Conformational Studies of the Phosphazenyl Side Chain in Cyclophosphazenes. Part 3.[1] Crystal and Molecular Structure of $N_3P_3Cl_4(NEt_2)(NPPh_3)$†,‡

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The crystal structure of $N_3P_3Cl_4(NEt_2)(NPPh_3)$ has been determined. The crystals are orthorhombic, space group *Pbca*, with $a = 8.208(1)$, $b = 21.890(1)$, $c = 31.722(2)$ Å, $Z = 8$, and m.p. = 146.5 °C. The structure was solved by direct methods and refined to a final *R* value of 0.045 for 2 025 independent reflections. The analysis reveals significant variations in the ring P–N bond lengths. The two nitrogenous substituents, $NPPh_3$ and NEt_2, reside on the same phosphorus atom. The latter, NEt_2, has an almost exact type II conformation (the plane NC_2 almost perpendicular to the local NPN plane) (the first observed for a dialkylamino-group in cyclophosphazenes), the former, $NPPh_3$, deviates from type II towards type III (in type III the plane P_{ring}–N–P_{exo} makes an angle of *ca.* 45° with the local N–P–N ring plane). The present structure is compared with others of triphenylphosphazenylcyclophosphazenes and the conformation of the $NPPh_3$ substituent and its electron supply in the ground and perturbed states are discussed.

THE crystal-structure analysis of $N_3P_3Cl_4(NEt_2)(NPPh_3)$ is part of a continuing series of studies on the structural aspects of cyclophosphazenes with triphenylphosphazenyl substituents. Basicity studies[2] of these compounds revealed two types of behaviour which were tentatively related to endocyclic and exocyclic protonation. It was postulated that these two types are functions of the conformation of the triphenylphosphazenyl side chain with respect to the local ring NPN segment and they were designated as type I and type II respectively.[3-6] Briefly, the N–P bond of the $NPPh_3$ substituent would be parallel (type I) or perpendicular (type II) to the local ring NPN segment in the two cases discussed. A conformation (type III) intermediate between type I and type II has also been proposed for geminal groupings.[3-6] The structures of four triphenylphosphazenylcyclophosphazenes have been previously solved.[7-10] In this paper, the structure of $N_3P_3Cl_4(NEt_2)(NPPh_3)$ is reported and five related structures are compared.

EXPERIMENTAL

The monodiethylamino-derivative, $N_3P_3Cl_4(NEt_2)(NPPh_3)$, was obtained by heating $N_3P_3Cl_5(NPPh_3)$ with two equivalents of diethylamine in boiling benzene for 6 h. The product was recrystallised from benzene–light petroleum (b.p. 60—80 °C) (1 : 4) to give crystals, m.p. 146.5 °C.[11] These are needle-shaped and have a square cross-section.

Crystal Data.—$C_{22}H_{25}Cl_4N_5P_4$, $M = 625.15$, Orthorhombic, $a = 8.208(1)$, $b = 21.890(1)$, $c = 31.722(2)$ Å, $U = 5\,700$ Å^3, $D_m = 1.44$ g cm^{-3}, $Z = 8$, $D_c = 1.46$, $F(000) = 2\,560$, space group *Pbca*, $\lambda(\text{Mo-}K_\alpha) = 0.710\,7$ Å, $\mu = 6.60$ cm^{-1}. Intensity data were collected on a CAD-4 diffractometer by the ω—2θ scan technique using Mo-K_α radiation. Of the 3 870 reflections measured in the range $0 < 2\theta < 45°$, 2 025 were above the threshold $[I > 3\sigma(I)]$.

Structure Solution and Refinement.—Intensities were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by direct methods using MULTAN.[12]

Except for the carbon atoms, all the other atoms of the molecule could be identified from the *E* map computed with the set of phases having the lowest Karle *R* value of 26.30. One cycle of least-squares refinement followed by a Fourier synthesis enabled the remaining atoms to be identified. Five cycles of least-squares refinement with isotropic thermal parameters and block-diagonal matrix approximation decreased the *R* index to 0.107. From the start of the refinement it was noticed that the methyl carbons C(3) and C(4) have high thermal parameters. At the end of the

