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COMPETITIVE FORMATION OF SPIRO AND ANSA DERIVATIVES IN THE REACTIONS OF TETRAFLUOROBUTANE-1,4-DIOL WITH HEXACHLOROCYCLOTRIPHOSPHAZENE: A COMPARISON WITH BUTANE-1,4-DIOL

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Abstract

Reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), in two stoichiometries (1:1.2 and 1:3) with the sodium derivative of the fluorinated diol, 2,2,3,3-tetrafluorobutane-1,4-diol, (**2**), in THF solution at room temperature afforded six products, whose structures have been characterized by X-ray crystallography and ^{1}H, ^{19}F and ^{31}P NMR spectroscopy: the mono-spiro compound, $N_3P_3Cl_4(OCH_2CF_2CF_2CH_2O)$, (**3**), its ansa isomer, (**4**), a di-spiro derivative $N_3P_3Cl_2(OCH_2CF_2CF_2CH_2O)_2$, (**5**), its spiro-ansa (**6**) and non-gem *cis* bis-ansa (**7**) isomers and a tri-spiro compound $N_3P_3(OCH_2CF_2CF_2CH_2O)_3$, (**8**). The tri-spiro derivative (**8**) was also formed in the reaction of the ansa compound (**4**) with diol (**2**) in a 1:3 ratio in THF at room temperature. The reactions of (**1**) with step-wise additions of (**2**) were also investigated at low temperature (-78^0C) to give the same range of products as at room temperature. The results of all reactions are compared with previous work on the reactions of (**1**) with butane-1,4-diol/pyridine mixtures and with the reaction of hexafluorocyclotriphosphazene, $N_3P_3F_6$ (**9**), with the silyl derivative of the diol (**2**), $(Me_3SiOCH_2CF_2)_2$, in a 1:0.4 mole ratio in the same solvent, THF.

Introduction

The reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**) (Figure 1) with difunctional reagents such as diols can give rise to four structural types: if only one functional group of the diol is used, this would give open-chain derivatives, whilst use of both functional groups of the diol can give rise to spiro, ansa and bridged derivatives. Reaction of (**1**) with ethane-, 1,3-propane- and 1,4-butane-diols (in the presence of pyridine to neutralize the HCl formed) predominantly gave spiro derivatives for all three diols, whereas ansa derivatives were rare products obtained only in small yields [1]. An open-chain and a bridged derivative were observed as minor products with 1,4-butanediol, indicating that chain length was a contributing factor in determining derivative-type [1]. Reaction of (**1**) with amino-alcohols, di-amines and their NMe derivatives, again showed a preference for spiro-derivatives, when the linking -$(CH_2)_n$- group of the reagent consisted of n = 2,3 moieties [2]. Bridged compounds became important for reactions of (**1**) with di-amines of increasing chain length (n = 4, 5) [3] and with chain lengths n >5 only bridged compounds were reported by Guerch *et al.* [4]. On the other hand, only ansa derivatives were obtained with structurally rigid di-functional reagents such as the di-lithium derivatives of ferrocene, ruthenocene and dibenzylchromium [5-8]. Herberhold and co-workers[9] reported that the reactions of the Li salt of the ferrocene (fc) diol with cyclophosphazenes, (**1**) and $N_3P_3F_6$ (**9**), gave ansa derivatives, but only spiro-derivatives were obtained when the Li salts of the di-thiol or di-selenol ferrocene were used as reagents, in spite of the larger linking atoms. This mirrors the behaviour of monofunctional oxygen and sulphur nucleophiles, whose attack on the hexachloride, (**1)**, are predominantly non-geminal (*cf* ansa with difunctional reagents) for the former [10,11] and predominantly geminal (*cf* spiro with difunctional reagents) for the latter [12]. A recent report on the reactions of the hexafluoride (**9**) with sodium phenoxide again shows a non-geminal pattern [13].

Reaction of (**1**) with the dilithiated diol, $FcCH_2P(S)(CH_2OLi)_2$, at –80^{o}C yielded one spiro and two ansa (endo and exo) derivatives in the ratio *ca*. 1:4 [14], whereas the reaction of the silyl derivative of 2,2,3,3-tetrafluorobutane-1,4-diol (**2**), $(Me_3SiOCH_2CF_2)_2$, with (**9**) afforded two products; the mono-spiro derivative, $N_3P_3F_4(OCH_2CF_2CF_2CH_2O)$, (**10**), and a derivative of the singly-bridged compound, $(N_3P_3F_5)_2(OCH_2CF_2CF_2CH_2O)$, (**11**) [15]. A second polymorph of (**10**) has been reported subsequently [16]. No other derivatives were observed and no reaction of the silyl reagent of (**2**) with the hexachloride (**1**) could be effected [15]. The purpose of the present study is to investigate the reaction of the sodium derivative of 2,2,3,3-tetrafluorobutane-1,4-diol (**2**) with hexachlorocyclotriphosphazene, (**1**) and compare the results with those obtained previously for reaction with butane-1,4-diol [1] and the other related reactions [14,15].

(Figure 1 about here)

Results and Discussion

(i) Reaction of hexachlorocyclotriphosphazene (1) with 2,2,3,3-tetrafluoro-1,4-butanediol (2) to form compounds (3)-(8).

We too observed no reactions between the hexachloride (**1**) and the silyl derivatives of alcohols in agreement with previous work [15], although it is known that silyl derivatives of the monophosphazene, $HN{=}PR_3$, do react with both the hexafluoride, (**9**), and hexachloride, (**1**), to give the analogous mono-substituted derivatives, $N_3P_3F_5(NPR_3)$ and $N_3P_3Cl_5(NPR_3)$ [17]. In the latter reaction the ease of formation of products decreased in the series [17]: $R_3 = (NMe_2)_3$, Me_3, Me_2Ph, $MePh_2$, Ph_3, $(OEt)_3$, which is in line with substituent basicity constants described and evaluated elsewhere [18]. It is clear that in addition to the driving force of formation of the Si-F (and to a lesser degree of the Si-Cl) bond, the nucleophilicity of the monophosphazene nitrogen atom plays a major role and, hence by implication, that of any other atom attached to the silyl reagent. It is also noted that silyl derivatives of alcohols should be less reactive than those of amines [17]. In order to overcome the lack of reactivity of silyl derivatives of alcohols with chlorophosphazenes, it was decided to use the sodium derivative of the fluorinated diol, (**2**), as the nucleophile.

Six products were isolated from the reaction of (**1**) with (**2**) in THF at two stoichiometries (1:1.2 and 1:3). The products were the mono-spiro compound, $N_3P_3Cl_4(OCH_2CF_2CF_2CH_2O)$, (**3**), its ansa isomer, (**4**), a di-spiro derivative $N_3P_3Cl_2(OCH_2CF_2CF_2CH_2O)_2$, (**5**), its spiro-ansa (**6**) and non-gem *cis* bis-ansa (**7**) isomers and a tri-spiro compound $N_3P_3(OCH_2CF_2CF_2CH_2O)_3$, (**8**). All reaction mixtures were analyzed by ^{31}P NMR spectroscopy and no other compounds were observed. The reaction of the hexachloride (**1**) with the sodium derivative of the fluorinated diol, (**2**), in THF was also investigated at a stoichiometry of 1:0.4 and examination of the reaction mixture showed largely the same range of products, spiro (**3**) > ansa (**4**) > di-spiro (**5**). Reaction of (**1**) with (**2**) in THF was also effected in the presence of pyridine at room temperature; in this case, although there was evidence of the formation of spiro (**3**) and ansa (**4**) compounds as major products of the reaction, many more minor derivatives were formed, including decomposition products. All the ansa and spiro derivatives reported in this work were found to be unaffected by exposure to air and/or moisture, in contrast to previous reports [14,19] that spiro isomers are highly unstable to air and/or moisture, though their ansa isomers are stable. The reaction of the hexachloride (**1**) with the sodium derivative of the fluorinated diol, (**2**) was also carried out at -78º, in order to compare our results most closely with those reported by Elias and co-workers

[14]. The reagent (**2**) was added step-wise, one mole at a time and the reaction mixtures were investigated by ^{31}P NMR spectroscopy. With a stoichiometry of 1:1, examination of the reaction mixture showed largely the same range of products as the reaction at room temperature, *viz* spiro (**3**) > ansa (**4**) ≈ di-spiro (**5**) > spiro-ansa (**6**) > tris-spiro (**8**). A similar range of products was formed at a stoichiometry of 1:2 though the relative proportions were changed; di-spiro (**5**) > spiro (**3**) > spiro-ansa (**6**) > ansa (**4**) > tris-spiro (**8**), whilst at a 1:3 ratio it was tris-spiro (**8**) >> di-spiro (**5**) > spiro-ansa (**6**). On addition of an excess of reagent only the tri-spiro compound (**8**) was observed. It was also found that reaction of the mono-ansa derivative (**4**) with an excess of reagent (**2**) converted it to the tri-spiro compound (**8**), which was confirmed by TLC, mpt. and ^{31}P NMR.

