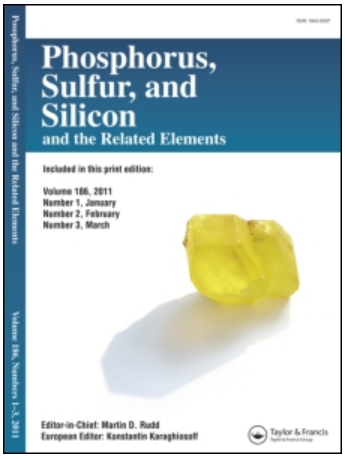

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X-RAY CRYSTALLOGRAPHIC INVESTIGATIONS OF SOME SPIRO-DERIVATIVES OF CYCLOTRIPHOSPHAZATRIENE

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X-RAY CRYSTALLOGRAPHIC INVESTIGATIONS OF SOME SPIRO-DERIVATIVES OF CYCLOTRIPHOSPHAZATRIENE

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The crystal structures of a number of spiro derivatives of cyclotriphosphazatriene are reported. Attempts are made to relate these to NMR and other physical properties.

We have reported previously X-ray crystallographic studies on spiro derivatives of cyclophosphazenes.[1,2] We now extend our investigations to other five-membered and six-membered spiro compounds and compare these with earlier findings, our own,[1,2] as well as those of other workers.[3,4]

We will commence with five-membered spiro derivatives. We have determined the structures of $N_3P_3[O(CH_2)_2NH]Cl_4$ (**1**) and its *N*-methylated analogue, $N_3P_3[O(CH_2)_2NMe]Cl_4$ (**2**), and compare these with that of $N_3P_3[O(CH_2)_2O]Cl_4$ (**3**) (Figure 1).

If we first compare compounds (**1**) and (**2**), there are no significant differences in these two structures either in bond angles or bond lengths, except that P(4)—N(5) is significantly longer in (**1**) than in (**2**). The reason for this becomes at once apparent, when we examine the hydrogen bonding in compound (**1**). The N—H of the spiro cycle is bonded to the N(5) atom of the N_3P_3 ring (see later).

The exocyclic nitrogen atoms in both compounds are trigonal planes. In both structures there appears to be a tendency for on P—Cl bond (of each PCl_2 group) to be longer than the other.

Whilst, as anticipated on chemical grounds, the P(2)—N(3) and the N(3)—P(4) bonds in (**1**) and (**2**) show a trend to be somewhat longer and shorter respectively, then those in compound (**3**), the differences are not statistically significant. However, as Coulson and coworkers[5–7] have shown that bond angles are a more reliable guide than bond lengths, it is reassuring that the angles N(1) P(2) N(3) in (**1**) [112.9 (2)°] and (**2**) [113.3 (2)°] are significantly smaller than those in (**3**) [115.5 (2)°], and that the P(2) N(3) P(4) β angles in (**1**) [124.6 (2)°] and (**2**) [124.3 (2)°] are significantly larger than those in (**3**) [122.9 (1)°]. This is indicative of the greater electron-releas-

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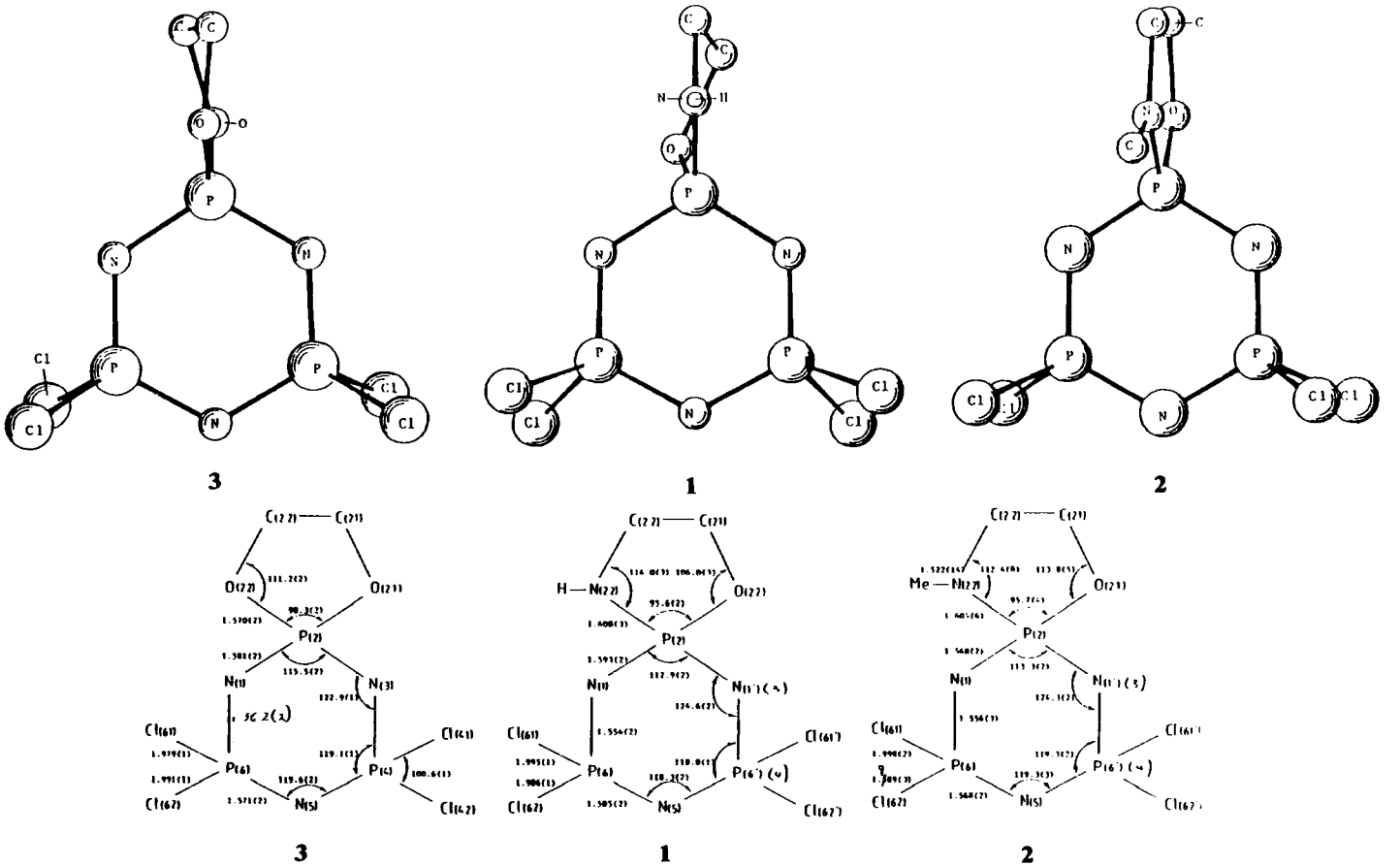


