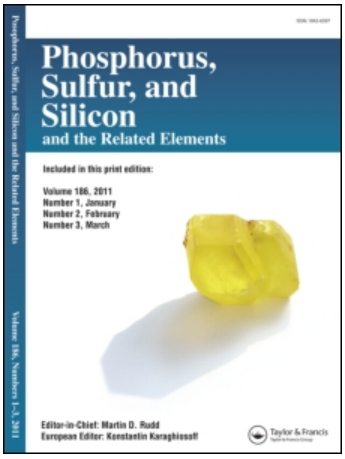

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THE REACTIONS OF $N_3P_3CL_6$ AND RELATED COMPOUNDS WITH DIFUNCTIONAL REAGENTS. COMPARISONS AND CONTRASTS

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THE REACTIONS OF $N_3P_3Cl_6$ AND RELATED COMPOUNDS WITH DIFUNCTIONAL REAGENTS. COMPARISONS AND CONTRASTS

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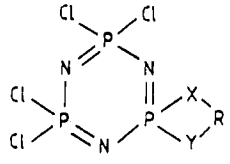
The reactions of $N_3P_3Cl_6$ with a variety of difunctional reagents are discussed. NMR spectroscopic and X-ray crystallographic investigations are presented.

The reactions of $N_3P_3Cl_6$ and its derivatives with difunctional reagents have aroused a good deal of attention, particularly in recent years. Four types of products have been realised with aliphatic reagents: spiro, ansa, bridging, dangling (monofunctional) (**1–4**).[1–18]



SPIRO

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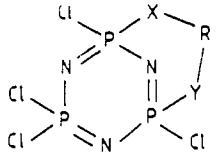

ANSA

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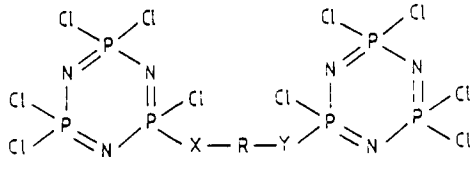
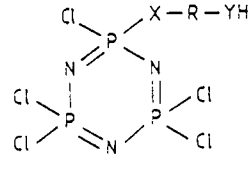


BRIDGING

3

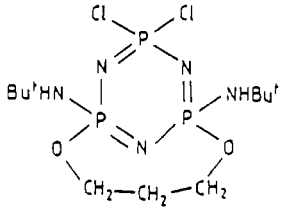


OPEN CHAIN
(DANGLING)

4

*Author to whom all correspondence should be addressed.

NMR spectroscopy, ^{31}P, ^{13}C and ^{1}H, has proved very useful for structure determination, but occasionally it can be rather misleading, as in the case of $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$, where NMR spectroscopy indicated an ansa-structure (**5**), but X-ray crystallography revealed a spiro grouping (**6**).[19]



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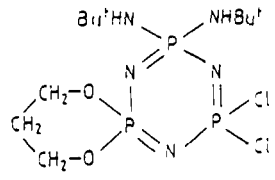


6

NMR spectroscopy here was misleading because of the accidental isochrony of the chemical shifts of the $\underline{P}(NHBu^t)_2$ and $\underline{P}[O(CH_2)_3O]$ groups; basicity measurements cannot distinguish (useful as they are for certain structure determinations) between these two particular structures.[20]

X-ray crystallography is the only certain way for structure determination and many of the structures we are discussing here have been determined in this manner.[21] Crystallography[21-25] in conjunction with NMR[20,22-25] and ^{35}Cl N.Q.R.[22] spectroscopy and basicity studies,[20] has revealed a wealth of information.

Let us consider the ^{31}P NMR data first. We will confine ourselves to the chemical shifts of the phosphorus nuclei carrying the spiro groups. The data are given in Table I.