(ii) Characterization of compounds (3)-(8) by ^{1}H, ^{31}P and ^{19}F NMR spectroscopy

Each of the compounds (**3**) - (**8**) was characterized by mass spectrometry and NMR spectroscopy, and the results are summarized in Table 1. The ^{31}P NMR spectra of cyclophosphazene derivatives containing the spiro moiety are observed as A_2X (or A_2B) spin systems with characteristic chemical shifts that reflects the number of spiro substituents in the compound, *i.e*. both the $>PCl_2$ and $>P(OR)_2$ chemical shifts move to high frequency (downfield) about 4.5 – 5.5 ppm per tetrafluorobutanedioxy moiety, as expected [20]. Similarly, the chemical shifts of the >P(OR)Cl group of the ansa derivatives move to high frequency (downfield) as the cyclophosphazene (**4**) is further substituted with spiro (**6**) or ansa (**7**) tetrafluorobutanedioxy moieties (Table 1). Whilst the chemical shifts of the PCl_2 [for isomers (**3**) and (**4**)] and $P(OR)_2$ groups [for isomers (**5**), (**6**) and (**7**)] seem to be insensitive to the nature of the disposition of the P-Cl bonds (geminal or *cis*-non-geminal), the shifts of the P(OR)Cl group [for isomers (**6**) and (**7**)] show some differences. It is noteworthy that in these isomers the two P-Cl bonds of (**7**) represent the only example in this series, where these two bonds are in a *trans*-relationship.

The proton-decoupled ^{19}F NMR spectrum of the spiro form of the 2,2,3,3-tetrafluoro-1,4-butanedioxy moieties exists as a single line with essentially the same chemical shift (Table 1) for compounds (**3**), (**5**), (**6**) and (**8**), whereas the ansa form gives rise to an AB spin system with ^{2}J(FF) *ca*. 283 Hz for compounds (**4**) and (**6**) and two AB spin systems with ^{2}J(FF) *ca*. 288 Hz for the non-gem *cis* bis-ansa compound (**7**). The magnitudes of ^{2}J(FF) are in line with previous results on geminal coupling [21]. It should be noted that the line-widths of the ^{19}F NMR signals of the spiro moiety are narrower than those for the ansa moiety, which might reflect the fact that the spiro moiety is more flexible than the ansa moiety.

The ^{1}H NMR spectra of the spiro compounds, (**3**),(**5**) and (**8**), are complex multiplets with similar chemical shifts (Table 1), whereas those for the mono-ansa moieties in compounds (**4**) and (**6**) are observed as two complex multiplets and for the non-gem *cis* bis-ansa compound (**7**) as four complex multiplets. Although analysis of these multiplets, in principle, could lead to ^{3}J(FH) and ^{3}J(PH) magnitudes and a conformational analysis of the spiro and ansa rings, in practice, this is not feasible because the appropriate Karplus-type relations for ^{3}J(FH) and ^{3}J(PH) magnitudes in such cyclophosphazene derivatives are not known. However, the conformations of the spiro and ansa rings have been determined by X-ray crystallography.

(iii) X-ray crystallographic characterization of compounds (3)-(8).

The X-ray crystal structures are reported for compounds (**3**) – (**8**) (Figures 2-7) and appropriate crystallographic data are summarized in Table 2.

Figures 2-7 and Table 2 (about here)

The ($OCH_2CF_2CF_2CH_2O$) moiety forms spiro derivatives in compounds (**3**), (**5**) and (**8**), ansa derivatives in (**4**) and (**7**), whereas compound (**6**) exhibits both spiro and ansa functionality. Each structure is composed of a cyclotriphosphazene core which, in all cases, exhibits no unusual deviations in geometry from either that of the parent $N_3P_3Cl_6$ structure (CSD code KAGKUY),[22] or from that observed in similar structures in the Cambridge Structural Database [23]. The cyclophosphazene rings are essentially planar, in which the deviation of individual atoms from the N_3P_3 plane in all the compounds reported here is less than 0.1 Å. However, the compounds are of structural interest in that they are systematically substituted at the phosphorus centres by an increasing number of ($OCH_2CF_2CF_2CH_2O$) moieties in either the spiro or ansa configurations.

The spiro rings in the spiro-substituted structures are all found to have similar twisted-chair conformations with a strictly alternating positive/negative torsion angle sequence around the ring and each ring component in a *gauche* conformation with respect to its neighbour. The twist of the seven-membered P($OCH_2CF_2CF_2CH_2O$) spiro moiety gives a sense of chirality to the individual molecules which have been denoted as positive (*p*) or negative (*n*) depending on the sign of the O-P-O-C dihedral angle [16]. For the compounds measured in this work, positive twist angles are observed for the mono-spiro derivative (**3**) and both spiro rings of one molecule of the di-spiro compound (**5**), whereas negative twist angles are observed for the spiro-ansa derivative (**6**) and both spiro rings of the second molecule in the unit cell of (**5**). Interestingly,

the tri-spiro derivative (**8**) has two *p* and one *n* form of twisted-chair conformation. A useful measure of ring conformation is puckering analysis [24], where calculation of the mean plane and puckering parameters afford a unique quantitative descriptor, the total puckering amplitude (Q), for a ring conformation. When subjected to ring puckering analysis the spiro substituted structures all have a total puckering amplitude, Q, in the range 0.7979 - 0.8359.

The spiro-containing structures exhibit intermolecular interactions, in that there are a large number of C-H···F close contacts present. Whilst not considered as 'classical' hydrogen-bonds, there is considerable evidence that interactions do exist between these moieties [25]. The range of D···A separations (some 20 in total for these 4 structures) varies from 3.073(6)Å for C1-H1A···F4 in (**8**) to an upper limit of 3.484(8)Å. Other notable D···A separations are: 3.102(6)Å for C8-H8B···F4 in (**5**); 3.134(4)Å for C1-H1A···F4 in (**3**); and 3.177(5)Å for C4-H4···F2 in (**6**). Also present in structures (**5**) and (**6**) are short F···F contacts, which are currently the subject of much discussion [26], e.g. F3···F10 = 2.730(7)Å in (**5**) and F1···F6 = 2.885(6)Å in (**6**).

The ansa-substituted structures in compounds (**4**), (**6**) and (**7**) adopt the same general nine-membered ring conformation, which can best be described as a deformed crown having an anti conformation about the CH_2-CF_2 bonds. The total puckering amplitude [24] of the ansa rings is in the range 1.1878 – 1.1882, showing a remarkable degree of consistency. There are only a few intermolecular interactions present in these systems ranging from D···A separations for C-H···F contacts of 3.177(6)Å in (**6**) to 3.301(7) in (**7**). The cyclophosphazene ring for the ansa compounds characterized in this work is essentially planar, which has also been observed for macrocyclic-phosphazene compounds having a sixteen-membered ansa ring [27, 28]; this is in contrast to that discussed for eight-membered ansa rings *(i.e.* propanedioxy, propanolamino and ruthenocene) [29] and propanedioxy derivatives where the central CH_2 has been replaced by the ferrocenylCH_2P(S) moiety [14]. For the eight-membered ansa ring derivatives of cyclophosphazene, the deviation from the N_3P_3 plane of the nitrogen atom between the phosphorus atoms carrying the ansa moiety is usually greater than 0.2 Å. [14, 29, 30] The difference in behavior of the ansa compounds is likely to reflect the higher degree of flexibility of the sixteen- and even the nine-membered rings compared to the eight-membered ansa ring system.

Whilst ansa structures of cyclophosphazenes have been known for about twenty years, ansa-ansa structures are relatively rare. There are two types of ansa-ansa structures; geminal, where the two ansa moieties share the same two phosphorus atoms, and non-geminal, where they share only one phosphorus atom. Published examples of the former all contain the tetraethyleneoxy macrocyclic group, $O(CH_2CH_2O)_4$, with the second group as either binaphthoxy [27a],

ethylenediamino [27b], or another tetraethyleneoxy macrocyclic group [27c]. The ansa-ansa compound **(8)** reported here is only the second bis non-geminal structure in chlorocyclotriphosphazenes, the other having one tetraethyleneoxy macrocyclic ring and one binaphthoxy group [27a]. A similar structure has been proposed for a fluorocyclotriphosphazene derivative, but no crystallographic data was presented [31].

(iv) Comparison of the electron-releasing capacity of a geminal pair of substituents for compounds derived from (1) by analysis of crystal structures.

