855. *Structure and Basicity. Part II.*[1] *The Basicity of Fully Aminolysed Cyclotriphosphazatrienes and Cyclotetraphosphazatetraenes in Nitrobenzene and Water.*

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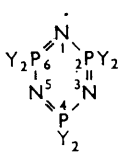
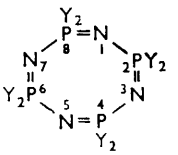
The basicities of a series of hexa-aminocyclotriphosphazatrienes, $N_3P_3(NRR')_6$, and octa-aminocyclotetraphosphazatetraenes, $N_4P_4(NRR')_8$ ($NRR' = NH_2$, NHMe, NHEt, $NHPr^n$, $NHPr^i$, $NHBu^n$, $NHBu^i$, $NHBu^t$, cyclohexylamino, NMe_2, NEt_2, piperidino), have been measured in nitrobenzene, and, where possible, also in water. The basicities are discussed in terms of the structure of, and the bonding in, these aminophosphazenes.

The observation that hydrochlorides of hexa-aminocyclotriphosphazatrienes, $N_3P_3(NHR)_6,HCl$, were isolated [2] from the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with an excess of primary aliphatic amines, NH_2R, led us to investigate this aspect quantitatively. It is also of interest that a number of aminophosphazenes show donor properties towards species other than the hydrogen ion.[3]

This Paper deals with the basic properties of fully aminolysed cyclotriphosphazatrienes (I) and cyclotetraphosphazatetraenes (II), in which Y = NH_2, NHMe, NHEt, $NHPr^n$, $NHPr^i$, $NHBu^n$, $NHBu^i$, $NHBu^t$, cyclohexylamino, NMe_2, NEt_2, piperidino.



(I)



(II)

A few of these aminophosphazenes are water-soluble, and values of pK_{a1}, and, in the tetraene series, in which they were high enough to be measured, of pK_{a2} also, are recorded for them in aqueous solution (Table 1). All except two are soluble in nitrobenzene, and

TABLE 1.

Aqueous solutions.*

R	$N_3P_3R_6$	$N_4P_4R_8$			R	$N_3P_3R_6$	$N_4P_4R_8$		
	pK_{a1}	pK_{a1}	pK_{a2}	ΔpK_a		pK_{a1}	pK_{a1}	pK_{a2}	ΔpK_a
NH_2	7·70	7·50	5·15	2·35	NHEt	8·65	8·70 †	6·10 †	2·60
NHMe	7·80	7·95	5·20	2·75	NMe_2.....	7·45	—	—	—

* pK_a values accurate to ±0·05 unit. † Measured in 3% methanol solution.

[1] Part I, Feakins, Last, and Shaw, *J.*, 1964, 2387.
[2] Ray and Shaw, *Chem. and Ind.*, 1961, 1173.
[3] Das, Shaw, Smith, Last, and Wells, *Chem. and Ind.*, 1963, 866.

the corresponding quantities in this solvent, pK_{a1}' and pK_{a2}', the latter now accessible for all the soluble compounds, are in Table 2. The Tables include values of ΔpK_a ($= pK_{a1} - pK_{a2}$) and $\Delta pK_a'$ ($= pK_{a1}' - pK_{a2}'$). Values for some reference compounds are in Table 3. The ensuing discussion will necessarily be based largely on the more numerous results for solutions in nitrobenzene, *i.e.*, on pK_a' and $\Delta pK_a'$ values rather than on pK_a and ΔpK_a values.

TABLE 2.

Solutions in nitrobenzene.*

	$N_3P_3R_6$			$N_4P_4R_8$		
R	pK_{a1}'	pK_{a2}'	$\Delta pK'_a$	pK'_a	pK'_{a2}	$\Delta pK'_a$
NHMe	8·8 ± 0·6	−2·0 ± 0·4	10·8	8·2	3·4	4·8
NHEt	8·2	−1·3	9·5	8·1	3·8	4·3
$NHPr^n$	7·9	−1·3	9·2	8·3	3·9	4·4
$NHPr^i$	8·4	−1·5	9·9	8·1	2·2	5·9
$NHBu^n$	7·9	−1·8	9·7	7·6	3·1	4·5
$NHBu^i$	—	—	—	8·0	3·2	4·8
$NHBu^t$	8·0	−1·7	9·7	8·8	0·4	8·4
Cyclohexylamino	7·9	−1·4	9·3	—	—	—
Piperidino	8·4	−3·2 ± 0·4	11·6	8·4	0·5	7·9
NMe_2	7·6	−3·3	10·9	8·3	0·6	7·7
NEt_2	8·5	−3·9	12·4	8·3	−0·9	9·2

