G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967).
(7) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 1600 (1976).
(8) (a) T. P. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964); (b) T. P. Onak, G. B. Dunks, F. R. Spielman, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **88**, 2061 (1966); (c) T. P. Onak, R. E. Williams, and H. G. Weiss, *ibid.*, **84**, 2830 (1962).
(9) R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, **13**, 1138 (1974).
(10) This reaction was originally discovered by Dr. Vernon Miller in this laboratory and was subsequently mentioned in a review: R. N. Grimes, *Pure Appl. Chem.*, **39**, 455 (1974).
(11) R. Weiss and R. N. Grimes, *J. Organomet. Chem.*, **113**, 29 (1976).
(12) N. N. Greenwood, C. G. Savory, R. N. Grimes, L. G. Sneddon, A. Davison, and S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, 718 (1974).
(13) J. Knight and M. J. Mays, *J. Chem. Soc. A*, 654 (1970).
(14) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976), and references therein.
(15) V. R. Miller, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 3090 (1974).
(16) I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *J. Am. Chem. Soc.*, **85**, 3167 (1963).
(17) (a) T. P. Onak, R. Drake, and G. B. Dunks, *J. Am. Chem. Soc.*, **87**, 2505 (1965); (b) S. R. Prince and R. Schaeffer, *Chem. Commun.*, 451 (1968).
(18) J. L. Boone, *J. Am. Chem. Soc.*, **86**, 5036 (1964).
(19) (a) K. Wade, *J. Chem. Soc. D*, 792 (1971); (b) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972); (c) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972); (d) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976); (e) R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974).
(20) The placement of one or more CO ligands in bridging locations has no effect on the overall formal electron count in the central polyhedral cage.
(21) J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, **16**, 3255 (1977).
(22) J. R. Pipal and R. N. Grimes, to be submitted for publication.
(23) Thermal rearrangement studies of metallocarboranes,[24] in fact, suggest that in general the most stable isomers have nonadjacent metal atoms. However, this is not universally true[24d] and the problem of metal–metal interactions in borane polyhedra is in a very early stage of exploration.
(24) (a) M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **94**, 6679 (1972); (b) D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, *ibid.*, **96**, 3085 (1974); (c) W. J. Evans, C. J. Jones, B. Stibr, and M. F. Hawthorne, *J. Organomet. Chem.*, **60**, C27 (1973); (d) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **97**, 4213 (1975); (e) W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *ibid.*, **99**, 4016 (1977).
(25) (a) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *Inorg. Chem.*, **15**, 1343 (1976); (b) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 4818 (1976); (c) W. M. Maxwell, K-S. Wong, and R. N. Grimes, *Inorg. Chem.*, **16**, 3094 (1977); C. G. Salentine, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **15**, 1832 (1976).
(26) B. P. Sullivan, R. N. Leyden, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 455 (1975).
(27) D. A. Franz and R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 387 (1971).
(28) D. Finster and R. N. Grimes, unpublished work.

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Studies of Phosphazenes. 5.[1] Synthesis and Nuclear Magnetic Resonance Spectra of Chloro(*N*-methylanilino)cyclotetraphosphazatetraenes

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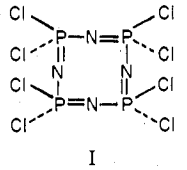
The reaction of $N_4P_4Cl_8$ (I) with *N*-methylaniline has been studied using a variety of experimental conditions, and the chloro(*N*-methylanilino) derivatives $N_4P_4Cl_{8-n}(NMePh)_n$ [n = 1, 2 (two isomers), 3, 4 (five isomers), and 6] have been isolated. Structures have been assigned to these compounds on the basis of ^1H NMR spectra (in some cases with the additional aid of ^{31}P NMR data) and chemical evidence. The methoxy derivatives $N_4P_4(OMe)_{8-n}(NMePh)_n$ [n = 2 (two isomers), 4 (two isomers), and 6] have also been prepared and in general their ^1H NMR spectra confirm the structures assigned to the chloro precursors. The chemical shifts of *N*-methyl and *O*-methyl protons and the "virtual-coupling" effects observed in the ^1H NMR spectra are discussed. *N*-Methylaniline replaces the chlorine atoms of $N_4P_4Cl_8$ by a predominantly nongeminal pathway. The results are compared with those observed in other aminolysis reactions of the octachloride I.

Aminolysis reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, have received a great deal of attention, and several hypotheses have been suggested to rationalize the halogen replacement patterns.[4-6] Systematic studies of the analogous reactions of the tetrameric chloride $N_4P_4Cl_8$ (I) have been



I

reported only recently. Ethylamine[7] and *tert*-butylamine[1] react with $N_4P_4Cl_8$ (I) to give chloro(alkylamino) derivatives which have nongeminal structures. In contrast, products formed in the reaction of *tert*-butylamine with $N_3P_3Cl_6$ and in the later stages of the analogous reaction of ethylamine have geminal structures.[5,6,8] Millington and Sowerby[9] have investigated the reaction of $N_4P_4Cl_8$ (I) with dimethylamine and isolated the derivatives $N_4P_4Cl_{8-n}(NMe_2)_n$ [n = 2, 3 (three isomers), 4 (four isomers), 5 (two isomers), 6, and 8]. The reaction proceeds predominantly via a nongeminal path. The reaction of *N*-methylaniline with $N_4P_4Cl_8$ (I) has been studied by Moeller and co-workers and two compounds, $N_4P_4Cl_6(NMePh)_2$, mp 146 °C, and $N_4P_4Cl_4(NMePh)_4$, mp 145 °C, have been isolated.[10] We have reinvestigated this reaction as part of a general program on the reactions of $N_4P_4Cl_8$ (I). The present study has revealed the great complexity of the system and the results are reported in this paper.

