Structure and Basicity. Part IX.[1] Triphenylphosphazenylcyclophosphazenes: Examples of Exo- and Endo-cyclic Protonations and the Relation of these to the Conformation of the Triphenylphosphazenyl Group

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The $pK'_{a,1}$ values of a series of triphenylphosphazenylcyclotriphosphazatrienes of known structure have been measured, *viz.* $N_3P_3Cl_5(NPPh_3)$, $N_3P_3Cl_4(NPPh_3)_2$ (three isomers), $N_3P_3PhCl_4(NPPh_3)$, $N_3P_3Ph_2Cl_3(NPPh_3)$, $N_3P_3Ph_4Cl(NPPh_3)$, $N_3P_3Cl_4(NMe_2)(NPPh_3)$ (two isomers), $N_3P_3Cl_3(NMe_2)_2(NPPh_3)$, $N_3P_3Cl_2(NMe_2)_3(NPPh_3)$, $N_3P_3Cl_4(NC_5H_{10})(NPPh_3)$ (two isomers), $N_3P_3Cl_4(NH_2)(NPPh_3)$, $N_3P_3Cl_4(NPPh_3)(OEt)$, $N_3P_3Ph(NMe_2)_4(NPPh_3)$, and $N_3P_3(NMe_2)_5(NPPh_3)$. In almost all the compounds an unambiguous assignment of the first sites of protonation can be made. These can be classified as (*i*) type (I), where the group on the same phosphorus atom as the Ph_3PN substituent is Cl or Ph_3PN and gives rise to ring protonation, or (*ii*) type (II), where the group is NH_2, NMe_2, or Ph and exocyclic protonation occurs. Type (I) and (II) behaviour is correlated with the conformation of the Ph_3PN group relative to the ring; this is borne out by *X*-ray crystallographic data. Basicity measurements are suggested as a tool to determine the conformation of phosphazenyl substituents. Values of $\Delta pK'_a$ ($= pK'_{a,1} - pK'_{a,2}$) enable the assignment of the two sites of protonation in doubly protonated species. Probable sites of protonation are adduced for $N_4P_4Cl_6(NPPh_3)_2$. In the ground state, the electron-releasing properties of the Ph_3PN group resemble those of NR'_2 and NHR' (R' = alkyl) groups; on protonation, however, the Ph_3PN group becomes by far the most powerful electron-releasing group observed to date in cyclophosphazene chemistry.

In our earlier studies on the basicities of cyclophosphazenes towards perchloric acid in nitrobenzene we showed that the first,[2] as well as the second,[2,3] site of protonation is an endocyclic nitrogen atom. This pertains even to the most basic compounds studied so far, the aminocyclophosphazenes, *e.g.* $N_3P_3R_6$ [R = NH_2, NHR', or NR'_2 (R' = alkyl)],[2] where protonation at the exocyclic nitrogen atom had to be considered. *X*-Ray crystallographic studies of the unperturbed molecules, $N_3P_3Cl_{6-n}(NMe_2)_n$,[4-6] $N_4P_4Cl_{8-n}(NMe_2)_n$,[7-11] and $N_6P_6(NMe_2)_{12}$,[12] revealed that a considerable