The structure of the mono-spiro compound (**3**) formed from the tetrafluorobutanediol (**2**) is compared with that of its butane-1,4-diol analogue (**12**), which does not have the fluorine atoms in the dioxy substituent, and also compared with a compound with an identical fluorinated spiro group, but having the 4 P-Cl bonds replaced by 4 P-F bonds, (**10**). The data are presented in Table 3 using the descriptions of bond lengths and angles shown in Figure 8.

(Figure 8 and Table 3 about here)

Comparison of the P-O bond length and POC bond angle of the butanedioxy derivative (**12**) with its tetrafluorobutanedioxy analogue (**3**) in Table 3 indicates that there is a considerably greater electron supply to the phosphazene ring of (**12**), as demonstrated by a shorter P-O bond and a greater POC bond angle, resulting from the greater lone-pair de-localization from the oxygen atom towards the N_3P_3 ring. Within the phosphazene ring there is also the usual pattern associated with a more electron-supplying substituent [32, 33]: a smaller α and a larger β angle, a longer P-N bond (*a*) adjacent to the electron-supplying substituent, concomitant with a shorter P-N bond adjacent to it (*b*). This results in the Δ(P-N) value (*a*-*b*, as defined in Table 3) of 0.031Å in the butanedioxy derivative (**12**) [32] compared to one of only 0.007Å in its tetrafluoroalkoxy analogue (**3**). Hence, there is only a very small electron-supply from the tetrafluorobutanedioxy group, which is barely distinguishable on this measure from that of a PCl_2 group.

Another approach to the electron-releasing capacity of a geminal pair of substituents is the effect this has on the average value of the P-Cl bonds in the two remaining PCl_2 groups (Table 3) compared with the value for compound (**1**) of 1.984Å [22]. Although the changes are small in the sequence, (**3**) 1.990, (**12**) 1.994 [32], 1.998Å for $N_3P_3Cl_4Ph_2$ [34] and 2.021Å for $N_3P_3Cl_4(NPPh_3)_2$ [35], they are in keeping with the electron-supply properties discussed above. For the tetra-substituted compounds the P-Cl bond lengths are, as expected, rather larger: 2.002Å for the di-spiro derivative (**5**) and 2.017Å for $N_3P_3Cl_2Ph_4$ [36]. This larger effect is not surprising, because in the latter compounds the effects of 4 donor groups are spread over only 2

P-Cl bonds, whereas for the di-substituted derivatives the effects of 2 donors are spread over 4 P-Cl bonds. Nevertheless, both the changes in Δ(P-N) values and the changes in average P-Cl bond lengths demonstrate that the spiro tetrafluorobutanedioxy group has a small, but definite, electron-releasing effect relative to a PCl_2 group.

Fluorine has a much greater electronegativity than chlorine, yet comparison of the data for compound (**3**) with compound (**10**) in Table 3 shows that most of the structural parameters of the compound containing 4 P-Cl bonds are very similar to the one containing 4 P-F bonds. Perhaps the greater inductive electron-withdrawing effect of fluorine is compensated for by a more pronounced tendency to a mesomeric back-donation from its lone pairs of electrons.

(v) Explanation of the difference in formation of spiro, ansa and bridged derivatives

It is necessary to explain the different nature of the products obtained with tetrafluorobutanediol in this work (spiro and ansa compounds) and that obtained earlier for butanediol (predominantly spiro). We also note that Shreeve and co-workers [15] reported only spiro and bridged compounds, although the same reaction solvent, THF, was used in their work as well as in ours. In both investigations the reaction mixtures were examined by NMR spectroscopy, so it can be assumed that all major products were accounted for. Shreeve and co-workers [15] found that heating the singly-bridged derivative caused partial conversion to the mono-spiro compound and it is therefore not clear how much of their spiro-derivatives are primary or secondary reaction products. Spiro derivatives are clearly the thermodynamically more stable form, which is also confirmed by the work of Elias and co-workers [30] on the transformation of fluorophosphazenes from ansa to spiro compounds in the presence of CsF. These authors also suggested that the absence of ansa compounds in the reactions with silylated reagents [15] was due to the catalytic conversion of these moieties to spiro groupings. As the PF_2 and PCl_2 groups are more electrophilic than either the PF(OR) or PCl(OR) moieties, the former would be the preferred reaction sites under kinetic control. The crystallographic data presented above show a slight, but definite, electron-supply by the spiro-tetrafluorobutanedioxy group and by implication also for the related PF(OR) and PCl(OR) groupings. However, in this work, reaction of (**1**) with the sodium salt of the diol (**2**) produced the ansa as well as the spiro derivative. For example, using the same molar ratio (1:0.4) of the cyclophosphazene (**1**) to the sodium salt of the diol (**2**) as used by Shreeve *et al.* [15], we observed by NMR spectroscopy approximately 60% unchanged $N_3P_3Cl_6$ and about 20% each of the mono-spiro (**3**) and the mono-ansa (**4**) derivatives, together with a trace of the dispiro compound (**5**).

We also compared the products of the starting material, $N_3P_3Cl_6$, (**1**) with the sodium and lithium salts of the tetrafluorobutanediol (**2**) in THF using a molar ratio of 1:0.5 to confine the products

to mono-substitution as much as possible. The ratio of mono-spiro (**3**):mono-ansa (**4**) was approximately 2:1 for the sodium derivative, but approximately 5:1 for the lithium reagent. As the lithium ion is smaller and its nuclear charge less shielded than that of the sodium ion, Li^+ is likely to form a stronger ion pair and hence make lithium alkoxides less reactive than their sodium analogues. THF is also probably solvating the sodium ion more strongly than the lithium ion and this too would enhance the reactivity of its alkoxide ion. Conductometric studies on the titration of alkali metal acetates with perchloric acid in acetic acid [37] and complexation studies of both the alkali metal ions with phosphazene lariat ethers by Bartsch *et al*. [38] indicate that ion-pairing will be stronger for lithium than for sodium alkoxides. The counter-n of the alkoxide is likely to be freer in the sodium reagent, making it more reactive than the lithium analogue, and hence proportionally more ansa derivative is obtained with the sodium alkoxide. A similar explanation can be offered for the observation that CsF acted as catalyst in the ansa to spiro tranformation in fluorocyclotriphosphazenes, but LiF was reported to be inactive [14]. Reaction of (**1**) with the dilithiated diol, $FcCH_2P(S)(CH_2OLi)_2$, at -80^oC yielded one spiro and two ansa (endo and exo) derivatives in the ratio *ca*. 1:4 [14]. Reactions of the ansa isomer with the disodium salt of propane-1.3-diol indicated partial conversion of the ansa group to the spiro isomer [14], again consistent with the greater reactivity of the sodium derivative in line with the explanation above. This reaction [14] differs from the present study on the reaction of (**1**) with the lithium derivative of (**2**), which gave significantly more spiro than ansa derivatives. The difference is likely to be a consequence of the reactions of the dilithiated diol, $FcCH_2P(S)(CH_2OLi)_2$, giving rise to spiro and ansa structures each containing one less atom then the ones reported here. The greater nucleophilic reactivity of the diol, $FcCH_2P(S)(CH_2OLi)_2$, than that of the sodium or lithium derivatives of tetrafluorobutanediol, (**2**), and the low temperature of -80˚C undoubtedly also play a part. Elias and co-workers [30] have shown that for fluorophosphazenes 8-membered ansa groupings rearrange in the presence of catalysts to the thermodynamically more stable 6-membered spiro moieties and that this accelerates with increasing temperature. Whilst Elias and co-workers report that ansa derivatives of chlorocyclotriphosphazenes do not rearrange to their spiro derivatives, we infer that a similar rearrangement does take place with the 9-membered ansa groupings to 7-membered spiro moieties. We deduce this, because the plethora of ansa derivatives **(4)**, **(6)** and **(7)**, observed, when the molar ratio of phosphazene (**1**) to diol (**2**) was 1:1.2, whilst with an excess of the sodium derivative of **(2**) only the tri-spiro derivative **(8**) was observed. Clearly the ansa moiety in all three ansa carrying species rearranged at some stage to a spiro group. To prove this we treated the most abundant of these, the mono-ansa derivative, **(4),** with an excess of the sodium

derivative of the reagent to yield the the tri-spiro derivative **(8)**. We cannot thus state, precisely, at which state of chlorine replacement this transformation occurred..

This raises the further question to what extent the spiro moieties observed in the reaction with a reactant ratio of 1:1.2 are primary reaction products or a result of a subsequent rearrangement. The answer was given by the NMR analysis of the low temperature reaction mixtures, which showed that the range of products and their ratios was largely the same as those observed at room temperature.

