Crystal Structure of 2,2,4,4-Tetrachloro-6,6-bis(trimethylsilylamino)cyclotriphosphazene, $N_3P_3Cl_4(NHSiMe_3)_2$†

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The *X*-ray crystal structure of $N_3P_3Cl_4(NHSiMe_3)_2$ has been determined. Crystals are monoclinic, space group *C2/c*, with a = 13.749(6), b = 7.343(3), c = 20.124(3) Å, β = 95.24(3)°, and Z = 4; R = 0.049 for 961 unique observed reflections. The phosphazene ring lies on a crystallographic two-fold axis and is planar within 0.031(2) Å. The *exo* P–N bond distance is 1.609(5) and the Si–N bond distance is 1.757(5) Å which suggests preferential nitrogen lone pair delocalization to the phosphorus atom. The P–N distances in the ring alternate (from the P with the *exo* N atoms) from 1.617(5) to 1.551(5) to 1.591(4) Å. The structural and ^{31}P n.m.r. parameters of $N_3P_3Cl_4(NHSiMe_3)_2$ are compared to those of the analogous t-butylamino derivative.

The π-donor interaction of exocyclic substituents with phosphorus centres in cyclophosphazenes is a topic of continuing interest and controversy. Spectroscopic evidence indicates that aryl π donation is non-existent[1] or low,[2] while in substituents containing lone pairs of electrons such as carbanions[3,4] and amines,[4–6] the π-donor effect is believed to be significant. In the most widely studied systems, the aminophosphazenes, the exocyclic nitrogen atom is in a trigonal-planar environment and the exocyclic phosphorus–nitrogen bonds are significantly shorter than the expected single bond distance.[5,6] The exceptions to these generalizations are the aziridine derivatives where the amine is tetragonal and the exocyclic phosphorus–nitrogen distances are longer than those found in other systems.[7] In this paper, we examine the effect of placing another second-row acceptor centre on the exocyclic nitrogen atom in $N_3P_3Cl_4(NHSiMe_3)_2$ and compare the results with the previously reported structure[8] of the carbon analogue, $N_3P_3Cl_4(NHCMe_3)_2$.

Experimental

Materials and Methods.—Hexachlorocyclotriphosphazene (Shin Nisso Kako) was converted to $N_3P_3Cl_4(NHSiMe_3)_2$[9] (**1**) and $N_3P_3Cl_4(NHCMe_3)_2$[8,10] (**2**) by previously reported procedures. The ^{31}P n.m.r. spectra (in $CDCl_3$) were recorded on a Bruker WM250 spectrometer operating at 101.2 MHz and using 85% H_3PO_4 as an external reference. The spectra were recorded under conditions of broad-band decoupling and chemical shifts upfield of the reference are assigned a negative sign.

X-*Ray Analysis of* $N_3P_3Cl_4(NHSiMe_3)_2$.—Crystals suitable for *X*-ray analysis were obtained from CCl_4 solution, $C_6H_{20}Cl_4N_5P_3Si_2$, M = 453.2, monoclinic, space group *C2/c*, a = 13.749(6), b = 7.343(3), c = 20.124(3) Å, β = 95.24(3)°, U = 2 023(2) Å^3, Z = 4, D_c = 1.49 g cm^{-3}, λ(Mo-K_α) = 0.710 73 Å, μ = 9.4 cm^{-1}, F(000) = 928 and T = 293 K.

