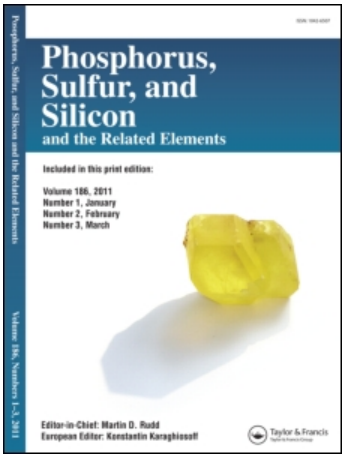

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THE PHOSPHAZENES-STRUCTURAL PARAMETERS AND THEIR RELATIONSHIPS TO PHYSICAL AND CHEMICAL PROPERTIES

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THE PHOSPHAZENES–STRUCTURAL PARAMETERS AND THEIR RELATIONSHIPS TO PHYSICAL AND CHEMICAL PROPERTIES‡

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A systematic study of crystallographic data has revealed a number of correlations between structural parameters, (e.g., bond angles, bond lengths, dihedral angles) and physical and chemical properties in phosphazenes and related compounds. These include (a) endocyclic bond angles NPN and PNP and their relationships to group electronegativities; (b) endocyclic bond angles NPN and PNP in geminal cyclotriphosphazatrienes, $N_3P_3RR'X_4$ (X = F, Cl) and their relationships to basicity; (c) deviations from some relationships due to ring puckering and the use of mathematical techniques to "flatten out" these rings; (d) ^{35}Cl nuclear quadrupole resonance frequencies and P—Cl bond lengths and other relationships; (e) exocyclic bond angles viz. OPO, NPN, ClPCl, CPC etc. versus ^{31}P NMR chemical shifts; (f) ring compression and deformation and unusual mass spectrometric and bulk polymerisation properties; (g) relationships in phosphazenylcyclophosphazenes between crystal structure, $^4J(PP)$ coupling constants, basicity and conformation; (h) relationships between spin-spin coupling constants, dihedral angles in, and conformations of, spiroderivatives of cyclophosphazenes—trigonal planar versus pyramidal nitrogen atoms.

X-ray crystallographic studies have three major focal points which affect the chemist, at present:[1] 1) the study of complex macromolecules of biological importance and origin; 2) structural problems in organic and inorganic chemistry, which have not yielded the necessary structural information, in spite of enormous progress in spectroscopic techniques (especially in NMR spectroscopy); 3) systematic and very accurate studies of series of related molecules which for instance (a) showed the preferred conformations in medium-sized rings, (b) gave data on chemical reaction paths for S_{N^1} and S_{N^2} types of reaction and (c) related the deformation of molecules from a given geometry to other physical and chemical properties.

The present paper is concerned with the last named type of study. In a series of papers devoted to the molecular geometry of substituted benzene derivatives, Coulson, Domenicano, Murray-Rust and Vaciago[2-4] came to the conclusion that, because of thermal effects, bond length data were much less reliable than bond angle data. By using the deformation of the internal bond angles α, β, γ and δ by a substituent X (Figure 1) from that of benzene itself, they showed a number of important relationships which can be gained from this data.

In particular, they demonstrated a linear relationship[3] between the internal bond angle α and the Pauling electronegativity for second-row elements (Figure 2).

Extension of this study[4] to para-disubstituted benzene derivatives (Figure 3) showed two independent effects that a substituent can exert on the angles of the

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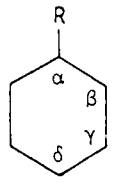


FIGURE 1 Bond angles in monosubstituted benzene derivatives.

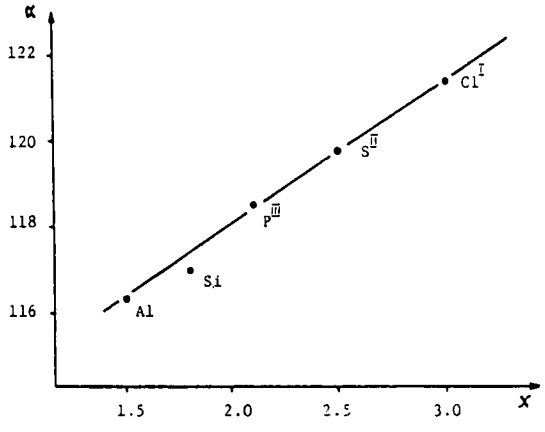
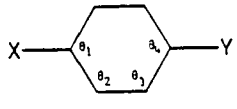


FIGURE 2 Plot of the bond angle α against the Pauling electronegativity for second-row elements.



$$\theta_1 = 120^\circ + \Delta\alpha_x + \Delta\delta_y ;$$

$$\theta_2 = 120^\circ + \Delta\beta_x + \Delta\gamma_y ;$$

$$\theta_3 = 120^\circ + \Delta\beta_y + \Delta\gamma_x ;$$

$$\theta_4 = 120^\circ + \Delta\alpha_y + \Delta\delta_x .$$

FIGURE 3 Bond angle deformations in *para*-disubstituted benzene derivatives.

benzene ring, α and β deformations being largely controlled by inductive effects, γ and δ deformations controlled by resonance effects.

A detailed analysis[4] gave a linear plot of $\Delta\alpha$ against Taft's inductive parameter σ_I, (Figure 4) and a curved relationship between $\Delta\gamma$ and the resonance parameter σ_R^0 (Figure 5).

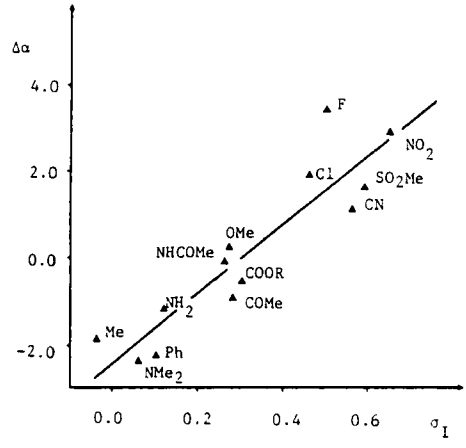


FIGURE 4 Plot of $\Delta\alpha$ against Taft's inductive parameters σ_I.

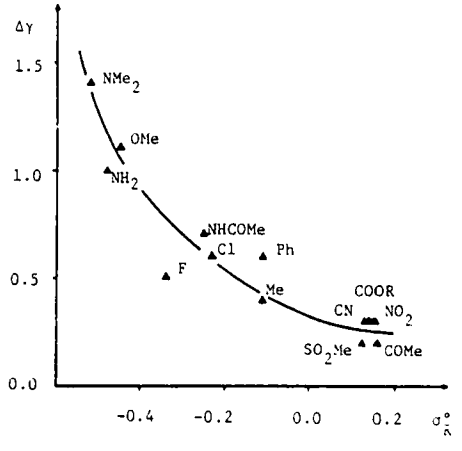


FIGURE 5 Plot of $\Delta\gamma$ against the resonance parameter σ_R^o.

A careful examination of the structural data already available on phosphazenes together with a great deal of very recent work, especially designed for this purpose, has revealed a number of relationships between structural parameters and physical and chemical properties.

We will first examine the relationship with electronegativity. Ahmed, Singh and Barnes[5] were the first to attempt this for cyclotriphosphazatrienes, $N_3P_3R_6$, and used Pauling's atomic electronegativity values. The range of compounds with different substituents was rather limited (R = F, Cl, Br and Ph) at that time, but several curved relationships were proposed (Figures 6 and 7).

Subsequently, Wagner[6] attempted a similar correlation for the eight-membered ring system, $N_4P_4R_8$, but found the use of both group and atom orbital electronegativities[7,8] more satisfactory (Figure 8).

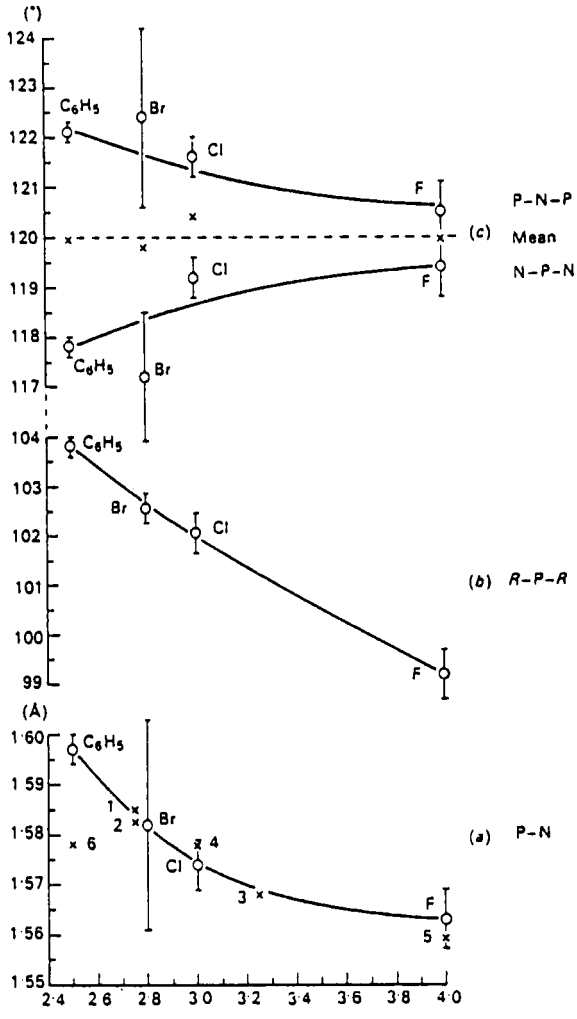


FIGURE 6 Plot of PNP, NPN, and RPR bond angles and of P—N bond lengths against Pauling's electronegativity values for N_3P_3 derivatives.

The range of derivatives available was larger (R = F, Cl, Br, NMe_2, OMe, Me) but the data was bedevilled by the erroneous structure determination[9] of $N_4P_4F_8$, which was reported as planar, with abnormally short P—N bonds, and abnormally large endocyclic PNP bond angles. Recently, it has been shown[10] that the structure is disordered, and a low temperature crystallographic investigation demonstrated[10] a puckered N_4P_4 ring with more acceptable bond lengths and bond angle values. The earlier and the more recent structural data are compared in Figure 9.