TABLE 1

Atomic co-ordinates with estimated standard derivations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cl(1)	0.307 6(7)	0.337 4(2)	0.177 1(2)
Cl(2)	0.593 5(5)	0.270 3(2)	0.136 0(2)
Cl(3)	0.179 5(8)	0.209 4(2)	0.022 2(1)
Cl(4)	−0.062 0(6)	0.287 0(2)	0.072 6(2)
P(1)	0.351 6(5)	0.262 4(2)	0.141 7(1)
P(2)	0.133 2(5)	0.232 5(2)	0.081 9(1)
P(3)	0.163 6(5)	0.156 1(2)	0.153 1(1)
P(4)	0.298 6(5)	0.040 8(2)	0.121 2(1)
N(1)	0.275 3(16)	0.275 5(6)	0.097 1(4)
N(2)	0.085 1(16)	0.175 4(5)	0.107 6(4)
N(3)	0.310 0(15)	0.203 3(5)	0.165 5(4)
N(4)	0.222 3(16)	0.087 1(5)	0.153 1(4)
N(5)	0.024 7(17)	0.160 5(6)	0.189 9(4)
C(1)	−0.038 7(26)	0.223 0(9)	0.200 8(7)
C(2)	0.031 3(30)	0.245 6(11)	0.241 6(6)
C(3)	−0.047 5(29)	0.107 5(10)	0.212 6(9)
C(4)	−0.195 3(34)	0.088 8(15)	0.194 0(11)
C(11)	0.427 5(18)	0.074 4(6)	0.081 8(5)
C(12)	0.546 6(21)	0.115 8(8)	0.094 7(5)
C(13)	0.649 9(22)	0.141 6(8)	0.065 4(6)
C(14)	0.632 9(22)	0.128 8(7)	0.023 0(6)
C(15)	0.516 7(23)	0.088 6(8)	0.009 7(5)
C(16)	0.414 0(20)	0.061 3(7)	0.038 8(5)
C(21)	0.148 1(18)	−0.003 5(6)	0.093 0(5)
C(22)	0.164 9(19)	−0.065 8(6)	0.085 2(5)
C(23)	0.049 1(20)	−0.096 9(7)	0.062 5(5)
C(24)	−0.084 6(22)	−0.066 1(7)	0.047 4(5)
C(25)	−0.104 2(21)	−0.004 4(8)	0.054 9(6)
C(26)	0.011 2(20)	0.026 5(7)	0.077 9(5)
C(31)	0.428 3(19)	−0.011 2(6)	0.150 0(5)
C(32)	0.401 1(21)	−0.019 1(8)	0.193 2(6)
C(33)	0.501 7(25)	−0.057 5(9)	0.216 3(6)
C(34)	0.626 2(25)	−0.088 5(8)	0.197 1(7)
C(35)	0.653 5(25)	−0.080 0(9)	0.154 7(7)
C(36)	0.553 0(22)	−0.041 5(8)	0.131 4(6)

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‡ 2,2,4,4-Tetrachloro-6-diethylamino-6-(2′,2′,2′-triphenylphosphazen-1′-yl)cyclotriphosphazatriene.

isotropic refinement, the thermal parameters of C(3) and C(4) were 9 and 17 Å^2 while for C(1) and C(2) they were 6.9 and 7.7 Å^2 respectively. A difference-Fourier map computed at this stage showed an elongated electron-density peak for C(3) and a more pronounced one for C(4), suggesting disorder.

At this stage anisotropy was introduced for the thermal parameters and two cycles of least-squares refinement reduced the R index to 0.057. The positions of the hydrogen atoms corresponding to the three phenyl rings and the methylene hydrogens of the ethyl groups were deduced from the molecular geometry and were included in the calculations. Another two cycles of least-squares refinement reduced the R index to 0.045. In the final cycle most parameter shifts were in the range 0.1 σ to 0.3 σ. The program for refinement was written by R. Shiono (University of Pittsburgh) and adapted for the IBM 360/44 by B. S. Reddy. The Fourier program was written by the latter for the above computer. The weighting scheme used was $w = 1/(0.176 + 0.036\,7|F_o| - 0.000\,08|F_o|^2)$. The scattering factors were taken from Cromer and Waber.[13] The final atomic co-ordinates of non-hydrogen atoms are given in Table 1. Observed and calculated structure factors, thermal parameters, and bond parameters of the phenyl rings are listed in Supplementary Publication No. SUP 22935 (21 pp.).*

