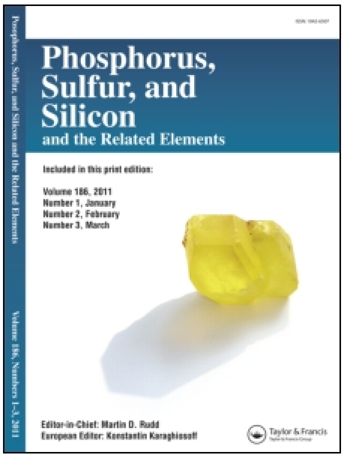

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POTENTIOMETRIC AND CONDUCTOMETRIC STUDIES OF THE BEHAVIOUR OF PHOSPHORUS NITROGEN COMPOUNDS TOWARDS PERCHLORIC ACID IN NON-AQUEOUS MEDIA

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POTENTIOMETRIC AND CONDUCTOMETRIC STUDIES OF THE BEHAVIOUR OF PHOSPHORUS NITROGEN COMPOUNDS TOWARDS PERCHLORIC ACID IN NON-AQUEOUS MEDIA

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The behaviour of phosphazenes, phosphazanes and other phosphorus-nitrogen compounds towards perchloric acid has been studied in nitrobenzene by potentiometry, and in nitrobenzene, in nitrobenzene/benzene (1:1), and in acetic acid by conductometry.

We report here some potentiometric and conductometric studies on cyclophosphazenes. Our potentiometric studies are well established. (For a summary, see ref. 1.) We have utilised these now to obtain basicity substituent constants for spirocyclic substituents, values which we needed for a relationship to endocyclic bond angles in cyclotriphosphazatrienes.[2, 3]

We have also used the same technique to help us in structural elucidation.

We also report the first conductometric titration studies of phosphazenes.

In Table I we give selected pK'_a values in nitrobenzene solution of cyclotriphosphazatrienes carrying spiro substituents.

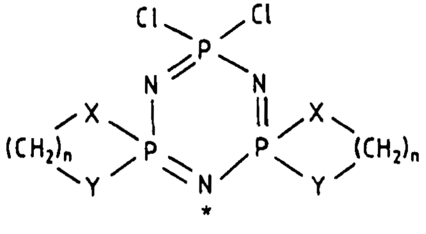
The compounds are arranged in order of increasing basicity. To evaluate the substituent constants, ∂_R, ideally we should have measured the bis-spiro derivatives

TABLE I

$pK'_{a,1}$ values in nitrobenzene solution of cyclotriphosphazatrienes with spiro substituents

Compound	$pK_{a,1}$
$N_3P_3[O(CH_2)_2O]PH_2Cl_2$	−4.93
$N_3P_3[O(CH_2)_3O]PH_2Cl_2$	−4.71
$N_3P_3[O(CH_2)_3NH]Ph_2Cl_2$	−2.25
$N_3P_3[O(CH_3)_2O](NHBu^t)_2Cl_2$	−1.20
$N_3P_3[MeN(CH_2)_3NMe]Ph_2Cl_2$	−0.42
$N_3P_3[HN(CH_2)_4NH]Ph_2Cl_2$	0.40
$N_3P_3[HN(CH_2)_3NH](NHBu^t)_2Cl_2$	3.82
$N_3P_3[O(CH_2)_3O](NHE^t)_4$	6.25

(**1**). (X = Y = O, NH, NMe or X ≠ Y; *n* = 2, 3, 4.) (Asterisks indicate preferred point of protonation.)



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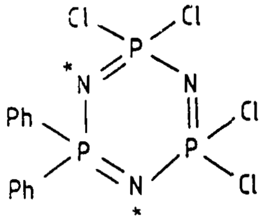
As a number of these have been difficult, or so far, impossible to obtain, *viz.*, $N_3P_3[X(CH_2)_2NH]_2Cl_2$ (X = O or NH), we decided to use the geminal compounds $N_3P_3Ph_2CL_4$ (**2**) and $N_3P_3(NHBu^t)_2CL_4$ (**3**) as starting materials and to synthesise their monospiro derivatives, $N_3P_3Ph_2[X(CH_2)_nY]Cl_2$ (**4**) and $N_3P_3(NHBu^t)_2[X(CH_2)_nY]Cl_2$ (**5**) (*n* = 2, 3, 4; X = Y = O, NH, NMe; X ≠ Y)[2].