There is a drastic drop in the chemical shift on passing from five-membered to six-membered spiro rings for the groupings $P[O(CH_2)_nO]$, $P[O(CH_2)_nNH]$ and $P[NH(CH_2)_nNH]$ ($\bar{n} = 2, 3$) 14–21 ppm, but not for the secondary amino group, $P[NMe(CH_2)_nNMe]$ ($n = 2, 3$), where it is only 3.3 ppm

A smaller increase in chemical shift is observed on passing from six-membered to seven-membered rings ($n = 3, 4$) for the compounds so far measured (3–7 ppm). Similar observations have been made on mononuclear phosphates, phosphites and

TABLE I

^{31}P chemical shifts of P(spiro) in phosphazenes with the spiro ring containing 5, 6, or 7 atoms

Compound	5-Ring	= 5-6	6-Ring	= 6-7	7-Ring
$N_3P_3[O(CH_2)_nO]Cl_4$	23.8	−21.4	2.4	7.2	9.2
$N_3P_3[O(CH2)_nNH]Cl_4$	24.4	−17.2	7.2	7.2	14.3
$N_3P_3[NH(CH_2)_nNH]Cl_4$	22.9	−15.4	7.5	5.3	12.8
$N_3P_3[NMe(CH_2)_nNMe]Cl_4$	20.4	−3.9	16.5		
$N_3P_3Ph_2[O(CH_2)_nO]Cl_2$	26.7	−21.3	5.4		
$N_3P_3Ph_2[O(CH_2)_nNH]Cl_2$	25.8	−15.8	10.0	6.9	16.9
$N_3P_3Ph_2[NH(CH_2)_nNH]Cl_2$	25.3	−14.1	11.2	3.3	14.5
$N_3P_3Ph_2[NMe(CH_2)_nNMe]Cl_2$	22.9	−3.3	19.6		

$n = 2$ (5-ring), $n = 3$ (6-ring), $n = 4$ (7-ring)

TABLE II

Comparison of the ^{31}P chemical shifts of related primary and secondary amino derivatives

Compound type	Primary amino derivative	Secondary amino derivative	Difference
$N_3P_3Ph_2[NR(CH_2)_2NR]Cl_2$ (R = H or Me)	25.3	22.9	−2.4
$N_3P_3Ph_2[NR(CH_2)_3NR]Cl_2$ (R = H or Me)	11.2	19.4	8.2
$N_3P_3(NRMe)_6$ (R = H or Me)	21.5	24.6	3.1
$N_3P_3(NREt)_6$ (R = H or Et)	18.0	22.5	4.5

related compounds pertaining to five-membered, six-membered and acyclic derivatives.[26,27]

When we compare similar types of primary and secondary amino derivatives, we observe considerable differences between spiro and acyclic structures (Table II).

On passing from primary to secondary amino derivatives, the chemical shift of the five-membered spiro ring decreases by 2.4 ppm, but increases by 8.2 ppm for the six-membered analogue. For acyclic analogues, $N_3P_3(NHR)_6$ and $N_3P_3(NR_2)_6$ (R = Me, Et), an increase of 3 to 4.5 ppm is observed.[28] These acyclics therefore occupy a position about half-way between the five- and six-membered spiro structures.

We shall make use of some of the above observations to deduce structures by NMR spectroscopy, where the reagent would allow five- or six-membered spiro rings to be formed.[29]

We also note the behaviour of the secondary amino six-membered spiro groups and will return to this when we discuss the ^{13}NMR spectra.

We now consider the ^{13}C data and confine ourselves to the spiro groups. In the six-membered rings the chemical shifts of all the compounds considered here were for $P—O\underline{C}H_2$ ~ 67.5 ppm, for $P—N—\underline{C}H_2$ ~ 41.0 ppm, with little scatter from these values. The only exception so far observed is compounds containing the