Results and Discussion

$N_4P_4Cl_8$ (I) reacts with *N*-methylaniline in organic solvents to give the chloro(*N*-methylanilino) derivatives $N_4P_4Cl_{8-n}(NMePh)_n$ [n = 1, 2 (two isomers), 3, 4 (five isomers), and 6] and *N*-methylaniline hydrochloride. Structural assignments for these compounds have been based mainly on ^1H NMR data which are summarized in Figure 1. Additional evidence for the structures of some of the compounds has been obtained from NMR data for the methoxy derivatives $N_4P_4(OMe)_{8-n}(NMePh)_n$ [n = 2 (two isomers), 4 (two isomers), and 6] (Figure 2).

The mono(*N*-methylanilino) compound (II) is conveniently prepared from a 1:2 $N_4P_4Cl_8$:*N*-methylaniline stoichiometric reaction carried out in benzene or methyl cyanide at ~25 °C. The two bis isomers $N_4P_4Cl_6(NMePh)_2$, mp 145 °C (III) and mp 105 °C (IV), have identical TLC R_f values. However, they can be separated by fractional crystallization from benzene; the high-melting isomer (III) crystallizes out preferentially. This observation may explain the previous isolation[10] of only one isomer (mp 145 °C). The ^1H NMR spectra of the mono

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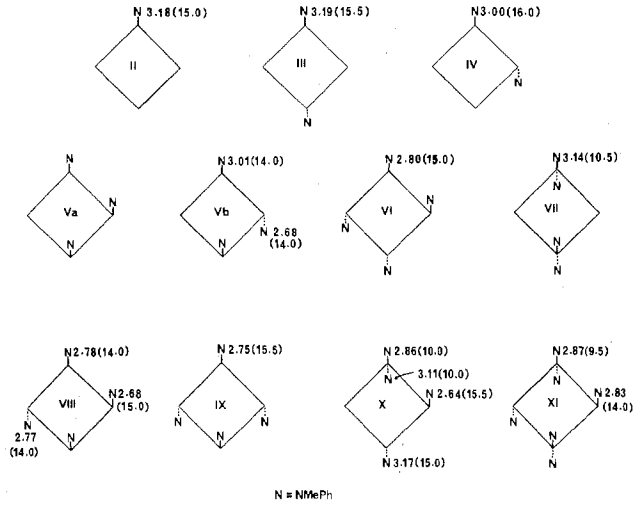


Figure 1. Proposed structures of chloro(*N*-methylanilino)cyclotetraphosphazatetraene derivatives. The values shown are the chemical shifts of *N*-methyl protons with $^3J^*$(P–H) in parentheses. (The corners of the square represent the phosphorus atoms; ring nitrogen and chlorine atoms are not shown.)

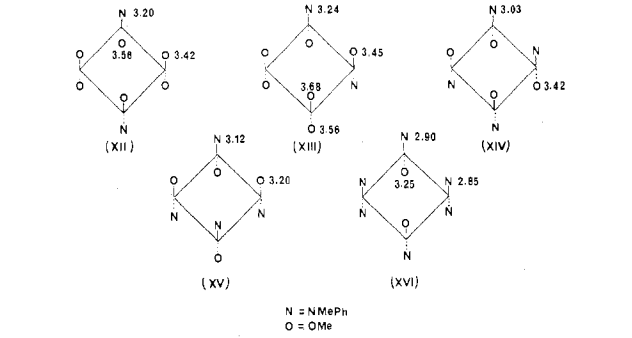


Figure 2. Structures of methoxy derivatives and their ^{1}H NMR data. The values shown represent chemical shifts of NCH_3 and OCH_3 protons; $^3J^*$(P–H) values (NCH_3, 9.5–11.5 Hz; OCH_3, 11.5–13.5 Hz) are unexceptional.

(II) and the bis derivatives (III and IV) have similar features: a doublet with strong "virtual coupling"[6] is observed for the *N*-methyl protons. The magnitude of $^3J^*$(P–H) is ca. 15.5 Hz which is characteristic of ≡PCl(NMePh) groups[11] and clearly indicates that the two bis isomers have nongeminal structures. The magnitude of $^3J^*$(P–H) for ≡P(NMePh)$_2$ groups lies in the range 9–11 Hz.[11] Similar trends in $^3J^*$(P–H) values have been utilized to distinguish ≡PR_2 and ≡PClR groups in many aminochlorocyclophosphazenes.[6]

The ^{31}P NMR spectrum of the bis isomer (III) is a singlet at δ −5.3 (lit.[12] −5.3). The proton spectrum of its methoxy derivative $N_4P_4(OMe)_6(NMePh)_2$ (XII) shows two doublets in the OMe region (relative intensity 1:2) indicating a 2,-trans-6[13] disposition of the *N*-methylanilino groups in this derivative and probably in the chloro precursor (III). The ^{31}P NMR spectrum of the bis isomer (IV) consists of 18 lines symmetrically placed around δ −4.0. This spectrum is clearly characteristic of an AA′BB′ spin system which implies a 2,4 arrangement of the *N*-methylanilino groups. Three methoxy doublets (relative intensities 1:1:1) are observed in the proton spectrum of the methoxy derivative $N_4P_4(OMe)_6(NMePh)_2$ (XIII). A distinction between 2,trans-4 and 2,cis-4 structures cannot be made from these data. X-ray crystallography establishes 2,trans-6[14a] and 2,trans-4[14b] structures for the two bis(*N*-methylanilino) isomers (III and IV), respectively.