Why ansa and not bridging compounds? In the reactions of $N_3P_3Cl_6$, (**1**), with mono-functional reagents, such as secondary amines, giving rise to non-geminally di-substituted derivatives, the yields of the *trans*-isomer are generally substantially larger than that of the *cis*-isomer and steric effects were invoked to rationalize these observations [39]. However, for the reaction of (**9**) with NaOR [13, 40, 41] the reverse behaviour was observed, producing a slight predominance of the *cis* over *trans*-isomer, which was rationalized in terms of the co-ordination of the sodium ion by the lone pairs of electrons of the oxygen atom in the P-OR group already present after mono-substitution. A similar sodium ion solvation was also postulated by Brandt and co-workers [27, 42] to account for the exclusive formation of *cis*-ansa macrocyclic-cyclophosphazene derivatives. Formation of such a *cis*-ansa product might be dictated by steric effects for short-chain diols, but for longer chain derivatives such as tetraethylene glycol, which were always used as sodium salts [27, 42], the sodium solvation step by the existing PCl(OR) moiety may well play an important role. On the other hand, with the silylated diol no such solvation is possible and, because PF_2 is marginally more reactive than PF(OR), reaction occurs to form bridging compounds, especially as the molar ratio employed showed an excess of $N_3P_3F_6$, (**9**).

It can be seen that the nature of the products (spiro, ansa, bridged) depends, amongst other factors, on the avidity for each other of the electrophilic phosphorus-containing reagent and nucleophilic activity of the diol. The present work has shown that with an unchanged electrophile the lowered reactivity of the nucleophile favours spiro over ansa. Other work with an unchanged nucleophile has also found that a reduction in the electrophilic character of the phosphazene has the same effect, *e.g*. on substitution of some chlorine atoms in $N_3P_3Cl_6$ by electron-releasing substituents such as the phenyl or tertiary-butylamino groups. However, this is not the whole story, because we have observed that in the reactions of the hexachloride **(1)** with the two diols, propane-1,3-diol and 2,2-dimethylpropane-1,3-diol (using pyridine as the hydrogen halide acceptor), the former forms only traces of the ansa compound, whilst the latter does so in significant quantities [43], which has been explained in terms of the Thorpe-Ingold Effect [44]. Thus relatively subtle changes between different nucleophiles can tilt significantly

the spiro/ansa balance, which is likely to be the reason why the sodium derivative of (**2**) gave such a range of products that differed markedly from those obtained by the reaction of compound (**12**) in the presence of pyridine [1]. In case the difference was due to the diol/pyridine reagent, we have also investigated the initial stages of the same reaction using the sodium derivative of butane1,4-diol and found substantially the same range of products as with diol/pyridine reagent and most noticeably the absence of ansa-derivatives. The case of the reaction of compound (**9**) with the silylated derivative of (**2**) provides another subtle change in the nature of the nucleophile, further complicated by this reaction being largely driven by the strengths of the Si-F being formed [17 and refs therein]. Much remains to be explained, such as the observation that the mono-ansa compound **(4)** reacts with pyrrolidine with retention of configuration [45].

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Otsuka Chemical Co., Ltd) was purified by fractional crystallisation from hexane. Sodium hydride, 60% dispersion in mineral oil (Merck), the latter removed by washing with dry heptane (Merck) followed by decantation. Hexane, heptane (Merck) and 2,2,3,3-tetrafluoro-1,4-butanediol (Aldrich) were used as received. THF was distilled over a sodium-potassium alloy under an atmosphere of dry argon. All reactions were performed under a dry argon atmosphere. For column chromatography silica gel (230-400 mesh Merck) was used.

Methods. Elemental analyses were obtained using a Carlo Erba 1106 Instrument. Mass spectra were recorded on a VG Zab Spec GC-MS spectrometer using the fast atom bombardment (FAB) method (35 kV) with MNBA as the matrix; ^{35}Cl values were used for calculated masses. Analytical Thin Layer Chromatography (TLC) was performed on Merck Silica gel plates (Merck Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck 60, 230-400 mesh; for 3g. crude mixture, 100g. silica gel was used in a column of 3 cm in diameter and 60 cm in length). ^{1}H, ^{19}F and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions on a Bruker DRX 500 MHz spectrometer using TMS as an internal reference for ^{1}H, $CFCl_3$ as an internal reference for ^{19}F and 85% H_3PO_4 as an external reference for ^{31}P. In order to assign the signals of some compounds both proton-coupled and proton-decoupled ^{19}F and ^{31}P NMR spectra were recorded.

Reaction of hexachlorocyclotriphosphazene (1) with 2,2,3,3-tetrafluoro-1,4-butanediol (2) in a 1:1.2 ratio to form compounds (3)-(7). Hexachlorocyclotriphosphazene, (**1**), (3.48 g, 10 mmol) and 2,2,3,3-tetrafluoro-1,4-butanediol (1.94 g, 12 mmol), (**2**), were dissolved in 300 mL of dry THF under an argon atmosphere in a 500 mL three-necked round-bottomed flask The

reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.96 g, 24 mmol) in 30 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction mixture was stirred for 2 h at room temperature and the reaction followed on TLC silica gel plates using hexane-dichloromethane (1:1) as eluant. Five products were observed and none of compound (**1**) remained. The reaction mixture was filtered to remove the sodium chloride formed and the solvent removed under reduced pressure. The resulting colorless oil was subjected to column chromatography, using hexane-dichloromethane (2:1) as eluant. The first product is the mono-spiro derivative [$N_3P_3Cl_4(OCH_2CF_2CF_2CH_2O)$], (**3**), (1.23 g, 28%, mp 95^0C). Anal. Calcd. for $C_4H_4Cl_4F_4N_3O_2P_3$: C, 11.00; H, 0.92; N, 9.62. Found: C, 10.97; H, 0.93; N, 9.52. The second product is the isomeric mono-ansa derivative [$N_3P_3Cl_4(OCH_2CF_2CF_2CH_2O)$], (**4**), (0.6 g, 14%, mp 145^0C). Anal. Found: C, 11.05; H, 0.93; N, 9.40. The third product is the bis-spiro derivative [$N_3P_3Cl_2(OCH_2CF_2CF_2CH_2O)_2$], (**5**), (0.39 g, 7%, mp 204^0C). Anal. Calcd for $C_8H_8Cl_2F_8N_3O_4P_3$: C, 18.27; H, 1.53; N, 7.99. Found: C, 18.27; H, 1.52; N, 7.65. The fourth product is the isomeric spiro-ansa derivative [$N_3P_3Cl_2(OCH_2CF_2CF_2CH_2O)_2$], (**6**), (0.22 g, 4%, mp 120^0C). Anal. Found: C, 18.38; H, 1.47; N, 7.64 and the fifth product is the isomeric non-gem *cis* bis-ansa derivative [$N_3P_3Cl_2(OCH_2CF_2CF_2CH_2O)_2$], (**7**), (0.1 g, 2%, mp > 270^0C). Anal. Found: C, 18.25; H, 1.52; N, 7.89. All of the new compounds were crystallized from hexane-dichloromethane (1:2) and obtained as colorless crystals.

Reaction of (1) with (2) in a 1:3 ratio to form compound (8)

(**1**) (1.74 g, 5 mmol) and (**2**) (2.425 g, 15 mmol) were dissolved in 100 mL of dry THF under argon atmosphere in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 1.2 g, 30 mmol) in 30 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction mixture was stirred for 24 h at room temperature and the reaction followed by TLC on silica gel plates using hexane-THF (1:1). Only one product was observed and no starting material (**1**) was detected. The reaction mixture was filtered to remove the sodium chloride formed, the solvent removed under reduced pressure and the resulting colorless oil subjected to column chromatography, using THF as eluant. The product is the tri-spiro derivative [$N_3P_3(OCH_2CF_2CF_2CH_2O)_3$], (**8**), (1.72, 56%, mp 332), a colorless solid, which was re-crystallized from THF-hexane (1:1). Anal. Calcd for $C_{12}H_{12}F_{12}N_3O_6P_3$: C, 23.43; H, 1.97; N, 6.83. Found: C, 23.45; H, 1.98; N, 6.81.

Reactions of hexachlorocyclotriphosphazene (1) with 2,2,3,3-tetrafluoro-1,4-butanediol (2) at -78^{0}C . Hexachlorocyclotriphosphazene, (**1**), (3.48 g, 10 mmol) and 2,2,3,3-tetrafluoro-1,4-butanediol (1.62 g, 10 mmol), (**2**), were dissolved in 90 mL of dry THF under an argon atmosphere in a 100 mL three-necked round-bottomed flask at ≈ -78^{0}C (acetone-liquid nitrogen). NaH (60% oil suspension, 0.8 g, 20 mmol) in 3 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction mixture was stirred for 3 h at low temperature (-78^{0}C) and the reaction followed on TLC silica gel plates using hexane-dichloromethane (3:1) as eluant. 1/3 of the reaction mixture was removed for NMR analysis; 3 products (**3**, **4** and **5**) were observed and no starting material (**1**) remained. Reagent **(2)** and NaH were then added to achieve a 1:2 stoichiometry under the same conditions and the reaction mixture stirred for a further 3 h. Half of this reaction mixture was removed for NMR analysis and five products (**3**, **4**, **5,** as well as **6, 7**) were observed. Reagent **(2)** and NaH were again added to the remaining reaction mixture to achieve a 1:3 stoichiometry. The reaction mixture was stirred for 3 h at -78^{0}C, followed by 20 h at room temperature and the reaction followed on TLC silica gel plates using hexane-dichloromethane (1:1) as eluant. It was observed that all the compounds were transformed into the tri-spiro compound (**8**) as confirmed by TLC, mpt. and ^{31}P NMR.