RESULTS AND DISCUSSION

Bond Distances and Angles.—A view of the molecule down the a axis is shown in Figure 1. Bond distances and angles are given in Table 2. The compound, whose structure was ambiguous from ^{1}H n.m.r. studies,[11] has been shown to have a geminal disposition of the four chlorine atoms. The phosphazene ring exhibits three distinct pairs of P–N bond distances, whose variations can be correlated with the nature of the substituents.[14] The two endocyclic P–N bonds adjacent to the $NPPh_3$ substituted phosphorus atom, P(3), are the longest bonds in the ring and are comparable to the exocyclic P(3)–N(5) bond of the P–NEt_2 group. At 1.634 Å (mean), they appear to be the longest cyclophosphazene bonds reported and indeed are close to values normally associated with phosphazane character.[5] The two bonds P(1)–N(3) and P(2)–N(2) (mean 1.541 Å) adjacent to these two long bonds are the shortest bonds in the ring; the remaining two (mean 1.574 Å) are intermediate in length. Whilst bond variations of the type discussed above have also been observed in the previous three structures,[7-9] the above seems to represent the most pronounced example of such behaviour in cyclotriphosphazatriene structures. The geminal P–Cl bonds are of two types, one short (mean 1.998 Å) and one long (mean 2.020 Å) on each phosphorus atom. This feature is also observed in $N_3P_3Cl_4Ph(NPPh_3)$,[7] $N_3P_3Cl_5(NPPh_3)$,[8] and $N_4P_4Cl_7(NPPh_3)$,[9] as well as in other structures, *viz.* *gem*-$N_3P_3Cl_4Ph_2$,[15] *gem*-$N_3P_3Cl_2Ph_4$,[16] and *gem*-$N_3P_3Cl_3(NMe_2)_3$.[17] The N–C and C–C bond distances in the present studies are unexceptional except for C(3)–C(4).