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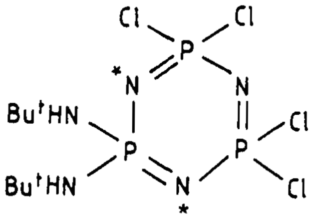

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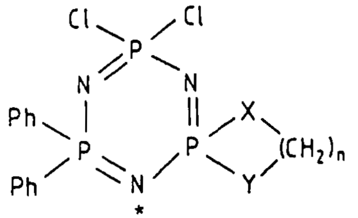

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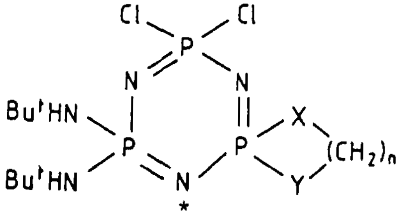

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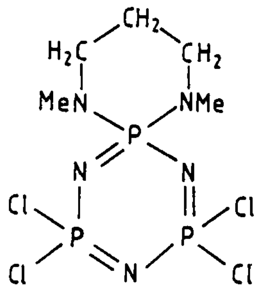
Most of the compounds were purposely made for the present study and their NMR spectra and a crystal structure are reported elsewhere.[2,4]

We note that compounds of type (**5**) are about 3.5 to 4.0 pK_a' units stronger bases than those of type (**4**). We further note that where the linking atoms are the same, e.g., in the spiro groups, $O(CH_2)_nO$, ($n = 2, 3, 4$) the differences in pK_a' values are relatively small. Change of linking atoms from O to NH increases the basicity by about 2.2 to 3 pK_a' units, e.g., the series

$$O(CH_2)_nO < O(CH_2)_nNH < NH(CH_2)_nNH.$$

We commented elsewhere[2,4] on the apparently anomalous behaviour of the $NMe(CH_2)_3NMe$ derivatives in NMR spectroscopy. The pK_a' value of -0.42 for $N_3P_3[NMe(CH_2)_3NMe]Ph_2Cl_2$ appears to be somewhat lower than that expected by comparison with related compounds. Whilst further measurements will be needed to confirm this, the crystal structure of $N_3P_3[NMe(CH_2)_3NMe]Cl_4$ (**6**)[4,5] when contrasted with that of $N_3P_3[NH(CH_2)_3NH]CL_4$[5,6] (**7**) gives us a clue to this lowering of basicity on passing from $NH(CH_2)_3NH$ substituents to $NMe(CH_2)_3NMe$ substituents. In the primary amino derivative (**7**) the exocyclic nitrogen atoms are trigonal planar and hence there is an optimum situation for back-donating their lone-pairs to phosphorus. In the secondary amino derivative (**6**), the exocyclic nitrogen atoms are deviating markedly from a trigonal planar structure and thus back conjugation will be diminished, with a resultant lowering of basicity of the ring nitrogen atoms.



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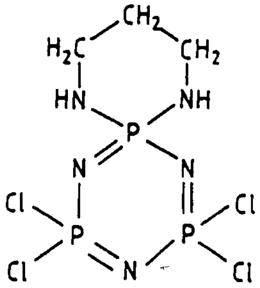

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We now demonstrate the use of pK_a' values in structure determinations and demonstrate this work with two examples.

We have mentioned elsewhere that the compound whose composition and molecular weight corresponded to $N_3P_3[O(CH_2)_3O](NHBu^t)_2Cl_2$ could have five possible structures (**8**–**12**) (Figure 1).