Reaction of (4) with (2) in a 1:3 ratio to form compound (8). Mono-ansa, (**4**), (0.65 g, 1.5 mmol) and 2,2,3,3-tetrafluoro-1,4-butanediol (0.73 g, 4.5 mmol), (**2**), were dissolved in 10 mL of dry THF under an argon atmosphere in a 100 mL three-necked round-bottomed flask at room temperature. NaH (60% oil suspension, 0.36 g, 9 mmol) in 2 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction mixture was stirred for 20 h at room temperature and the reaction followed on TLC silica gel plates using hexane-dichloromethane (1:1) as eluent. It was observed that all of compound (**4**) was transformed into the tri-spiro compound (**8**), as was confirmed by TLC, mpt. and ^{31}P NMR.

X-ray structure determinations

Data were collected by means of combined phi and omega scans on a Bruker-Nonius KappaCCD area detector situated at the window of a rotating anode (λMo-k$_\alpha$ = 0.71073Å). The structures were solved by direct methods, SHELXS-97 and refined using SHELXL-97 [46]. Hydrogen atoms were included in the refinement, but thermal parameters and geometry were constrained to ride on the atom to which they are bonded. The data were corrected for absorption effects using SORTAV [47]. Supplementary data in the form of CIF files have been deposited with the Cambridge Crystallographic Data Centre with deposition numbers CCDC 277314 - 277319 inclusive.

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Table 1. MS [a] and NMR (^{1}H, ^{31}P and ^{19}F) [b] data on compounds (**3**) – (**8**).

Cpd	No.[c]	**3**	**4**	**5**	**6**	**7**	**8**
	Type[d]	sp	an	di-sp	sp-an	di-an	tri-sp
Mpt.	^{o}C	95	145	204	120	>270	>280
M, m/z	Obs./ Calc	435.9/ 435.8	436.0/ 435.8	526.0/ 525.9	525.9/ 525.9	525.8/ 525.9	615.9/ 616.0
$\delta(^{31}P)$/ppm	$>PCl_2$	25.2	25.2	29.5		-	-
	$>P(OR)_2$	8.6	-	14.4	13.9	13.9	19.9
	>P(OR)Cl		23.6	-	28.5	31.2	-
$^{2}J_{P\text{-}P}$ /Hz		75.0	65.0	81.5	86.5	85.4	
$\delta(^{19}F)$/ppm	$>CF_2$(sp)	-127.8	-	-127.9	-127.8	-	-127.9
	$>CF_2$(an)	-	-115.5/ -116.6	-	-115.5/ -116.7	-111.5/-115.1 -117.3/-119.3	-
$^{2}J_{F\text{-}F}$/Hz			283.5	-	282.5	288.4/288.5	
$\delta(^{1}H)$/ppm	$>CH_2$(sp)	4.39		4.35	4.36		4.24
	$>CH_2$(an)		4.42		4.36	4.27/4.40	
			4.75		4.74	4.62/4.75	

[a] MS (FAB + LCSIMS). Mass quoted for observed MH^+ peak and calculated for the ^{35}Cl isotopomer.

[b] 500 MHz ^{1}H NMR chemical shifts (ppm) with respect to internal TMS, 200 MHz ^{31}P NMR chemical shifts (ppm) with respect to external 85% H_3PO_4 and 470 MHz ^{19}F NMR chemical shifts (ppm) with respect to internal $CFCl_3$ observed on a Bruker 500 MHz DRX spectrometer

[c] Structures of compounds are summarized in Figure1.

[d] sp = spiro and an = ansa

Table 2. Crystal data and refinement parameters for **(3), (4), (5), (6), (7)** and **(8)**.

	3	***4***	***5***	***6***	***7***	***8***
Empirical formula	$C_4H_4Cl_4F_4N_3O_2P_3$	$C_4H_4Cl_4F_4N_3O_2P_3$	$C_8H_8Cl_2F_8N_3O_4P_3$	$C_8H_8Cl_2F_8N_3O_4P_3$	$C_8H_8Cl_2F_8N_3O_4P_3$	$C_{12}H_{12}F_{12}N_3O_6P_3$
Formula weight	436.81	436.81	525.98	525.98	525.98	615.16
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$Cmc2_1$	P-1	$C2/c$	$Pbcn$	P-1
a (Å)	5.89280(10)	11.3916(6)	11.4831(2)	30.6471(10)	17.0002(6)	6.6961(2)
b (Å)	13.5413(4)	11.4294(6)	12.8030(2)	6.1108(2)	11.1130(3)	10.8514(4)
c (Å)	17.6863(6	10.9340(4)	13.0505(2)	24.0233(10)	8.9716(2)	15.2892(6)
α (°)	90	90	98.4420(10)	90	90	92.1960(10)
β (°)	99.1310(10)	90	110.7170(10)	129.546(3)	90	102.5230(10)
γ (°)	90	90	100.0350(10)	90	90	107.157(3)
Volume ($Å^3$)	1393.42(7)	1423.60(12)	1721.29(5)	3469.3(2)	1694.94(8)	1030.00(6)
Z	4	4	4	8	4	2
Density (calc) (Mg/m^3)	2.082	2.038	2.030	2.014	2.061	1.983
Absorption coefficient (mm^{-1})	1.240	1.214	0.763	0.757	0.775	0.436
F(000)	856	856	1040	2080	1040	612
Crystal size (mm)	0.20 × 0.05 × 0.02	0.50 × 0.02 × 0.02	0.40 × 0.32 × 0.05	0.14 × 0.05 × 0.05	0.54 × 0.04 × 0.03	0.38 × 0.08 × 0.02
θ_{max} (°)	27.44	27.43	27.47	27.47	27.50	27.47
Reflections collected	12316	5884	24664	7789	9472	13843
Independent reflections	3099	1591	7674	3786	1938	4556
R(int)	0.0490	0.0758	0.0695	0.0446	0.0743	0.0429
Final R indices $F^2>2\sigma F^2$	R1 = 0.0297 wR2 = 0.0628	R1 = 0.0364 wR2 = 0.0735	R1 = 0.0381 wR2 = 0.1043	R1 = 0.0401 wR2 = 0.0780	R1 = 0.0377 wR2 = 0.0953	R1 = 0.0376 wR2 = 0.0860
Δρ max / min ($eÅ^{-3}$)	0.371 / –0.463	0.461 / –0.389	0.587 / –0.619	0.588 / –0.472	0.502 / –0.588	0.341 / –0.434

Table 3. Parameters of molecular framework of mono-spiro cyclophosphazene compounds.

Structural Parameter [a]	Cyclophosphazene spiro-compound [b]		
	(**12**)[c]	(**3**)	(**10**)[d]
θ	106.1(1)	104.6(1)	104.3(2)
α	116.1(1)	117.7(1)	118.2(2)
β	122.3(1)	121.7(1)	121.2(2)
γ	119.3(1)	118.6(1)	119.5(1)
δ	120.1(2)	120.0(1)	120.1(3)
a	1.592(2)	1.577(1)	1.576(3)
b	1.561(2)	1.570(1)	1.570(3)
c	1.575(2)	1.584(1)	1.569(3)
Δ(P-N) [e]	0.031(3)	0.007(1)	0.006(4)
P-O	1.561(2)	1.579(1)	1.578(2)
POC	121.9(2)	122.7(1)	119.8(3)
P-Cl	1.994(3)	1.990(2)	

[a] Structural parameters defined in Figure 8

[b] Comparisons are made between spiro compounds,(**12**), $N_3P_3Cl_4[OCH_2CH_2CH_2CH_2O]$, and (**3**), $N_3P_3Cl_4[OCH_2CF_2CF_2CH_2O]$, and between compounds (**3**) and (**10**), $N_3P_3F_4[OCH_2CF_2CF_2CH_2O]$

[c] Ref. 32

[d] Ref.14

[e] Δ(P-N) = (*a*-*b*)

Captions for figures

Figure 1. Structures of compounds.

Figure 2. The molecular structure of **(3),** showing the atomic numbering scheme.