TABLE III

^{13}C NMR data

Compound	$P—O\underline{C}H_2$ ppm	$^2J(P,C)$ Hz	$C—CH_2—C$ ppm	$^3J(P,C)$ Hz
$N_3P_3[O(CH_2)_3O]Cl_4$	68.1	6.6	25.8	7.3
$N_3P_3[O(CH_2)_3O]_2Cl_2$	67.4	5.9	25.9	7.3
$N_3P_3[O(CH_2)_3O]_3$	66.9	5.5	26.1	7.0
$N_3P_3Ph_2[O(CH_2)_3O]Cl_2$	67.3	7.3	26.0	6.1
$N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$	66.9	5.9	26.1	6.7
$N_3P_3[HN(CH_2)_3O]Cl_4$	68.4	7.3	25.5	6.1
$N_3P_3Ph_2[HN(CH_2)_3]Cl_2$	67.6	6.7	25.8	6.1
$N_3P_3(NHBu^t)_2[HN(CH_2)_3O]Cl_2$	67.3	7.3	25.1	5.9

TABLE IV

^{13}C NMR data

Compound	P—NCH_2 ppm	^2J(P, C) Hz	C—CH_2 ppm	^3J(P, C) Hz
$N_3P_3[HN(CH_2)_3NH]Cl_4$	40.5	2.9	25.6	6.6
$N_3P_3Ph_2[HN(CH_2)_3NH]Cl_2$	41.3	3.6	26.2	6.1
$N_3P_3(Bu^tNH)_2[HN(CH_2)_3NH]Cl_2$	41.2	2.9	26.5	5.9
$N_3P_3[O(CH_2)_3NH]Cl_4$	40.9	3.1	25.5	6.1
$N_3P_3Ph_2[O(CH_2)_3NH]Cl_2$	41.1	3.6	25.8	6.1
$N_3P_3(NHBu^t)_2[O(CH_2)_3NH]Cl_2$	41.1	3.0	25.1	5.9
$N_3P_3[MeN(CH_2)_3NMe]Cl_4$	50.1	0.0	25.1	2.6
$N_3P_3Ph_2[MeN(CH_2)_3NMe]Cl_2$	50.4	0.0	25.3	0.0
$N_3P_3[NHBu^t]_2[MeN(CH_2)_3NMe]Cl_2$	50.5	0.0	24.6	0.0

$N_3P_3[NMe(CH_2)_3NMe]$ fragment for which $\delta^{13}C$ for P—N—$\underline{C}H_2$ is approximately 50 ppm. All of the above compounds give δCH_2—$\underline{C}H_2CH_2$ signals at approximately 26 ppm, regardless of whether the hetero-atoms are oxygen and/or nitrogen (NH).

Two-bond coupling constants ^2J(P—O—C) are 6.4 ± 0.9 Hz, and ^2J(P—N—C) 3.2 ± 0.4 Hz. Three-bond coupling constants, ^3J(P—X—C—C) (X = O, NH), are for all these six-membered rings 6.5 ± 0.8 Hz.

Compounds containing the $N_3P_3[NMe(CH_2)_3NMe)]$ fragment again proved to be an exception as ^2J(P—N—C) and ^3J(P—N—C—C) values are zero and only 2.6 Hz, respectively.

In the seven-membered ring systems the chemical shifts of P—O—C and P—N—C were similar to those of the six-membered ring systems, with perhaps marginally lower values. The shifts of CH_2—$C\underline{H}_2$—CH_2, however, fell into two groups, P—O—C—C being near 29 ppm, whilst P—N—C—C is at 31–32 ppm. This allowed assignment in the mixed ring system $P[O(CH_2)_4NH]$. Coupling constants show much larger differences than chemical shifts, when comparing six- and seven-membered spiro rings. For ^2J(P—O—C) an average value for the seven-membered ring system is 5.7 Hz, about 1 Hz less than for the six-membered ring system. The change for ^2J(P—N—C) is more dramatic, being zero for the seven-membered against approximately 3.2 Hz for the six-membered system. Even more dramatic are the values for ^3J(P—X—C—C) (X = O, NH). In the seven-membered rings the