The new bond length data are in keeping with a detailed analysis of a whole range of P—N bond lengths (with phosphorus in different valency states and with different coordination numbers), where it was shown that, in general, F_2P—N bonds were approximately 0.04 Å shorter than Cl_2P—N bonds.[11]

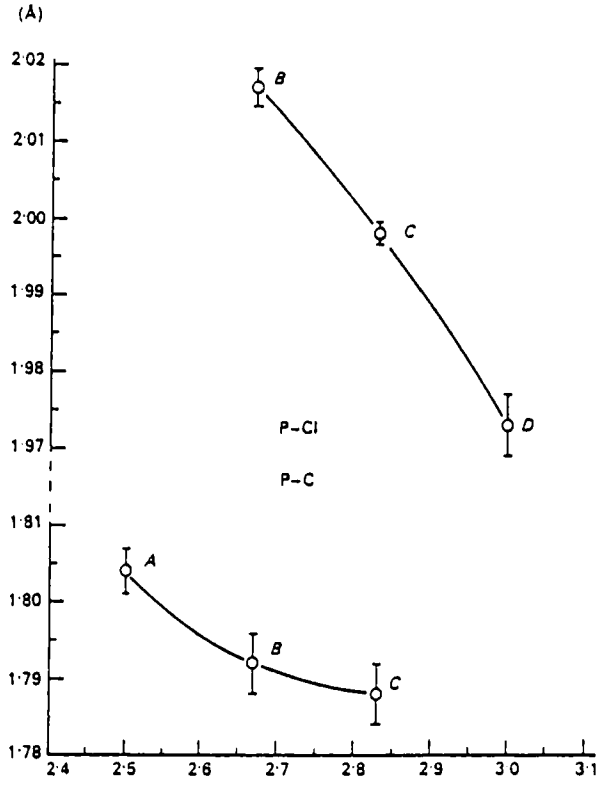


FIGURE 7 Plot of P—C and P—Cl bond lengths against Pauling's electronegativity values for N_3P_3 derivatives.

Crystal structure determinations of some derivatives of $N_4P_4F_8$[12,13] report very short P—N bond lengths and very large PNP bond angles; hence low temperature crystallographic data on these compounds would be interesting.

The availability of data for a large number of $N_3P_3R_6$ derivatives, together with more accurate redeterminations of earlier structures, allows a fresh look to be made at the above relationships. In particular, the use of Pauling electronegativities for nitrogen groups as diverse as NMe_2,[7] $N_2C_3H_2$ (imidazolyl) and NCS[8] (which cover the whole range of bond angles discussed here) pointed to the shortcomings of this approach. We have therefore used both group and Pauling electronegativities (where appropriate). Plots of these properties against NPN and PNP endocyclic bond angles are shown in Figure 10.

Satisfactory curved relationships are established for the eight compounds where both electronegativity and bond angle data are available. In particular, the electronegative nature of the NCS substituent[8] is highlighted, though regrettably the accuracy of the crystal structure[20] is low by modern standards. Generally the NPN bond data have fewer complications than the corresponding PNP values. The ring nitrogen atoms (and their PNP bond angles) are very sensitive to intra- or intermolecular interactions. Thus whilst in $N_3P_3Br_6$[16] the NPN angles are not significantly different, the PNP angles show significantly different values, 119.3(6) and

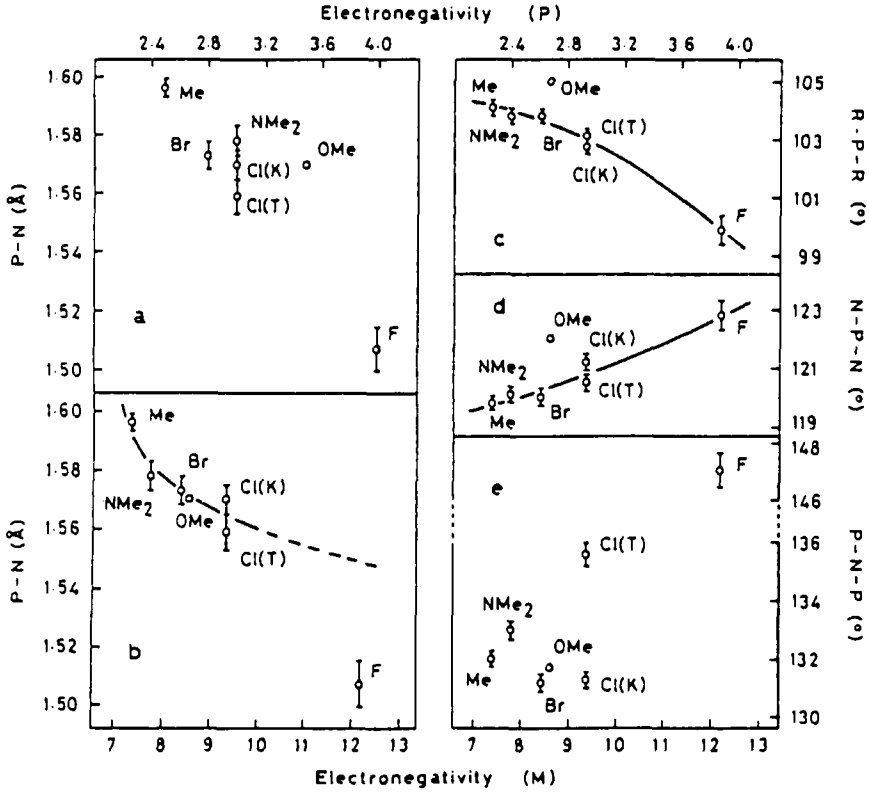
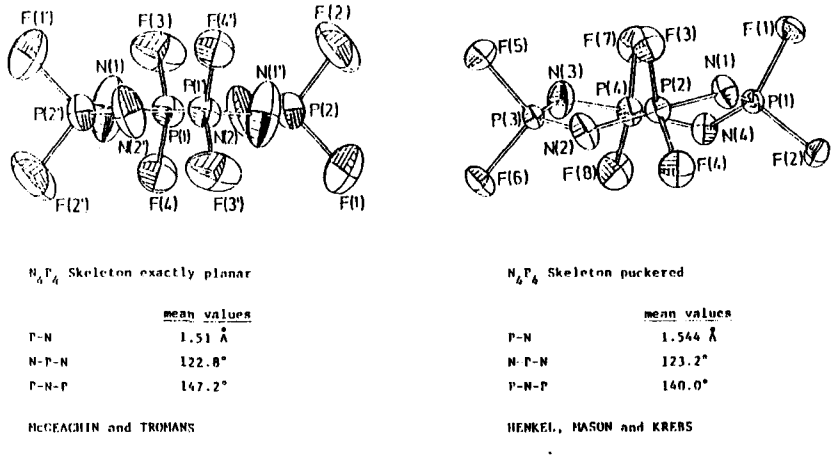


FIGURE 8 Plot of P—N bond lengths and of NPN. PNP, and RPR bond angles against Pauling's or group electronegativities in N_4P_4 derivatives.



N_4P_4 Skeleton exactly planar

	mean values
P-N	1.51 Å
N-P-N	122.8°
P-N-P	147.2°

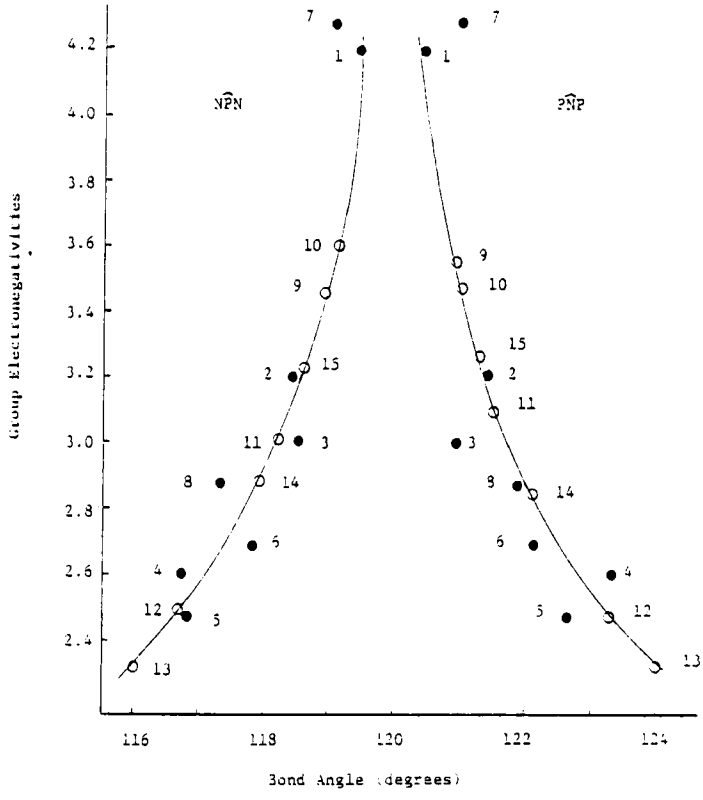
McGEACHIN and TROTMAN

N_4P_4 Skeleton puckered

	mean values
P-N	1.544 Å
N-P-N	123.2°
P-N-P	140.0°

HENKEL, MASON and KREBS

FIGURE 9 The crystal structure of $N_4P_4F_8$.



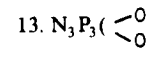
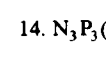
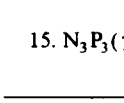
	$\widehat{NPN}$(Mean)	$\widehat{PNP}$(Mean)	Electronegativity
1. $N_3P_3F_6$	119.4	120.35	4.0
2. $N_3P_3Cl_6$	118.4	121.4	3.0
3. $N_3P_3Br_6$	118.5	120.85	2.8
4. $N_3P_3(NMe_2)_6$	116.7	123.3	2.4
5. $N_3P_3Me_6$	116.8	122.6	2.27
6. $N_3P_3Ph_6$	117.8	122.1	2.49
7. $N_3P_3(NCS)_6$	119.0	121.0	4.17
8. $N_3P_3(OPh)_6$	117.3	121.9	2.68
9. $N_3P_3(SPh)_6$	118.9	120.9	
10. $N_3P_3(N_2C_3H_3)_6$	119.1	121.0	
11. N_3P_3()$_3$	118.2	121.5	
12. $N_3P_3(NC_2H_4)_6$	116.7	123.3	
13. N_3P_3()$_3$	116.3	123.7	
14. N_3P_3()$_3$	117.9	122.1	
15. N_3P_3()$_3$	118.6	121.2	

FIGURE 10 Plot of NPN and PNP bond angles against group electronegativities for $N_3P_3R_6$ derivatives.

122.4(5)°, the smaller one pertaining to a nitrogen atom with a probable intermolecular interaction with a Br atom of another molecule. If we ignore this smaller angle, we find that both the NPN and the PNP data give us commensurate results. As both curves give us closely related results, our confidence in their applicability is strengthened.

We now use bond angle data to deduce group electronegativities, when the latter have apparently not yet been evaluated by other methods. Using similar provisos as for $N_3P_3Br_6$ regarding some PNP bond angles, we deduce group electronegativity for $N_3P_3R_6$ derivatives as follows: R = SPh,[21] 3.30, R = $N_2C_3H_2$ (imidazolyl),[22] 3.34, R = NC_2H_4 (aziridinyl),[23] 2.30, R_2 = 2,2′-dioxybiphenyl,[24] 3.02, R_2 = *o*-phenylenedioxy,[25], 2.82, R_2 = 1.8-dioxynaphthalene,[26] 2.67, R_2 = 2,3-dioxynaphthalene,[27] 2.16 and these too are shown in Figure 10. The agreement between the NPN and PNP curves is gratifying, but it must be stressed, that relatively small errors in bond angles can alter the group electronegativities considerably, and some of the bond angle e.s.d.'s are by no means small! Hence this method can give us a guideline, albeit not a very accurate one, to group electronegativities.