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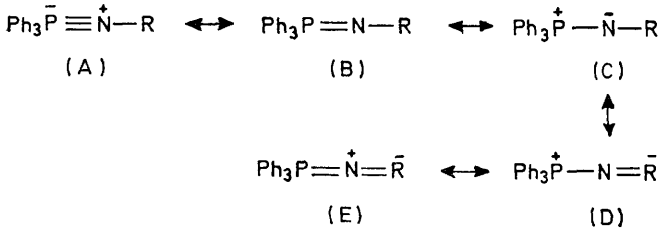
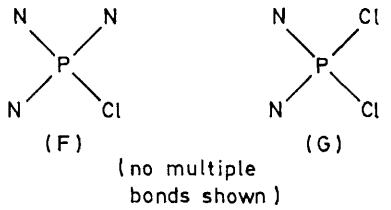
delocalisation of the lone-pair electrons of the exocyclic nitrogen atom towards the cyclophosphazene ring occurs in the ground state, as witnessed by the near coplanarity of the three substituents of the dimethylamino-nitrogen atom (sums of bond angles tend towards 360°) and the relatively short exocyclic P–N bond distances. This shortening is enhanced in the protonated species [*gem*-$N_3P_3Cl_2H(NHPr^i)_4]Cl$ [13] and $[N_3P_3H(NMe_2)_6]_2[Mo_6O_{19}]$ [14] studied by *X*-ray crystallography. The former, very accurate, study [13] also confirmed that protonation occurred on the endocyclic nitrogen atom flanked by two $\equiv P(NHPr^i)_2$ moieties.

PPP-Triphenylphosphazene, $Ph_3P{=}NH$, is a strong base and a strong nucleophile.[15] The basicities of its derivatives, $Ph_3P{=}NR$,[15] are strongly dependent on the nature of R; if the latter is an electron acceptor the basicity is reduced.[15] *X*-Ray crystallographic studies, where R is an electron-acceptor group, reveal rather short N–R bonds.[16–18] For any triphenylphosphazenyl derivatives (or related compounds), five canonical forms (A)—(E) may be considered. Some evidence for



contributions from (E) was obtained in a recent study by Phillips and Skapski [19] on a related compound, $[RuCl_3(NPEt_2Ph)(PEt_2Ph)_2]$. For most compounds the resonance forms (B)—(D) will probably be the major ones and their relative importance will depend on the steric and polar effects of R.

We have shown elsewhere [20] the difficulty of introducing more than two Ph_3PN residues into $N_3P_3Cl_6$, and



suggested steric hindrance as a major cause. A linear relation between P–Cl bond lengths and ^{35}Cl n.q.r. coupling constants has been demonstrated [21] for a number of cyclophosphazenes, where the substituents on phosphorus are nitrogen and chlorine [(F) and (G)]. If the same pertains, as appears likely, to triphenylphosphazenylcyclotriphosphazatrienes, then, in the two compounds so far studied, $N_3P_3Cl_5(NPPh_3)$ [20] and *gem*-$N_3P_3Cl_4(NPPh_3)_2$,[22] the effect of the Ph_3PN group in the ground state (as measured by ^{35}Cl n.q.r. frequencies) is similar to that of NR'_2 and NHR' groups.[22] In stark contrast to this is the behaviour of triphenylphosphazenylcyclophosphazene derivatives in basicity studies.

All monosubstituted, $N_3P_3Cl_5R$, and disubstituted derivatives, $N_3P_3Cl_4R_2$, of hexachlorocyclotriphosphazatriene hitherto studied are well below the level of detection ($pK'_a < -6$) of our present technique.[23,24] Whilst the triphenylphosphazenyl derivative, $N_3P_3Cl_5(NPPh_3)$ (I), has a pK'_a value of <-6, the three disubstituted derivatives, $N_3P_3Cl_4(NPPh_3)_2$ [(IIa)—(IIc)], are well within our range of measurements. The geminal isomer,[25] (IIa), m.p. 199—201 °C, has a pK'_a value of 0.4. The two non-geminal isomers [20] of m.p. 225, (IIb), and 230 °C, (IIc), respectively, believed to have a *cis–trans* relation, each have the same pK'_a value of 0.2. We have demonstrated earlier that (*i*) the contributions of a substituent, R, on a phosphorus atom α or γ to a cyclic nitrogen atom are α_R and γ_R respectively [24] and that $\alpha_R \approx 2\gamma_R$,[3,26] (*ii*) the additivity [26] of these substituent constants (except at very high pK'_a values when the 'saturation effect' [3] comes into play), and (*iii*), for two or three sites of equal basicity, statistical quantities of 0.3 and 0.5 respectively [26] must be added to the calculated pK'_a values.