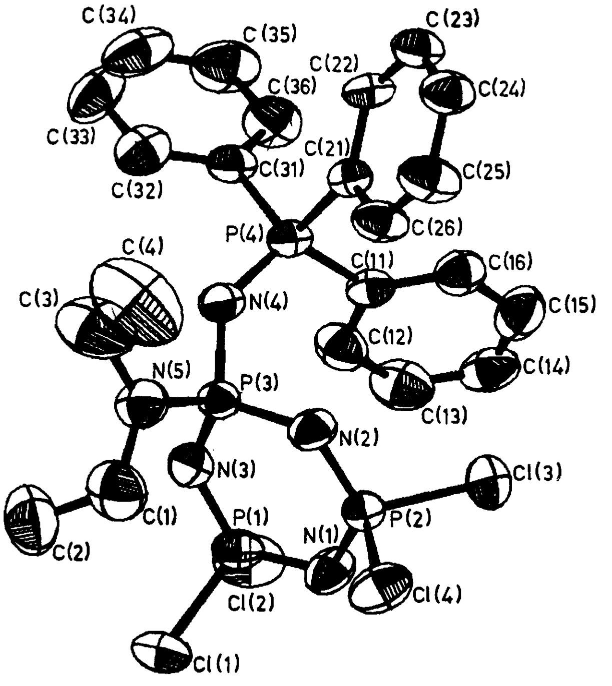

FIGURE 1 View of the molecule $N_3P_3Cl_4(NEt_2)(NPPh_3)$ down the a axis

TABLE 2

Bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses

P(1)–Cl(1)	2.022(6)	P(3)–N(4)	1.59(1)
P(1)–Cl(2)	2.001(6)	P(3)–N(5)	1.64(1)
P(2)–Cl(3)	1.996(6)	P(4)–N(4)	1.56(1)
P(2)–Cl(4)	2.018(6)	P(4)–C(11)	1.79(2)
P(1)–N(1)	1.57(1)	P(4)–C(21)	1.81(2)
P(1)–N(3)	1.54(1)	P(4)–C(31)	1.81(2)
P(2)–N(1)	1.57(1)	N(5)–C(1)	1.51(2)
P(2)–N(2)	1.55(1)	N(5)–C(3)	1.49(3)
P(3)–N(2)	1.64(1)	C(1)–C(2)	1.50(3)
P(3)–N(3)	1.63(1)	C(3)–C(4)	1.41(4)
N(1)–P(1)–N(3)	120.5(7)	N(2)–P(2)–Cl(3)	110.2(5)
N(1)–P(1)–Cl(1)	106.3(5)	N(2)–P(2)–Cl(4)	110.6(5)
N(1)–P(1)–Cl(2)	107.4(5)	Cl(3)–P(2)–Cl(4)	99.4(3)
N(3)–P(1)–Cl(1)	111.8(5)	N(2)–P(3)–N(3)	109.9(6)
N(3)–P(1)–Cl(2)	109.7(5)	N(2)–P(3)–N(4)	111.5(7)
Cl(1)–P(1)–Cl(2)	99.0(3)	N(2)–P(3)–N(5)	109.9(7)
N(1)–P(2)–N(2)	120.7(7)	N(3)–P(3)–N(4)	112.3(6)
N(1)–P(2)–Cl(3)	107.5(5)	N(3)–P(3)–N(5)	107.6(7)
N(1)–P(2)–Cl(4)	106.2(5)	N(4)–P(3)–N(5)	105.5(7)
P(1)–N(1)–P(2)	117.5(8)	N(4)–P(4)–C(31)	108.5(7)
P(2)–N(2)–P(3)	125.1(8)	C(11)–P(4)–C(21)	106.2(7)
P(1)–N(3)–P(3)	125.2(8)	C(11)–P(4)–C(31)	105.3(7)
P(3)–N(4)–P(4)	137.6(8)	C(21)–P(4)–C(31)	108.3(7)
P(3)–N(5)–C(1)	117(1)	P(4)–C(11)–C(12)	118(1)
N(3)–N(5)–C(3)	125(1)	P(4)–C(11)–C(16)	123(1)
C(1)–N(5)–C(3)	117(1)	P(4)–C(21)–C(22)	123(1)
N(5)–C(1)–C(2)	111(1)	P(4)–C(21)–C(26)	118(1)
N(5)–C(3)–C(4)	111(2)	P(4)–C(31)–C(32)	118(1)
N(4)–P(4)–C(11)	114.9(7)	P(4)–C(31)–C(36)	122(1)
N(4)–P(4)–C(21)	113.2(7)		

We now consider the exocyclic $NPPh_3$ group. The nature of the second substituent X [on the $NPPh_3$-substituted phosphorus atom, $PX(NPPh_3)$] would be expected to influence the P–N bond strengths and hence the bond lengths. When this second substituent is an electron-withdrawing group, *e.g.* X = Cl, the two P–N bond lengths would be expected to be different from those

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

where the second substituent is an electron-donating group, *e.g.* X = Ph or NEt_2. These two cases are exemplified by the structures of $N_3P_3Cl_5(NPPh_3)$ [8] and of $N_4P_4Cl_7(NPPh_3)$,[9] on the one hand, and by those of $N_3P_3Cl_4Ph(NPPh_3)$ [7] and $N_3P_3Cl_4(NEt_2)(NPPh_3)$ on the other.

TABLE 3

Comparison of acyclic P–N bond distances in triphenylphosphazenyl–phosphorus compounds, $Ph_3P{=}N{-}R$

R	P–N in $Ph_3P{=}N$/ Å	P–N in N–R/ Å	PNP/ °	Ref.
$N_3P_3Cl_4(NEt_2)$	1.563(12)	1.585(12)	137.6(8)	This work
$N_3P_3Cl_4Ph$	1.576(6)	1.585(6)	131.7(4)	7
$N_3P_3Cl_5$	1.597(9)	1.614(9)	134.8(9)	8
$N_4P_4Cl_7$	1.586(9)	1.564(9)	133.0(6)	9
$P(O)Ph_2$	1.557(2)	1.604(2)	146.0(2)	18
$P(O)Cl_2$	1.582(2)	1.558(2)	139.7(2)	18
PPh_3^+ (linear)	1.539(2)	1.539(2)	180	19
PPh_3^+ (angular)	1.570—1.586	1.570—1.586	135—142	19

An inspection of the data in Table 3 shows that the two exocyclic P–N bond distances in each of the triphenylphosphazenylcyclophosphazenes investigated are short and have phosphazene character.[7–9] Within the limits of the accuracy of the results, these two exocyclic P–N bond distances are equal within each structure (three-centre delocalisation) and they do not vary significantly from structure to structure, *i.e.* they are apparently not affected by the conformation of the $NPPh_3$ substituent relative to the phosphazene ring or by the nature of the second substituent X on the ring phosphorus atom. This observation may be contrasted with data for acyclic analogues $Ph_3P{=}N{-}P(O)X_2$ (X = Cl or Ph[18]) (see Table 3 and also ref. 5), where significant differences in P–N bond lengths are observed which reflect the electron-withdrawing (supplying) character of the second substituent discussed above. Thus, Table 3 shows as great a variation between long, 1.614 Å, and short, 1.563 Å, P–N bonds for the cyclic structures as for the acyclic ones, 1.604 and 1.557 Å. However, the latter range was observed in the same compound and is consistent with chemical reasoning. The former values come from a series of compounds and are not chemically meaningful. Probably the effect of changing two substituents X at the same time in acyclic compounds and compensating factors from the ring in cyclic compounds contribute to this observation.