* pK_a' values accurate to ±0·25 unit in the range −3·3 to 7·6 pH′, and ±0·4 unit outside this, except where indicated.

TABLE 3.

Aqueous solutions.*

	NH_3	NH_2Me	NH_2Et	$NHMe_2$	$NH_2{\cdot}NH_2$	$NH_2{\cdot}[CH_2]_2{\cdot}NH_2$	$NH_2{\cdot}[CH_2]_3{\cdot}NH_2$
pK_{a1}	9·25	10·62	10·63	10·77	8·11	10·09	10·62
pK_{a2}	—	—	—	—	−0·88	7·00	8·64
ΔpK_a	—	—	—	—	8·99	3·09	1·98

Solutions in nitrobenzene.†

	NH_2Me	NH_2Et	NH_2Pr^i	$NHMe_2$	$NHEt_2$	$PO(NMe_2)_3$ ‡
pK_{a1}'	6·9	7·1	6·5	7·5	7·1	−1·2

* Values from Robinson and Stokes, "Electrolyte Solutions," Butterworths, London, 2nd edn., 1959, pp. 517—526. † From Part I,[1] except for $PO(NMe_2)_3$. ‡ K_{ass} ~10^5.

Some of the bases, B, are associated with their conjugate monoprotonated acids BH^+

$$BH^+ + B \rightleftharpoons BHB^+$$

for which

$$K_{ass} = [BHB^+]/[BH^+][B]$$

(See Part I [1] for further details of pK_a, pK_a', and K_{ass}.) All the compounds substituted with primary amino-groups have $K_{ass} = 10^3$—10^4 l. mole^{-1}. Those substituted with secondary amino-groups are not detectably associated.

pK_a and pK_a' values were measured as before.[1] For the preparation of the amino-phosphazenes, see ref. 4.

DISCUSSION

The basic centres in all the phosphazenes discussed in this Paper are thought to be nitrogen atoms. For the most part it is adequate to assume that the charge-densities on these atoms in the neutral molecules, if the addition of the first proton is being considered, or in the monoprotonated bases for the addition of a second, determine the dissociation constants of the respective conjugate acids.

This view is obviously naïve, and refinements of it will be introduced in this series as needed, but one simple one may be mentioned at the outset, namely, that it may be

[4] Ray and Shaw, *J.*, 1961, 872; Ray, Shaw, and Smith, *J.*, 1963, 3236; Shaw and Stratton, *J.*, 1962, 5004.

important to consider the electron-distribution in the final protonated or diprotonated states, respectively, as well as in the initial neutral or monoprotonated bases, respectively.

The Positions of Protonation.—In general, high basicities might be expected for both the cyclic and the exocyclic nitrogen atoms in these compounds. A nitrogen atom of a particular type, cyclic or exocyclic, in the neutral base will be attacked by the first proton, as being of higher intrinsic basicity. The second proton may not necessarily attack at a second nitrogen atom of the same type, for the effect of the first proton may be to make it less basic than one of the other type of atom. In this work, any equivalence points after the second would be inaccessible under our experimental conditions.

In a preliminary communication,[5] we suggested that protonation of the cyclic rather than the exocyclic nitrogen atoms occurred in the aminophosphazenes, at least for the first proton. Moeller and Kokalis [6] have since offered confirmation of this from a study of the infrared and nuclear magnetic resonance spectra. With the aid of new data, we can now expand the arguments which led to our original conclusion.