The properties of the exo- and endo-cyclic phosphazenyl nitrogen atoms are probably similar. Hence, it is not easy to predict *a priori* where protonation will be preferred. If exocyclic nitrogen atoms are the first to be protonated in compounds (II), $\alpha_R - \gamma_R = 0.2$ ($R = NPPh_3$) and hence $\alpha_R \approx 0.4$, a nonsensical answer in view of the high pK'_a values of these compounds. If endocyclic protonation [type (I) behaviour] is assumed, however, we would expect, in the light of all previous experience, that the protonated ring-nitrogen atoms would be those where the sum of the substituent constants (α_R and γ_R) is greatest. Hence, the only difference in pK_a' values expected between the non-geminal and geminal isomer is 0.3 (two equivalent sites); [26] 0.2 was observed. We have estimated earlier the pK'_a value of $N_3P_3Cl_6$ as -20.4.[27] Hence, we deduce $\alpha_{NPPh_3} = 10.3$ [for type (I) behaviour], by far the

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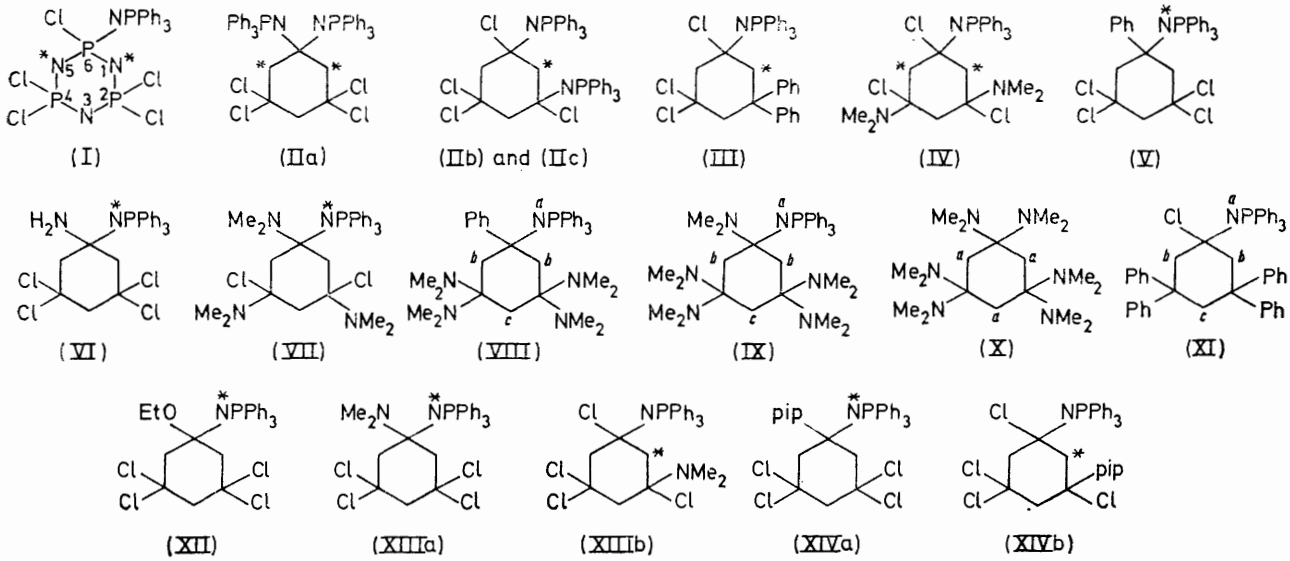
[27] R. A. Shaw, *Endeavour*, 1968, 74.