A colourless platelet of approximate dimensions 0.02 × 0.40 × 0.46 mm, mounted on a glass fibre was used for data collection on an Enraf-Nonius CAD-4 diffractometer using variable-speed (3—17 ° min^{-1}) ω–2θ scans. D_m was not measured. The unit cell was determined from a least-squares fit of the angle data for 25 reflections with $18 < 2\theta < 22°$. The analytical absorption correction[11] based on crystal shape varied from 0.68 to 1.00. Data were collected to a value of sin θ/λ of 0.60; $-6 \leqslant h \leqslant 0$, $-8 \leqslant k \leqslant 0$, $-23 \leqslant l \leqslant 23$. The data were collected in two shells. Three standard reflections (-6 0 4, -3 -3 -3, -1 -1 9) decayed by 32% over 16.2 h of data collection; anisotropic correction was applied. 2 304 Reflections were measured, 1 775 unique (R_{int} = 0.02), 814 reflections with $I < 3\sigma(I)$ were considered unobserved. The structure was solved by direct methods (MULTAN)[12] and refined by full-matrix least-squares minimized $\Sigma w(\Delta F)$.[2] Methyl hydrogen atom orientations were determined on difference maps and methyl hydrogen atoms were constrained to idealized (C–H = 0.95 Å) positions with isotropic U = 1.2 × U of the bonded carbon atom. The hydrogen atom on nitrogen was located on a difference map and was refined with a constrained isotropic thermal parameter. All non-hydrogen atoms were refined anisotropically for a total of 92 variables. The final refinement with observed data gave R = 0.049, R' = 0.062 and goodness of fit = 1.32, where non-Poisson w^{-1} = $[\sigma^2(I) + 0.0036 I^2]/4F^2$. Final $(\Delta/\sigma)_{max.}$ < 0.07, with maximum and minimum peaks of 0.40(6) and $-0.40(6)$ e Å^{-3} on the final difference map. The atomic scattering factors and anomalous dispersion corrections were from ref. 13 and the programs used were those of the Enraf SDP package.[11]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

The crystal and molecular structure of (**1**) was determined in order to ascertain the effect of the replacement of a carbon atom by a silicon atom on the exocyclic nitrogen atom in an aminocyclotriphosphazene. The final atomic co-ordinates of all unique atoms are given in Table 1. Selected bond lengths and angles are given in Table 2 and an ORTEP drawing, together with the atom-numbering scheme, is shown in the Figure. The observed molecular structure of (**1**) confirms the geminal configuration of the trimethylsilylamino groups, which was previously predicted on a chemical basis,[9] based on the known geminal configuration of $N_3P_3Cl_4(NH_2)_2$,[14] the chemical precursor to (**1**). In a comparison of the structure of (**1**) with its t-butylamino analogue, (**2**),[8] a striking similarity of structural

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

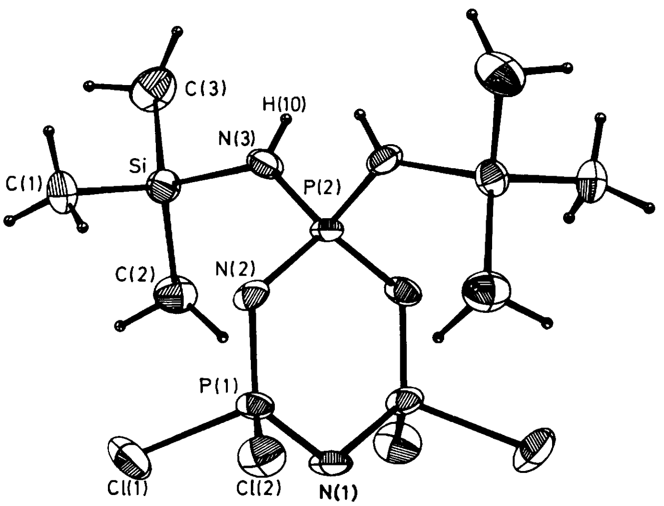

Figure. View of $N_3P_3Cl_4(NHSiMe_3)_2$ with the atomic numbering scheme

Table 1. Final positional parameters for compound (**1**)

Atom	*x*	*y*	*z*
Cl(1)	0.086 9(1)	0.288 5(3)	0.623 9(1)
Cl(2)	0.211 5(1)	0.281 4(3)	0.757 6(1)
P(1)	0.082 2(1)	0.192 6(2)	0.717 6(9)
P(2)	0.000	−0.142 3(3)	0.750
Si	−0.077 0(2)	−0.235 5(3)	0.606 60(9)
N(1)	0.000	0.305(1)	0.750
N(2)	0.078 2(3)	−0.018 5(7)	0.715 1(3)
N(3)	−0.048 3(4)	−0.274 3(7)	0.692 3(2)
C(1)	0.037 1(6)	−0.226(1)	0.563 6(3)
C(2)	−1.455 1(6)	−0.020(1)	0.592 2(4)
C(3)	−0.155 7(6)	−0.431(1)	0.578 1(4)

Table 2. Bond distances (Å) and angles (°) for $N_3P_3Cl_4(NHSiMe_3)_2$ with estimated standard deviations in parentheses