Each ΔpK_a or $\Delta pK_a'$ value in Tables 1—3 may be the sum of contributions from a number of effects, of which perhaps three are the most important. First, the electronic effect. The protonation of one basic centre will lower the electron-density at the others by a number of mechanisms including, for example, the conventional mesomeric and inductive effects. Secondly, a form of the direct-field effect. The free energy of the diprotonated ion will be higher than that of the monoprotonated ion because of the mutual repulsion of the two positive charges. Thirdly, there will be specific solvation effects.

An approximate idea of the values of ΔpK_a and $\Delta pK_a'$ expected for various separations (r) of the basic centres when the second effect alone is operating, which we may call ${}^{f}\Delta pK_a$ and ${}^{f}\Delta pK_a'$, has been obtained as follows. The values of ΔpK_a for hydrazine [7] and the aliphatic diamines [8] were assumed to depend only on the direct-field effect and were identified with ${}^{f}\Delta pK_a$ values. A graph of these values against r^{-1} is approximately rectilinear, and values of ${}^{f}\Delta pK_a$ for various r can be interpolated from it.

Values of ${}^{f}\Delta pK_a'$ could not be found in the same way because pK_a' values of sufficient accuracy could not be obtained for the model compounds. Values of ${}^{f}\Delta pK_a'$ were therefore obtained from the assumption that

$$ {}^{f}\Delta pK_a' = \rho\,{}^{f}\Delta pK_a \qquad (1) $$

An estimate of ρ, $1{\cdot}71 \pm 0{\cdot}05$, was made from data on the two aminophosphazenes with which determinations both of ΔpK_a and $\Delta pK_a'$ were possible, putting

$$ \rho = \Delta pK_a'/\Delta pK_a \qquad (2) $$

The value of ρ from eqn. (2) will only approximate to the true value of eqn. (1) since the measured $\Delta pK_a'$ and ΔpK_a values for a given aminophosphazene probably contain contributions from other effects. A simple electrostatic model [9] gives $\rho = 2{\cdot}2$, suggesting that the value chosen is of the right order.

Table 4 shows the ${}^{f}\Delta pK_a$ and ${}^{f}\Delta pK_a'$ values expected for diprotonation at various centres in triene and tetraene derivatives. For the purpose of this argument, the N—N distances were assumed to be the same for all the six-membered ring compounds on the one hand and all the eight-membered ring compounds on the other. For the latter, the distances were obtained from Bullen's [10] data for octakisdimethylaminocyclotetraphosphazatetraene, taking mean values where necessary. For the six-membered ring, a planar model with the P–N bond lengths and exocyclic bond angles of the eight-membered ring compound, above, was adopted. Where there is a choice of positions,

[5] Feakins, Last, and Shaw, *Chem. and Ind.*, 1962, 510.
[6] Moeller and Kokalis, *J. Inorg. Nuclear Chem.*, 1963, **25**, 875.
[7] Schwarzenbach, *Helv. Chim. Acta*, 1936, **19**, 178.
[8] Bertsch, Fernelius, and Block, *J. Phys. Chem.*, 1958, **62**, 444.
[9] Bjerrum, *Z. phys. Chem.*, 1923, **106**, 219.
[10] Bullen, *J.*, 1962, 3193.

only those likely to lead to the smallest direct-field effect have been considered. Protonation on the N(1) and N(3) positions of the cyclotetraphosphazatetraene is unlikely when the N(1)—N(5) configuration is available for protonation, for example.

TABLE 4.

Centres	r (Å)	ΔpK_a	$\Delta pK_a'$
Hexa-aminocyclotriphosphazatrienes			
Ring N(1)—Ring N(3)	2·7	4·5	7·7
Ring N(1)—Exocyclic N on P(4)	4·5	2·4	4·1
Exocyclic N on P(2)—Exocyclic N on P(4) (*trans*)	5·3	$1{\cdot}8_5$	3·3
Octa-aminocyclotetraphosphazatetraenes			
Ring N(1)—Ring N(5)	4·0	2·8	4·7
Ring N(1)—Exocyclic N on P(4)	5·0	2·0	3·4
Exocyclic N on P(2)—Exocyclic N on P(6) (*trans*)	6·5	1·4	2·3

