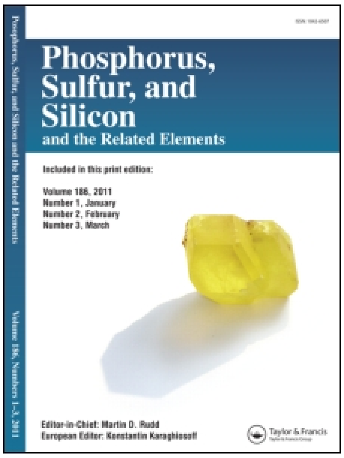

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ISOLATION, NMR SPECTRA AND X-RAY CRYSTAL STRUCTURES OF TWO ISOMERIC $N_3P_3CL_2[O(CH_2)_3O]_2$ DERIVATIVES. THE FIRST EXAMPLE OF DISPIRO / SPIRO-ANSA ISOMERISM IN PHOSPHAZENE CHEMISTRY. COMPARISONS OF TRANS-ANNULAR BRIDGED CYCLOPHOSPHAZENES

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ISOLATION, NMR SPECTRA AND X-RAY CRYSTAL STRUCTURES OF TWO ISOMERIC $N_3P_3Cl_2[O(CH_2)_3O]_2$ DERIVATIVES. THE FIRST EXAMPLE OF DISPIRO / SPIRO-ANSA ISOMERISM IN PHOSPHAZENE CHEMISTRY. COMPARISONS OF TRANS-ANNULAR BRIDGED CYCLOPHOSPHAZENES

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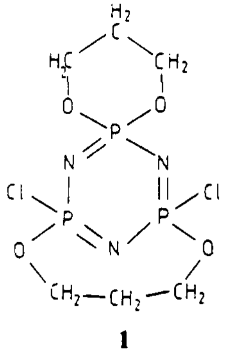
From the reaction of $N_3P_3Cl_6$ with 1,3-dihydroxypropane two isomeric $N_3P_3Cl_2[O(CH_2)_3]_2$ derivatives were isolated, whose NMR spectra suggest, and crystal structures prove, them to represent an example of dispiro/spiro-ansa isomerism, the first of its kind in phosphazene chemistry. The crystal structures and NMR spectra are discussed. Extension of the work with difunctional reagents is reported.

We have already reported[1] the isolation of the first pair of isomeric dispiro/spiro-ansa derivatives, $N_3P_3Cl_2[O(CH_2)_3O]_2$, (**1** and **2**). We briefly discussed their NMR spectra and some aspects of their structure as determined by X-ray crystallography.[1]



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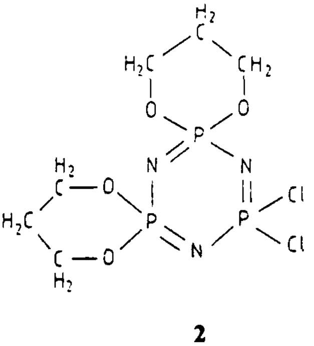

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We now take a closer look at aspects of the above ansa-structure (**1**) and compare it with others, which have since been reported.[2,3] Ansa-derivatives of cyclotriphosphazatrienes are just a special case of the more general class of *trans*-annular bridged compounds. Those of cyclotetraphosphazatetraenes have been known considerably longer[4-13] than those of cyclotriphosphazatrienes,[1-3,14] and four examples

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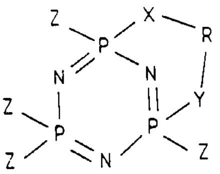

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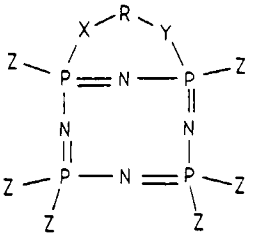

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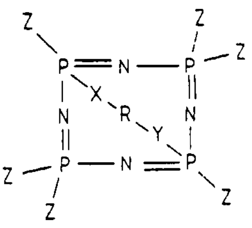

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of the former have been crystallographically investigated.[2,4,8,9,12,13] We can describe *trans*-annular bridged compounds (with one such bridge) based on the N_3P_3 and N_4P_4 ring systems by the general structures (**3**–**5**).