We give below each structure the calculated pK_a' value. The experimental value of -0.8 definitely rules out structures **8**, **11** and **12**, and clearly points to either structure **9** or **10**. It cannot however distinguish between these two.[1] In this particular case our NMR data[2] would have given us the erroneous structure (**10**) because of accidental isochrony of the chemical shifts of $\underline{P}(NHBu^t)_2$ and $\underline{P}[O(CH_2)_3O]$, but X-ray crystallography decisively demonstrated structure (**9**).[2,5]

We have shown elsewhere[7,8] that the alcoholysis of the geminal compound $N_3P_3(NH_2)_2Cl_4$ can proceed with or without rearrangements of NH_2 groups from a

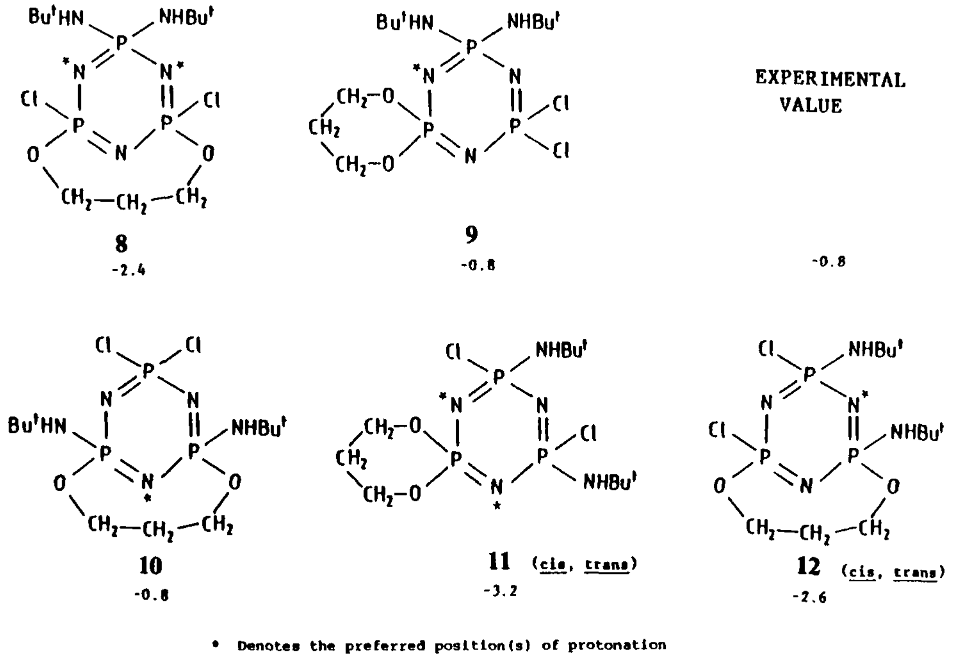
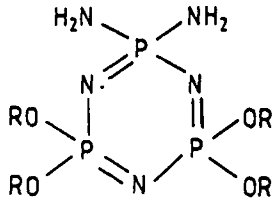


FIGURE 1 Possible Structures for $N_3P_3[O(CH_2)_3O](NHBu^t)_2Cl_2$ and their calculated pK_a' values.

geminal to two nongeminal positions. In addition to fully alcoholysed derivatives $N_3P_3(NH_2)_2(OR)_4$, unrearranged (**13**) and rearranged (**14**), we also isolated partially alcoholysed compounds, $N_3P_3(NH_2)_2(OR)_2Cl_2$(R = Et, Pr^i) (**15**–**19**) (Figure 2).