TABLE V

^{13}C NMR data

Compound	P—OCH_2 ppm	^2J(P, C) Hz	O—C—CH_2—C ppm	^3J(P, C) Hz
$N_3P_3[O(CH_2)_4O]Cl_4$	67.7	5.9	28.9	0.0
$N_3P_3[O(CH_2)_4O]Cl_2$	66.8	5.9	29.0	0.0
$N_3P_3[O(CH_2)_4O]_3$	65.9	5.1	29.1	0.0
$N_3P_3[O(CH_2)_4NH]Cl_4$	67.3	5.9	29.7	0.0
$N_3P_3Ph_2[O(CH_2)_4NH]Cl_2$	66.0	5.9	29.8	0.0
$N_3P_3(NHBu^t)_2[O(CH_2)_4NH]Cl_2$	65.7	6.0	29.9	0.0

TABLE VI

^{13}C NMR data

Compound	N—$\underline{C}H_2$ ppm	^2J(P,C) Hz	N—C—$\underline{C}H_2$ ppm	^3J(P,C) Hz
$N_3P_3[HN(CH_2)_4NH]Cl_4$	40.4	0.0	31.6	0.0
$N_3P_3[HN(CH_2)_4NH]_2Cl_2$	40.5	0.0	32.8	0.0
$N_3P_3Ph_2[HN(CH_2)_4NH]Cl_2$	40.4	0.0	31.9	0.0
$N_3P_3(NHBu^t)[HN(CH_2)_4NH]Cl_2$	40.4	0.0	32.1	0.0
$N_3P_3[O(CH_2)_4NH]Cl_4$	40.4	0.0	30.8	0.0
$N_3P_3Ph_2[O(CH_2)_4NH]Cl_2$	40.2	0.0	31.1	0.0
$N_3P_3(NHBu^t)_2[O(CH_2)_4NH]Cl_2$	40.2	0.0	31.3	0.0

values are zero in contrast to the six-membered rings, where the corresponding values are approximately 6.5 Hz.

Data on the five-membered spiro rings are rather more scarce. As a group, this type of compound is rather prone to decomposition. Chemical shifts for P—O—$\underline{C}$ are marginally lower than in six- or seven-membered ring analogues, whilst for P—N—$\underline{C}$ the values differ little from that of the higher ring systems. The odd one out is again a secondary amino derivative, $N_3P_3Ph_2[NMe(CH_2)_2NMe]Cl_2$, with a chemical shift of 47.2 ppm Whilst in the six-membered ring system the effect of changing P—NH—$\underline{C}H_2$ to P—NMe—$C\underline{H}_2$ increases the chemical shift from 41 to 50, i.e., by about 9 ppm, this effect is only half as pronounced in the five-membered system, where corresponding values are 42 to 47, i.e., 15 ppm. We are currently extending these studies.

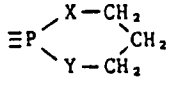
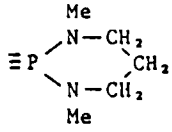
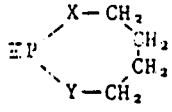
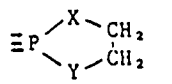
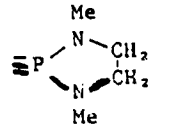
Coupling constants are radically different from the higher ring systems. The difficulty of interpretation is increased as the coupling constant experimentally observed is probably a combination of the effects via two and three bonds. J(P—O—$\underline{C}$) values vary from 0 to 2.9 Hz. It is possible that some of the zero values conceal small coupling constants, as multiplicities of three or greater could arise from long-range virtual coupling. Not only do we have groups with identical chemical shift, but also others with closely related chemical shifts arising from PCl_2 and PPh_2 groups.[19] J(P—N—$\underline{C}$) values are also drastically different from those of the higher ring systems. For J(P—NH—$\underline{C}H_2$) a value of 8.8 Hz and for J(P—NMe—$\underline{C}H_2$) one of 117 Hz contrast sharply with the values reported above.

We summarise our data in Table VIII.