Examples of all three types (**3**–**5**) are now crystallographically documented.[1-4,8,9,12,13]

Historically the first of these are compounds of type (**5**), which were isolated under some conditions during the aminolysis of $N_4P_4Cl_8$ and certain of its derivatives[4-10] (Figures 1 and 2).

This was followed shortly by an example (**6**) of type (**4**) (Figure 3).[11-13]

We will now examine the non-bonding distances P ··· P, both across the ring to the far phosphorus atoms in the eight-membered ring, and to the neighbouring

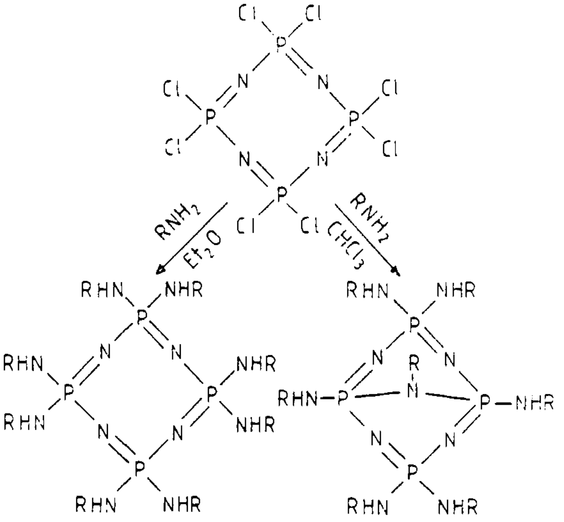

FIGURE 1 The reactions of $N_4P_4Cl_8$ with NH_2R to give monocyclic and bicyclic compounds.

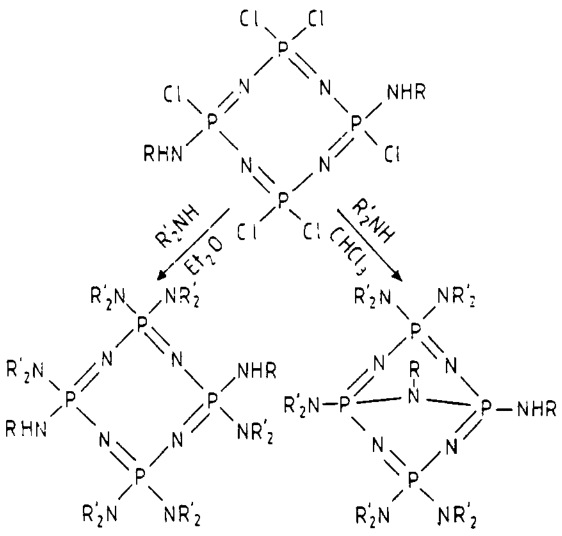

FIGURE 2 The reactions of $N_4P_4(NHR)_2Cl_6$ with NHR'_2 to give monocyclic and bicyclic compounds.

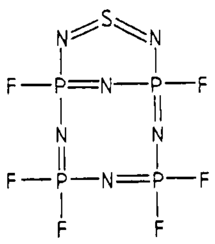

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FIGURE 3 The bridged compound $N_4P_4F_6(N_2S)$.

phosphorus atoms in the six- as well as the eight-membered ring structures. In Figure 4 are diagrams of monocyclic tetramer molecules, $N_4P_4Z_8$, of type (**7**), where the distances x and y represent the P ··· P non-bonding distances to the far and to the neighbouring phosphorus atoms, respectively.

Such non-bonding distances in homogeneously substituted monocyclic tetramer derivatives, $N_4P_4Z_8$, are assembled in Table I.