When dealing with compounds of a type other than $N_3P_3R_6$, the situation is more complex and will be discussed elsewhere.

As far as the $N_4P_4R_8$ system is concerned, the new crystal structure of $N_4P_4R_8$ by Henkel, Mason and Krebs[10] removes the major anomalies both in bond length and in PNP bond angles, in Wagner's diagrams,[6] and this system will be discussed elsewhere.

I now wish to turn attention to systems where we have a net transfer of electrons from one part of the molecule to another part of the same molecule. I concentrate on structures of the type geminal $N_3P_3RR'X_4$ (X = F or Cl; R, R′ are the same or different, acyclic or spirocyclic), and we examine the changes in endocyclic bond angles NPN and PNP (Figure 11).

We now report a relationship between endocyclic bond angles in cyclotriphosphazatrienes and basicity substituent constants, which are obtained by the titration of the phosphazene derivative with perchloric acid in nitrobenzene solution.

When plotting the sum of the basicity substituent constants $\Sigma\alpha_R$, which describes the contribution of a substituent R on a phosphorus atom α to a ring nitrogen atom (ring nitrogen atoms being the site of protonation in the vast majority of phosphazene derivatives) against the endocyclic NPN bond angle α, a straight line (for the angle range 109–115° and for $\Sigma\alpha_R$ 8–13) is obtained with a negative slope (Figure 12). A linear regression analysis of the points gives the equation $y = a + bx$ ($x = \Sigma\alpha_R$, $y = \alpha$) with a value for $a = 123.78 \pm 0.89°$, $b = -1.018 \pm 0.089$ and a

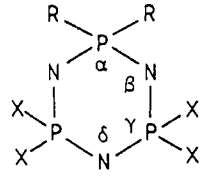


FIGURE 11 Bond angles in 2,2-disubstituted-4,4,6,6-tetrahalogenocyclotriphosphazatrienes (X = F or Cl).

correlation coefficient, $r = 0.974$, y residuals -0.7 to $0.6°$. Increase in $\Sigma\alpha_R$ decreases the angle α. Thus the electron release in the crystalline ground state, as observed by X-ray crystallography, parallels the electron release in the state perturbed by protonation in solution. Deviations from the straight line are minor and generally well within three e.s.d.'s (determined from crystallographic data) (error bars in Figure 12), although effects arising from hydrogen bonding cannot be ruled out at this stage.

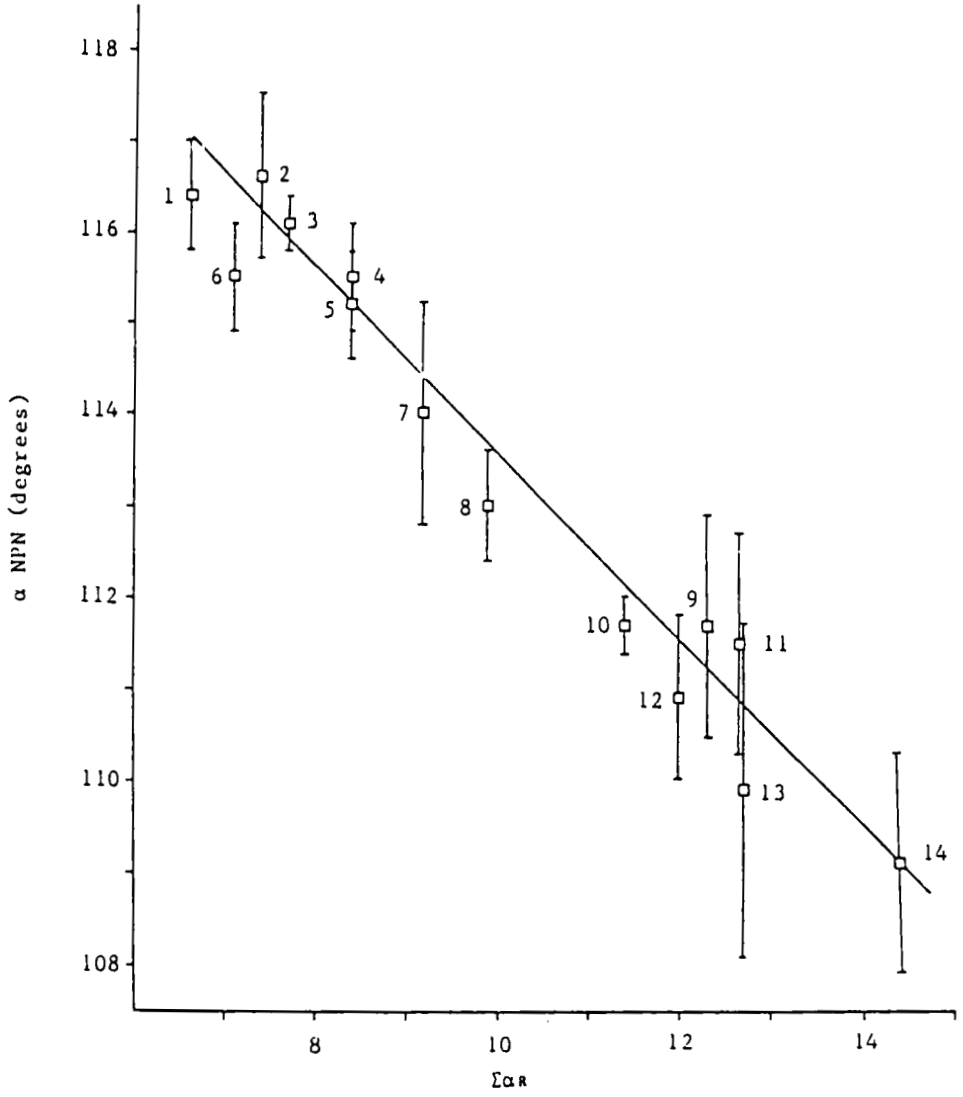


FIGURE 12 Plot of NPN bond angle α against sum of basicity substituent constants $\Sigma\alpha_R$. References refer to crystal structure determinations. 1. $N_3P_3(SPh)_2Cl_4$,[28] 2. $N_3P_3[O(CH_2)_3O]Cl_4$,[29] 3. $N_3P_3[O(CH_2)_4O]Cl_4$,[29] 4. $N_3P_3Ph_2F_4$,[30] 5. $N_3P_3Ph_2Cl_4$,[31] 6. $N_3P_3[O(CH_2)_2O]Cl_4$,[29] 7. $N_3P_3Me_2F_4$,[32] 8. $N_3P_3[O(CH_2O_2NH]Cl_4$,[33] 9. $N_3P_3(NHBu^t)_2Cl_4$,[34] 10. $N_3P_3(NPPh_3)PhCl_4$,[35] 11. $N_3P_3[NH(CH_2)_3NH]Cl_4$,[36] 12. $N_3P_3(NH_2)_2F_4$,[37] 13. $N_3P_3(NPPh_3)(NEt_2)Cl_4$,[38] 14. $N_3P_3(NPPh_3)_2Cl_4$.[39]

At α angles $> 115°$ and for $\Sigma\alpha_R < 8$ significant deviations occur from the straight line (Figure 12). (We are currently investigating whether these are special cases or whether the relationship changes in that region from a straight line to a curve.)

To test the validity of the above relationship, we have determined (i) the crystal structure[33] and (ii) the basicity substituent constant of 2,2-(1′-amino-2′-oxyethane)-4,4,6,6-tetrachlorocyclotriphosphazatriene, $N_3P_3[O(CH_2)_2NH]Cl_4$. The data for this compound beautifully fit our line in a region where we had relatively few points before. Basicity constants, α_R, were taken for acyclic substituents from the literature,[40-42] and were evaluated for cyclic substituents in the present study, as conformational constraints and effects arising from these,[43] are likely to be of greater importance in the latter type of substituent.

We need to comment on the substituent constant for the $NPPh_3$ group. We have earlier evaluated $\alpha_{NPPh_3} = 10.3$.[44] If such a value had been used in the present calculations, the points for compounds 10, 13 and 14 would deviate widely from our plot. We have, however, shown that the value of 10.3 holds for Type I conformation[11,45-47] (the N—P segment of the substituent being approximately parallel to the N_3P_3 ring) and endocyclic protonation,[44] whilst for compounds 10,[35] 13,[38] and 14[39] Type II conformations[11,45-47] (the N—P segment approximately perpendicular to the N_3P_3 ring) pertain, and that in the latter case exocyclic protonation of the phosphazenyl groups occurs.[44] Hence we cannot obtain α_{NPPh_3} for Type II conformations from our experimental basicity data. By deducing it, however, from the bond angle of $N_3P_3(NPPh_3)_2Cl_4$ (compound 14)[39] and its intercept with the proposed line, we obtain a value of $\alpha_{NPPh_3 II}$ of 7.2 (in contrast to $\alpha_{NPPh_3 I}$ of 10.3). If we use this value of 7.2 for $\alpha_{NPPh_3 II}$, we find that compounds 10 and 13 also now nicely fit our relationship, and thus validate our method of deducing $\alpha_{NPPh_3 II}$. We have earlier demonstrated the dependence of α_R of other substituents on conformation.[43]

We can use the relationship established here to deduce the electron-releasing capacity of substituents for which no basicity data is available. We exemplify this by the examination of the crystal structure determination of geminal $N_3P_3Me[Fe(CO)_2C_5H_5]Cl_4$.[48] The relevant α-angle is 111.8(1)°. This corresponds to a $\Sigma\alpha_R$ of approximately 11.8. As $\alpha_{Me} = 4.6$, $\alpha_{Fe(CO)_2C_5H_5} \simeq 7.2$ i.e., approximately the same electron-releasing capacity as $\alpha_{NPPh_3 II}$.

As in beneze derivatives, bond angle changes in the cyclotriphosphazatriene derivatives reported here are not confined to the α angle, although the effects are most pronounced there.

In the latter class of derivatives, plotting of $\Sigma\alpha_R$ values against angles β, γ and δ, give rise to positive, positive and negative slopes respectively, those of the γ angles being the least sensitive to changes in $\Sigma\alpha_R$. Some major deviations from linearity occur with the plots of β, γ and δ angles caused by deviation of one or more ring P or N atoms from the planarity of the rest of the ring.

To overcome this we use some mathematical manipulations, details of which will be published elsewhere. These are exemplified by the plot of β bond angles versus $\Sigma\alpha_R$. The point for geminal $N_3P_3(NPPh_3)_2Cl_4$ deviates widely from the line (Figure 13a). This is because atom P(2) (Figure 14a) which carries the two $NPPh_3$ substituents is markedly out of the plane of the four atoms N(1) N(3) P(4) P(6).