Attempts to isolate a tris(*N*-methylanilino) derivative, $N_4P_4Cl_5(NMePh)_3$, from the reactions of the octachloride (I) with 6 equiv of *N*-methylaniline were unsuccessful. The

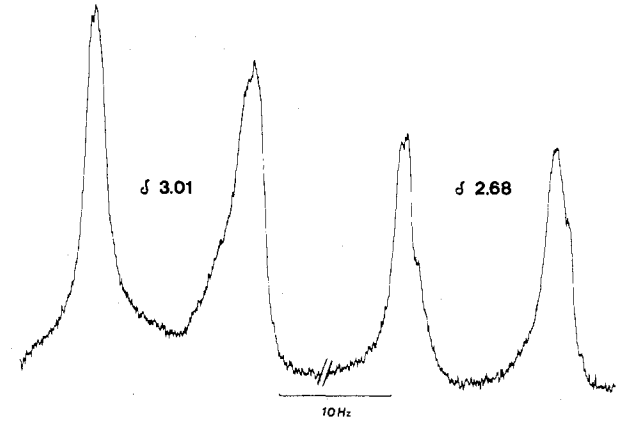


Figure 3. ^{1}H NMR spectrum (220 MHz) of the tris(*N*-methylanilino) derivative 2,2,4,6,8-$N_4P_4Cl_5(NMePh)_3$ (V).

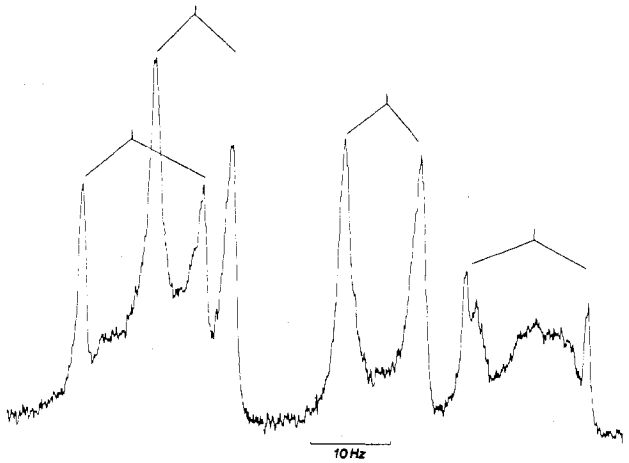


Figure 4. ^{1}H NMR spectrum (100 MHz) of 2,2,4,6-$N_4P_4Cl_4(NMePh)_4$ (X).

tris(*N*-methylanilino) compound (V) was obtained in <1% yield from a 1:8 stoichiometric reaction in boiling benzene (carried out by adding $N_4P_4Cl_8$ (I) to *N*-methylaniline). The 220-MHz ^{1}H NMR spectrum of compound V consists of two doublets (relative intensity 2:1) for the *N*-methyl protons (Figure 3). The magnitude of $^3J^*$(P–H) (14.0 Hz) associated with the two doublets indicates the presence of only ≡PCl-(NMePh) groups. Two structures, Va and Vb, are compatible with these observations. Structure Vb is favored because a compound with structure Va cannot be formed from *either* of the bis isomers (III and IV) without an isomerization step (see later).

Five tetrakis(*N*-methylanilino) derivatives $N_4P_4Cl_4(NMePh)_4$, mp 199 (VI), 162 (VII), 128 (VIII), 145 (IX), and 166 °C (X), have been isolated from 1:8 stoichiometric reactions. The relative yields of these isomers depend markedly on the reaction solvent. The isomer VI is the major product in all 1:8 reactions (and also in reactions involving higher stoichiometries). It is sparingly soluble in organic solvents at room temperature and coprecipitates with *N*-methylaniline hydrochloride (see Experimental Section).

There are ten possible positional and geometrical isomers at the tetrakis stage of chlorine replacement in reactions of $N_4P_4Cl_8$ (I).[6,15] The observation of a doublet without "virtual coupling" and the magnitude of $^3J^*$(P–H) (10.5 Hz) clearly indicate that the isomer VII has the 2,2,6,6 structure. The 2,2,6,6 assignment is further supported by the ^{31}P NMR spectrum which is of the A_2B_2 type. The alternative geminal structure (2,2,4,4) is unlikely because (a) virtual coupling is absent[16] and (b) the ^{31}P NMR spectrum would be of the AA′BB′ pattern.

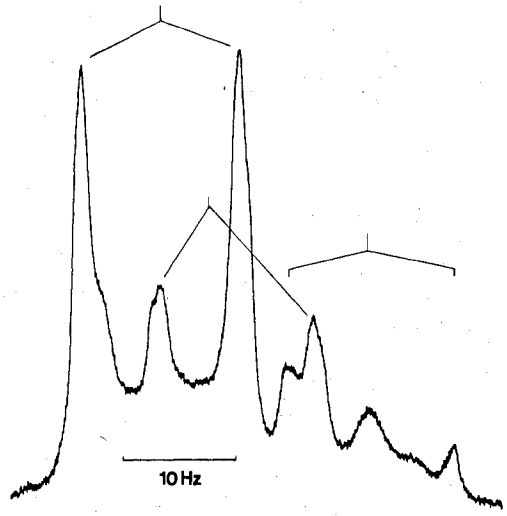
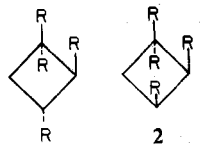


Figure 5. ^{1}H NMR spectrum (220 MHz) of 2, *cis*-4,*cis*-6,*trans*-8-$N_4P_4Cl_4(NMePh)_4$ (VIII) in C_6D_6.

The ^{1}H NMR spectrum of the tetrakis compound X is shown in Figure 4. Since four distinct *N*-methyl proton environments are observed, the compound must have one of two structures (**1** and **2**). The lowest and the highest field

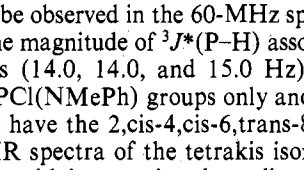


1 **2**

doublets (δ 3.17 and 2.64) are associated with a ^3J*(P–H) of 15.0 and 15.5 Hz, respectively, and arise from ≡PCl(NMePh) groups; the other two doublets (δ 3.11 and 2.86) are attributed to geminal ≡P(NMePh)$_2$ groups as ^3J*(P–H) is 10.0 Hz. We assign structure **1** to this compound because of the appearance of a ≡PCl(NMePh) resonance at δ 3.17. For structure **2** this resonance would be expected to occur at a considerably higher field (cf. chemical shifts shown in Figure 1).