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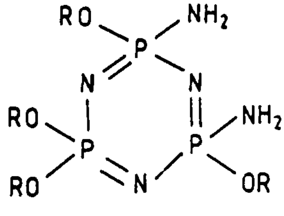

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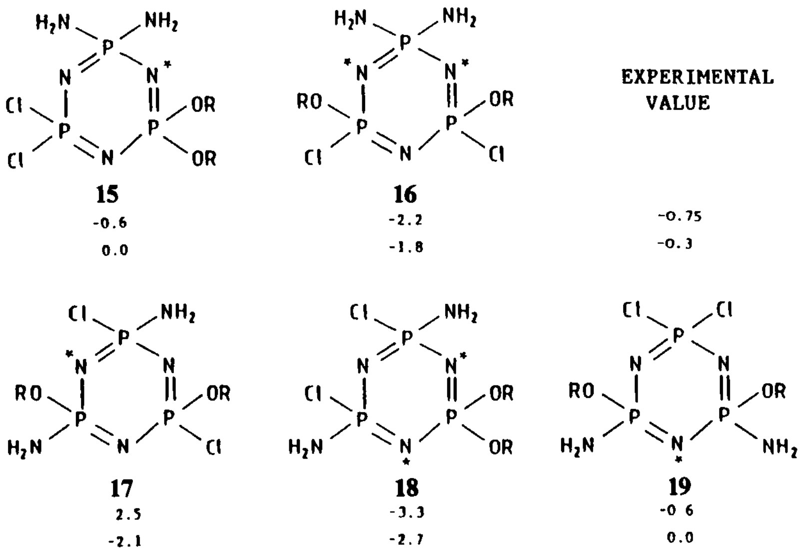
The experimentally observed pK_a' values for $N_3P_3(NH_2)_2(OR)_2Cl_2$, were for R = Et − 0.75 and for R = Pr^i − 0.3. These decisively exclude structures (**16**–**18**), and clearly point to either structure (**15**) or (**19**). The alcoholysis of $N_3P_3Cl_6$ proceeds overwhelmingly by a non-geminal pathway. (For a recent summary see ref. 9). This, together with the NMR spectroscopy of these two compounds[8] makes structural type (**15**) unlikely unless, of course, we have another case of accidental isochrony, as in the compound $N_3P_3[O(CH_2)_3O](NHBu^t)_2Cl_2$. Hence, we prefer



* Denotes the preferred position(s) of protonation

FIGURE 2 Possible Structures for $N_3P_3(NH_2)_2(OR)_2Cl_2$ and their Calculated pK_a' Values. R = Et upper value, R = Pr^i lower value.

structural type (**19**), although we cannot decide at present between *cis* and *trans* structures.

We now discuss the titration curves obtained in potentiometric and conductometric studies. Examples are given in Figures 3–5.

Comparing the two techniques, it can be seen that second end-points in cyclotriphosphazatriene derivatives are much more readily observed by conductometric studies.

In Figure 3 we see the curves for $N_3P_3(NMe_2)_6$. The potentiometric titration shows clearly the first end-point and indicates a second one. Both are very clearly seen in the conductometric curves. In particular, in nitrobenzene + benzene (1 : 1) both end points are especially clearly marked.

In Figure 4 we observe that for $N_3P_3[O(CH_2)_3O](NC_4H_8)_4$, a slightly weaker base than $N_3P_3(NMe_2)_6$, a similar problem is apparent, except that in the potentiometric curve no indication of a second end-point can be seen. Additionally, the second end-points in the conductometric curves are less marked.

In Figure 5 we show similar data on a consideraly weaker base, $N_3P_3(NHC_6H_4\text{-}p\text{-}Me)_6$. Only in conductometric studies in nitrobenzene + benzene (1 : 1) do we now observe a second end-point. This again demonstrates that this solvent system is the most useful of the three investigated for observing clear end-points.

Time and space do not permit here a detailed discussion of the shapes of the conductometric curves, which will be given elsewhere.[10] It is obvious that we deal with complex equilibria involving dissociated ions as well as ion-pairs.