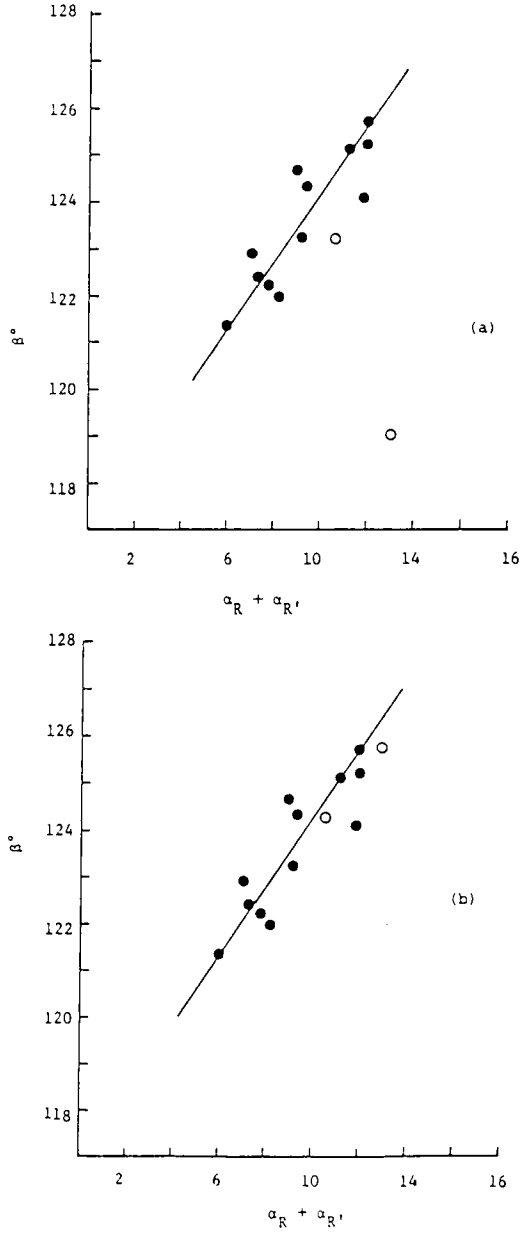
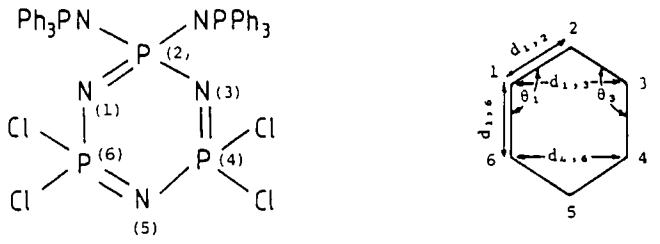


FIGURE 13 Plot of $\Sigma\alpha_R$ for geminal $N_3P_3RR'X_4$ (X = F, Cl) against β-angle (a) uncorrected, and (b) corrected for puckering of N_3P_3 ring.

As there is a mirror plane along the line P(2) N(5), we can use the following expression based on Figure 14b.

$$\theta_3 = \theta_1 = 90° + \sin^{-1}\left(\frac{d_{4,6} - d_{1,3}}{2d_{1,6}}\right) + \cos^{-1}\left(\frac{d_{1,3}}{2d_{1,2}}\right)$$



$$\theta_3 = \theta_1 = 90° + \sin^{-1}\left(\frac{d_{4,6} - d_{1,3}}{2d_{1,6}}\right) + \cos^{-1}\left(\frac{d_{1,3}}{2d_{1,2}}\right)$$

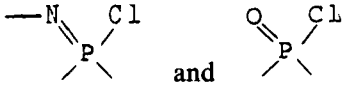
FIGURE 14 Mathematical formula to flatten a puckered ring. Example: geminal $N_3P_3(NPPh_3)_2Cl_4$.

Where θ_3 and θ_1 are the endocyclic bond angles at positions 3 and 1 respectively and $d_{4,6}$, $d_{1,3}$ and $d_{1,2}$ are the respective distances between positions 4 and 6, 1 and 3, and 1 and 2.

The mathematically corrected bond angle, i.e., the angle which would have pertained, had the molecule not puckered, now nicely fits our line (Figure 13b). A similar, but less marked deviation from the straight line occurs with geminal $N_3P_3(NPPh_3)PhCl_4$ (Figure 13a) which is again corrected (Figure 13b) by use of the above equation. The remaining deviations are minor and will be investigated in detail. Some deviations could be due to large e.s.d.'s and, in addition, many of these structures which show minor anomalies contain hydrogen bonds, which might affect the relationship. A detailed discussion of the manipulations shown above and the implications which result will be published elsewhere.

We now turn to a consideration of the relationship of X-ray crystallographic structural and nuclear quadrupole resonance (NQR) spectroscopic data, both relating to crystalline molecules in their ground state.

We have shown earlier[49,50] that a straight line relationship exists between P—Cl bond lengths (determined at room temperature) and ^{35}Cl NQR frequencies (determined at 77 K) (Figure 15), and that different slopes arise from the groupings



. We shall see in a later section that the nature of the multiple-bonded atom also affects the graphical plots of ^{31}P NMR chemical shifts against exocyclic bond angles.

We have discussed the NQR–bond length relationship in greater detail elsewhere in this Symposium,[51] as well as the solid-state phase changes we have observed by ^{35}Cl NQR spectroscopy and the conclusions which can be drawn from these changes.[51]

This relationship deals only with the immediate environment of the chlorine nucleus, i.e., the P—Cl bond itself. We now ask: Are there long range effects, which can be similarly quantified? The endocyclic NPN bond angles γ (Figure 11) in geminal $N_3P_3RR'X_4$ derivatives (see above) are adjacent to the PCl_2 groups. Is there a relationship between some property of the substituents R and R', the endocyclic

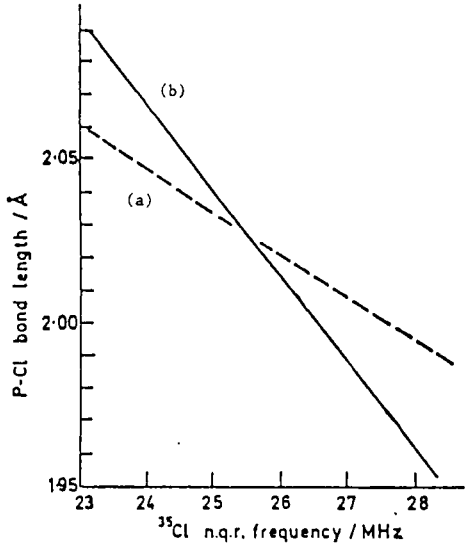


FIGURE 15 Plot of P—Cl bond length (not corrected for librational motions) against ^{35}Cl NQR frequency for (a) —N=PR_2—Cl and (b) O=PR_2—Cl.

NPN bond angle γ and the ^{35}Cl NQR frequency of the immediately adjacent chlorine nuclei? The general trend is in the expected direction as when R = R′ = Cl (i.e., $N_3P_3Cl_6$) the NQR frequencies are higher, the P—Cl bond length is shorter and the bond is less ionic than when R and R′ are electron-releasing groups. Thus the mean ^{35}Cl NQR frequencies at 77 K are: $N_3P_3Cl_6$ 28.48,[49] $N_3P_3[O(CH_2)_3O]Cl_4$ 27.95,[51] $N_3P_3Ph_2Cl_4$ 27.76[49] and $N_3P_3(NPPh_3)_2Cl_4$ 27.60 MHz.[56] Undoubtedly, a trend towards lower frequencies with increasing electron-releasing capacity of the substituents R and R′, and hence a greater ionic character of the P—Cl bond, exists. However, the exact shape of the relationship will have to await further data.

Unfortunately, the bond angles γ are the least sensitive of all the endocyclic bond angles α, β, γ and δ to changes in the substituents R and R′. Furthermore NQR data is not always available over the complete temperature range, and there could be phase changes, so far unobserved. Hence we must await further results before attempting to find new quantitative relationships for the above.

We have so far confined ourselves to endocyclic NPN and PNP bond angles in cyclophosphazenes. We now consider exocyclic bond angles.

Gorenstein has reported[52] earlier an empirical correlation between OPO bond angles in the PO_4 tetrahedra of mononuclear phosphates and their ^{31}P NMR chemical shifts. The OPO angles chosen were the smallest for a given group, i.e., those where the electron density in the bonds in question is the least and, hence, the smallest repulsion between the bonds.

The curve showed a pronounced minimum in ^{31}P chemical shift value near 107°. Most points were on the branch of the curve representing bond angles < 107°. A later version of the curve by the same author[53] omitted the points > 107°. We have slightly modified this curve[29] by omitting points based on P—O—C_{sp^2} moieties and reinstated the upward sweep of the curve at angles > 107° with the inclusion of the

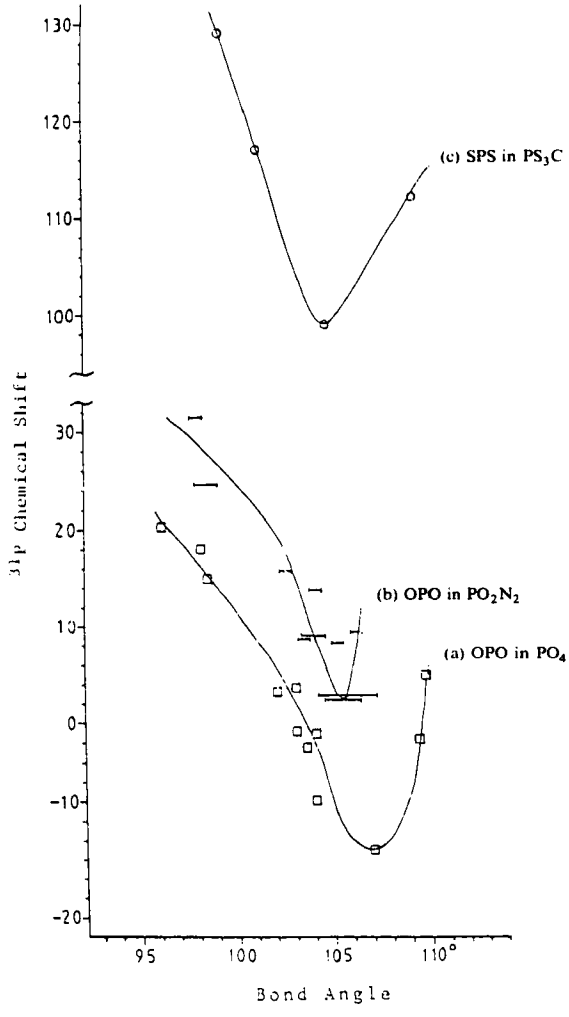
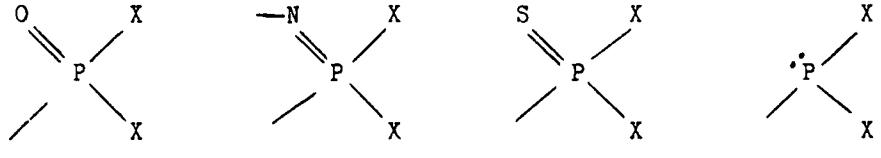


FIGURE 16 Plot of δ ^{31}P against (a) OPO bond angles in PO_4 terahedra, (b) OPO bond angles in PO_2N_2 tetrahedra, (c) SPS bond angles in PS_3C tetrahedra.

very large OPO bond angle in 2′,5′-arabinosylcytidine cyclic monophosphate, δ ^{31}P −1.84 ppm (Figure 16a)

We have deduced a similar, but displaced, curve for OPO bond angles in PO_2N_2 tetrahedra (Figure 16b), again excluding any P—O—C compounds where the carbon atom is not sp^3-hybridised. The minimum in our curve fell near 105.5°. As mentioned in the section (above) devoted to NQR spectra, we observe related, but not identical relationships when the multiple bonded atom is changed, and hence one would expect different curves for XPX bond angles in the moieties



One other such curve based on SPS bond angles in PS_3C tetrahedra has also been reported by Martin and Robert (Figure 16c).[54] It is based on only four points, one of which is obtained by calculation. In terms of chemical shift it is well displaced from the other two curves, but again it shows a minimum in the same region.