highest α_R value observed to date. In the aminocyclotriphosphazatriene series (three-co-ordinate exocyclic nitrogen atom, one lone pair of electrons available for back conjugation to the phosphorus atom), α_R values trend in the opposite direction to inductive effects, *e.g.* α_{NH_2} 6.0 > α_{NHMe} 5.8 > α_{NMe_2} 5.6 and α_{NHEt} 5.8 > α_{NMe_2} 5.6.[3] The reverse is observed for alkoxycyclotriphosphazatrienes [28] (two-co-ordinate exocyclic oxygen atom, two lone pairs of electrons available for back-conjugation to the phosphorus atom), *e.g.* α_{OMe} 3.6 [26] < α_{OEt} 3.9 [29] < α_{OPri} 4.3 [estimated from $\alpha_R \approx 2\gamma_R$; p$K'_a$ for $N_3P_3(OPr^i)_6$ is 1.4]. Triphenylphosphazenyl substituents (two-co-ordinate exocyclic nitrogen atom, two lone pairs of electrons potentially available for back conjugation), taking into account both electronic and steric factors, have obviously greater electron-releasing potential than either amino- or alkoxy-substituents.

If we now use previously determined substituent constants α_{Ph} 4.2,[24] α_{NMe_2} 5.6,[26] and γ_{NMe_2} 2.8,[26] we obtain excellent agreement between the observed and calculated (endocyclic) pK'_a values for compounds (II)—(IV). On the other hand, the observed pK'_a values for compounds (V)—(VII) differ by 0.9, 0.9, and −1.6 pK'_a units respectively from those predicted assuming endocyclic protonation (Table).

X-Ray crystallographic investigations of chloro(dimethylamino)-cyclotriphosphazatrienes [4-6] and -cyclotetraphosphazatetraenes [7-11] have shown that the con-



* Denotes position(s) of protonation; *a*, *b*, and *c* denote different potential protonation sites.

Observed and calculated p$K'_{a,1}$ values and ΔpK'_a values for some triphenylphosphazenylcyclotriphosphazatrienes

Compound	p$K'_{a,1}$ obs.	p$K'_{a,1}$ calc. (*endo*) [a]	p$K'_{a,1}$ calc. (*exo*) [a]	p$K'_{a,2}$	ΔpK'_a [b]
(I)	< −6.0	−9.8	−8.9		
(IIa)	0.4	0.5	1.7		
(IIb) and (IIc)	0.2	0.2 (standard)	−4.7		
(III)	−1.8	−1.7	−4.3		
(IV)	−1.6	−1.4	−3.3		
(V)	−4.7	−5.6	−4.7 (standard)		
(VI)	−2.9	−3.8	−2.9		
(VII)	2.6	4.2	2.3	*ca.* −5.0	*ca.* 7.6
(VIII)	8.7	> 6.5 (N^1, N^5), > 7.1 (N^3)	6.5	−1.8	10.5
(IX)	9.1	> 7.9 (N^1, N^5), > 7.6 (N^3)	7.9	−1.3	10.4
(X)	7.5			−3.1	10.6
(XI)	2.5	3.2 (N^1, N^5), 1.6 (N^3)	0.3	*ca.* −5.0	*ca.* 7.5
(XII)	−5.2	−5.9	−5.0		
(XIIIa)	−2.0	−4.2	−3.0		
(XIIIb)	−4.8	−4.7	−3.6		
(XIVa)	−2.0	−4.2	−3.0		
(XIVb)	−4.7	−4.7	−3.6		

[a] For assumptions made in the calculations, see text. [b] p$K'_{a,1}$ − p$K'_{a,2}$.

[28] D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw, *J. Chem. Soc.*, 1965, 2804.

[29] R. Das, R. A. Shaw, B. C. Smith, and M. Woods, *J.C.S. Dalton*, 1973, 709.

formation of the Me_2N group relative to its nearest ring segment, NPN, differs markedly between the groups $\equiv PCl(NMe_2)$ and $\equiv P(NMe_2)_2$. Obviously steric effects play a major part. Similar investigations on acyclic ylides [30] and related compounds (*e.g.* Ph_3PN derivatives) [16] show a marked dependence of conformations and dihedral angles on structural effects in other parts of the molecule.[16,30]

If the replacement of the chlorine atom on the phosphorus carrying the Ph_3PN group by a phenyl group changes the conformation of the Ph_3PN group (see later) in such a manner that the electron release to the phosphazene ring is decreased, exocyclic protonation becomes feasible [type (**II**) behaviour]. Assuming that this is the case for compound (V), $N_3P_3PhCl_4(NPPh_3)$, using known substituent constants, α_{NH_2} 6.0,[3] *etc.* we obtain excellent agreement between observed and calculated (exocyclic) pK'_a values for compounds (V)—(VII).