Towards the addition of the first proton, the hexa-aminocyclotriphosphazatrienes are all bases comparable in strength with the parent amines. This high strength would only be compatible with exocyclic protonation in the absence of any multiple bonding between the exocyclic nitrogen atoms and the ring, for such bonding would drain charge from them. In the absence of multiple bonding the exocyclic groups would be almost completely independent of each other electronically. Thus, if the first proton attacked an exocyclic nitrogen atom, as being of higher intrinsic basicity than a cyclic one, the second proton should attack a second exocyclic atom for the same reason. The resulting diprotonated configuration would also be the most favoured by the direct-field effect (Table 4). If the groups were independent electronically, the $\Delta pK_a'$ value would be close to the expected $^{f}\Delta pK_a'$ value (3·3) for this configuration. The lowest $\Delta pK_a'$ value is, in fact, 9·5, and this rules out attack by the first proton, or by both protons on exocyclic nitrogen atoms. The $\Delta pK_a'$ values observed are compatible with cyclic protonation for both protons for which $^{f}\Delta pK_a' = 7{\cdot}7$.

The whole of this analysis also applies to the tetraene series. In neither series, however, does it exclude the possibility that, while the first proton attacks a cyclic centre, the second attacks an exocyclic centre, for, although this may be of lower intrinsic basicity than a cyclic nitrogen atom, the direct-field effect for such a configuration would be lower than for that in which two cyclic nitrogen atoms had been protonated (Table 4).

A second, closely similar but independent, argument rests on the values of the P–N (exocyclic) bond lengths found in octakisdimethylaminocyclotetraphosphazatetraene, $N_4P_4(NMe_2)_8$, by Bullen,[10] which are compatible with a degree of multiple bonding, which of necessity involves charge-transfer from the exocyclic nitrogen atoms to the phosphorus atoms. In these circumstances, it is unlikely that the exocyclic nitrogen atom could give rise to the high basicities towards the first proton, found in this work. It may be assumed that this conclusion applies to phosphazenes substituted with other amino-residues, and to the six- as well as to the eight-membered ring derivatives.

That appreciable multiple bonding of amino-nitrogen atoms to quinquevalent phosphorus can occur is also apparent from the low basicity in nitrobenzene of hexamethylphosphoric triamide, $PO(NMe_2)_3$ ($pK_a' = -1{\cdot}2$; Table 3), compared with that of dimethylamine ($pK_a' = 7{\cdot}5$; Table 3).

Thirdly, consider octaphenylcyclotetraphosphazatetraene, $N_4P_4Ph_8$, for which $\Delta pK_a' = 8{\cdot}0$. Here protonation must occur on the ring nitrogen atoms, as it must also do in octaethylcyclotetraphosphazatetraene, $N_4P_4Et_8$, where $\Delta pK_a'$ has a very similar value (7·4). These values are higher than would be expected from the direct-field effect alone (4·7) for protonation on these positions, and indicate the participation of other effects. The $\Delta pK_a'$ values for the octa-amino-derivatives vary from 4·3 to 9·2 units (Table 2). The $\Delta pK_a'$ values for five non-geminally substituted tetra-aminotetraphenyl compounds, $N_4P_4Ph_4(NRR')_4$ (Table 5), are all close to the means of values for the octaphenyl derivative

and the corresponding octa-amino-derivatives. This would be unlikely if the protonation pattern changed from the octaphenyl derivative to the octa-amino-derivatives, and it may

TABLE 5.

	pK_{a1}'	pK_{a2}'	$\Delta pK_a'$	"Mean" $\Delta pK_a'$ *
$N_4P_4Ph_8$	2·2	−5·8	8·0	—
$N_4P_4Et_8$	7·6	0·2	7·4	—
$N_4P_4(NHMe)_4Ph_4$	5·4	−1·2	6·6	6·4
$N_4P_4(NHPr^n)_4Ph_4$	5·7	−1·0	6·7	6·2
$N_4P_4(NHPr^i)_4Ph_4$	6·0	−0·9	6·9	7·0
$N_4P_4(NMe_2)_4Ph_4$	4·5	−3·2	7·7	7·9
$N_4P_4(piperidino)_4Ph_4$	4·9	−3·0	7·9	8·0

* Mean of values for $N_4P_4Ph_8$ and the corresponding fully aminolysed compound, $N_4P_4(NRR')_8$.

be concluded that protonation on two ring nitrogen atoms occurs in all the octa-amino-compounds, the differences in ΔpK_a and $\Delta pK_a'$ among individual compounds being due to other effects.