The 100-MHz ^{1}H NMR spectrum of the tetrakis isomer VIII is not very informative because of overlap of signals and pronounced virtual coupling. The spectrum recorded at 220 MHz (Figure 5) shows the presence of three distinct *N*-methylanilino proton environments (relative intensities 2:1:1) which can also be observed in the 60-MHz spectrum after ^{31}P decoupling. The magnitude of ^3J*(P–H) associated with each of the doublets (14.0, 14.0, and 15.0 Hz) establishes the presence of ≡PCl(NMePh) groups only and this compound must therefore have the 2,cis-4,cis-6,trans-8 structure.

The ^{1}H NMR spectra of the tetrakis isomers VI and IX exhibit a doublet with intense virtual coupling for the *N*-methyl protons [^3J*(P–H) 15.0 and 15.5 Hz, respectively]. Hence, each compound must have one of the three structures (**3**–**5**) shown below. The 2,4,6,8 structures for the two isomers are



3 **4** **5**

confirmed by ^{1}H and ^{31}P NMR data of their respective methoxy derivatives, $N_4P_4(OMe)_4(NMePh)_4$ (XIV and XV) (Figure 2). The single line observed in the ^{31}P NMR spectrum of isomer IX is also consistent with the assignment of a 2,4,6,8 structure.[17] It is necessary to consider chemical evidence in order to deduce the exact structures of the two tetrakis isomers

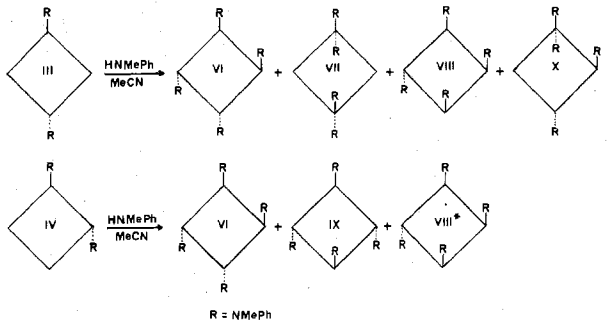


Figure 6. Products isolated from the reactions of the bis(*N*-methylanilino) compounds III and IV with *N*-methylaniline (* indicates product not isolated but detected by TLC).

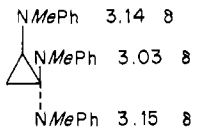
VI and IX. The products obtained from the reactions of the 2,trans-6 and 2,trans-4 bis derivatives (III and IV) with 4 equiv of *N*-methylaniline are shown in Figure 6. The tetrakis isomer VI is obtained as the major product from both the reactions and hence this compound is assigned the 2,cis-4,trans-6,trans-8 structure (**3**). Structures **4** and **5** are unlikely because a compound with either structure cannot be obtained from the 2,trans-6 bis isomer III unless there is net inversion. However, independent experiments show that the two bis (III and IV) and the tetrakis (VI) derivatives do not isomerize in the presence of *N*-methylaniline hydrochloride. It may be pointed out that the major tetrakis isomer formed in the reaction of $N_4P_4Cl_8$ (I) with dimethylamine also has the 2,cis-4,trans-6,trans-8 structure.[9,18] The tetrakis isomer IX is assigned the 2,trans-4,cis-6,trans-8 structure (**4**) as it is obtained only from the 2,trans-4 bis isomer IV. Additional support for this assignment is provided by the observed chemical shift of the OMe protons in compound XV.[19] The structures assigned to the other tetrakis isomers (VII, VIII, and X) are also consistent with the results shown in Figure 6.

The hexakis(*N*-methylanilino) compound (XI) has been obtained in very low yields from a 1:20 reaction in boiling toluene as well as from a 1:6 reaction in the presence of 6 equiv of triethylamine; in both reactions, the tetrakis compound VI is the major product. The ^{1}H NMR spectrum of compound XI at 100 MHz is not sufficiently well resolved to measure the ^3J*(P–H) values. The spectrum recorded at 220 MHz shows two distinct doublets for *N*-methyl protons (intensity ratio 2:1) with ^3J*(P–H) values of 9.5 and 14.0 Hz, respectively. This compound must therefore have the 2,trans-6:2,4,4,6,8,8 structure.

We now turn our attention to a detailed consideration of the observed proton chemical shifts for the *N*-methylanilino derivatives II–XVI. In general, the proton chemical shifts of cyclophosphazene derivatives are determined by (a) inductive and conjugative electron flow and (b) neighbor anisotropy effects (including that of the aromatic ring current). The chemical shifts of the NMe_2 protons in the dimethylamino derivatives $N_3P_3Cl_{6-n}(NMe_2)_n$ (δ 2.75–2.66)[20] and $N_4P_4Cl_{8-n}(NMe_2)_n$ (δ 2.75–2.49)[9] are largely explicable in terms of the electronic effect. It is found that δ_{NMe_2}(gem) < δ_{NMe_2}(cis nongem) < δ_{NMe_2}(trans nongem). For the phenoxydimethylamino-[21] and phenyldimethylaminocyclophosphazenes,[22,23] the shielding of NMe_2 protons increases with the number of phenyl groups cis to the dimethylamino substituent(s). The chemical shifts of the *N*-methyl protons in the tetrameric derivatives (II–XVI) occur over a wide range (δ 3.24–2.64) whereas the *N*-methyl resonances for *N*-methylanilinocyclotriphosphazene derivatives $N_3P_3Cl_{6-n}(NMePh)_n$, span a much narrower range (δ 3.18–3.02).[11] The OMe chemical shifts in the methoxy derivatives (XII–XVI) vary from δ 3.68 to δ 3.20. As OMe and NMePh groups are much weaker electron-releasing substituents than NMe_2,[24] the

considerable variation of NMePh and OMe chemical shifts must be due to the aromatic ring current effect.[27] It appears that this effect is much more pronounced in the *N*-methylanilino tetrameric derivatives than in the corresponding trimeric derivatives.