These were calculated from the fractional atomic coordinates of the published structures.[15] The distances (x) between the far non-bonded phosphorus atoms are fairly constant at 4.00 ± 0.08 Å (with those for $N_4P_4F_8$ perhaps marginally longer), whilst the corresponding values (y) for the neighbouring phosphorus atoms are 2.87 ± 0.04 Å. In Figure 5 is the diagram of 2,6-*trans*-annular bridged compounds of type (**5**). Here (x') and (x) represent the distances between the bridged and non-bridged phosphorus atoms and (y) the same as above.

In Figure 6 we show the three compounds (**8, 9, 10**) of this type (**5**), which have been crystallographically determined.

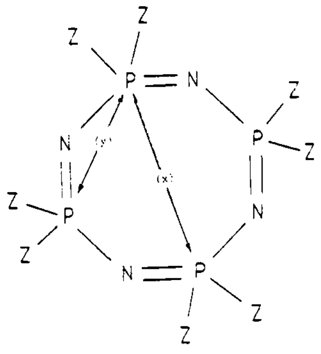

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FIGURE 4 Non-bonded P ··· P distances in $N_4P_4Z_8$.

The data (again calculated as above) are summarised in Table II together with the mean values for unbridged compounds from Table I.

Table II makes at once apparent the dramatic reductions to 2.78–2.79 Å in compounds (**8**) and (**9**) of the P ··· P distances, x', between those atoms where bridging has occurred. These, as well as the neighbouring distances, y, are commensurate with those of monocyclic trimer derivatives (see below). By contrast the non-bonding distances, x, between the far non-bridged phosphorus atoms have now expanded to 4.17 and 4.24 Å.

By contrast the changes in the metallocene bridged tetramer (**10**) are more modest. The distances x and y are barely different from those of the monocycles, $N_4P_4Z_8$, and x', the bridged distance has been reduced by only about 0.2 Å compared to the 1.2 Å in compounds (**8**) and (**9**). It is probably this marked reduction in distances, comparable to those in trimer derivatives, which causes the remarkable ^{31}P chemical shift changes to values in the trimer region.[4–7,10]

TABLE I

Compound	Mean P ··· P non-bonded distances (Å)	
	x	y
$N_4P_4F_8$[16] (low temperature form)	4.100	2.899
$N_4P_4F_8$[16] (high temperature form, split atoms model)	4.115	2.909
$N_4P_4Cl_8$[17] (K-form)	3.919	2.860
$N_4P_4Cl_8$[18] (T-form)	3.961	2.885
$N_4P_4Br_8$[19]	3.920	2.865
$N_4P_4(OMe)_8$[20]	4.048	2.870
$N_4P_4(NMe_2)_8$[21]	4.062	2.894
$N_4P_4(NC_4H_8)_8$[22]	4.002	2.844
$N_4P_4Ph_8$[23]	3.955	2.857
$N_4P_4Me_8$[24]	4.081	2.915

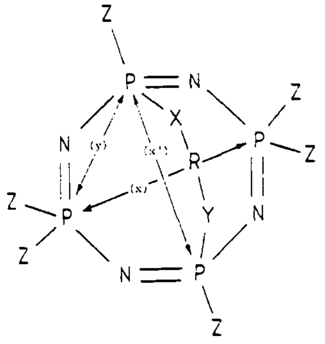

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FIGURE 5 Non-bonded P · · · P distances in 2,6-bridged $N_4P_4Z_6(XRY)$.