TABLE VII

Compound	P—O—$\underline{C}H_2$ ppm	^2J(P,C) Hz	P—N—$\underline{C}H_2$ ppm	^2J(P,C) Hz
$N_3P_3[O(CH_2)_2O]Cl_4$	66.6	2.2	—	—
$N_3P_3[O(CH_2)_2O]_2Cl_2$	66.3	0.0	—	—
$N_3P_3[O(CH_2)_2O]_3$	66.0	0.0	—	—
$N_3P_3Ph_2[O(CH_2)_2O]Cl_2$	66.0	0.0	—	—
$N_3P_3(NHBu^t)_2[O(CH_2)_2O]Cl_2$	65.6	0.0	—	—
$N_3P_3[O(CH_2)_2NH]Cl_4$	67.3	2.2	42.5	8.1
$N_3P_3(Bu^tNH)_2[O(CH_2)_2NH]Cl_2$	66.4	2.9	42.4	8.8
$N_3P_3Ph_2[MeN(CH_2)_3NMe]Cl_2$	—	—	47.2	11.7

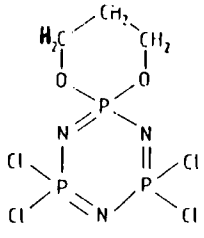
TABLE VIII

Spiro ring[a]	δP—O—C ppm	^2J(POC) Hz	δP—N—C ppm	^2J(PNC) Hz	δP—X—C—C ppm	^3J(PXCC) Hz
	67.5	6.4	41.0	3.2	26.0	6.5
	—	—	50.3	0.0	25.0	2.6
	66.5	5.7	40.5	0.0	30.8[b]	0.0
	66.0	0.3	42.5	8.8	29.7[c] —	0.0 —
	—	—	47.2	11.7	—	—

[a] X = Y = O, NH [b] X = O
X = O, Y = NH [c] X = NH

This highlights the anomalous properties of N—Me derivatives in the five- and six-membered ring systems. (Note our earlier remarks on their ^{31}P NMR spectra).

As crystallographic data is available on a number of five-, six- and seven-membered spiro ring systems,[1,2,7-10,12-15,17-25] we have investigated the X-ray crystal



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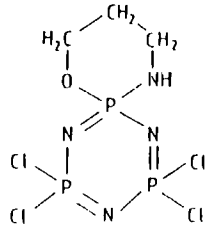

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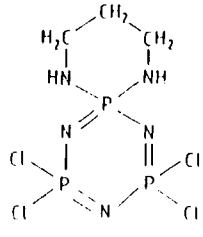

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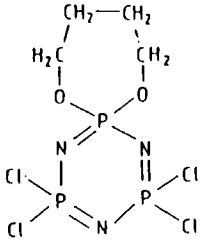

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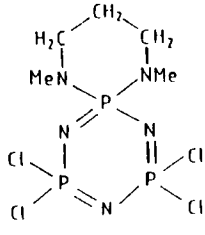