Compounds (I)—(IV) have either a chlorine atom or a two-co-ordinate nitrogen atom of a phosphazenyl group on the same phosphorus as the Ph_3PN substituent. Compounds (V)—(VII) have sterically more demanding groups in a similar position. It appears, therefore, that the choice between endo- and exo-cyclic protonation is largely governed by the nature of the group adjacent to the Ph_3PN substituent. *X*-Ray crystallographic studies on a variety of ylides and related compounds suggest that they adopt only a relatively small number of different conformations.[16,30] The same appears to pertain to the compounds discussed here by the clear division of $pK'_{a,1}$ values between the two groups of compounds, (I)—(IV) and (V)—(VII). We shall call these two conformations for brevity type (**I**) and (**II**) respectively. We can calculate the pK'_a value of the exocyclic nitrogen atom in compound (I) in the type (**II**) conformation as —8.9, and for the adjacent endocyclic nitrogens with the substituent in the type (**I**) conformation as —9.8. That there is merit in assuming only a small number of conformations (or groups of closely related conformations) for the Ph_3PN substituent can be seen from the observed pK'_a values of compounds (V)—(VII), which deviate both positively and negatively from the highest possible values, if the substituents were free to adopt conformations which could supply the highest electron density to either *endo-* or *exo*-nitrogen atoms. Compound (IIa), assuming *exo* protonation and using α_{NPPh_3} 10.3 from compounds (IIb), (IIc), (IV), and (V), would give rise to a pK'_a value of 1.7, at variance with the observed basicity. Similarly, compounds (IIb) and (IIc), using the measured pK'_a value of 0.2 and assuming *exo* protonation, would give a substituent constant $\gamma_{NPPh_3} \approx 9.1$; alternatively, using α_{NPPh_3} (10.3) $\approx 2\gamma_{NPPh_3}$, would give a calculated pK'_a value of —4.7. Both values are at variance, the former with all previous experience, the latter with experimental observations.

Compounds (VIII) and (IX) have observed $pK'_{a,1}$ values of a magnitude which necessitates consideration of whether the ' saturation effect ' [3] is operative. From the above discussion, we can assume the Ph_3PN substituent to be in the type (**II**) conformation, and hence we can calculate the basicities of the *exo*-nitrogen atoms; in both compounds these are well below the observed values. If we take for the substituent constants of the Ph_3PN group [in the type (**II**) conformation] as lower limits the α and γ values of the Me_2N group [they are likely to be considerably higher; *cf.* $pK'_{a,1}$ 9.1 for compound (IX) and 7.5 for (X), $N_3P_3(NMe_2)_6$], this leaves little doubt that the now accumulated electron density from the substituents gives rise to ring protonation by the first proton, although whether this is α or γ to the Ph_3PN substituent will depend on the actual magnitudes of these constants.

Further confirmation that [in compounds (VIII) and (IX)] $pK'_{a,1}$ arises from *endo* protonation, comes from a consideration of $\Delta pK'_a$ ($= pK'_{a,1} - pK'_{a,2}$) values (Table). Whilst $\Delta pK'_a$ values for compounds (VIII)—(X) are 10.4—10.6, that of compound (VII) is only *ca.* 7.6. We have shown elsewhere that $\Delta pK'_a$ for the tetramer $N_4P_4(NMe_2)_8$ has a value (uncorrected for statistical effects) of 8.0,[1,2] in close agreement with that for compound (VII) and in contrast with that [$\Delta pK'_a$ 10.6 (uncorrected)] [2] of compound (X). For compound (VII) we therefore assign $pK'_{a,1}$ to protonation at site *a* and $pK'_{a,2}$ at site *c*. In compounds (VIII) and (IX), $pK'_{a,1}$ values arise from *endo* protonations; $\Delta pK'_a$ values (*ca.* 10.5) indicate a steric and/or polar relation as in compound (X). If the first protonations occur at sites *c*, the second take place at sites *b*. If the $pK'_{a,1}$ values derive from protonations at sites *b*, however, the present data do not permit determination of whether $pK'_{a,2}$ values arise from protonation at sites *a* or *c*.