The acyclic PNP bond angles are in the range 131.7—137.6° for the cyclophosphazenes with the compound reported here having the largest value. No obvious relationship with the nature of the substituents emerges, as is also the case for the two acyclics,[18] where still larger bond angles (139.7—146.0°) are observed. All of the PNP angles are considerably larger than the trigonal planar value of 120° but other triphenylphosphazenyl derivatives have PNP values as low as 121° and as high as 180° $[(Ph_3P{=}N{-}PPh_3)^+]$.[4,6,19]

In $N_3P_3Cl_4(NEt_2)(NPPh_3)$ the endocyclic angles at P(1) and P(2) are 120.5 and 120.7° respectively and the corresponding exocyclic ClPCl angles are also equal (99.0 and 99.4°). These values are similar to those in $N_3P_3Cl_6$.[20] However, at P(3), the ring atom carrying the two nitrogenous substituents, the geometry approaches a regular tetrahedral character, the endocyclic and exocyclic angles being 109.9 and 105.5° respectively. Both the substituents at P(3) are electron-donating groups, whereas at the other phosphorus atoms the substituents are electron-withdrawing chlorine atoms. This reduction in the endocyclic angle at the $NPPh_3$-substituted phosphorus atom has also been observed in the three earlier structures.[7–9] However, the angle (109.9°) reported here is the smallest endocyclic one so far observed in cyclotriphosphazatrienes and appears to be related to the electron-donating properties of the substituents.

In the present compound and the two related ones,[7,8] the endocyclic angle at the nitrogen atom opposite to the phosphorus atom carrying the $NPPh_3$ group is small compared with the other two angles at ring nitrogen atoms. Some bond angles and lengths of these three compounds, together with those of $N_3P_3Cl_6$ [20] and *gem*-$N_3P_3Cl_4Ph_2$, [15] are shown in Figure 2.

It seems worthwhile to compare the following parameters in these five structures [bearing in mind that the data for $N_3P_3Cl_5(NPPh_3)$ are the least accurate]. In general, the electron release from substituents X, Y (relative to X = Y = Cl) increases considerably a and e, increases marginally f, decreases considerably b and d, and decreases marginally g (for definition of a—g see last diagram in Figure 2). The above vary, on the whole, in a reasonably consistent manner. Angle c also increases, but no trend is apparent. Thus, if we compare the series $N_3P_3Cl_4X(NPPh_3)$, we deduce that in the ground state the electron supply is $Cl < Ph < NEt_2$. We have earlier drawn attention to the fact that it is necessary to distinguish between ground-state (*X*-ray, ^{35}Cl n.q.r. spectroscopy) and perturbed-state (basicity studies) measurements.[3,4] The above data suggest that the grouping PXY ($X = NPPh_3$, Y = Ph or NEt_2) supplies in the ground state more electron density to the ring than does PPh_2. The non-geminal P–Cl bond length of $N_3P_3Cl_5(NPPh_3)$,[8] together with the ^{35}Cl n.q.r. spectrum [21] of this compound, suggest however that this P–Cl bond is as much (or more) affected by electron release from an adjacent NMe_2 [17,22–27] group than by the $NPPh_3$ substituent. Thus, the evidence for the relative electron release by the NR_2 and $NPPh_3$ substituents in the ground state is ambivalent.

In basicity studies, however, there is no doubt that the $NPPh_3$ substituent is by far the most electron-releasing substituent as yet studied in phosphazene chemistry.[2] The $pK_{a,1}'$ values for some relevant phosphazenyl derivatives $[N_3P_3Cl_4X(NPPh_3)]$ X = Cl, < -6.0; X = Ph, -4.7; X = NMe_2, -2.0; X = NC_5H_{10}, -2.0, X = $NPPh_3$, 0.4, bear this out. Thus in the perturbed state the electron release is markedly $Cl < Ph < NR_2 < NPPh_3$.