The crystal structures of the two bis(*N*-methylanilino) isomers (III and IV) have been determined.[14] The P–N ring in the 2,trans-6 isomer (III) has a chair conformation and the two *N*-methylanilino groups are as far apart as possible.[14a] In the 2,trans-4 isomer (IV), the ring has a boat conformation;[14b] the two NMePh groups occupy equatorial positions and are oriented in such a way that the methyl protons of one of the NMePh groups comes into the shielding zone of the phenyl ring of the other NMePh group. These x-ray data would explain the greater shielding of the NMe protons in the 2,-trans-4 isomer (IV) assuming that there is no change in gross structural features between the solid and solution states. Thus, it appears that the shielding effect of the aromatic ring current can be pronounced even when groups are trans to each other; this may well be due to the flexibility of the eight-membered ring which can adopt one of several conformations.[29] For the geminally substituted compounds (X, XI) and the methoxy derivatives (XII–XVI), the shielding effect of the aromatic ring current seems to be greater in the cis than in the trans disposition. However, the mutual effect of the groups cis to each other need not be the same as shown by the observed shifts for *gem*-$N_3P_3Cl_3(NMePh)_3$[11] where the assignments are



(Cl atoms not shown)

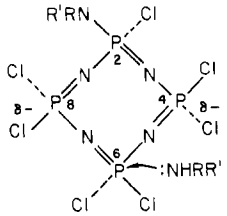
unambiguous. The chemical shifts shown in Figures 1 and 2 can be largely explained on the basis of the above arguments although one or two individual assignments must remain tentative.

In conclusion, the data discussed above suggest that for tetrameric derivatives containing ≡PCl(NMePh) groups (type I conformation of the substituent[30]), the aromatic ring current effect from groups in trans positions on adjacent phosphorus atoms can be comparable to that from groups in cis positions. For compounds containing ≡P(NMePh)$_2$ and ≡P-(NMePh)OMe structural units (which will probably have type III conformation[30]), however, the effect from groups in trans positions is much smaller than that from groups in cis positions.

A notable feature in many of the ^{1}H NMR spectra discussed above is the appearance of pronounced "virtual-coupling" effects. One of the essential conditions for the occurrence of virtual coupling is that the chemical shifts between ^{31}P nuclei involved in these effects is small or zero.[31,32] Although ^{31}P chemical shifts for a large number of cyclophosphazene derivatives have been determined and some trends discerned,[4,6,32] reliable guidelines for predicting phosphorus chemical shifts for cyclophosphazene derivatives containing different substitutents have not yet been established. In the absence of a comprehensive theoretical treatment of ^{31}P chemical shifts in cyclophosphazene derivatives, it is a priori difficult to ascertain in which systems and to what extent virtual coupling will occur.

Intense virtual coupling is observed in the ^{1}H NMR spectra of the two bis isomers III and IV and the two tetrakis isomers VI and IX whereas the spectrum of the 2,2,6,6-geminal isomer VII is a clean doublet as anticipated from the ^{31}P chemical shifts for these compounds (see Experimental Section). It has been noted previously that the strength of virtual-coupling effects or their absence can be useful for assigning structures to isomeric compounds. For example, the geminal 2,2,6,6- and 2,2,4,4-$N_4P_4Ph_4(NMe_2)_4$ isomers[16] as well as 2,4:2,4,6,6,8,8- and 2,6:2,4,4,6,8,8-$N_4P_4(NHBu^t)_2(NMe_2)_6$ isomers[28] have been distinguished.[33] Both 2,4- and 2,6-$N_4P_4(NMePh)_2Cl_6$ and their methoxy derivatives cannot be differentiated on this basis. The ^{1}H NMR spectra of 2,4- and 2,6-N_4P_4-$(NHBu^t)_2(OMe)_6$ also exhibit pronounced virtual coupling.[28] Consequently virtual-coupling effects as a criterion for structural assignments may be useful in favorable circumstances (when the ^{31}P chemical shift differences happen to be large) but may not be of general applicability.

It is interesting to compare the results obtained in this study with those reported for the reaction of $N_4P_4Cl_8$ (I) with dimethylamine.[9] In both cases, replacement of chlorine atoms takes place by a predominantly nongeminal pathway. An $S_N2(P)$ mechanism[34] would be consistent with this behavior. In the latter system, the 2,trans-6 isomer $N_4P_4Cl_6(NMe_2)_2$ is formed almost exclusively at the bis stage of chlorine replacement. With the more sluggishly reacting *N*-methylaniline, two bis isomers (III and IV) are formed in comparable yields and they have 2,trans-6 and 2,trans-4 structures, respectively. Similarly, a reactive primary amine (ethylamine[7]) gives the 2,trans-6 bis compound predominantly whereas a slowly reacting primary amine (*tert*-butylamine,[8] benzylamine[35]) affords 2,4 and 2,6 bis isomers. The results obtained in the secondary-amine reactions can be rationalized on the following lines. After the replacement of the first chlorine



atom from $N_4P_4Cl_8$ (I), electron release by the amino substituent at P(2) into the ring would preferentially deactivate the adjacent phosphorus atoms P(4) and P(8), thereby favoring nucleophilic attack at the distant phosphorus atom P(6). This preferential deactivation is likely to be less with the *N*-methylanilino group because it is a weaker electron-releasing substituent than dimethylamine. On statistical grounds alone, the 2,4 isomer should predominate. A delicate balance between these two factors would explain the formation of the two bis(*N*-methylanilino) isomers (III and IV) in comparable yields. In the primary-amine systems, additional mechanistic features[5,36] may have to be considered.