The evidence that the first proton in the cases of both the tri- and tetra-phosphazenes, and both protons in the case of the tetraphosphazene compounds, attack cyclic nitrogen atoms is thus strong. The evidence that cyclic diprotonation occurs in the triphosphazene series is weaker. However, an approximately linear relationship exists between the $\Delta pK_a'$ values for corresponding members of each series, only the t-butyl derivatives being exceptional. This suggests the same diprotonation pattern, *i.e.*, cyclic, for both types of ring.

Interpretation of the pK_a *and* pK_a' *Values.*—Craig and Paddock's [11] analysis shows that the electronic situation in the phosphazene rings is of considerable complexity. It is convenient to define, as they do, a set of local axes for each phosphorus atom (see their Fig. 1). The bonds from the phosphorus atom to the neighbouring cyclic nitrogen atoms define the XY-plane, with the Y-axis as the bisector of the NPN ring-angle, and the Z-axis as the local normal. Groups attached exocyclically lie in the YZ-plane, the exocylic bond angle being approximately the tetrahedral one. Both these authors and Dewar, Lucken, and Whitehead [12] consider that the p_z-orbitals of the cyclic nitrogen atoms combine with d-orbitals of the phosphorus atoms to form delocalised molecular orbitals. Dewar, Lucken, and Whitehead assume that, in planar rings, d_{xz}- and d_{xy}-orbitals are used equally, and that this results in a system of weakly interacting three-centre orbitals covering each P–N–P group. Craig and Paddock point out that, if for any reason these two orbitals are used unequally, cyclic delocalisation must occur, and that in non-planar rings the $d_{x^2-y^2}$ and d_{xy}-orbitals can also overlap the p_π-orbitals of the cyclic nitrogen atoms. Large deviations from planarity are likely in some of the compounds under discussion here. Back-donation of electrons from the lone-pair sp-hybrid orbitals of the ring-nitrogen atoms into the $d_{x^2-y^2}$- and d_{xy}-orbitals of phosphorus, in planar rings, and into all except the d_{z^2}-orbitals in non-planar rings, introduces additional multiple (π') bonding in the ring.

Many of the arguments already advanced imply multiple bonding between the exocyclic nitrogen and cyclic phosphorus atoms, with electron-transfer from nitrogen to phosphorus, and this bonding will now be examined, from the restricted standpoint of symmetry only.

On an exocyclic nitrogen atom the lone-pair orbital is an sp-hybrid. Some combination of the s-component of this with the d_{z^2}-, d_{yz}-, and $d_{x^2-y^2}$-orbitals of the phosphorus atoms is at least allowable on symmetry grounds. As the bond angles at the exocyclic nitrogen atom are, in general, unknown, the degree of s-character in the hybrid cannot be assessed. In octakisdimethylaminocyclotetraphosphazatetraene, $N_4P_4(NMe_2)_8$, for example, the mean C–N–C angle is 116°; [10] the s-character of the lone-pair orbitals is therefore small, and s–d-bonding will be unimportant in this compound.

[11] Craig and Paddock, *J.*, 1962, 4118.
[12] Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.

If, in fact, the lone-pair orbital is practically a pure *p*-orbital, its axis will lie perpendicular to the phosphorus–exocyclic nitrogen bond and may take up orientations between two extreme positions. In position (1) its axis is parallel to the *X*-axis. Position (2) is perpendicular to this, and its axis lies in the *YZ*-plane. In position (1) combination with the d_{xy}- and d_{xz}-orbitals is permissible symmetrically, and in position (2) with the d_{z^2}-, $d_{x^2-y^2}$-, and d_{yz}-orbitals. In both positions, the relative importance of each *d*-orbital in combining with the *p*-orbital will depend to some extent on the exocyclic N–P–N bond angle.