Phosphazene Ring.—The ring in most cyclotriphos-

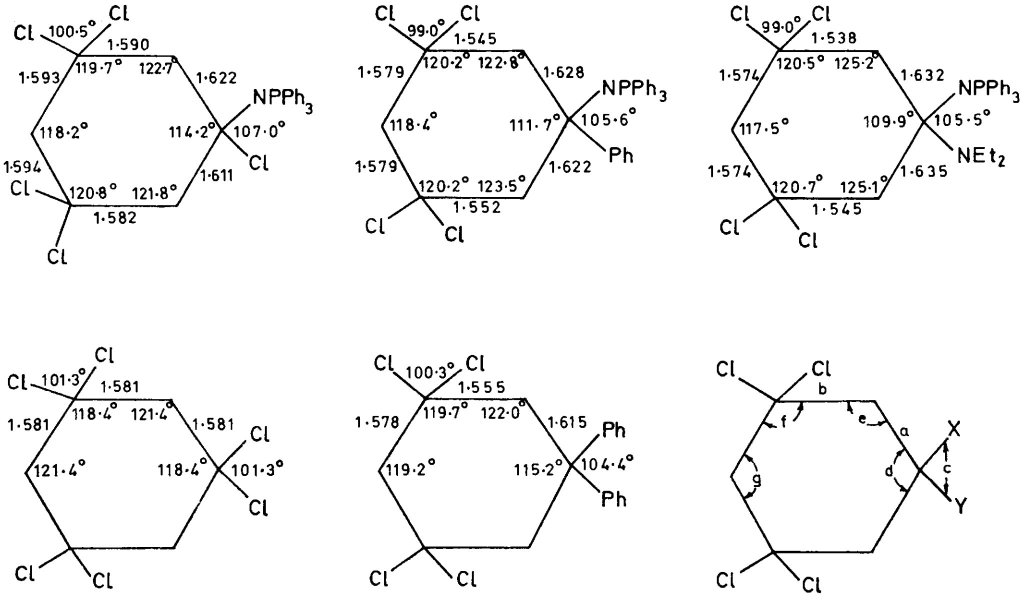


FIGURE 2 Bond lengths (Å) and angles of the compounds $N_3P_3Cl_5(NPPh_3)$, $N_3P_3Cl_4Ph(NPPh_3)$, $N_3P_3Cl_4(NEt_2)(NPPh_3)$, $N_3P_3Cl_6$, and *gem*-$N_3P_3Cl_4Ph_2$

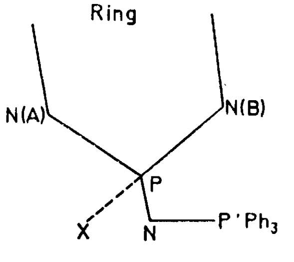
phazatrienes and related six-membered inorganic ring systems deviates from planarity (*cf.* refs. 14, 22—24, 27—29). In the present structure the maximum deviation from planarity is 0.06 Å [at P(1)], while at P(3) it is only 0.02 Å. In both $N_3P_3Cl_5(NPPh_3)$ [8] and $N_3P_3Cl_4Ph(NPPh_3)$ [7] the triphenylphosphazenyl substituted phosphorus atom deviates by a larger amount from the plane formed by the other ring atoms, *i.e.* 0.23 Å and 0.15 Å respectively. The deviation of the former has been attributed to inter- and intra-molecular contacts.[8]

Conformation of the $NPPh_3$ *Group*.—Arguments developed in earlier discussions [3, 7] would lead one to expect that the $NPPh_3$ group in the present compound would adopt a type II conformation. The relevant torsion angles (estimated standard deviations ~1°) given in Table 4, however, show considerable deviations from the expected values and indicate a conformation intermediate between type II and type III. The diethylamino-group, on the other hand, exhibits an almost exact type II conformation [N(4)–P(3)–N(5)–C(1) 173(1)°], the first one observed for a dialkylamino-substituent. The configurations of the ethyl groups are such that the methyl carbons C(2) and C(4) are on opposite sides of the plane formed by P(3), N(5), C(1), and C(3). The corresponding torsion angles are P(3)–N(5)–C(1)–C(2) −104(2)° and P(3)–N(5)–C(3)–C(4) −95(2)°.