Figure 3. The molecular structure of **(4),** showing the atomic numbering scheme and with disorder omitted from the tetrafluorobutanedioxy backbone for the purposes of clarity.

Figure 4. The molecular structure of **(5),** showing the atomic numbering scheme and only one of the two independent molecules depicted for purposes of clarity.

Figure 5. The molecular structure of **(6),** showing the atomic numbering scheme.

Figure 6. The molecular structure of **(7),** showing the atomic numbering scheme.

Figure 7. The molecular structure of (**8**), showing the atomic numbering scheme.

Figure 8. Definition of bond lengths and bond angles for cyclophosphazene compounds (**3**), (**10**) and (**12**); Y = F or H, X = F or Cl.

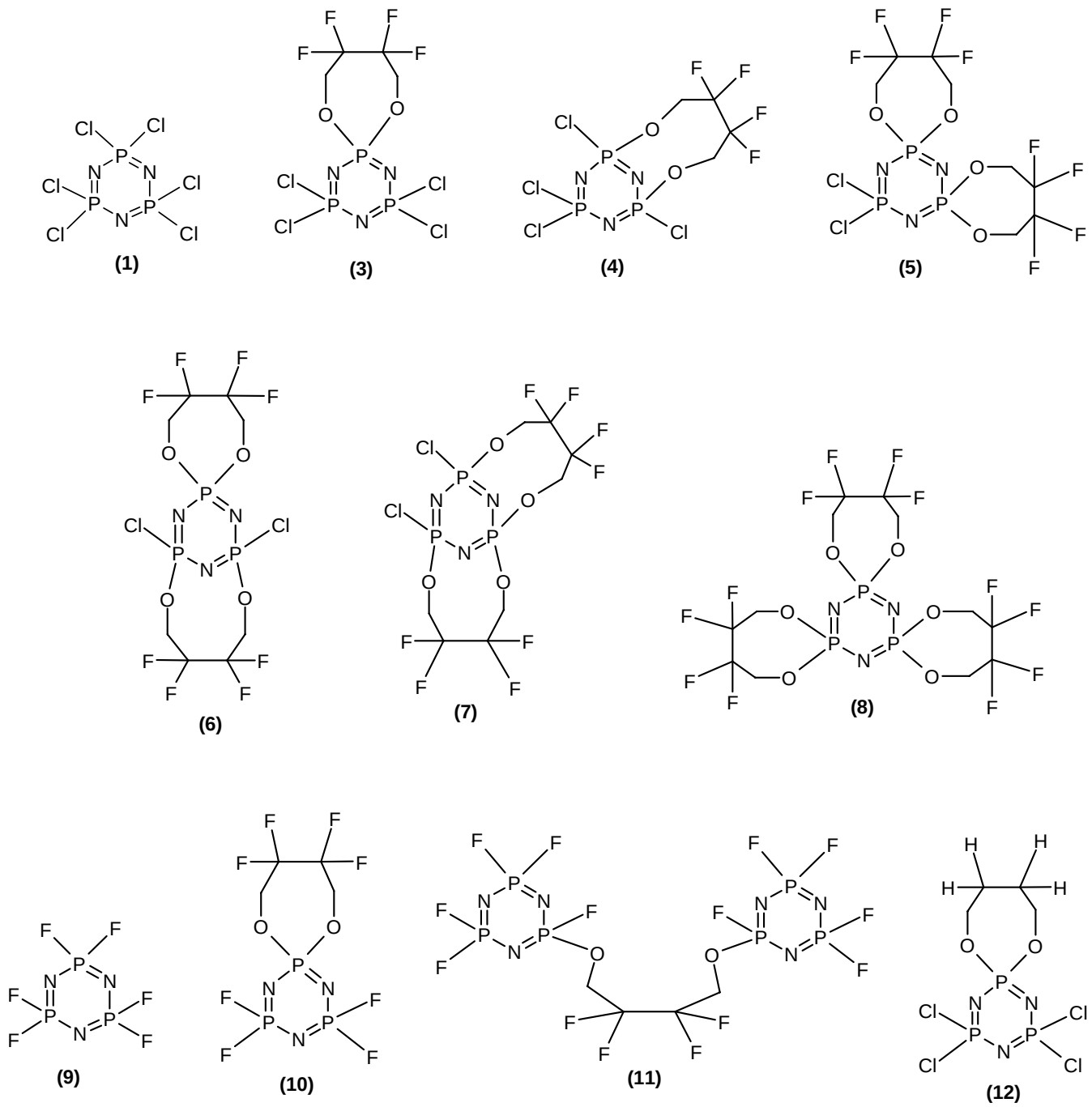

Figure 1. Structures of compounds.

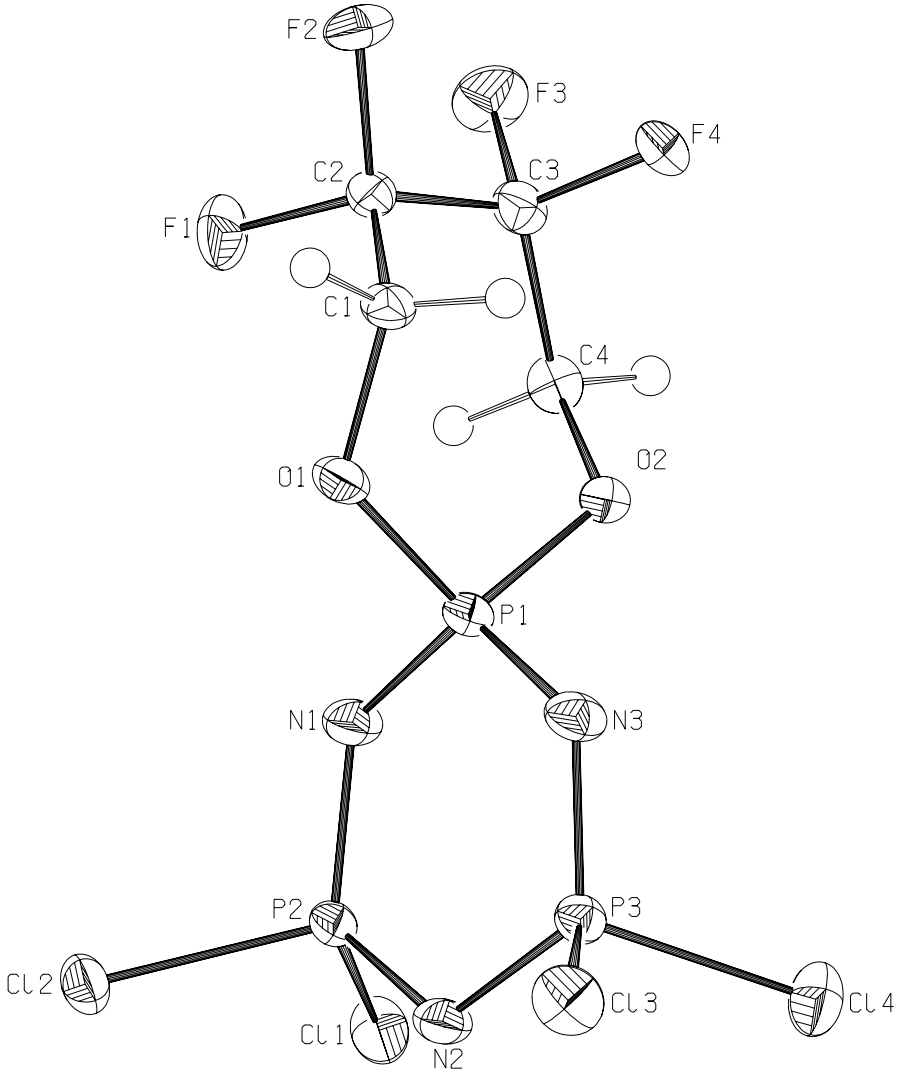

Figure 2. The molecular structure of **(3),** showing the atomic numbering scheme.

