ 8·56—8·59],[25] and give no evidence of ring currents. The n.m.r. spectra of the quaternaries (Figure 1) also indicate, by comparison with those of *N*-methylpicolinium iodides,[26] that transmission of magnetic influences is more restricted in the phosphazenes. Base strengths might be expected to follow the trend of 2-electron localisation energies, either homomorphic or heteromorphic (Table 2), but they do not, because even measurements of gas-phase proton affinities would require for their interpretation a (quantitatively unknown) allowance for hybridisation changes; [27] in solution solvation effects are important,[28] and might be crucial.[29]

TABLE 2

Two-electron localisation energies [a]

	N_3P_3	N_4P_4	N_5P_5
Homomorphic	1·754	1·466	1·612
Heteromorphic	1·364	1·466	1·511

[a] Units of β; $\rho = 1$.

The u.v. spectra of the methylphosphazenes are potentially more informative. Absorption is still increasing at 186 nm, and the transition, which is not attributable to the methyl group, is clearly allowed. Although the sensitivity of the band intensity to pH suggests that the transition is centred on nitrogen, the numerical details differ in both neutral and acid solution, and the transitions cannot be regarded as simple lone pair excitations. For $N_4P_4Me_8$, the results are consistent with the scheme of Figure 3, which shows, for a single π-system in an eight-membered ring, the effect of localising two electrons on nitrogen; the minimum excitation energy is increased on protonation.

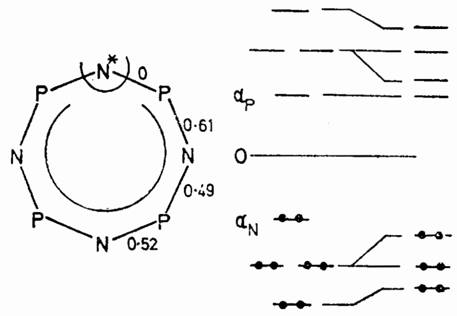

FIGURE 3 Bond orders (l.h.s.) of N_4P_4 ring in which two electrons are localised on N*, calculated for $\rho = 2$, and (r.h.s.) the changes in energy levels on localisation

As a consequence of the localisation, the orders of

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successive π-bonds are no longer equal. Quantitative detail on the interaction of methylphosphazenes with acceptors is added by the determination of the crystal structures of $N_4P_4Me_9Cr(CO)_5I$,[16] $(N_4P_4Me_8H)_2CoCl_4$,[15] $N_4P_4Me_8HCuCl_3$,[9] and $N_5P_5Me_{10}H_2CuCl_4,H_2O$.[17] A summary of structural information is given in Figure 4. If localisation on nitrogen is complete, the lengths of the ring bonds to the protonated or quaternised nitrogen atom should correspond to a single π-component, and it is noticeable that in these bonds (Figure 4a) the deficit from the 1·77 Å characteristic of a single P–N bond with no π-character[30] is approximately halved, the actual bond lengths being close to those in oxophosphazane[31] (1·663 Å) and metaphosphimate[32] (1·68 Å) structures, in which only two electrons in each monomer unit contribute to the π-bonding. In the 8-membered ring, the results of Figure 3 show that the second bond is expected to be the shortest, and the third to be intermediate between the first two, as found. The fourth should be intermediate between the second and third, and is so found to be in $N_4P_4Me_8H^+$; in $N_4P_4Me_9^+$ it is (marginally) shorter than either, possibly a reflection of (experimentally established) disorder in the crystal. The same model is applicable to the doubly protonated pentamer (Figure 4c), the π-electrons being now localised in 5-atom and 3-atom segments. The Figure shows that in this molecule also, the qualitative pattern of bond lengths is, to a first approximation, adequately described by the theoretical model. The structure of the complex $N_4P_4Me_8HCuCl_3$ (Figure 4b) has a further interest, in showing that electron localisation is less complete on co-ordination to a metal, the lower pair (1·64, 1·60 Å) being respectively shorter and longer than the upper pair (1·69, 1·56 Å). Bond length measurements therefore allow us to assess the interactions of the three acceptor groups with the $N_4P_4Me_8$ ring as $H^+ \geqslant Me^+ > CuCl_3^+$. The ready displacement of a methyl group by a proton suggests that the inequality holds.

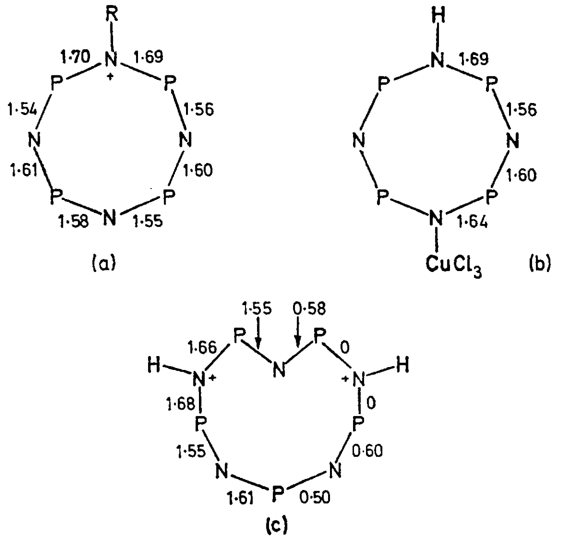

FIGURE 4 (a) (l.h.s., R = Me). Mean bond lengths in $N_4P_4Me_9^+$ [H. P. Calhoun and J. Trotter, *J.C.S. Dalton*, 1974, 377], and (r.h.s., R = H) mean bond lengths in $N_4P_4Me_8H^+$ [J. Trotter and S. H. Whitlow, *J. Chem. Soc.* (*A*), 1970, 460]. (b) Mean bond lengths in $N_4P_4Me_8HCuCl_3$ [J. Trotter and S. H. Whitlow, *J. Chem. Soc.* (*A*), 1970, 455]. (c) (l.h.s.) Lengths of bonds symmetrically related to the two protons in $N_5P_5Me_{10}H_2^{2+}$, averaged in pairs, and (r.h.s.), bond orders (ρ = 2) calculated for the localisation of two electron pairs on the N_5P_5 ring

It is an important feature of the above discussion that relative orbital electronegativity affects different molecular properties to different extents, so that, for instance, moderate base strengths, suggestive of electron localisation, are compatible with the bond length inequalities which are inter-related through delocalisation theory. As a final illustration, we can explain an important feature of the co-ordination of phosphazenes to transition metals. Since p_π–d_π interactions are important within the ring, the phosphazenes might also be π-donors to metals, through use of their acceptor levels. Even in complexes with metal carbonyls, however, the methylphosphazenes act as σ-donors.[7] The principal reason again is probably that the formally unshared electrons on nitrogen form part of the π-system, so that good base properties are achieved through small 2-electron localisation energies, a consequence of large differences in orbital electronegativity. As Figure 3 shows, and in agreement with the u.v. spectra, formation of a σ-bond to the acceptor makes the antibonding levels still less accessible. This behaviour is to be contrasted with that of such heteroaromatics as bipyridyl, in which the lone pair electrons are not involved in the π-system. The π-levels are not changed, to a first approximation, by complex formation, and the ligand can accept electrons from the metal, without significant change in its bond lengths.

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