This work had reached the above stage *ca.* 2 years ago; it seemed desirable, however, to test some of the above conclusions with further basicity data and, if possible, *X*-ray crystallographic investigations. Hence compounds (XI)—(XIII) were resynthesised,[20] and (XIV) newly synthesised (see Experimental section). There is no doubt that in compound (XI) $pK'_{a,1}$ arises from protonation on the ring [type (**I**), chlorine adjacent to Ph_3PN group], although the data do not permit distinction between sites *b* and *c* (Table). The $\Delta pK'_a$ value of *ca.* 7.5 suggests that in the diprotonated species the sites are *c* and *a*.

Whether compound (XII), an ethoxy-derivative, is of type (**I**) or (**II**) is *a priori* less easy to predict. The oxygen atom is two-co-ordinate and has two lone pairs of electrons (*cf.* the nitrogen of Ph_3PN), but the steric demands of the EtO group relative to that of Ph_3PN are less easy to assess. The $pK'_{a,1}$ value suggests, but does not confirm, type (**II**) behaviour, *i.e.* exocyclic protonation.

Compounds (XIII) and (XIV) are two pairs of isomers and their structures represent an excellent test for type (**I**) and (**II**) behaviour. The structures of

[30] A. F. Cameron, N. J. Hair, and D. G. Morris, *J.C.S. Perkin II*, 1972, 1071, 1331; A. F. Cameron, personal communication.

compounds (XIII) were confirmed by ^{1}H n.m.r. spectroscopy.[20] Compounds (XIV) were prepared by analogous routes. The structures of all four compounds were confirmed by ^{31}P n.m.r. spectroscopy.[31] The non-geminal compounds (XIIIb) and (XIVb) are, as predicted, the weaker bases, in excellent agreement with calculated values for type (**I**) (endocyclic) protonation. The geminal compounds (XIIIa) and (XIVa) are the stronger bases; their $pK'_{a,1}$ values were somewhat higher than calculated, but they are a clear case of type (**II**) (exocyclic) protonation. [For the calculations for compounds (XIII) and (XIV), (IV) and (VII) were used as the reference points.]

Two tetramer derivatives were also investigated. The monosubstituted derivative, $N_4P_4Cl_7(NPPh_3)$ (XV), had a $pK'_{a,1}$ value of <-6.0. The other is a non-geminally substituted bis derivative, $N_4P_4Cl_6(NPPh_3)_2$ (XVI). This has the same local environment as compounds (I)—(IV) and hence it can be assumed that the Ph_3PN substituents have the type (**I**) conformation. Compound (XVI) had a pK'_a value of -4.6, *ca.* 5 pK'_a units lower than those of compounds (IIb) and (IIc), and hence the two Ph_3PN substituents have undoubtedly a 2,6-relation.[20] Making the, to date, unproven assumption that the substituent constant relations of the trimer rings are applicable to the tetramer system, we calculate from the pK'_a values of compounds (IIb) and (IIc) a pK'_a value for compound (XVI) of -4.4 [making a statistical allowance for four equivalent sites (0.6 pK'_a units)]. The excellence of the agreement is probably fortuitous, but shows the essential correctness of our assignment. This has since been confirmed by an *X*-ray crystallographic investigation.[32]

The evidence at present shows that the electron-releasing properties of the Ph_3PN group in the ground state are of the order of that of NR'_2 and NHR' groups, but that, at the demand of a proton, they become by far the most powerful electron-releasing substituents known to date in cyclophosphazene chemistry.