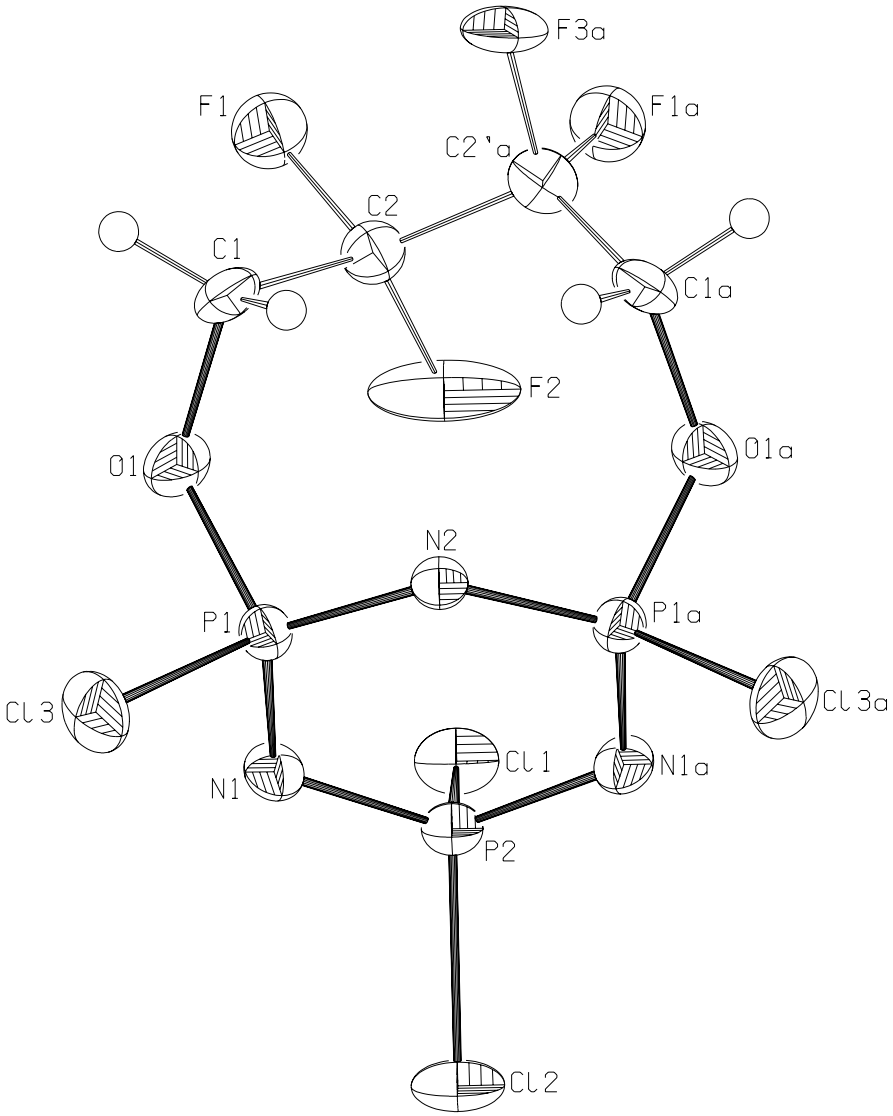

Figure 3. The molecular structure of **(4),** showing the atomic numbering scheme and with disorder omitted from the tetrafluorobutanedioxy backbone for the purposes of clarity.

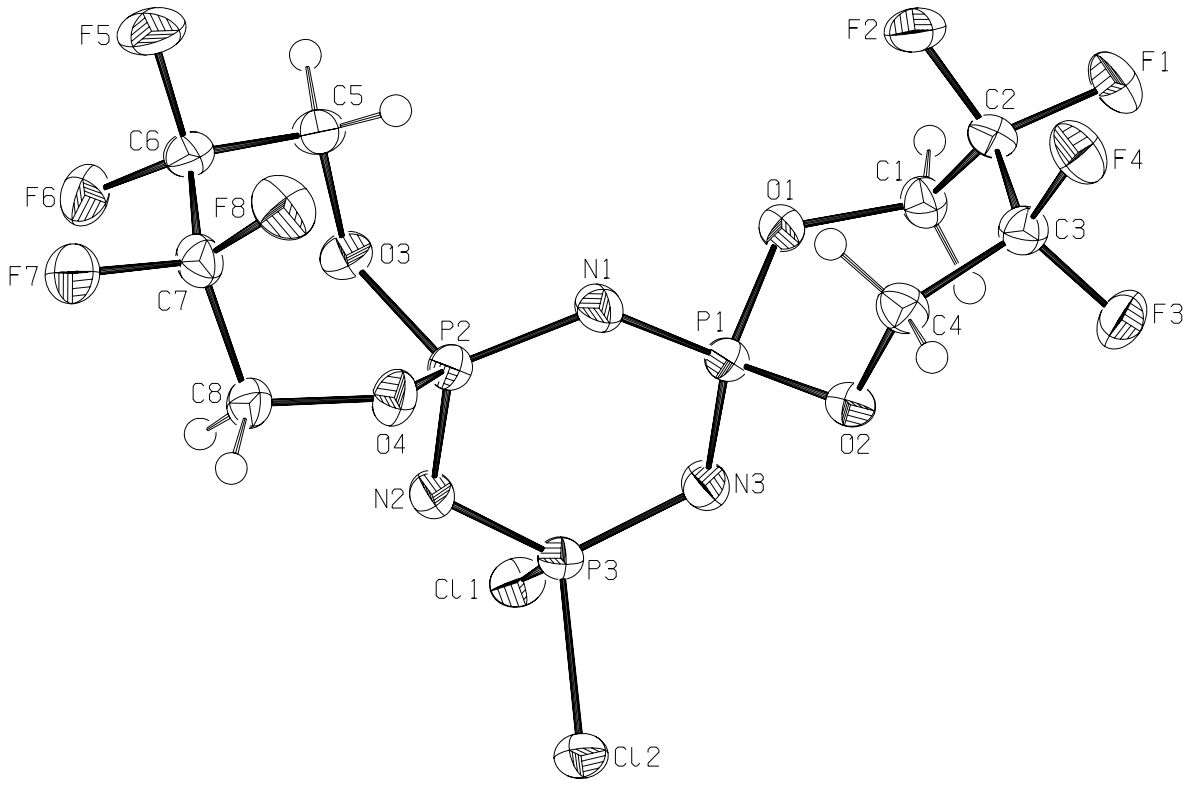

Figure 4. The molecular structure of **(5),** showing the atomic numbering scheme and only one of the two independent molecules depicted for purposes of clarity.

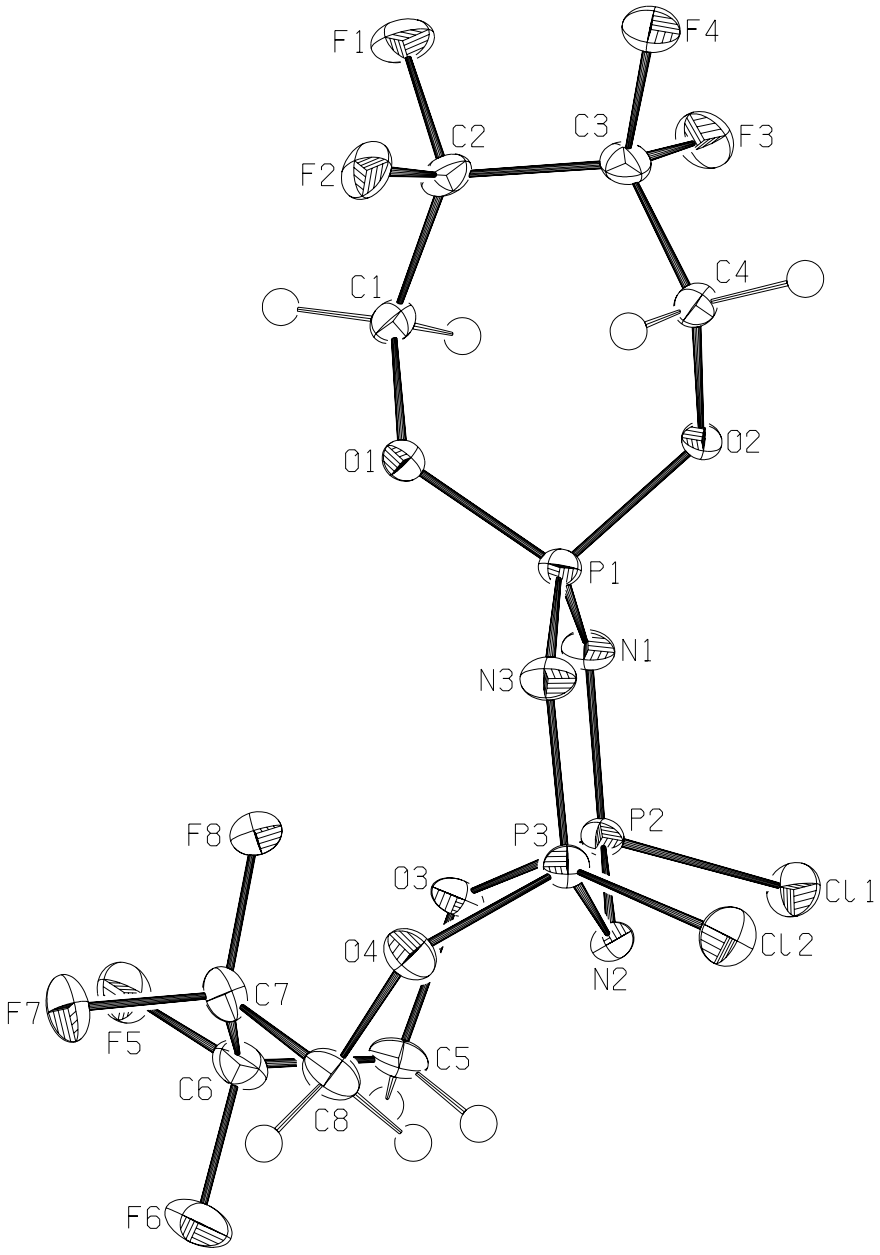

Figure 5. The molecular structure of **(6),** showing the atomic numbering scheme.