Position (1) ensures through-conjugation of the exocyclic nitrogen atom at least to the cyclic nitrogen atoms nearest to it, through π- and π′-bonding. In position (2), for exocyclic bond angles close to the tetrahedral value, the most important bonding involves the d_{z^2}- and $d_{x^2-y^2}$-orbitals, and that involving the d_{z^2}-orbital does not lead to through-conjugation. In octakisdimethylaminocyclotetraphosphazatetraene, $N_4P_4(NMe_2)_8$, the orientation of the *p*-orbital on one exocyclic atom at each phosphorus is fairly close to position (1), that on the other lying roughly half-way between the two positions.

Reference to Tables 1—3 shows that for monoprotonation the aminophosphazenes $[NP(NRR')_2]_n$ ($n = 3,4$) are 2—3 pK units weaker than the parent amines, NHRR′, in aqueous solution, but in nitrobenzene are stronger by up to about 2 pK' units. Solvation effects frequently cause this inversion of the order of basic strength in two solvents, but it is also possible that conformational changes in the phosphazene molecules between the two solvents are responsible for it. The results are no more fundamental in one solvent than in the other.

These high basicities arise from the release of electrons from the exocyclic nitrogen to the cyclic phosphorus atoms. These electrons may affect the π- and π′-electrons either mesomerically, if there is through-conjugation, or inductively, if there is not, causing increases in the π- or π′-electron-densities at the adjacent cyclic nitrogen atoms compared with the values in the weakly basic parent chlorides. The inductive effect referred to must be distinguished from the normal base-weakening inductive effect expected from the exocyclic nitrogen atoms.

The differences between pK_{a1}' values for corresponding compounds in the six- and eight-membered ring series are small (mean value: ±0·4 pK' unit) and random in sign. This is also true for the pK_{a1} data.

In both series, the pK_{a1}' values fall within the range 7·6—8·8, and there are no trends which could be rationalised in terms of the electronic and steric properties of the exocyclic groups. The apparent dependence of the basicities in aqueous solutions of the compounds $[NP(NHR)_2]_{3 \text{ or } 4}$ (R = H, Me, and Et) upon the electron-releasing powers of the alkyl groups does not extend to the compounds with R = Me and Et in nitrobenzene, or to the compound $[NP(NMe_2)_2]_3$ in water. The most striking feature of the results is the much bigger range of pK_{a2}' values, which, incidentally, have no correlation with the pK_{a1}' values. In both series, the orders in which the pK_{a2}' values lie is broadly the reverse of that which would be expected if the inductive electron-releasing properties of the various alkyl groups were controlling the pK_{a2}' values. In the tetraene series, the value of pK_{a2}' decreases, in general, with the increasing bulk of the amino-group. This is true in the triene series to the more limited extent that the compounds containing secondary amino-groups have uniformly lower pK_{a2}' values than those containing primary amino-groups.

We shall discuss a number of possible explanations of these facts.

First the steric and polar characteristics of the substituents will cause variations in the shapes of the rings, which may in turn affect their electronic properties and hence their basicities. Unfortunatly, there is insufficient structural evidence to enable this important factor to be further discussed.

Secondly, on monoprotonation, molecules of nitrobenzene enter, to solvate the positive centre, between the exocyclic groups attached to the phosphorus atoms which are

neighbours to the protonated cyclic nitrogen atom. To an extent dependent on the bulkiness of these groups, a conformational change may be forced on the molecule, such that other cyclic nitrogen atoms become shielded to solvation by the close approach of the exocyclic groups on the phosphorus atoms flanking them. This shielding will be further enhanced if these groups are also bulky. Thus, the bulkier the substituents, the greater will be the steric hindrance to the solvation of the second protonated position, and the lower the value of pK_{a2}'.

Thirdly, a purely electronic explanation may be advanced. The levelling of the pK_{a1}' values compared with the pK_{a2}' values means that the electron-densities on the cyclic nitrogen atoms of the neutral molecules must be roughly the same in each series, and no differentiation must occur even in the monoprotonated bases. This suggests some mechanism in the molecule, or " saturation effect," which, during the attack of the first proton, limits the charge-densities on the cyclic nitrogen atoms to values lying within the electron-releasing powers of all the amino-groups studied here. Diprotonation, however, calls for a further release of electrons from the exocyclic groups, causing their electron-releasing powers to be distinguished. This leads, in turn, to a spread of pK_{a2}' values.