Particularly noteworthy are the shapes of the curves of the stronger bases in acetic acid. The addition of the first equivalent of perchloric acid, $HClO_4$, causes a

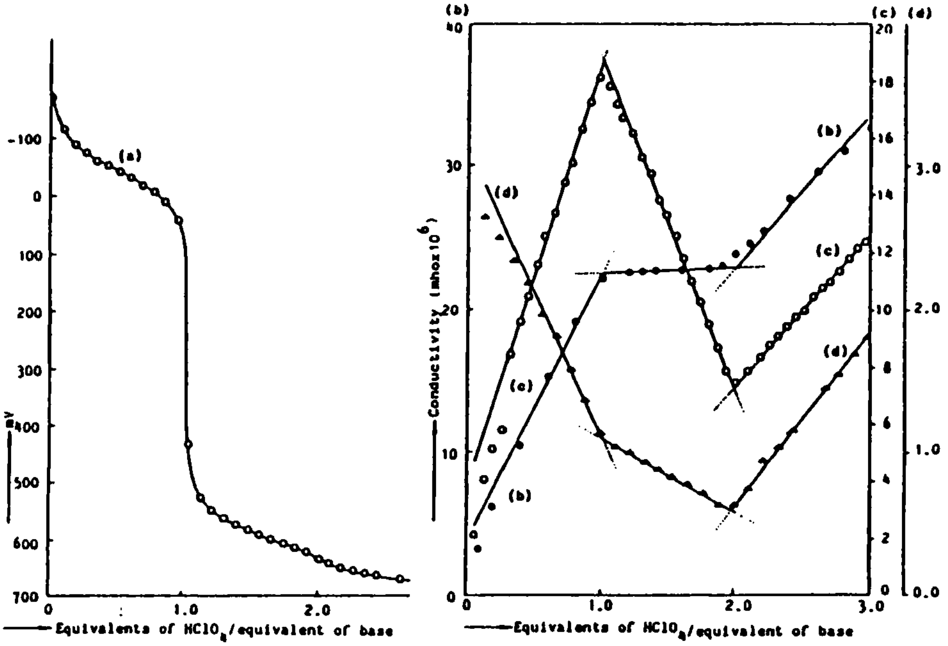


FIGURE 3 Titration curves of $N_3P_3(NMe_2)_6$: a) Potentiometric in nitrobenzene; b) Conductometric in nitrobenzene; c) Conductometric in nitrobenzene + benzene (1 : 1); d) Conductometric in acetic acid.

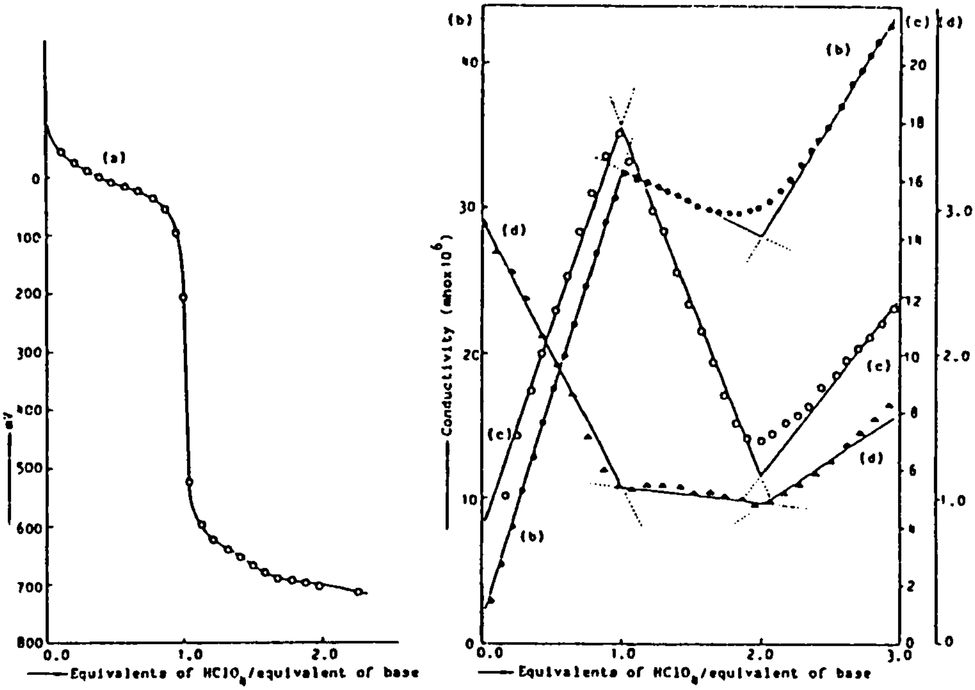


FIGURE 4 Titration curves of $N_3P_3[O(CH_2)_3O](NC_4H_8)_4$: a) Potentiometric in nitrobenzene; b) Conductometric in nitrobenzene; c) Conductometric in nitrobenzene + benzene (1 : 1); d) Conductometric in acetic acid.