FIGURE 1 (a) Molecular diagrams (b) averaged molecular dimensions of $N_3P_3[O(CH_2)_2O]Cl_4$, $N_3P_3[O(CH_2)_2NH]Cl_4$ and $N_3P_3[O(CH_2)_2NMe]Cl_4$.

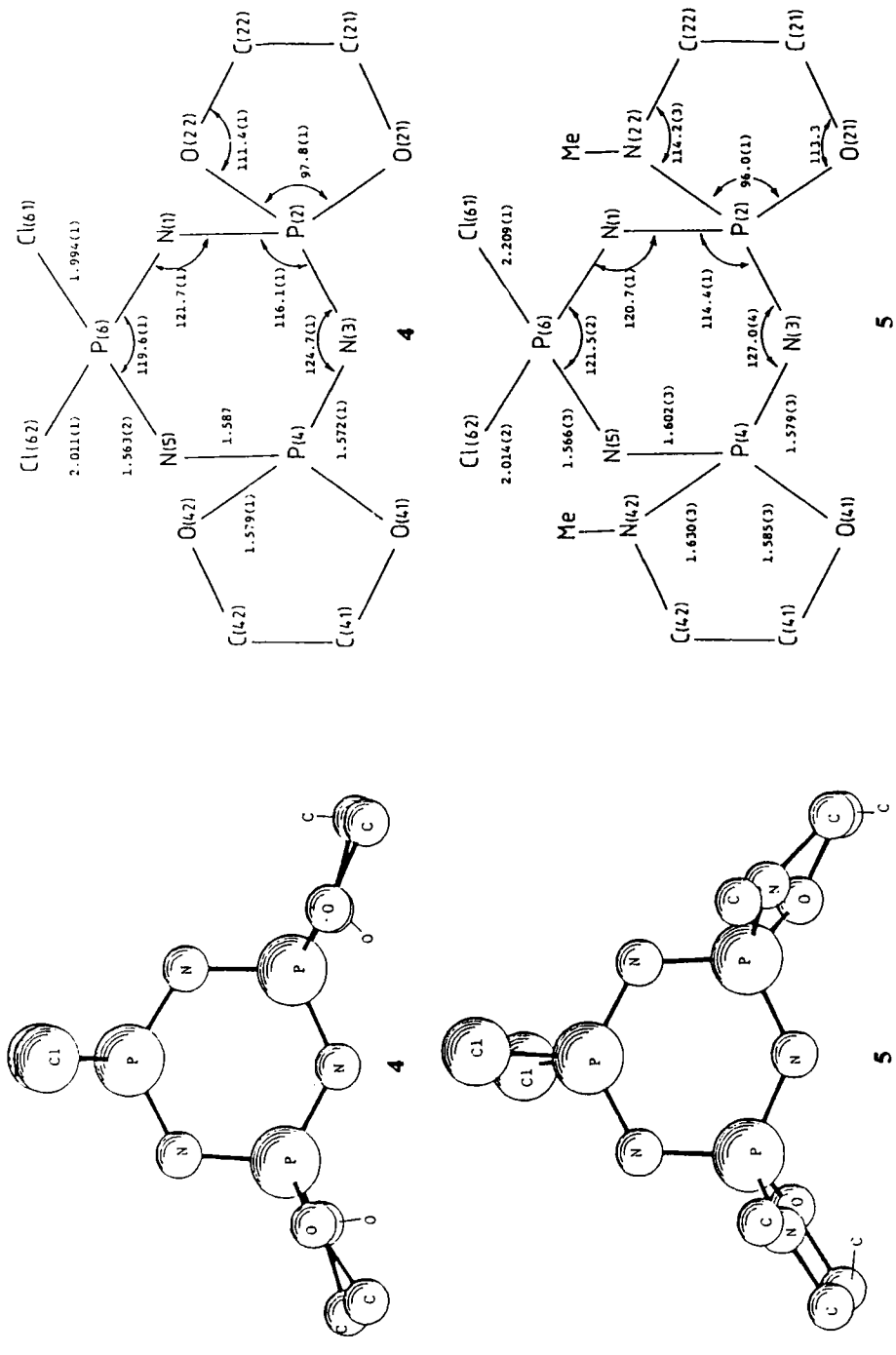


FIGURE 2 (a) Molecular diagram (b) averaged molecular dimensions of $N_3P_3[O(CH_2)_2O]_2Cl_2$ and $N_3P_3[O(CH_2)_2]_2NMe]_2Cl_2$.

ing capacity of the $[O(CH_2)_2NH]$ and $[O(CH_2)_2NMe]$ substituents compared to that of $[O(CH_2)_2O]$.[8] In all three compounds (**1**), (**2**), and (**3**), the N(3) P(4) N(5) and the P(4) N(5) P(6) angles neither differ significantly from each other within each compound nor from each other within this group of three compounds.

The average P—Cl bond lengths in (**1**) and (**2**) are marginally longer than those in (**3**), and this should be reflected in their ^{35}Cl N.Q.R. frequencies.[9-11]

We now compare two bis five-membered spiro-ring structures, viz. $N_3P_3[O(CH_2)_2O]_2Cl_2$ (**4**) with the previously reported *cis*-$N_3P_3[O(CH_2)_2NMe]_2Cl_2$ (**5**)[4] (Figure 2).

As in the related monospiro derivatives (**2**) and (**3**), so in the dispiro derivatives (**4**) and (**5**), the $[O(CH_2)_2NMe]$ substituent is more electron-releasing than $[O(CH_2)_2O]$ towards the N_3P_3 ring. We note a few salient features. The endocyclic bond angle NPN of the phosphorus atom carrying the spiro group is 116.1 (1)° for (**4**) and 114.4 (1)° for (**5**). The PNP angle between the two phosphorus atoms carrying spiro groups is 124.7 (1)° for (**4**) and 127.0 (4) for (**5**). Both are indicative of the greater electron-releasing power of the $[O(CH_2)_2NMe]$ substituent compared to that of $[O(CH_2)_2O]$. This is also reflected in the greater mean P—Cl bond length in (**5**) 2.022 (1) Å compared to (**4**) 2.003 (1) Å, both compounds having incidentally non-equivalent P—Cl bond lengths. Both these features should be reflected in their ^{35}Cl N.Q.R. spectra.