The isolation of only one tris(*N*-methylanilino) derivative in very low yields and the apparent absence of pentakis derivatives, compared with the isolation of three tris- and two pentakis(dimethylamino) derivatives,[9] would suggest that there is undoubtedly a greater tendency for *N*-methylanilinocyclophosphazenes containing an odd number of chlorine atoms to react further to yield derivatives with an even number of chlorine atoms. Our results also confirm the observation of Moeller and co-workers[10] that the replacement of chlorine atoms by *N*-methylaniline beyond the tetrakis stage is difficult.

Experimental Section

Octachlorocyclotetraphosphazatetraene (I) was purified by recrystallization from petroleum ether (bp 60–80 °C) to constant mp 124 °C. Petroleum ether (bp 60–80 °C unless stated otherwise), benzene, toluene, chloroform, and methyl cyanide were purified by conventional methods. *N*-Methylaniline (Riedel, Hannover, Germany) was dried with KOH pellets and distilled over Zn dust [89 °C (3 mm)].

Chromatographic procedures were as mentioned previously.[7] ^{1}H NMR spectra ($CDCl_3$ solution, Me_4Si internal standard) were recorded with Jeol MH 100 and Varian HR 220 spectrometers. ^{31}P{^{1}H} NMR spectra were obtained on Jeol C 60 HL and Varian XL-100 spectrometers using CH_2Cl_2 solutions and 85% phosphoric acid as external standard. Chemical shifts are expressed on the δ scale with upfield shifts negative.

Table I. Preparative Details[a]

Cyclotetraphosphazene	Amt		Amt of *N*-Methylaniline		Solvent	Solvent vol, cm^{-3}	Reacn time, h	Products and yields		
	g	mmol	g	mmol				No.	g	%
I	5	11	2.36	22	C_6H_6	25	2.5	I	0.75	15.0
								II	0.25	4.4
								III + IV	0.50	7.7
I	2	4.3	0.95	9	C_6H_6	10	24[b]	I	0.30	15.0
								II	0.40	17.4
								III + IV	0.10	3.8
I	5	11	2.36	22	CH_3CN	125	24[b]	I	0.50	10.0
								II	1.25	21.8
								III + IV	0.25	3.8
I	5	11	4.70	44	C_6H_6	35	10	II	0.10	1.7
								III	0.75	11.5
								IV	1.00	15.3
I	5	11	4.70	44	$CHCl_3$	50	24	II	0.10	1.7
								III	0.60	9.2
								IV	1.25	19.2
I	5	11	4.70	44	CH_3CN	25	16	III	1.30	19.5
								IV	0.60	9.2
I	5	11	7.08	66	C_6H_6	50	24	III	0.15	2.3
								VI	0.15	1.9
								IX	0.25	3.0
I	10	22	18.80	176	C_6H_6	60	48	VI	1.50	9.3
								VII	0.075	0.5
								IX	0.20	1.2
I	5	11	9.40	88	$C_6H_5CH_3$	25	12	VI	1.50	18.6
								IX	0.15	1.8
								VII	0.05	0.6
I	10	22	18.80	176	C_6H_5	150	65[d]	III	0.10	0.8
								V	0.10	0.7
								VI	1.60	10.0
								VIII	0.05	0.30
								IX	0.30	1.80
I	5	11	9.40	88	CH_3CN	50	44	VI	2.25	28.6
								VII	0.25	3.0
								VIII	0.20	2.5
								X	0.10	1.2
I	5	11	7.08	66[c]	CH_3CN	30	70	VI	1.40	17.5
								XI	0.03	0.3
I	5	11	23.50	220	C_6H_5	125	60[d]	VI	0.4	5.0
								VII	0.05	0.6
I	5	11	23.50	220	$C_6H_4(CH_3)_2$	50	100	VI	0.5	6.2
								XI	0.05	0.5
III	0.6	0.9	0.42	4.0	CH_3CN	25	20	VI	0.2	30.0
								VII	0.05	7.5
								VIII	0.05	7.5
								X	0.02	3.0
IV	0.6	0.9	0.42	4.0	CH_3CN	25	20	VI	0.08	12.0
								IX	0.06	9.0
								VIII[e]		

[a] *N*-Methylaniline, diluted with solvent, was added dropwise for 1 h to a boiling solution of $N_4P_4Cl_8$ (I) in the solvent specified. [b] At room temperature. [c] Triethylamine (6.4 g, 64 mmol) was added. [d] Procedure of Moeller and co-workers.[10] [e] TLC evidence—not isolated.

Preparative Details. Reactions of $N_4P_4Cl_8$ (I) with *N*-methylaniline have been carried out in different organic solvents using various relative proportions of reactants. The reactivity of $N_4P_4Cl_8$ (I) toward *N*-methylaniline is greater than that of $N_3P_3Cl_6$[11] in the initial stages. Each reaction gives a complex mixture of products and the low yields recorded are largely due to the considerable loss of material that occurs during chromatographic separations. The general experimental procedure is described below. Details of the reactions are summarized in Table I.