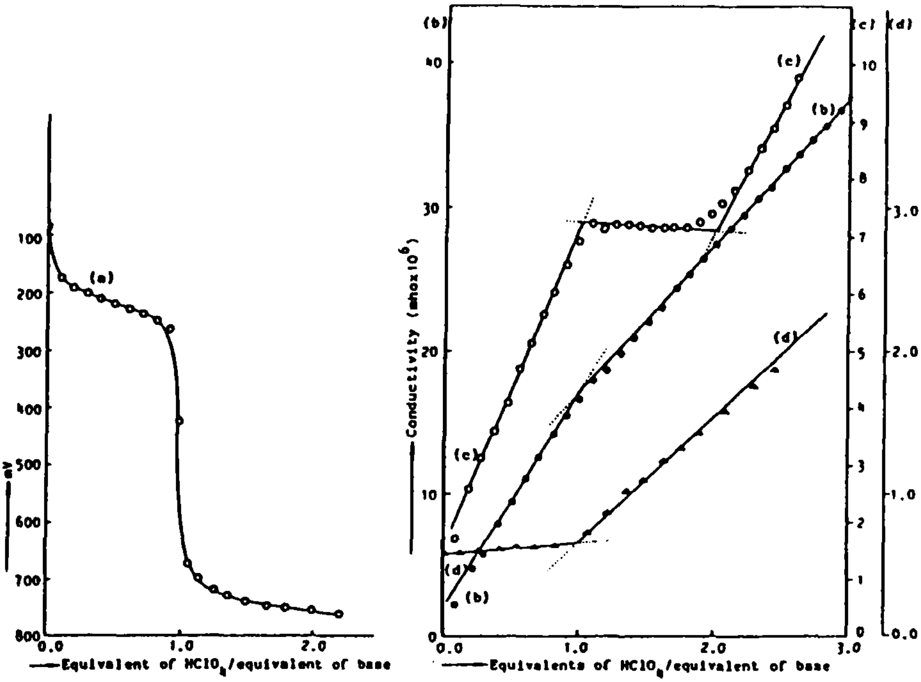


FIGURE 5 Titration curves of $N_3P_3(NHC_6H_4\text{-}p\text{-}Me)_6$ a) Potentiometric in nitrobenzene; b) Conductometric in nitrobenzene; c) Conductometric in nitrobenzene + benzene (1 1); d) Conductometric in acetic acid.

reduction in conductivity. We tentatively explain this by contribution from the following equilibria (B = base).

$$BH^+OCOMe^- \rightleftharpoons BH^+ + OCOMe^- \qquad (1)$$

$$BH^+ + OCOMe^- + HClO_4 \rightleftharpoons BH^+ + ClO_4^- + HOCOMe \qquad (2)$$

$$MeCOO^- + HOCOMe \rightleftharpoons MeCOOH + {}^-OCOMe \qquad (3)$$

The strong bases in acetic acid solution give largely dissociated pairs of ions and equilibrium (1) lies largely on the right-hand side. Addition of perchloric acid to this converts the protonated base acetates to perchlorates, again largely dissociated, the acetate ion converting to undissociated acetic acid, i.e., equilibrium (2) also lies largely on the right-hand side. The removal of acetate ions from the scene inhibits a proton-jump mechanism (equilibrium 3), and hence the overall result on the addition of the first equivalent of perchloric acid to strongly basic phosphazenes in acetic acid solution is a drop in conductivity.

We are currently actively pursuing these studies with a wide range of bases, phosphazenes and others.

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