We now turn our attention to six-membered spiro rings. The structures of $N_3P_3[O(CH_2)_3O]Cl_4$ (**6**)[1,2] and $N_3P_3[NH(CH_2)_3NH]Cl_4$ (**8**)[3] have been previously reported. We now describe those of $N_3P_3[O(CH_2)_3NH]Cl_4$ (**7**) and of $N_3P_3[NMe(CH_2)_3NMe]Cl_4$ (**9**). We first compare the structures of (**6**), (**7**) and (**8**) (Figure 3).

We observe, as we replace the spiro substituent $[O(CH_2)_3O]$ successively by $[O(CH_2)_3NH]$ and $[NH(CH_2)_3NH]$, a lengthening of the ring P—N bond adjacent to the P(spiro) group and a marginal shortening of the N—P bond adjacent to the longer one. As mentioned earlier, we find, however, bond angles to be a more reliable guide than bond lengths. As mentioned elsewhere in this Symposium,[11] in geminal disubstituted derivatives, $N_3P_3RR^1Cl_4$, the bond angles α show the most marked effect of the substituents R and R^1, followed by a somewhat lesser effect in β angles and lesser ones still in γ and δ angles. These bond-angle changes clearly show the increased electron donation to the ring as we replace $[O(CH_2)_3O]$ successively by $[O(CH_2)_3NH]$ and $[NH(CH_2)_3NH]$. Interestingly, the first replacement of O by NH seems to be about twice as effective as the second replacement.

We have remarked elsewhere in this Symposium[12] on the differences in the ^{31}P and ^{13}C NMR spectra of the related primary amino, $N_3P_3[NH(CH_2)_3NH]Cl_4$ (**8**) and secondary amino derivatives, $N_3P_3[NMe(CH_2)_3NMe]Cl_4$, (**9**). Thus δ ^{31}P for $P[NH(CH_2)_3NH]$ is 7.5 ppm, whilst δ ^{31}P for $P[NMe(CH_2)_3NMe]$ is 16.5 ppm. Additionally, in the ^{13}C NMR spectra of these two compounds, there are dramatic changes in coupling constants. Thus for compounds (**8**) and (**9**) $^2J(PC)$ are 2.9 and 0.0 Hz respectively, whilst $^3J(PC)$ are 6.6 and 2.6 Hz respectively.