The following compounds were isolated. $N_4P_4Cl_7(NMePh)$ (II): mp 65 °C; R_f [TLC (silica gel; eluent benzene–petroleum ether (1:1))] 0.96; ^{31}P NMR complex multiplet δ −6.5. Anal. Calcd for $C_7H_8Cl_7N_5P_4$: C, 15.7; H, 1.5; N, 13.1. Found: C, 15.8; H, 1.5; N, 13.3. $N_4P_4Cl_6(NMePh)_2$ (III): mp 145 °C, lit.[10] mp 146 °C; R_f 0.93. Anal. Calcd for $C_{14}H_{16}Cl_6N_6P_4$: C, 27.8; H, 2.7; N, 13.9. Found: C, 28.0; H, 3.0; N, 13.8. $N_4P_4Cl_6(NMePh)_2$ (IV): mp 105 °C; R_f 0.93. Anal. Found: C, 28.0; H, 2.7; N, 13.5. $N_4P_4Cl_5(NMePh)_3$ (V): mp 144 °C; R_f 0.84. Anal. Calcd for $C_{21}H_{24}Cl_5N_7P_4$: C, 37.3; H, 3.6; N, 14.5. Found: C, 37.0; H, 3.5; N, 14.3. $N_4P_4Cl_4(NMePh)_4$ (VI): mp 199 °C; R_f 0.70. Anal. Calcd for $C_{28}H_{32}Cl_4N_8P_4$: C, 45.1; H, 4.3; N, 15.3. Found: C, 45.6; H, 4.3; N, 15.3. $N_4P_4Cl_4(NMePh)_4$ (VII): mp 162 °C; R_f 0.80; ^{31}P NMR δ_{PCl_2} −11.5, $\delta_{P(NMePh)_2}$ −5.4, $^2J(P-P)$ = 37.1 Hz. Anal. Found: C, 45.1; H, 4.3; N, 15.1. $N_4P_4Cl_4(NMePh)_4$ (VIII): mp 128 °C; R_f 0.66; ^{31}P NMR δ −2.1. Found: C, 44.9; H, 4.4; N, 15.0. $N_4P_4Cl_4(NMePh)_4$ (IX): mp 145 °C, lit.[10] mp 145 °C; R_f 0.56. Anal. Found: C, 44.9; H, 4.3; N, 14.7. $N_4P_4Cl_4(NMePh)_4$ (X): mp 166 °C; R_f 0.75. Anal. Found: C, 45.6; H, 4.5; N, 14.7. $N_4P_4Cl_2(NMePh)_6$ (XI): mp 192 °C; R_f 0.68. Anal. Calcd for $C_{42}H_{48}Cl_2N_{10}P_4$: C, 56.2; H, 5.4; N, 15.6. Found: C, 55.9; H, 5.4;

N, 15.2. The following methoxy derivatives have been obtained in 70–80% yield from the reactions of chloro(*N*-methylanilino) derivatives with sodium methoxide in benzene at 50–60 °C (3 days). $N_4P_4(OMe)_6(NMePh)_2$ (XII): liquid. $N_4P_4(OMe)_6(NMePh)_2$ (XIII): liquid (both isomers were characterized by NMR spectroscopy). $N_4P_4(OMe)_4(NMePh)_4$ (XIV): mp 71 °C; ^{31}P NMR δ 1.1. Anal. Calcd for $C_{32}H_{44}O_4N_8P_4$: C, 52.7; H, 6.1; N, 15.4. Found: C, 52.7; H, 6.2; N, 15.2. $N_4P_4(OMe)_4(NMePh)_4$ (XV): mp 119 °C; ^{31}P NMR δ 1.7. Anal. Found: C, 53.2; H, 6.1; N, 15.5. $N_4P_4(OMe)_2(NMePh)_6$ (XVI): mp 110 °C. Anal. Calcd for $C_{44}H_{54}O_2N_{10}P_4$: C, 61.2; H, 6.3; N, 16.2. Found: C, 60.1; H, 6.3; N, 16.2.

General Experimental Procedure. After the reaction was terminated, the reaction mixture was filtered to remove *N*-methylaniline hydrochloride. The filtrate was evaporated to obtain an oily residue which was crystallized from a suitable solvent or a mixture of solvents (usually petroleum ether and/or benzene). In many instances, crystallization did not occur even after prolonged cooling, and chromatography over silica gel was essential to isolate the *N*-methylanilinochlorocyclotetraphosphazatetraene derivatives. In some cases, successive crops were enriched in one or other of the derivatives, and these were further purified by fractional crystallization. For example in 1:4 $N_4P_4Cl_8$:amine stoichiometric reactions, the 2,-*trans*-6-bis(*N*-methylanilino) isomer (III) crystallized out first and the subsequent crops consisted mostly of the 2,trans-4 isomer (IV). After the removal of the crystalline crops, the residual reaction mixture was chromatographed.

In 1:8 and higher stoichiometric reactions, the tetrakis derivative VI, being sparingly soluble in cold organic solvents, coprecipitated with *N*-methylaniline hydrochloride. The precipitate was washed with water and extracted several times with hot benzene to recover compound VI.

Thin-layer chromatography was used to monitor the course and extent of the reactions and also to identify the components of various fractions collected during column chromatographic separations.

Attempted Preparation of Octakis(*N*-methylanilino)cyclotetraphosphazatetraene. Two methods were tried for the preparation of the title compound. The reaction of the tetrakis(*N*-methylanilino) derivative VI with 8 equiv of *N*-methylaniline (in the presence of triethylamine) in boiling toluene (36 h) resulted in the recovery of the starting material (VI): TLC indicated the absence of any products. The reaction of $N_4P_4Cl_8$ (I) with 20 equiv of the amine in boiling toluene (48 h) gave a dark brown oil and a precipitate from which compound VI (10%) was recovered. Crystallization of the brown oil from petroleum ether at 0 °C gave compound XI (5%). The mother liquor was chromatographed over silica gel (eluent benzene), and various oily residues were obtained. One of these residues crystallized in petroleum ether to give a substance of mp 230–234 °C. Found: C, 61.9; H, 6.2; N, 17.2. TLC and the complex proton NMR spectrum indicated that this substance was a mixture. The mixture could not be separated by standard techniques. More drastic conditions (sealed tube, temperature >150 °C) were avoided owing to the tendency of *N*-methylaniline to undergo dealkylation in the presence of phosphorus(V) chlorides.[11,37]

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Registry No. I, 2950-45-0; II, 61153-55-7; III, 54633-24-8; IV, 65242-44-6; Vb, 65878-87-7; VI, 65914-77-4; VII, 65878-86-6; VIII, 65914-76-3; IX, 65914-75-2; X, 65878-85-5; XI, 65878-84-4; XII, 65878-83-3; XIII, 65878-82-2; XIV, 65914-74-1; XV, 65878-81-1; XVI, 65878-80-0; *N*-methylaniline, 100-46-9.