We now demonstrate that this appears to be a phenomenon of much wider occurrence in phosphazenes and related compounds. We describe similar relationships for NPN (Figure 17), CPC (carbon as part of an aromatic system) (Figure 18),

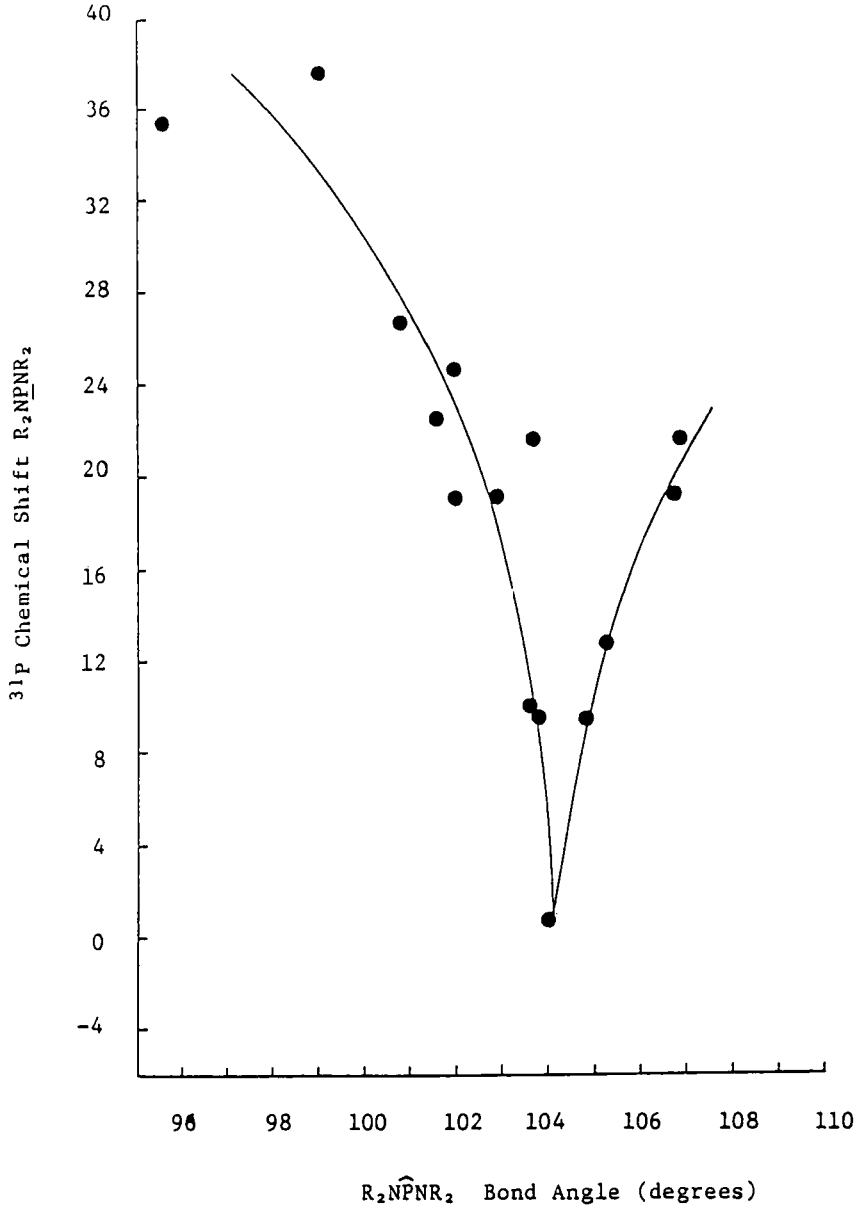


FIGURE 17 Plot of δ ^{31}P against exocyclic NPN bond angles in phosphazenes and related compounds.

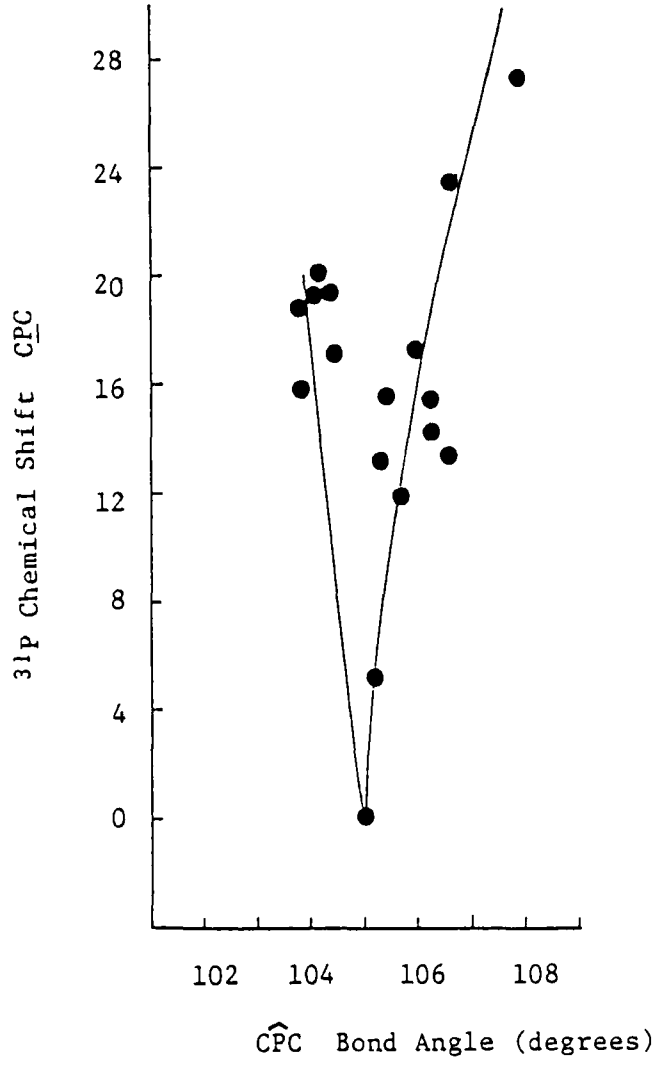


FIGURE 18 Plot of δ ^{31}P against CPC (C is sp^2-hybridised bond angles in phosphazenes and related compounds.

and ClPCl (Figure 19) exocyclic bond angles and we compare these with the curve derived for OPO bond angles[29] for these compounds (Figure 20).

We note the following: 1) all curves show large changes in ^{31}P NMR chemical shift with relatively small changes in bond angle, particularly near their minima; 2) for the OPO, NPN and CPC curves, the minima occur close to 105°; for the ClPCl curve (second row element substituents) near 102°; 3) with the exception of the OPO curves for phosphazenes[29] and for mononuclear phosphates;[29,52,53] where only a few points occur on the curve at bond angles greater than those corresponding to the minima, the other curves are relatively well populated on either side of the minimum; 4) the range of spread of bond angles reported here are in the order

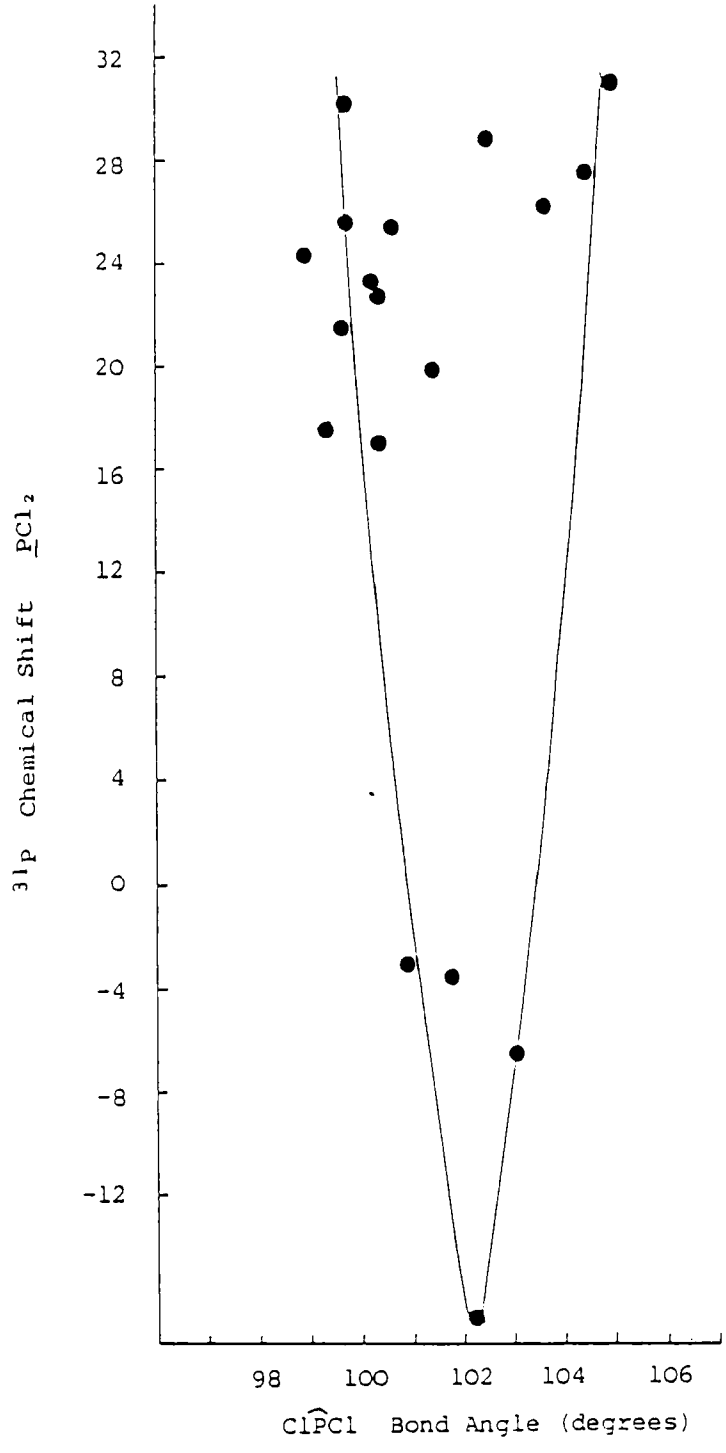


FIGURE 19 Plot of δ ^{31}P against ClPCl bond angles in phosphazenes and related compounds.