Since completion of the basicity work, *X*-ray crystallographic data have become available for compounds (V)[18] and (XVI).[32] The former, $N_3P_3PhCl_4(NPPh_3)$, shows electron delocalisation over the exocyclic P–N–P segment, both P–N bonds being very short and of the same length; indeed, they are shorter than the ring P–N bonds at the point of attachment of the Ph_3PN substituent and as short as those of the Cl_2P–N–N–PCl_2 segment. The plane of the exocyclic P–N–P segment is perpendicular to that of the trimer ring.[18] Compound (XVI), although not fully refined, has a 2,6-*trans*-configuration. Here the exocyclic P–N–P segments are turned through *ca.* 90° compared to that of compound (V).[32] Whilst the data quoted pertain to the free bases in the solid state, it appears that type (**I**) and (**II**) behaviour is associated with exocyclic P–N–P segments parallel or perpendicular to the adjacent N–P–N ring segments. Assuming an approximately sp^2 hybridised exocyclic nitrogen atom [in compound (V) the angle P–N–P is *ca.* 132°], its p_z orbital is approximately parallel [compound (V)] or perpendicular [compound (XVI)] to the above mentioned ring segments. Some of the small differences between calculated and observed values [compounds (XI), (XIIIa), and (XIVa)] could be due to changes in the exocyclic P–N–P angles or the conformations of the exocyclic P–N–P segment. A discussion of the conformations of the Ph_3PN, and of the Me_2N and Ph, groups has been given in greater detail elsewhere.[33] Basicity measurements on phosphazenylcyclophosphazenes appear a promising tool for the conformational analysis of the exocyclic phosphazenyl group.

EXPERIMENTAL

The technique of measuring basicities in nitrobenzene [34] and the preparation of the compounds [except (XIV), see below] have been described elsewhere.[20,25]

2,2,4,4-*Tetrachloro*-6-*piperidino*-6-N-(2′,2′,2′-*triphenylphosphazenyl*)*cyclotriphosphazatriene*, (XIVa).—To a solution of compound (I) [20] (5.8 g, 0.01 mol) in diethyl ether (250 cm^3) was added dropwise with stirring a solution of piperidine (1.6 g, 0.02 mol) in diethyl ether (25 cm^3). The mixture was then heated under reflux for 0.5 h, after which the precipitated piperidinium chloride was filtered off. The filtrate was evaporated to dryness and the residue dissolved in hot benzene (*ca.* 20 cm^3). An equal volume of light petroleum was added and the solution set aside to cool. On standing, crystals of compound (XIVa) were obtained (4 g, 64%), m.p. 150—160 °C (Found: C, 43.1; H, 4.0; N, 10.8; P, 19.5. $C_{23}H_{25}Cl_4N_5P_4$ requires C, 43.3; H, 4.0; N, 11.0; P, 19.5%). Repeated crystallisation failed to change the melting-point range.

2,4,4,6-*Tetrachloro*-2-*piperidino*-6-N-(2′,2′,2′-*triphenylphosphazenyl*)*cyclotriphosphazatriene*, (XIVb).—To a solution of 2,4,4,6,6-pentachloro-2-piperidinocyclotriphosphazatriene [35] (3.9 g, 0.01 mol) in benzene (100 cm^3) was added *PPP*-triphenylphosphazene (5.5 g, 0.02 mol) in benzene (50 cm^3). The mixture was heated under reflux for 4 h and the precipitated aminotriphenylphosphonium chloride filtered off. The filtrate was evaporated to small bulk and light petroleum added. On standing, crystals of compound (XIVb) were obtained (3.5 g, 57%), m.p. 179—181° C (Found: C, 43.2; H, 3.9; N, 10.9; P, 19.4. $C_{23}H_{26}Cl_4N_5P_4$ requires C, 43.3; H, 4.0; N, 11.0; P, 19.5%).

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