We therefore undertook a crystal structure determination of compound (**9**) to compare it with that of compound (**8**), in the hope to discover the origin of this difference in behaviour in NMR spectroscopy. Their structures are compared in Figure 4.

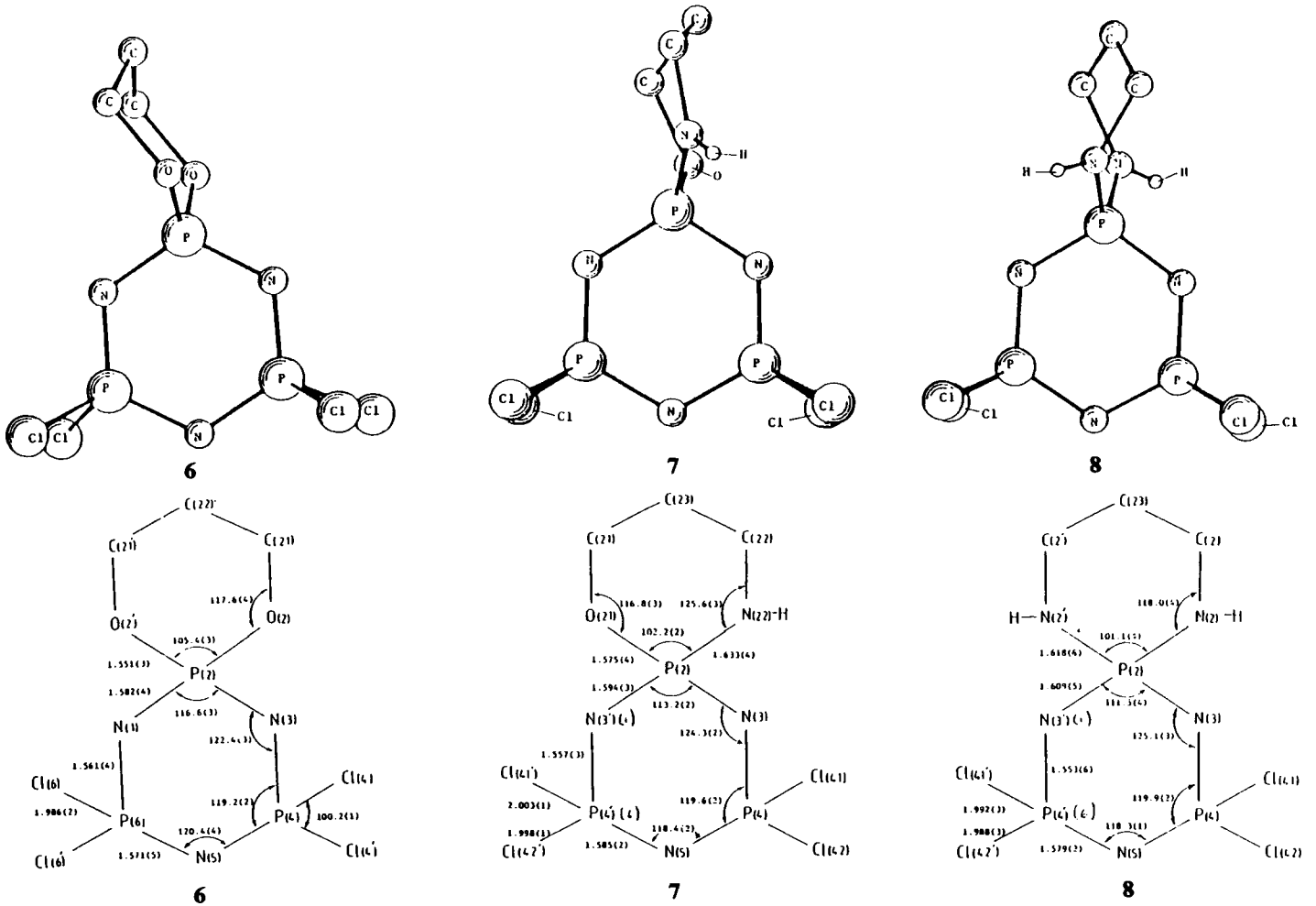
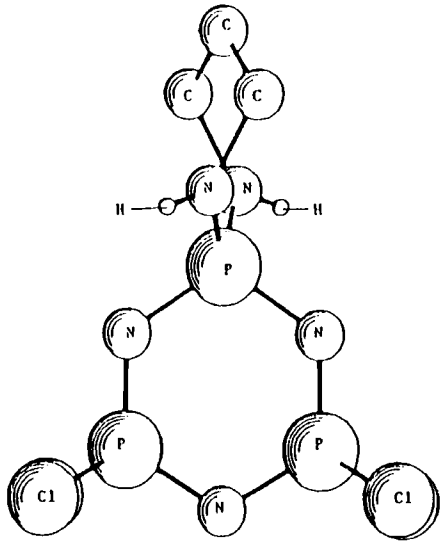


FIGURE 3 (a) Molecular diagram (b) averaged molecular dimensions of $N_3P_3[O(CH_2)_3O]Cl_4$, $N_3P_3[O(CH_2)_3NH]Cl_4$ and $N_3P_3[NH(CH_2)_3NH]Cl_4$.