It is of interest to compare the conformations of the $NPPh_3$ group in the structures so far solved. A type I conformation was reported for $N_3P_3Cl_5(NPPh_3)$ [8] and a type II for $N_3P_3Cl_4Ph(NPPh_3)$.[7] In the latter, the phenyl group also exhibits an almost perfect type II conformation being perpendicular to the plane of the local NPN segment. On the other hand, the structure of

TABLE 4

Conformations of $NPPh_3$ groups



Torsion angles:

a P'—N—P—N(A)
b P'—N—P—N(B)
c P'—N—P—X

Compound	X	Torsion angles (°) *a*	*b*	*c*	Type	Ref.
$N_3P_3Cl_5(NPPh_3)$	Cl	34	164	−83	I	8
$N_3P_3Cl_4(NEt_2)(NPPh_3)$	NEt_2	35	−89	154	II–III	This work
$N_4P_4Cl_7(NPPh_3)$	Cl	58	−172	−59	I–III	9
$N_3P_3Cl_4Ph(NPPh_3)$	Ph	−60	67	−178	II	7
$N_4P_4Cl_6(NPPh_3)_2$	Cl Molecule 1	25	154	−99	I	*
	Cl Molecule 2	48	−172	−61	I–III	

* G. J. Bullen, personal communication.

$N_4P_4Cl_7(NPPh_3)$ [9] showed a triphenylphosphazenyl group with a conformation tending from type I to type III. The deviation from exact type I in the last case was tentatively attributed to steric factors. In the present structure, $N_3P_3Cl_4(NEt_2)(NPPh_3)$, however, the reasons for the deviation from type II to type III are less obvious as there are no unfavourable steric contacts of the phenyl groups with the rest of the molecule. Whilst the results are not very accurate due to disorder, it is noteworthy that in the structure of the non-geminal 2,6-*trans*-$N_4P_4Cl_6(NPPh_3)_2$ (two molecules differing in ring conformation are present in the unit cell)[10] the relevant torsional angles of one of these molecules have values (−61°) close to that observed for $N_4P_4Cl_7(NPPh_3)$ (−59°) and are thus conformational type I—III. In the second molecule the angles (−99°) are close to that of type I. The torsion angles for all of these structures are given in Table 4. It is noteworthy that the mean torsion angle (−75.5°) of the structures with conformations I or I—III differs from ideal type I by 14.5° and the same mean angle (166°) for compounds with conformations II or II—III differs by 14° from ideal type II.

It is clear that conformations in the solid state [7-10] are closely related to the preferred conformation in solution [as indicated by the four-bond spin–spin coupling constants ${}^4J(P-P)$] [30] and that these in turn bear a relationship to the basicities in nitrobenzene solution.[2-4]

It seems that if an axially symmetric substituent such as chlorine resides on the same phosphorus atom as the phenyl, dialkylamino-, or triphenylphosphazenyl groups, the preferred conformation of these groups is of type I. Type II conformation has to date been observed only if either one of the two substituents has a two-co-ordinate atom adjacent to the phosphorus to which it is attached (*e.g.* a $NPPh_3$ group) and thus minimises edge-on steric interference, or when both substituents are sterically constrained to such a conformation (*e.g.* a five-membered ring structure).[31] A likely reason for the adoption of type III conformation is the mutual repulsion of two axially non-symmetric substituents with their attendant filled p_z orbitals.

In the present structure the $NPPh_3$ substituent deviates from type II behaviour by 26°, the NEt_2 substituent by 8°, both in the same rotational sense (clockwise or anticlockwise, as viewed from the ring phosphorus atom along the bond to be rotated). In the type III behaviour of geminal phenyl or dimethylamino-groups the rotation of both substituents (from type I or II) in *gem*-$N_3P_3Cl_4Ph_2$,[15] *gem*-$N_3P_3Cl_2Ph_4$,[16] $N_3P_3Ph_6$,[14] *gem*-$N_3P_3Cl_3(NMe_2)_3$,[17] *gem*-$N_3P_3(NHCH_2CH_2NH)(NMe_2)_4$,[31] and in $N_3P_2CPh_4(NMe_2)$ [32] is again in the same rotational sense, giving rise to a dihedral angle between the planes of the two substituents close to 90°. It may be that the same driving forces are responsible for the deviations from type II towards type III conformation in the present structure. It seems clear that conformational studies on phosphazenes in the solid state, as well as in solution, and their correlation with other physical and chemical properties, will continue to be a fertile field.

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