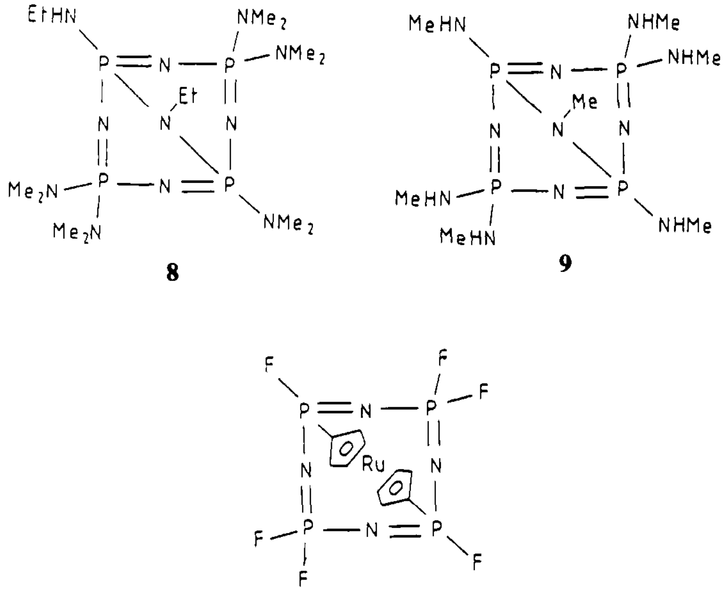

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FIGURE 6 The three 2,6-bridged N_4P_4 derivatives, whose crystal structures have been determined.

We now consider the one example (**6**) of a bridge spanning neighbouring phosphorus atoms in cyclotetraphosphazatetraenes,[12,13] i.e. an example of type (**4**). In Figure 7 we show the non-bonded distances involved in compounds of type (**4**).

The bridged distance, y', between neighbouring phosphorus atoms has contracted to 2.75 Å, i.e. to the trimer region; y'' involving one bridging atom and one non-bridged one, at 2.83 Å, is perhaps marginally shorter than those of monocyclic tetramer derivatives (Tables I and II). The distance, y, involving two non-bridged atoms, at 2.96 Å, is somewhat longer than the values in monocycles. The non-bonded

TABLE II

Compound	Mean P · · · P non-bonded distances (Å)		
	x	x'	y
$N_4P_4(NMe_2)_5(NHEt)(NEt)$[4,8] **(8)**	4.169	2.793	2.807
$N_4P_4(NHMe)_6(NMe)$[9] **(9)**	4.243	2.784	2.781
$N_4P_4F_6[(C_5H_4)_2Ru]$[2] **(10)**	3.986	3.736	2.862
$N_4P_4Z_8$ (mean value)	4.00		2.87

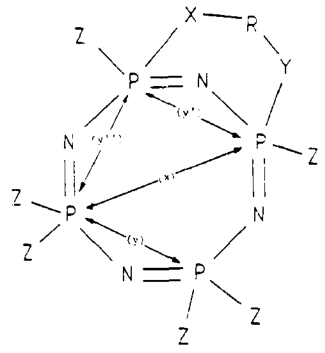

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FIGURE 7 Non-bonded P · · · P distances in 2,4-bridged $N_4P_4Z_6(XRY)$.

distance between the far phosphorus atoms, x, at 4.02 Å is in the region of these unbridged monocycles of type (7), and especially close to that for $N_4P_4F_8$.

We now consider the homogeneously substituted cyclotriphosphazatriene derivatives, $N_3P_3Z_6$ without *trans*-annular bridging. Some of this data are collected in Table III.

We note that the mean non-bonded distance, y, between neighbouring phosphorus atoms at 2.77 ± 0.03 Å (except for $N_3P_3F_6$ which has a value of 2.71 Å) is rather shorter than the corresponding mean distance, y, for monocyclic tetramer derivatives at 2.87 Å, and close to those of the two bridged tetrameric phosphazenes (**8**) and (**9**) at 2.79 Å.

We now compare the above values with those obtained for the three bridged (ansa) cyclotriphosphazatriene derivatives. A general structure of type (**3**) is given in Figure 8.

Here the distance y'' represents the two bridged phosphorus atoms, whilst y and y' (which may be the same or different, depending on whether $X = Y$ or $X \neq Y$) are the distances between one bridged and the unbridged phosphorus atoms.