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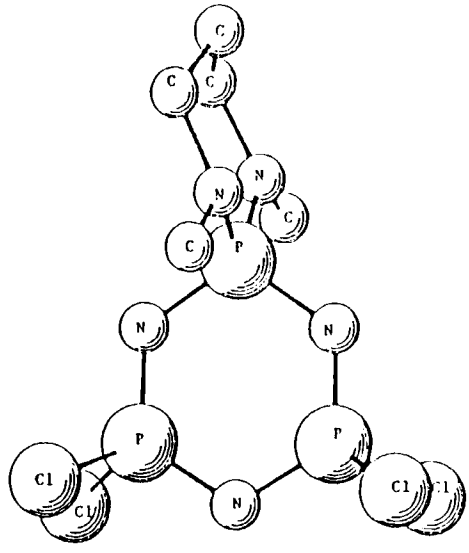

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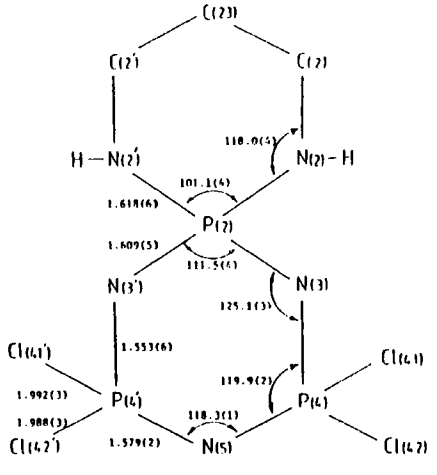

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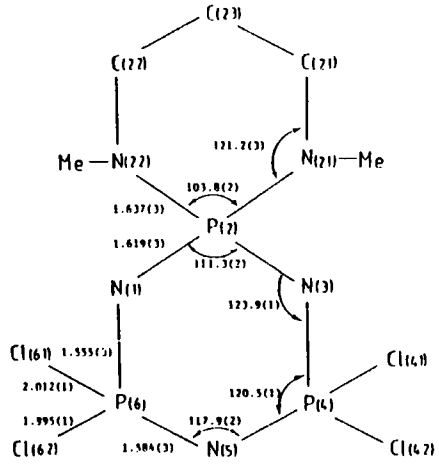

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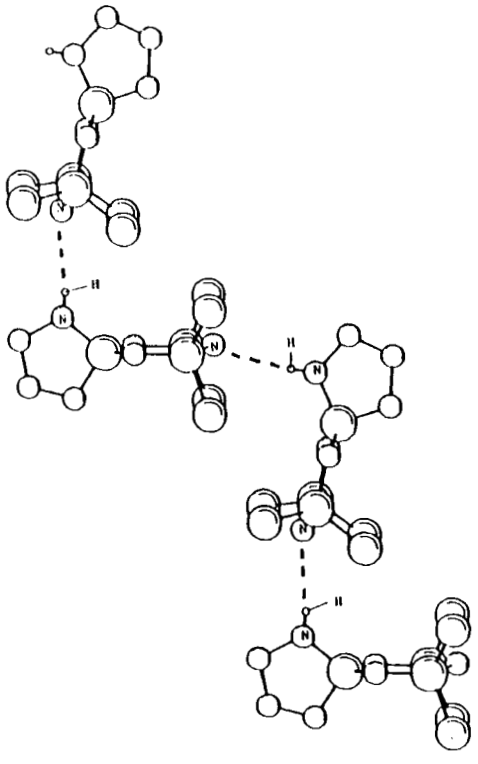
FIGURE 4 (a) Molecular diagrams (b) averaged molecular dimensions of $N_3P_3[NH(CH_2)_3NH]Cl_4$ and $N_3P_3[NMe(CH_2)_3NMe]Cl_4$.

The striking finding, which emerges, is the close similarity between most features of these two compounds. There is perhaps a suggestion (from bond angle data) that compound (**8**) supplies marginally more electron density than compound (**9**) to the N_3P_3 ring. This is supported by basicity data in solution.[9] The most marked differences between these two structures are in the spiro rings. The HNPNH angle in (**8**) is 101.1 (4)°, whilst the MeNPNMe angle in (**9**) is 103.8 (2)°. The PNC angle in