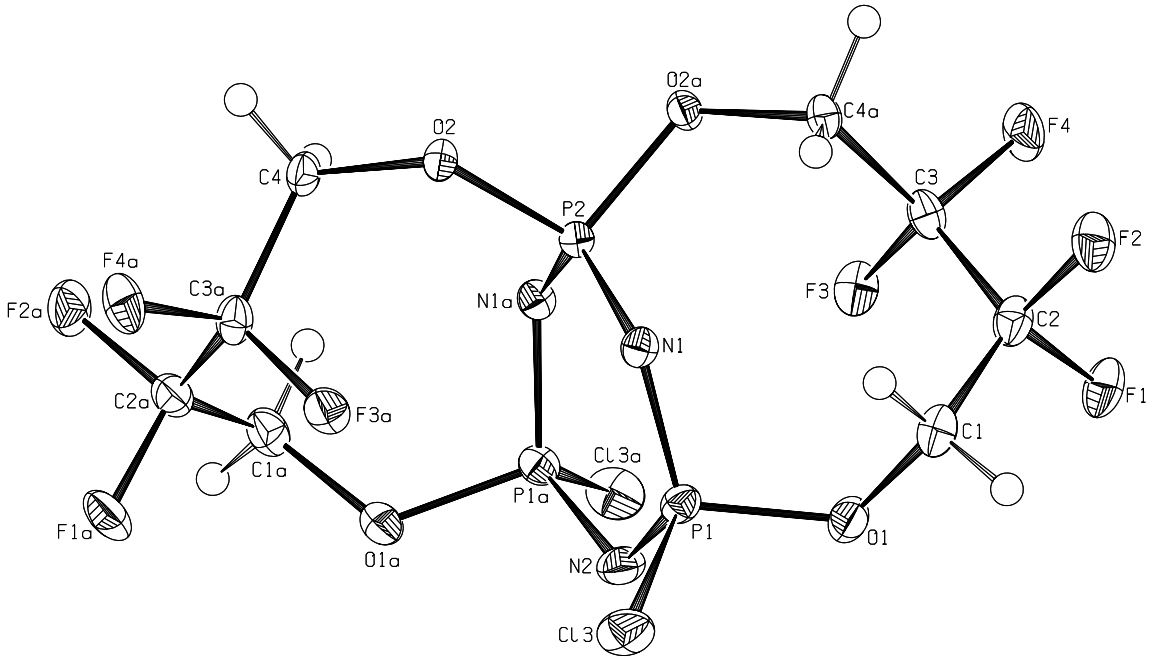

Figure 6. The molecular structure of **(7),** showing the atomic numbering scheme.

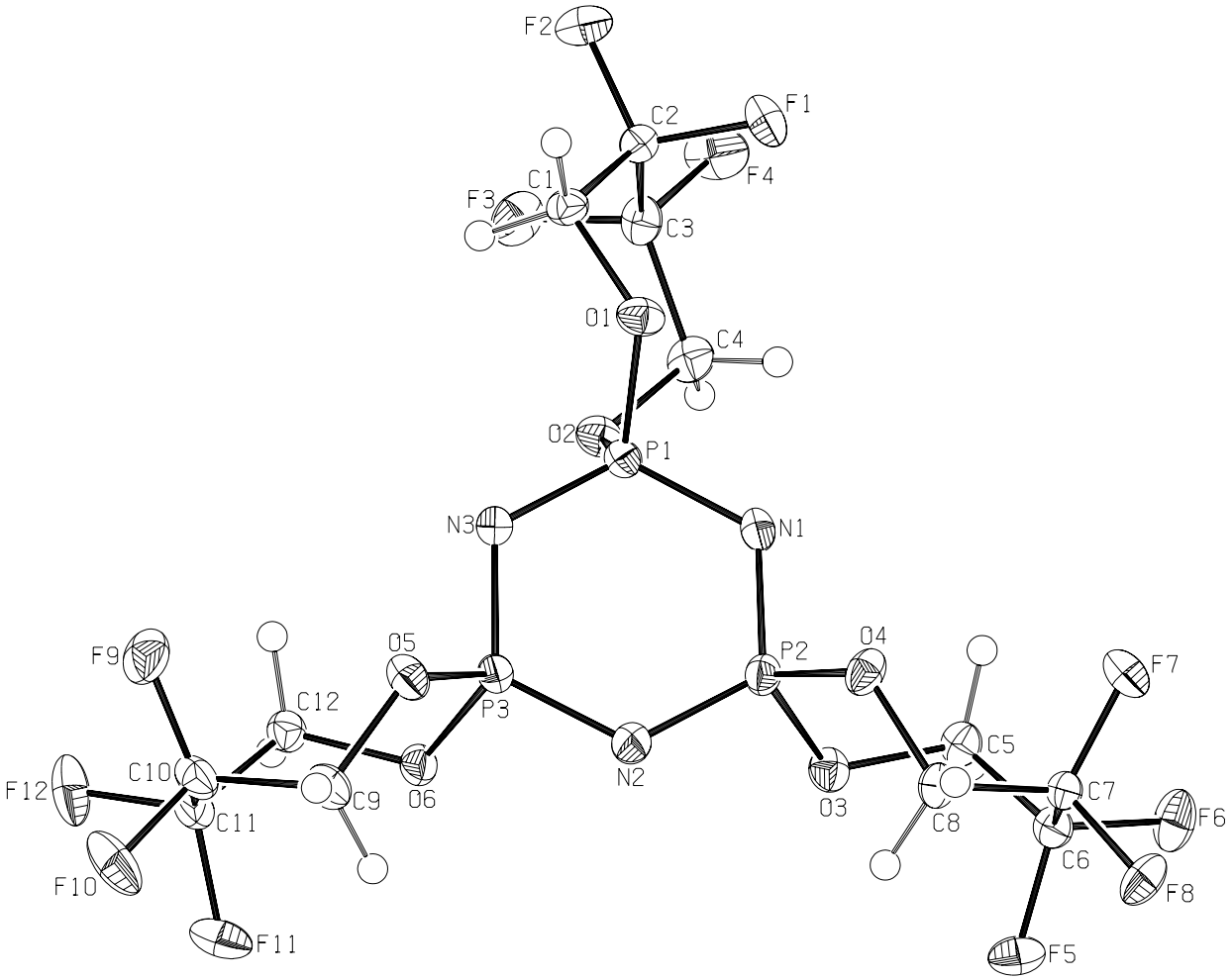

Figure 7. The molecular structure of (**8**), showing the atomic numbering scheme.

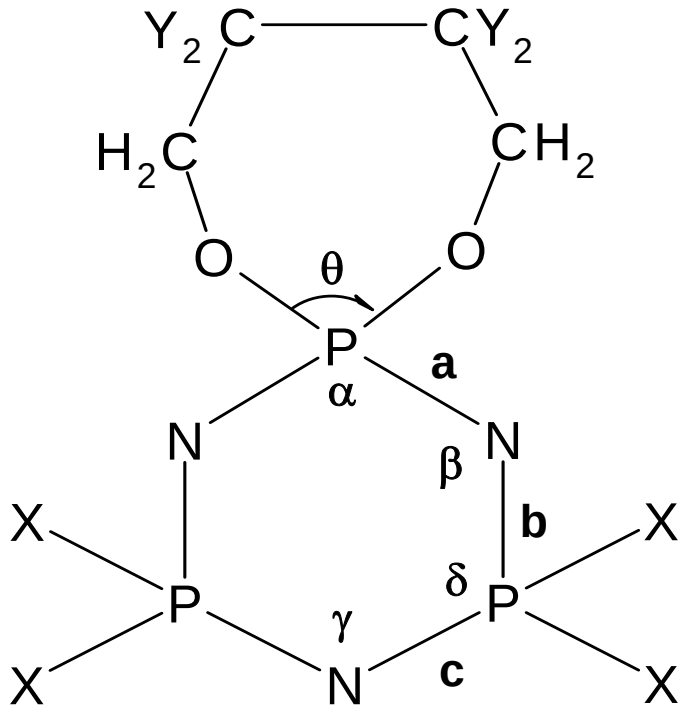

Figure 8. Definition of bond lengths and bond angles for cyclophosphazene compounds (**3**), (**10**) and (**12**); Y = F or H, X = F or Cl.