References and Notes

(1) Part 4: S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. A. Shaw, M. Woods, and R. Keat, *J. Chem. Soc., Dalton Trans.*, 1980 (1977).
(2) Indian Institute of Science.
(3) Birkbeck College, University of London.
(4) H. R. Allcock, "Phosphorus-Nitrogen Compounds", Academic Press, New York, N.Y., 1972; *Chem. Rev.*, **72**, 315 (1972).
(5) R. A. Shaw, *Z. Naturforsch., B*, **31**, 641 (1976).
(6) S. S. Krishnamurthy, A. C. Sau, and M. Woods, *Adv. Inorg. Chem. Radiochem.*, in press.
(7) S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. Keat, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1405 (1976).
(8) S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 5032 (1965).
(9) D. Millington and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 2035 (1972).
(10) K. John, T. Moeller, and L. F. Audrieth, *J. Am. Chem. Soc.*, **82**, 5616 (1960); **83**, 2608 (1961).
(11) S. S. Krishnamurty, M. N. Sudheendra Rao, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *Indian J. Chem., Sect. A*, **14A**, 823 (1976).
(12) T. Moeller, unpublished results quoted in *Top. Phosphorus Chem.*, **5**, 401 (1967).
(13) For nomenclature, see B. W. Fitzsimmons, R. A. Shaw, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962).
(14) (a) Y. S. Babu, K. Bhandari, and H. Manohar, *Acta Crystallogr., Sect. B*, **33**, 3548 (1977); (b) Y. S. Babu and H. Manohar, *Cryst. Struct. Commun.* **6**, 803 (1977).
(15) D. B. Sowerby, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two*, 127 (1972).
(16) M. Biddlestone, S. S. Krishnamurthy, R. A. Shaw, M. Woods, G. J. Bullen, and P. E. Dann, *Phosphorus*, **3**, 179 (1973).
(17) ^{31}P NMR spectrum of compound VI could not be obtained because of its poor solubility in organic solvents.
(18) G. J. Bullen and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, 2437 (1972).
(19) The chemical shift of the methyl protons of 2,*cis*-4,*cis*-6,*cis*-8-$N_4P_4Ph_4(NMe_2)_4$ is δ 2.66[22] and is comparable to δ 2.57 observed for $N_4P_4(NMe_2)_8$. The considerable shielding of OMe protons for compound XV (δ 3.2, Figure 2) (compared to $N_4P_4(OMe)_8$, δ 3.58) rules out an all-cis structure.
(20) R. Keat, S. K. Ray, and R. A. Shaw, *J. Chem. Soc.*, 7193 (1965).
(21) D. Dell, B. W. Fitzsimmons, R. Keat, and R. A. Shaw, *J. Chem. Soc. A*, 1681 (1966).
(22) B. Grushkin, A. J. Berlin, J. L. McClanaham, and R. G. Rice, *Inorg. Chem.*, **5**, 172 (1966).
(23) S. Das, R. A. Shaw, and B. C. Smith, *J. Chem. Soc., Dalton Trans.*, 1883 (1973).
(24) This conclusion is supported by (a) basicity measurements (cf. pK'_a values: $N_3P_3(NMe_2)_6$, 7.6;[5] $N_3P_3(NMePh)_6$, 3.5;[25] $N_3P_3(OMe)_6$, −1.9[5]) and (b) P–Cl bond length data obtained from x-ray crystallography (NMe_2P–Cl = 2.06 Å;[26] NMePhP–Cl = 2.04 Å[14a]).
(25) D. Feakins, R. A. Shaw, P. Watson, and S. N. Nabi, *J. Chem. Soc. A*, 2468 (1969).
(26) G. J. Bullen and P. E. Dann, *J. Chem. Soc., Dalton Trans.*, 1453 (1973).
(27) In many mixed methoxy(alkylamino)cyclotetraphosphazatetraene derivatives, the resonances for methoxy protons present in different environments are poorly resolved (if at all) and provide little structural information.[7,28]
(28) A. C. Sau, Ph.D. Thesis, Indian Institute of Science, Bangalore, 1976.
(29) S. S. Krishnamurthy, R. A. Shaw, and M. Woods, *Curr. Sci.*, **45**, 433 (1976).
(30) The conformations of R groups (R = NMe_2, Ph) in geminal ($\equiv PR_2$) and nongeminal ($\equiv PClR$) cyclophosphazene derivatives have been defined as type III and type I, respectively. For a detailed discussion of these terms and the relevant x-ray crystallographic data see ref 5.
(31) E. G. Finer, *J. Mol. Spectrosc.*, **23**, 104 (1967).
(32) R. Keat, R. A. Shaw, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1582 (1976).
(33) For the use of virtual coupling in structural assignments of cyclotriphosphazene derivatives, see ref 5.
(34) R. F. Hudson in "Structure and Mechanism in Organophosphorus Chemistry", Academic Press, London, 1969, Chapter 3.
(35) K. Ramachandran, unpublished results.
(36) R. N. Das, R. A. Shaw, B. C. Smith, and M. Woods, *J. Chem. Soc., Dalton Trans.*, 709 (1973).
(37) C. Y. Cheng and R. A. Shaw, *J. Chem. Soc., Perkin Trans. 1*, 1739 (1976).