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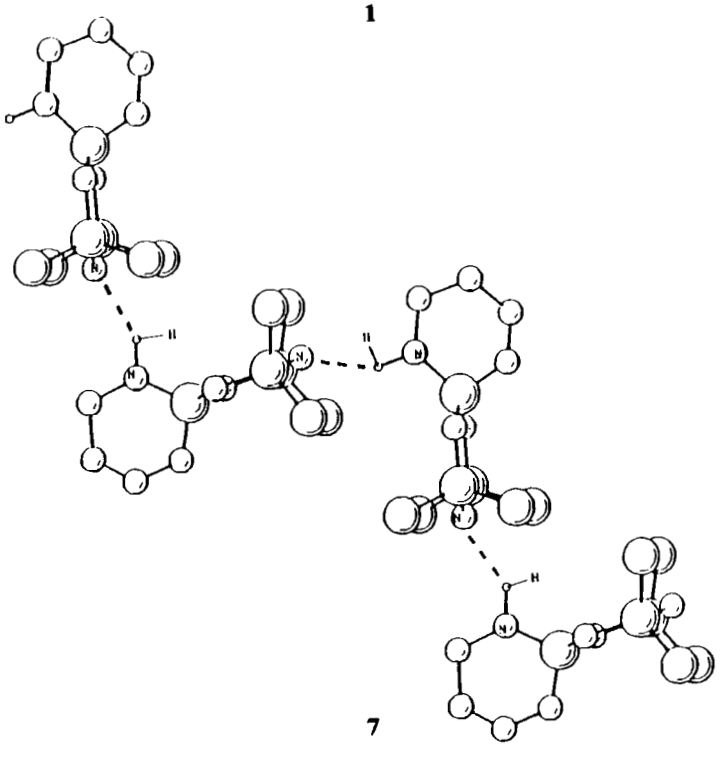

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FIGURE 5 Hydrogen bonding diagrams for (a) $N_3P_3[O(CH_2)_2NH]Cl_4$ and (b) $N_3P_3[O(CH_2)_3NH]Cl_4$.

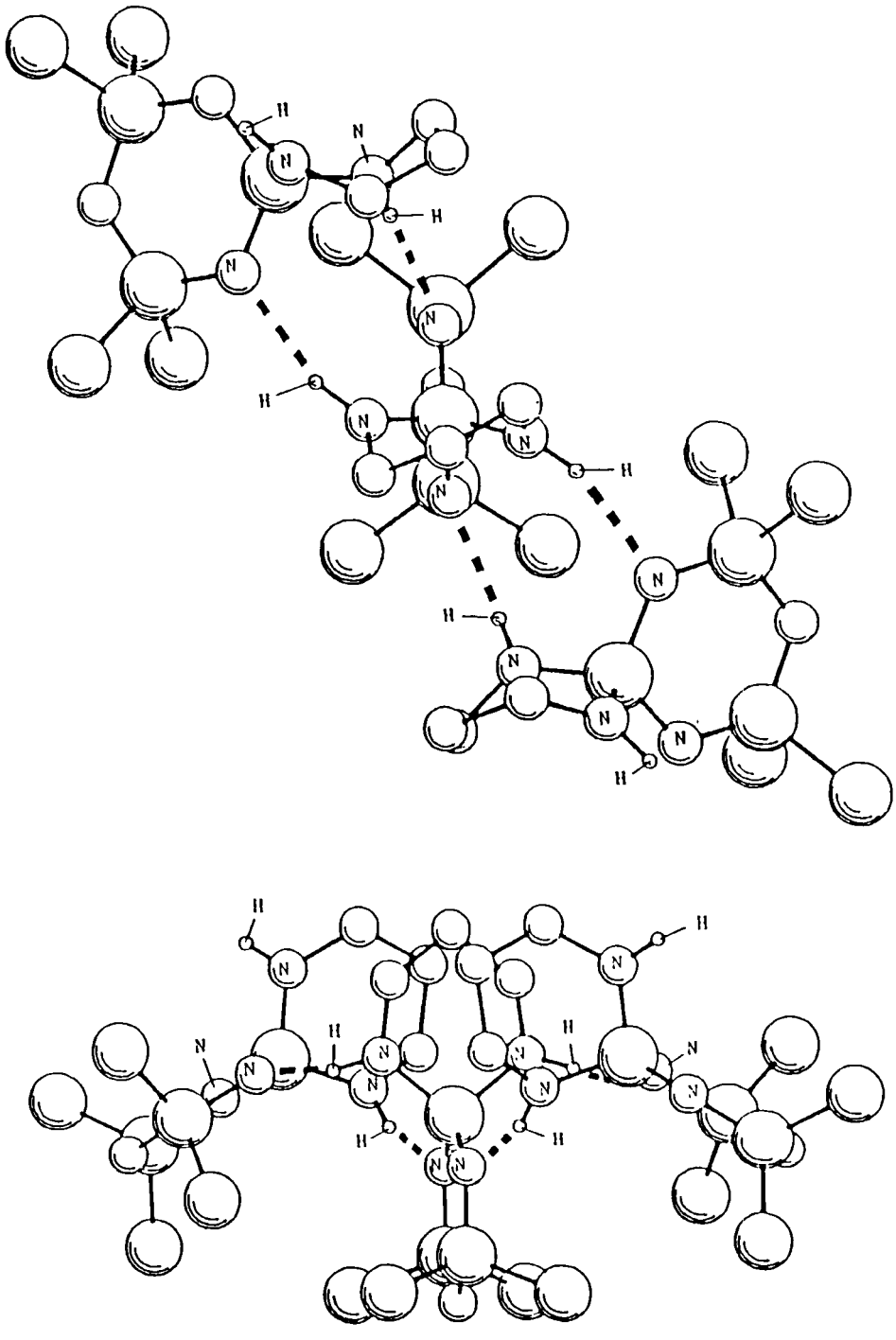

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FIGURE 6 Hydrogen bonding diagrams for $N_3P_3[NH(CH_2)_3NH]Cl_4$.