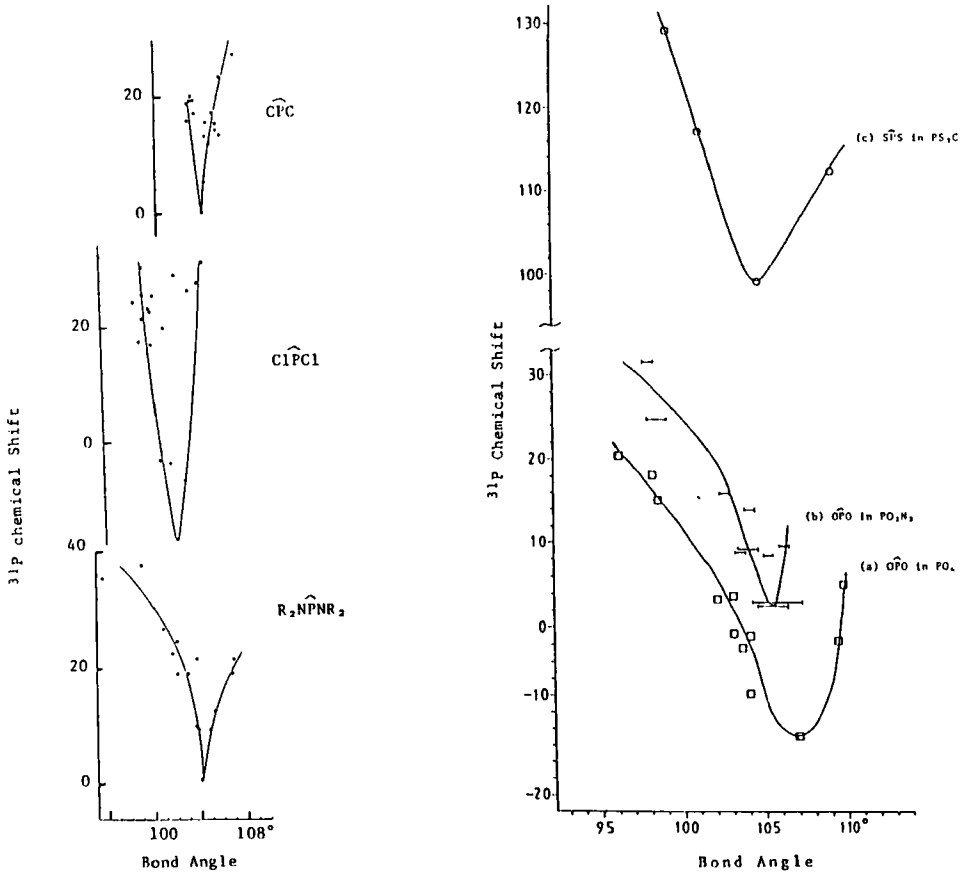


FIGURE 20 Comparison of plots of δ ^{31}P against OPO, NPN, CPC, and ClPCl bond angles in phosphazenes and related compounds.

NPN(11.3°) > OPO(9.0°) > ClPCl(6.5°) > CPC(2.8°) and appears to be related to the ability of the substituents to back conjugate to the ring phosphorus atom; 5) with the exception of the ClPCl system (δ ^{31}P 32 to -17 p.p.m.), the ^{31}P NMR chemical shifts range from 40 to 0 p.p.m.; 6) these curves allow structural assignments to be made. Thus for the compound in Figure 21 three singlets at δ 18.7, 17.1 and 0.0 p.p.m., with approximate intensities 2:1:1, were reported in the ^{31}P NMR

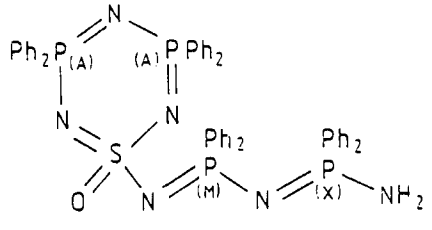


FIGURE 21 Structure of $N_3P_2Ph_4S(O)NPPh_2NPPh_2NH_2$ and assignments of chemical shifts.

spectrum.[55] These were not assigned. The relative intensity of two makes the assignment at 18.7 p.p.m. an obvious one for the ring phosphazene atoms (A). The use of our curve allows the signals at 17.1 p.p.m. (CPC 105.9°) and 0.0 p.p.m. (CPC 105.0°) to be assigned to the phosphazene moities adjacent to the ring (M) and at the end of the side-chain (X), respectively.

A few deviations from our curves have been observed. Some of these can be rationalised. For example, intermolecular hydrogen bonding in the solid state may affect bond angles. These deviations and a detailed discussion of the data given above will be presented elsewhere. Here we wish to stress that the closer the chemical relationship of the measured compounds, the better the approximation to the curve. Thus we have included only alkoxyphosphazenes (sp^3-hybridised carbon atoms) in our OPO curve.

No doubt other substituent groupings will give other similar curves, but as yet there is a paucity of data. All those compounds so far described have two identical substituents i.e. $\equiv PX_2$ groupings. In $\equiv PXY$ moieties, where there are donor-acceptor relationships between X and Y, we have some data for OPN and ClPN groupings indicating the outlines of curves, but as yet the data is insufficiently complete to be reported here.

We are currently investigating relationships similar to those described above for phosphorus systems other than phosphazenes.

We now examine briefly the structures of transannular bridged cyclotriphosphazatrienes and cyclotetraphosphazatetraenes and their relationships to bulk phase and mass spectrometric gas phase polymerisations. Details of the intramolecular compressions by bridging groups in these compounds have been examined in some detail, elsewhere in this Symposium.[57]

The three types of these compounds, which have so far been crystallographically examined are given in Figure 22.

We will consider first that type, which is based on an N_3P_3 ring. Three crystal structures of this type have so far been reported[58–60] and these are shown in Figure 23.

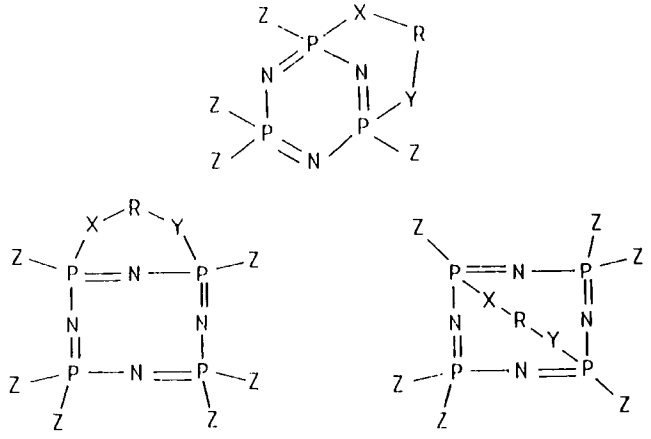
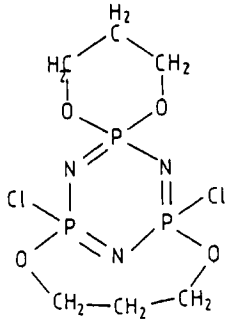


FIGURE 22 Three types of *trans*-annular bridged cyclotriphosphazatrienes and cyclotetraphosphazatetraenes.



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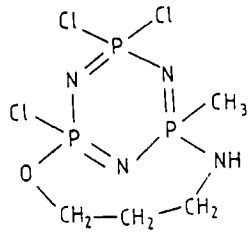

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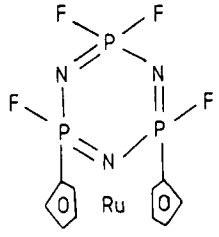

(12)

FIGURE 23 The three N_3P_3 ansa compound, which have been crystallographically examined.

The normal, mean non-bonded P · · · P distance for homogeneously substituted $N_3P_3Z_6$ derivatives (except Z = F) is around 2.77 Å[57] (for Z = F, it is 2.71 Å).[57] For non-homogeneously substituted compounds, $N_3P_3Z_{6-n}Z_n$ such as

$$N_3P_3Cl_4[O(CH_2)_3O]\ (2.726, 2.758, 2.748\ \text{Å}),^{29}$$

$N_3P_3Cl_2[O(CH_2)_3O]_2$(2.768, 2.745, 2.746 Å),[58,61] $N_3P_3Ph_2Cl_4$ (2.722, 2.770, 2.776 Å),[31] $N_3P_3Ph_4Cl_2$ (2.803, 2.738, 2.759 Å),[62] it does not appear to be less than 2.72 Å. At least two of the compounds, in Figure 23, viz. $N_3P_3Cl_2[O(CH_2)_3O]_2$ and $N_3P_3F_4[(C_5H_4)_2Ru]$, show signs of intermolecular compression.[57] Apart from the shortening of the non-bonded P · · · P distances of those phosphorus atoms involved in the transannular bridge, the nitrogen atoms between them are forced out of the plane of the cyclotriphosphazatriene rings.[58-60]

This ring compression and deformation seem to be implicated in the increased ability of these compounds towards polymerisation. Thus it has been reported that the ferrocene analogue, $N_3P_3F_4[(C_5H_4)_2Fe]$, of the ruthenocene, $N_3P_3F_4[(C_5H_4)_2Ru]$, discussed above, undergoes ring-opening polymerisation more readily in the bulk phase, than its unbridged analogue.[63] Recent studies have indicated that polymerisations in a mass spectrometer, operating in the chemical ionisation mode, seem to follow a closely parallel, perhaps even an identical, mechanism to that in the bulk phase. Both polymerisations are apparently initiated only by $N_3P_3X_5^+$ species, which then attack, in the propagation step, the ring nitrogen atoms of neutral molecules, $N_3P_3X_6$[64-67] (Figure 24).

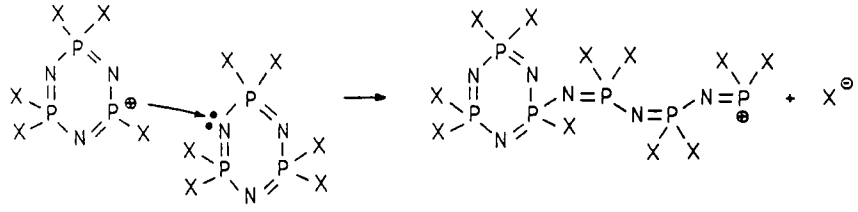

FIGURE 24 Proposed mechanism for bulk phase and for gas phase polymerisation.

When our ansa-derivative, $N_3P_3Cl_2[O(CH_2)_3O]_2$[58-61] was studied by this method, a unique feature was observed in that more than one cationic species derived from fragment cations initiated the polymerisation.[68] Undoubtedly, this can be attributed to ring strain, which accompanies the ring compression and deformation commented on[57] above. It seems that the introduction of ring strain can promote the polymerisation of cyclophosphazenes and studies in these directions may well be very fruitful.