Consider the pK_{a2}' values first. The analysis made above shows that the orientation of the exocyclic groups will determine which *d*-orbitals of the phosphorus atom are used in exocyclic multiple bonding, and to what extent. There might well be an optimum orientation, determined, for example, by the strength of the multiple bonding and the degree of through-conjugation to the cyclic nitrogen atoms, which leads to the highest charge-density on these atoms. It is likely that only the smaller groups on a given phosphorus atom could take up position (**1**), and this, or something close to it, is probably the optimum position. With increasing steric hindrance between the exocyclic groups, the orientations of one or both substituents on each phosphorus atom move away from this position, the charge-densities available on the cyclic nitrogen atoms for the second proton fall and so do the pK_{a2}' values.

Consider now the saturation effect. It has been suggested that the strength of bonding involving the *d*-orbitals of phosphorus depends critically on the electron-density on the phosphorus atom,[13] being weaker the higher it is above a certain value. It may well be that the critical electron-density on the phosphorus atoms is reached by transfer of charge from the exocyclic groups in all these amino-compounds, and no more can flow to the ring without raising this electron-density and weakening the multiple bonding.[14] The charge-densities on the cyclic phosphorus atoms will be approximately independent of the amino-substituent, and will control the charge-densities on the cyclic nitrogen atoms so that these are also approximately the same in all the amino-compounds.

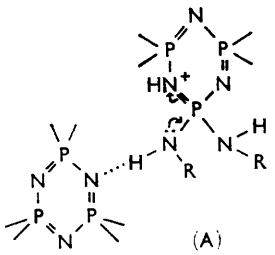
On diprotonation, the charge-density on the phosphorus atoms probably falls below the critical value, at least in the more sterically hindered compounds, enabling the electron-densities on the cyclic nitrogen atoms to be controlled directly by the polar and steric properties of the exocyclic groups.

The Association of Base and Conjugate Acid.—The tendency for aminophosphazenes formed from primary amines to associate with the protonated base in solutions in nitrobenzene, in contrast to the behaviour of those formed from secondary amines may be explained as follows. The structures (A) and (B) involve the strongest proton-acceptors, *i.e.*, cyclic nitrogen atoms. While the derivatives of primary amines can take up structure (A), leading to a strong association, those of secondary amines can only take up the more sterically hindered structure (B), leading to an association which would be undetectable in our measurements.

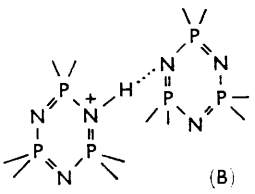
The results discussed above, and their interpretation, raise points of some general chemical interest. In general, a group X when attached to a phosphorus atom, P–X,

[13] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1953, **332**; Jaffé, *J. Phys. Chem.*, 1954, **58**, 185.
[14] Hudson and Keay, *J.*, 1960, 1859.

tends to resemble chemically the same group when attached to an acyl group, R'C(:O)X,[15,16] but shows little or no resemblance to the corresponding alkyl, Alk–X, or aryl derivatives, Ar–X. For example, an amino-group attached to a phosphorus atom



(A)



(B)

P–NHR, possesses, in general, amide rather than amine properties. Thus, hexamethylphosphoric triamide, like acetamide, is a weak base.

The analogy is seen to extend also to amino-groups attached to phosphazene rings, the comparatively high basicity of the aminophosphazenes deriving from the cyclic rather than the exocyclic nitrogen atoms. These compounds are structurally analogous to the derivatives of melamine, $N_3C_3(NRR')_3$, which also have appreciable basic strengths [17] and other donor properties.[3] Other chemical and physical analogies between phosphazenes and 1,3,5-triazines have been observed.[3,18,19]

It has frequently been reported (cf. ref. 19) that it is difficult to remove all the amine hydrochloride or ammonium chloride from aminophosphazenes in the working-up of reaction mixtures derived from aminolysis or ammonolysis reactions of halogenophosphazenes. This can now be seen to be due largely or wholly to formation of the hydrochlorides of the relevant aminophosphazenes.

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