(**8**) is 118.0 (4)°, whilst in (**9**) it is 121.2 (3)°. The dihedral angle PNCC in (**8**) is 62.4°, whilst those in (**9**) are −47.0 and 50.9°, hardly a likely cause of this difference in $^3J(PC)$ values. A detailed look at the stereochemistry of the substituent nitrogen atoms revealed that in compound (**9**) the nitrogen atoms deviate markedly (0.27 Å) from the planes of the three atoms to which they are bonded. The sums of the bond angles around these nitrogen atoms are 351.1°. In compound (**8**) the comparable nitrogen atom is trigonal planar, the sum of its bond angles being 360.0°. The same trigonal planar structure has also been observed for $N_3P_3[O(CH_2)NH]Cl_4$ (**1**), for $N_3P_3[O(CH_2)_2NMe]Cl_4$ (**2**) and for $N_3P_3[O(CH_2)_3NH]Cl_4$ (**7**). In $N_3P_3[O(CH_2)_2NMe]_2Cl_2$ (**5**),[4] one nitrogen atom is trigonal planar (sum of bond angles = 359.95°), the other has a slight pyramidal

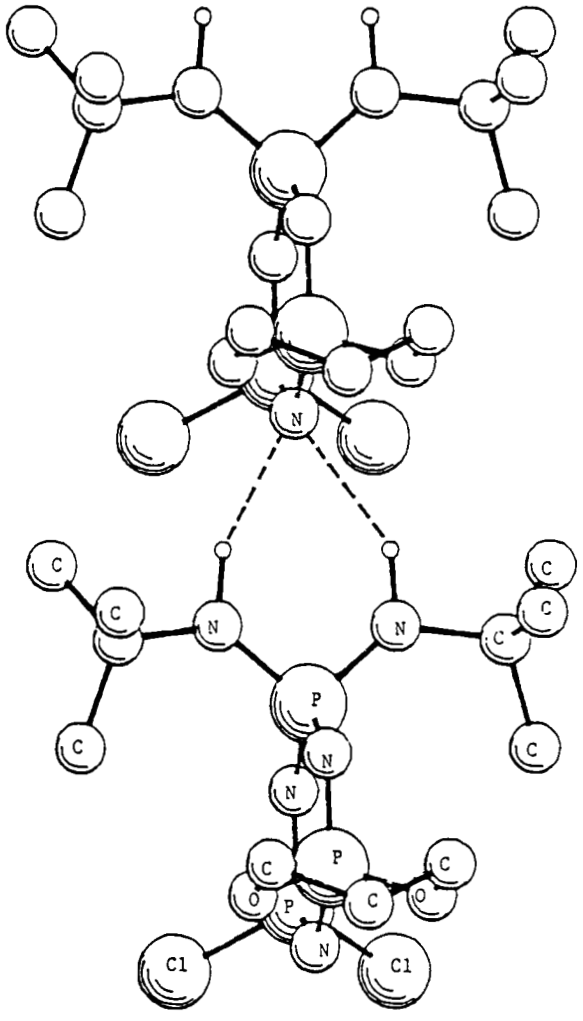

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FIGURE 7 Hydrogen bonding diagram for $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_4$.

character (sum of angles = 358.6°) and it lies 0.1 Å below the plane of its three neighbours. We suggest that this deviation of the nitrogen atoms from planarity and the resulting reduced back-donation of their lone pairs of electrons to phosphorus is a major cause of the anomalies we have observed in comparing compound (**9**) with related structures.

Finally, we would like to make a few comments on the hydrogen bonding in the structures discussed here. Compounds (**1**), $N_3P_3[O(CH_2)_2NH]Cl_4$ and (**7**) $N_3P_3[O(CH_2)_3NH]Cl_4$ behave very similarly, the N—H bonds of the substituents hydrogen bond to ring nitrogen atoms *para* to the substituents (Figure 5).

In both compounds an infinite chain structure results.

Compounds (**1**) and (**7**) have similar unit cells and melting points. These are a reflection of the close similarity of their structures, including their hydrogen-bonded array.

By contrast compound (**8**), $N_3P_3[NH(CH_2)_3NH]Cl_4$,[3] forms a complex hydrogen-bonded array from both of the N—H bonds of the substituents to ring nitrogen atoms *ortho* to these substituents (Figure 6).