We now turn our attention in the next section to triphenylphosphazenylcyclophosphazenes. We have postulated earlier two types of behaviour in our basicity studies.[44] 1. Protonation on the endocyclic nitrogen atoms (as in phosphazenes with a whole range of other types of substituents) and 2. Protonation on the exocyclic nitrogen atoms of the phosphazenyl substituent. We deduced that this difference in behaviour on protonation was a function of the conformation of the substituent, with respect to the local NPN segment of the cyclophosphazene ring. This was later borne out by X-ray crystallography.[35,38,39,69-72] Based on the conformational behaviour of the substituents $NPPh_3$, NMe_2 (and other amino groups), and Ph, we have postulated three major types of conformation.[45-47] 1) Those where the p_z-orbital of the sp^2-hybridised linking atom (N or C) of the substituent is parallel to the reference plane (for a definition of this plane see refs. 45–47), which we call Type I. 2) Those where this p_z-orbital is approximately perpendicular to the reference plane, which we call Type II, and 3) Those where the p_z-orbital is half-way between Types I and II, which we call Type III. The last-named type occurs frequently in geminal NMe_2 groups, $P(NMe_2)_2$. (Figure 25).

Making these definitions crystallographically more precise, we can define the dihedral angle ABCD (see Figure 26) as $\pm 90°$ for Type I, 180° or 0° for Type II, and $\pm 45°$, $\pm 135°$ for Type III.[73]

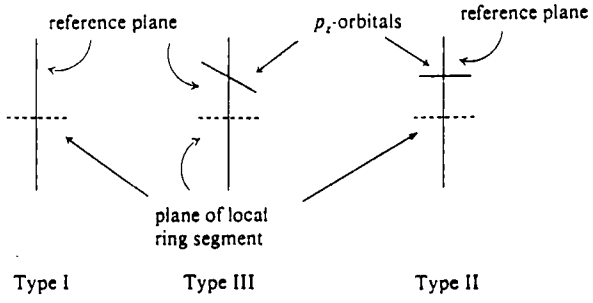

FIGURE 25 The three types of conformations of substituents in phosphazenes and related compounds.

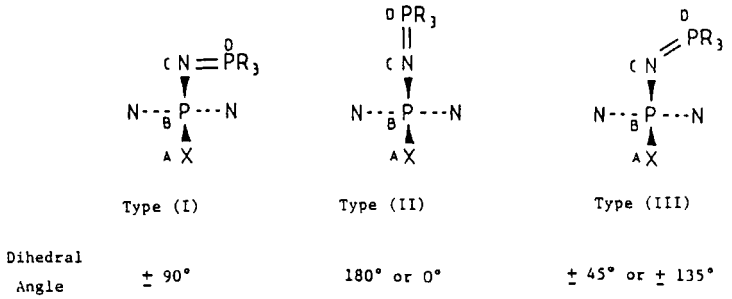

FIGURE 26 Details of conformations Types I, II and II.

As an example of almost perfect Type I behaviour (dihedral angle −83°) has been reported for $N_3P_3(NPPh_3)Cl_5$.[70] An even better approximation to Type II (dihedral angle −178°) has been found for geminal $N_3P_3(NPPh_3)PhCl_4$.[35] Type III behaviour, although common in $P(NR_2)_2$ groups, has so far been absent in phosphazenyl compounds, though a conformation in between Types II and III has been reported (dihedral angle 154°) for geminal $N_3P_3(NPPh_3)(NEt_2)Cl_4$.[38]

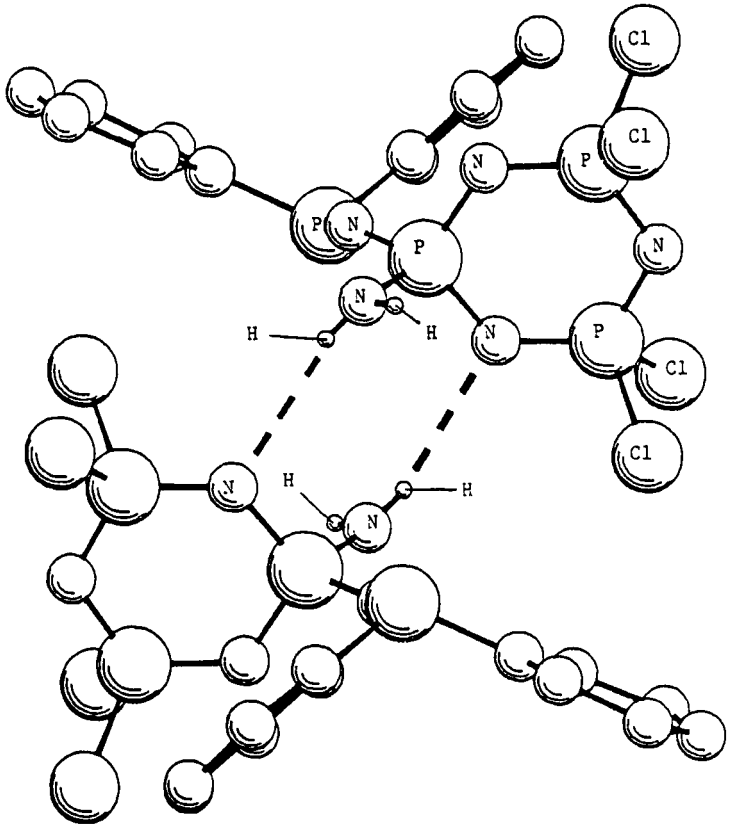

FIGURE 27 Hydrogen bonding in geminal $N_3P_3(NPPh_3)$ $(NH_2)Cl_4$. (One Ph group from each molecule omitted for clarity.)

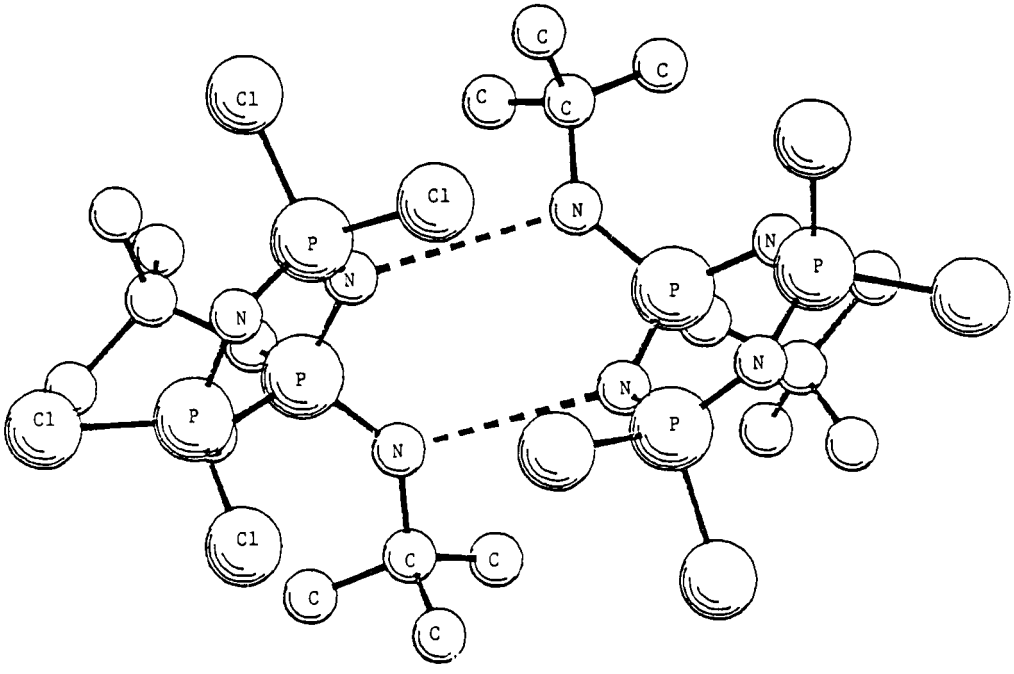

FIGURE 28 Hydrogen bonding in geminal $N_3P_3(NHBu^t)_2Cl_4$.

We now report an almost perfect example of Type III conformation in the solid state for the geminal compound, $N_3P_3(NPPh_3)(NH_2)Cl_4$ (dihedral angle $-139.2°$). This compound forms hydrogen-bonded dimers based on eight-membered rings (Figure 27), analogous to those of geminal $N_3P_3(NHBu^t)_2Cl_4$[34] (Figure 28).

This hydrogen-bonding behavior contrasts with that of the geminal spiro derivative, $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$,[74] where six-membered hydrogen-bonded rings give rise to infinite chains (Figure 29).

The hydrogen-bonding behavior of geminal and cis-nongeminal $N_3P_3(NH_2)_2(OMe_2)_4$ and of trans-nongeminal $N_3P_3(NH_2)_2(OPr^n)_4$ is even more complex.[75]

We now need to refine our conformational types further. In Type I, if the two PCl_2 groups in $N_3P_3(NPPh_3)Cl_5$ are made non-equivalent as in trans-nongeminal $N_3P_3(NPPh_3)(NEt_2)Cl_4$,[70] then the $NPPh_3$ substituent can be either *syn* or *anti* to the $PCl(NEt_2)$ group. In the compound mentioned, the $NPPh_3$ group is *syn* to the $PCl(NEt_2)$, in the solid state. (In an earlier paper[73] we had erroneously it as *anti*). In the *syn* and *anti* conformational change the bond N(C)—P(D) describes and arc of 180° around the bond N(C)—P(B).

If a similar rotation is effected in the Type II conformation, we have again *syn*-conformers with the $NPPh_3$ substituent turning towards the phosphazene ring and *anti*-conformers, when this substituent turns away. All of the Type II compounds show the *syn*-structure bar one. The exception is the geminal compound $N_3P_3(NPPh_3)_2Cl_4$,[39] where one $NPPh_3$ group is *syn*, and the other is *anti*. Thus of

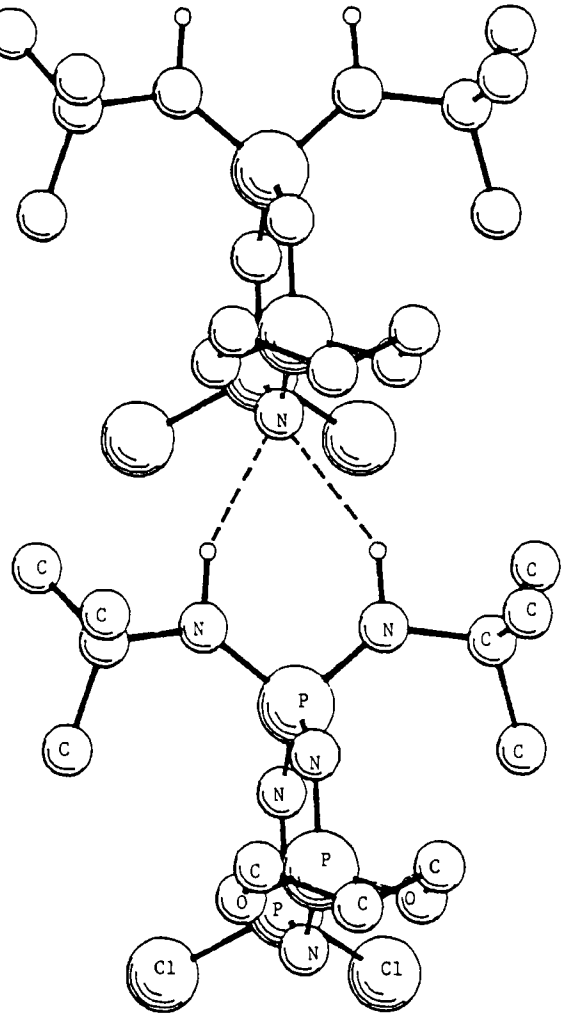

FIGURE 29 Hydrogen bonding in the geminal spiro derivative, $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$.

the three conformational groupings which might be imagined: *syn/syn/*, *anti/anti*, *syn/anti*, the last one is the only one so far observed in the solid state.