In Figure 9 we display the three bridged (ansa) structures (**1**), (**11**) and (**12**).

For compound (**1**) we note the contraction of (y'') to 2.644 Å and a marginal shortening of (y) to 2.733 Å. For compound (**11**) (y'') has only been reduced to

TABLE III

Compound	Mean P · · · P non-bonded distances (Å) y
$N_3P_3F_6$[25]	2.713
$N_3P_3Cl_6$[26]	2.746
$N_3P_3Br_6$[27]	2.747
$N_3P_3(NMe_2)_6$[28]	2.789
$N_3P_3(OPh)_6$[29]	2.751
$N_3P_3Ph_6$[30]	2.794
$N_3P_3Me_6$[31]	2.796

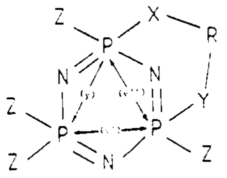

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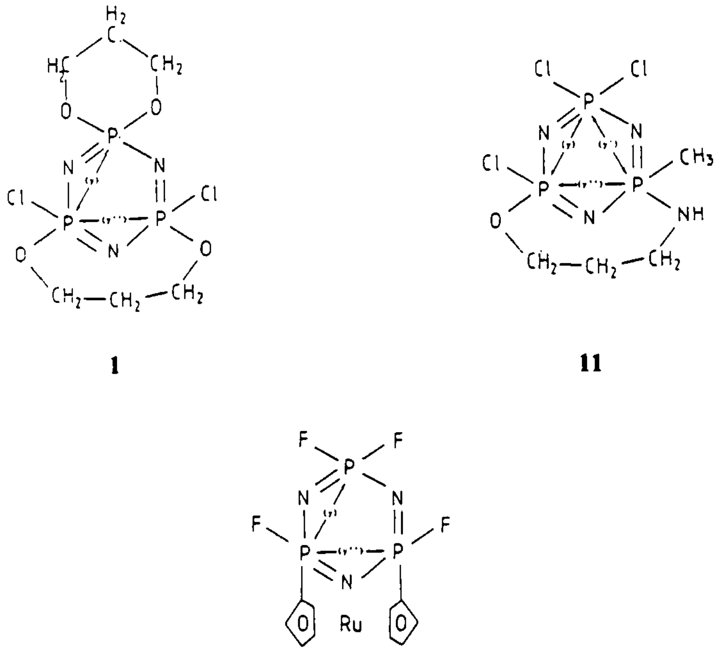
FIGURE 8 Non-bonded P · · · P distances in bridged N_3P_3 derivatives.



1 **11**

12

FIGURE 9 The three bridged N_3P_3 derivatives whose crystal structures have been determined.

2.720 Å, (y) also to 2.726 Å and (y') has a normal value of 2.787 Å. Compound (**12**), the metallocene derivative, has (y'') at 2.649 Å and (y) at 2.708 Å. The latter is normal, as in $N_3P_3F_6$, (y) is 2.713 Å.

It is clear that all three compounds are compressed relative to comparable monocyclic cyclotriphosphazatriene derivatives, which have a mean value for (y) of 2.77 Å. The compression is least marked for compound (**11**).

This compression of the non-bonded distances between the two phosphorus atoms which are bridged is accompanied by a deviation of the nitrogen atom between them from the plane of the remaining phosphorus and nitrogen ring atoms. These deviations are 0.523, 0.4 and 0.56 Å respectively for compounds (**1**), (**11**) and (**12**). Again that for compound (**11**) is the least marked, and this derivative appears to be less compressed than the other two. Clearly there is some relationship between the compression of (y) to (y'') and the deviation of the above nitrogen atom from the rest of the cyclotriphosphazatriene ring. It will require, however, more data for this relationship to be defined more precisely.

The relationship of these ring compressions to bulk polymerisation and to mass spectrometry is referred to elsewhere.[32]

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