A similar result has been observed with $N_3P_3(NHBu^t)_2$ derivatives.[11] The geminal derivative, $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_2$ (**10**),[8] utilises both of the N—H bonds of

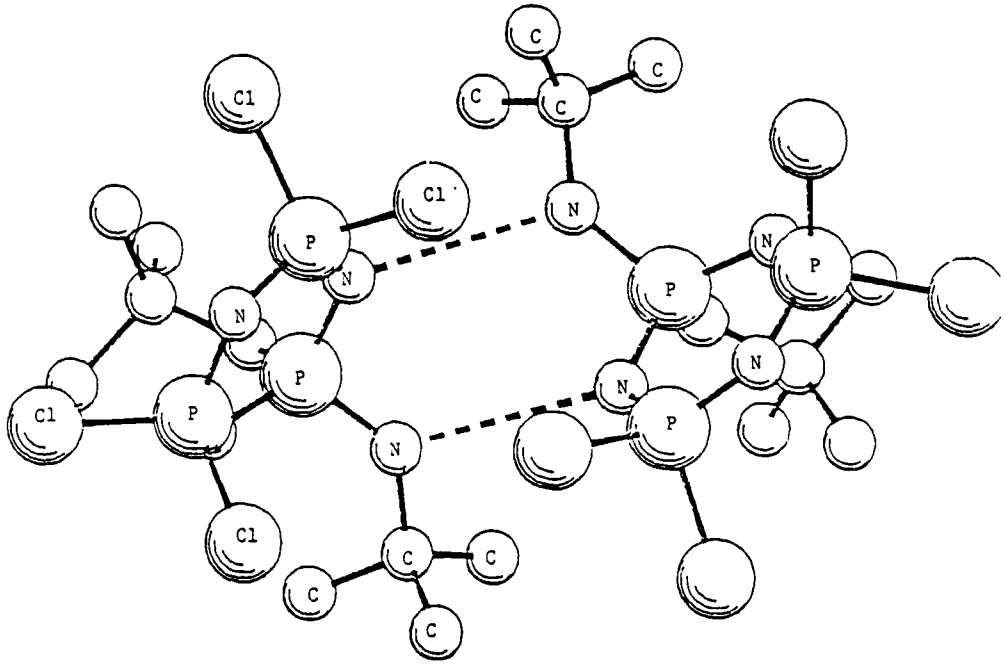

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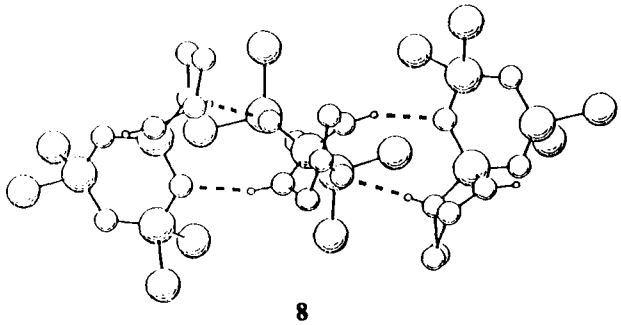
FIGURE 8 Hydrogen bonding diagram for $N_3P_3(NHBu^t)_2Cl_4$.



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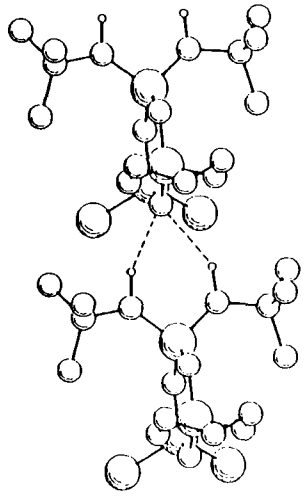

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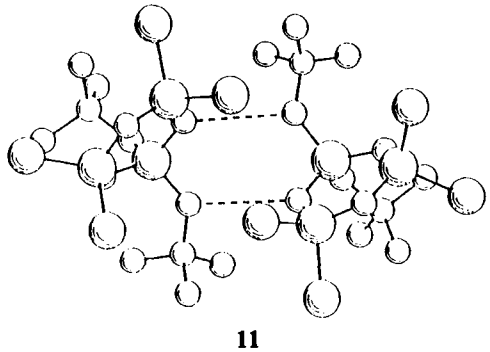

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FIGURE 9 Summary of hydrogen bonding diagrams for $N_3P_3[NH(CH_2)_3NH]Cl_4$, $N_3P_3(NHBu^t)_2[O(CH_2)_3O]Cl_4$ and $N_3P_3(NHBu^t)_2Cl_4$.

the two $NHBu^t$ groups to form a chelated, six-membered hydrogen bonded structure to the ring nitrogen atom *para* to the $P(NHBu^t)_2$ group (Figure 7).

The overall result is again an infinite structure.

By contrast, $N_3P_3(NHBu^t)_2Cl_4$,[13] (**11**) forms discrete dimers, utilising the N—H bond of only one $NHBu^t$ group (Figure 8).

In two of the above structures, (**8**) and (**11**), the hydrogen-bonded rings are eight membered, in one (**10**) they are six membered (Figure 9).

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