Orthographic projections[76] to illustrate these conformational groupings are shown in Figure 30.

We have demonstrated that four bond ^4J(PP) coupling is a good guide to the conformational behaviour of phosphazenyl groups in solution.[73,77] Preferred Type I conformational behavior of $NPPh_3$ substituents gives rise to relatively large ^4J(PP) values (3.3 to 5.7 Hz). Those compounds where the preferred conformation is Type II, have ^4J(PP) values close to zero. This type of behaviour has been observed also for the geminal derivative, $N_3P_3(NPPh_3)(NH_2)Cl_4$, where no ^4J(PP) coupling has so far been discerned. This fits in with our earlier views on its basicity behaviour, when it behaved in a fashion similar to geminal $N_3P_3(NPPh_3)PhCl_4$, and related com-

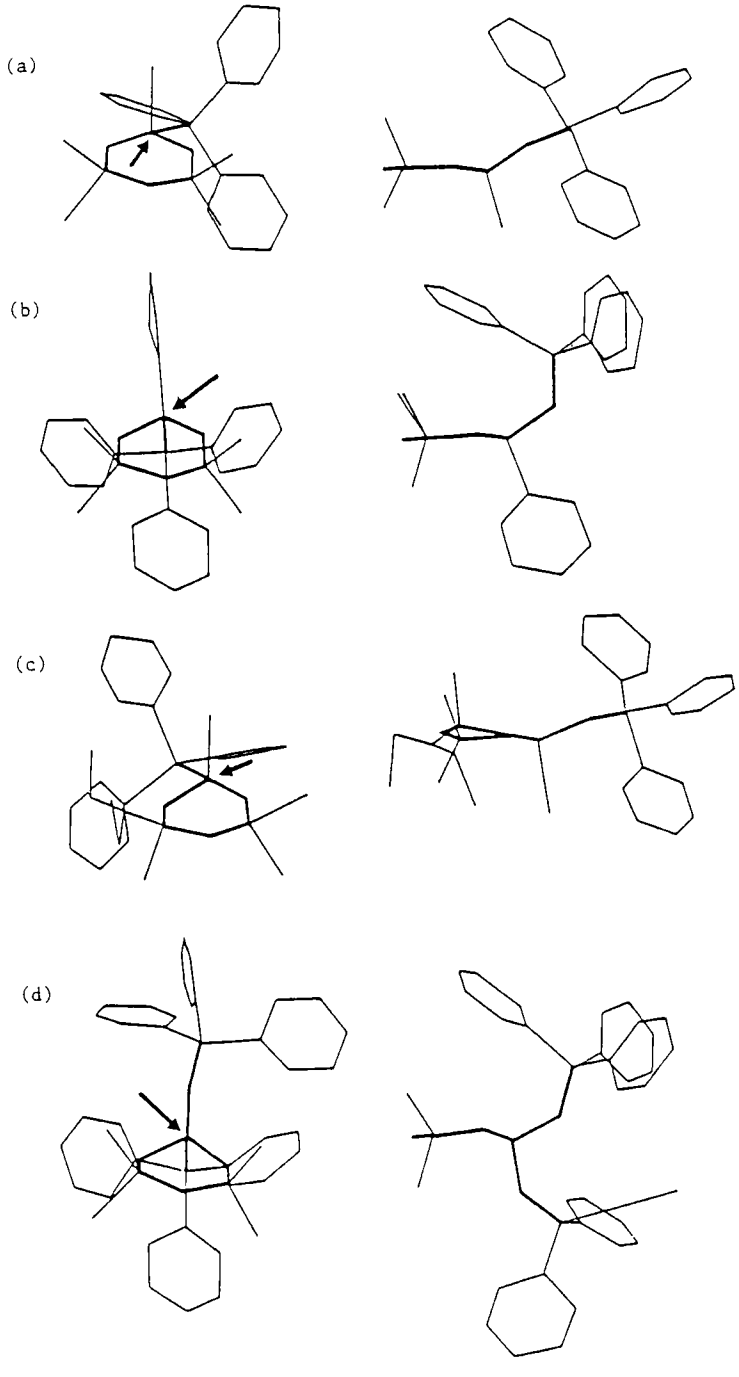

FIGURE 30 Solid state conformational features of phosphazenylcyclophosphazenes. Bolder lines show the P—N skeletal detail, except that for the P—NEt_2 bonds. The left-hand column shows a projection along the first *exo* P—N bond (arrowed), and the right-hand column shows a projection across the cyclophosphazene ring approximately perpendicular to the same P—N bond. (a) $N_3P_3Cl_5(N{=}PPh_3)$,[69] (b) $N_3P_3Cl_4Ph(N{=}PPh_3)$ (geminal),[35] (c) $N_3P_3Cl_4(NEt_2)$ $(N{=}PPh_3)$ nongeminal,[70] (d) $N_3P_3Cl_4(N{=}PPh_3)_2$ (geminal).[39]

pounds. We can illustrate the utility of the relationship between ^4J(PP) in solution and the conformation observed by X-ray crystallography in the solid state. In a recent study[78] of the reaction of $N_4P_4Cl_8$ with monolithiated ferrocene, a ring contraction to a six-membered ring, $N_3P_3\{NPCl[Fe(C_5H_5)(C_5H_4)]_2\}Cl_5$, was noted.[78] This paralleled our findings of 20 years ago that in the reaction between $N_4P_4Cl_8$ and PhMgBr, *inter alia*, a ring contracted derivative, $N_3P_3(NPPh_3)PhCl_4$, was formed.[35,79,80] The more recent ferrocene derivative showed a ^4J(PP) spin-spin coupling of 4 Hz.[78] Although the authors reported the crystal structure,[78] they did not comment on the conformation of the phosphazenyl side-chain. The ^4J(PP) value suggested a Type I conformation and we calculated from the fractional atomic coordinates a dihedral angle of $-97°$, in excellent agreement with this conformation.

For my final section I wish to deal with another conformational topic. Whilst collating various NMR parameters for spirocyclic phosphazenes, we observed some very pronounced differences between individual ring systems.[81] In particular, the phosphorus-carbon spin-spin coupling constants showed marked variations. Detailed discussion of these and of the relevant crystal structures[33] have been presented elsewhere in this Symposium, and I wish to highlight a few aspects. I will attempt to relate these coupling constants and the dihedral angles of the compounds, which exhibit them, to other properties. These results are summarised in Table I.

Whilst the variation in ^3J(POCC) and dihedral angle POCC is likely to fit a Karplus type relationship, with a minimum in coupling constants at dihedral angles near 90°, a similar explanation does not seem to be satisfactory for the two nitrogen-containing spiro rings. A closer look at the stereochemistry of the nitrogen atoms involved shows that whilst those in $N_3P_3[NH(CH_2)_3NH]Cl_4$[36] are trigonal planar (sum of bond angles 360.0°), those in $N_3P_3[NMe(CH_2)_3NMe]Cl_4$[33] show a marked pyramidal character (sum of bond angles 351.1°), with the nitrogen atoms about 0.27 Å out of the planes of their bonding partners. Such non-planarity seems to be rare as the nitrogen atoms in the spiro compounds so far examined, $N_3P_3[O(CH_2)_2NH]Cl_4$,[33] $N_3P_3[O(CH_2)_2NMe]Cl_4$,[33] $N_3P_3[O(CH_2)_3NH]Cl_4$,[33], and $N_3P_3[NH(CH_2)_3NH]Cl_4$,[36] are all trigonal planar. $N_3P_3[O(CH_2)_2NMe]_2Cl_2$[82] has however only one nitrogen atom planar whilst the other has a slight pyramidal character (sum of bond angles 358.6°).

TABLE I

Dihedral angles and ^3J(PXCC) (X = O, NH, NMe) spin-spin coupling constants of some spirocyclic derivatives of N_3P_3

Compound	Dihedral angle (°)	^3J(PXCC) (Hz)	Bonding around N atom
$N_3P_3[O(CH_2)_4O]Cl_4$	89	0.0	
$N_3P_3[O(CH_2)_3O]Cl_4$	53	7.3	
$N_3P_3[O(CH_2)_3NH]Cl_4$	37 (X = O) 69 (X = NH)	6.1	trigonal planar
$N_3P_3[NH(CH_2)_3NH]Cl_4$	62	6.6	trigonal planar
$N_3P_3[NMe(CH_2)_3NMe]Cl_4$	49	2.6	tends to pyramidal

By contrast, in compounds that contain acyclic secondary amino groups, (e.g. NMe_2 groups), such non-planarity is common, though by no means universal. (Cf. Refs. 17, 83–88) Camerson[89,90] has pointed out a relationship between the sums of the bond angles around the amino-nitrogen atoms and the exocyclic P—N bonds. We feel that further exploration of the relationships between the stereochemistry of these nitrogen atoms, conformation, NMR parameters, basicity, etc. would be fruitful.

On the present, rather limited data, it appears that secondary amino groups, when attached to phosphorus, show a greater propensity towards non-planar structures than do primary amino groups, though in the latter case the situation is further complicated by hydrogen bonding.

It may well be, that this greater tendency towards pyramidality could be part of the explanation, why $N_3P_3Cl_{6-n}(NMe_2)_n$ compounds methylate (with $Me_3O^+BF_4^-$) on the exocyclic NMe_2 groups,[91] whilst primary amino derivatives, as well as $N_3P_3Ph_6$, methylate on ring nitrogen atoms.[91] Ring nitrogen alkylation occurs also when $N_3P_3Me_6$ and $N_4P_4Me_8$ are treated with methyl or ethyl iodide.[92]

In this lecture, I have endeavoured to show the enormously fruitful interplay of the results obtained by systematic and careful X-ray crystallography with a variety of physical and chemical properties. I hope that I have succeeded. I think that we are moving towards a stage in scientific development, where quantitative relationships become feasible and allow predictions of structure and properties to be made with a fair degree of assurance.

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