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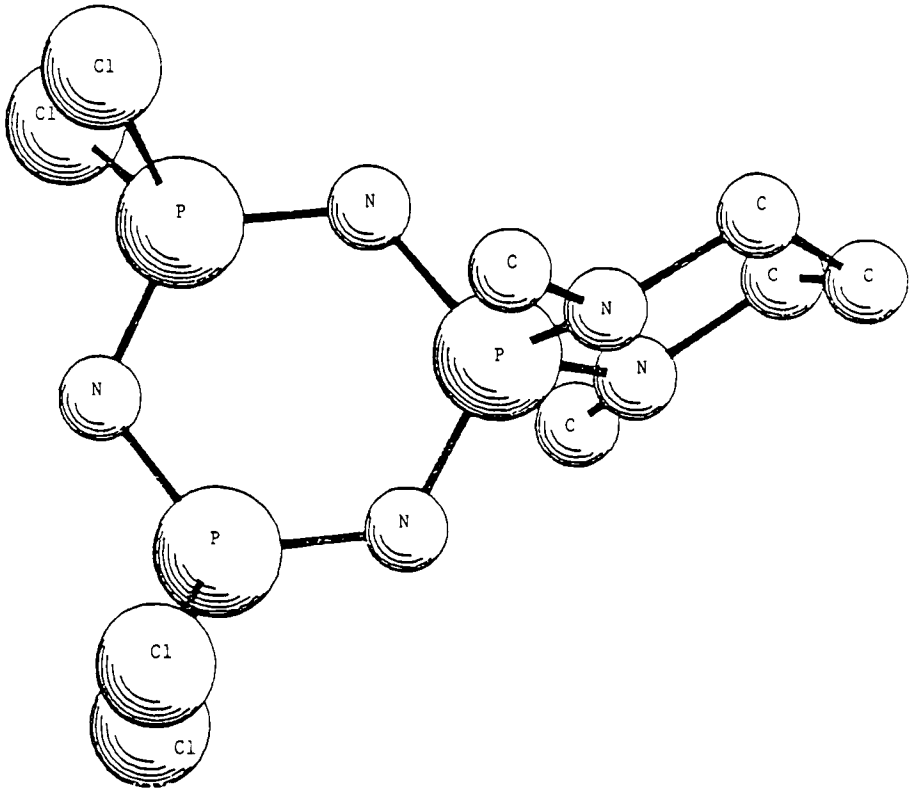

FIGURE 1 Molecular diagram of $N_3P_3[NMe(CH_2)_3NMe]Cl_4$

structure of $N_3P_3[NMe(CH_2)_3NMe]Cl_4$ to discover the cause of its contrast with other six-membered ring systems.

The dihedral angles POCC in the crystalline state for a number of compounds containing the $P[O(CH_2)_3O]$ group (e.g., **7**) are 53–57°. The same angle in $N_3P_3[O(CH_2)_3NH]Cl_4$, (**8**), a disordered structure, is 37°, whilst its nitrogen analogue PNCC is 69°. The dihedral angle PNCC in $N_3P_3[NH(CH_2)_3NH]Cl_4$ (**9**) is 62°. In the seven-membered ring $N_3P_3[O(CH_2)_4O]Cl_4$ (**10**) POCC is 89°.

In the structure we report here, $N_3P_3[NMe(CH_2)_3NMe]Cl_4$ (**11**), we find the dihedral angles PNCC to be 47 and 51°. The spiro ring is in a chair form (Figure 1). There is no simple relationship between dihedral angles PXCC (X = O, NH, NMe) in the crystalline state and the P—X—C—C (X = O, NH, NMe) coupling constants in solution; indeed, because of the different nature of the linking atoms, one would not have expected one.

The clue to the difference in behaviour of the compounds containing the $N_3P_3[NMe(CH_2)_3NMe]$ fragment and the others lies in the stereochemistry of the nitrogen atom. In $N_3P_3[NH(CH_2)_3NH]Cl_4$[13] (**9**), the exocyclic nitrogen atom is trigonal planar (sum of bond angles 359.9°). Its lone pair thus participates in a major way in back-bonding to phosphorus. The same pertains to the P—NH—CH_2 section of $N_3P_3[O(CH_2)_3NH]Cl_4$[21] (**8**). The oxygen atom in this compound, as well

as those in $N_3P_3[O(CH_2)_3O]Cl_4$,[21] (7-c) has two lone pairs available and hence will be able to effectively back bond over a considerable range of conformations.

By contrast, in $N_3P_3[NMe(CH_2)_3NMe]Cl_4$, (**11**), the exocyclic nitrogen atoms deviate ~ 0.27 Å from the plane of the three atoms to which they are bonded. The sum of their bond angles is approximately 351°. Hence, these nitrogen atoms have an appreciable amount of sp^3-character, and are less able to back conjugate than the other compounds mentioned above.

This structural feature is the likely cause of the drastic reduction in coupling constants. It also explains the reduced basicity,[20] as well as probably the ^{31}P chemical shift.

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