Cl(1)–P(1)	2.011(2)	Si–N(3)	1.757(5)
Cl(2)–P(1)	1.997(2)	Si–C(1)	1.861(7)
P(1)–N(1)	1.591(4)	Si–C(2)	1.848(7)
P(1)–N(2)	1.551(5)	Si–C(3)	1.856(7)
P(2)–N(2)	1.617(5)	N(3)–H(10)	0.75(6)
P(2)–N(3)	1.609(5)		
Cl(1)–P(1)–Cl(2)	99.3(1)	N(3)–Si–C(2)	109.1(3)
Cl(1)–P(1)–N(1)	106.9(2)	N(3)–Si–C(3)	104.5(3)
Cl(1)–P(1)–N(2)	109.2(2)	C(1)–Si–C(2)	110.6(3)
Cl(2)–P(1)–N(1)	107.5(2)	C(1)–Si–C(3)	112.2(3)
Cl(2)–P(1)–N(2)	111.4(2)	C(2)–Si–C(3)	110.4(4)
N(1)–P(1)–N(2)	120.4(3)	P(1)–N(1)–P(1′)	117.4(4)
N(2)–P(2)–N(2′)	111.6(3)	P(1)–N(2)–P(2)	125.0(3)
N(2)–P(2)–N(3)	105.8(2)	P(2)–N(3)–Si	130.7(3)
N(2)–P(2)–N(3′)	113.9(3)	P(2)–N(3)–H(10)	115.0(5)
N(3)–P(2)–N(3′)	105.9(4)	Si–N(3)–H(10)	114.0(5)
N(3)–Si–C(1)	109.8(3)		

parameters, with some subtle differences, is noted. In the structure of (**2**), a well developed hydrogen-bond network exists between an exocyclic amino hydrogen atom and an endocyclic nitrogen atom. This gives rise to two different orientations of the t-butylamino groups. In (**1**), both of the trimethylsilylamino groups are in the same configuration and the closest intermolecular contacts are between the exocyclic amino nitrogen atom and N(1) of the next molecule along a two-fold axis. The observed N(3) ··· N(1) distance is 3.34 Å placing it at the outer limit of N–H ··· N hydrogen bonds (2.8—3.4 Å). Hydrogen-bonding arrays of this type have been observed in other cyclophosphazene derivatives.[15] The N_3P_3 ring in (**1**) is planar within 0.031(2) Å while that in (**2**) exhibits a slight boat conformation. The exocyclic nitrogen atoms in (**1**) are in the centre of a trigonal planar array.

Table 3. Selected ^{31}P n.m.r. data for compounds (**1**) and (**2**)

Compound	δ[≡P(NHMMe$_3$)][a]	δ(PCl$_2$)[a]	$^2J_{PP}$[b]
(**1**)	9.4	22.1	50.9
(**2**)	2.3	19.6	44.7

[a] In p.p.m. [b] In Hz.

The phosphorus–nitrogen bond lengths and angles in (**1**) and (**2**) are nearly identical. Particular points of interest are the exocyclic phosphorus–nitrogen bond lengths [1.609(5) in (**1**) and a mean distance of 1.609 in (**2**)] and the exocyclic N–P–N angles [105.9(4) in (**1**) and 104.1(8), 103.9(6) for the two independent molecules of (**2**)]. It has been proposed that a relationship exists between exocyclic O–P–O bond angles and ^{31}P n.m.r. chemical shifts in cyclophosphazenes.[16] The ^{31}P n.m.r. data for (**1**) and (**2**) are given in Table 3 and a significant chemical shift difference for the ≡P(NHMMe$_3$) (M = C or Si) centres is found, but any attempted correlation with the exocyclic N–P–N angle should be viewed with caution since all these angles in (**1**) and (**2**) lie within three standard deviations and hence must be considered statistically indistinguishable.

The range of bond lengths in unconstrained silicon–nitrogen fragments is 1.688—1.759 Å,[17] so the value observed for (**1**) [1.757(5) Å] is amongst the longest of these bonds. An analogous situation occurs in disilylamino centres where one of the silicon atoms has silicon–fluorine bonds. In these cases, the silicon–nitrogen bond to the fluorinated silicon centre is short and the remaining silicon–nitrogen bond is longer.[18,19] Since the exocyclic phosphorus–nitrogen distances in (**1**) and (**2**) are equivalent, the delocalization of the exocyclic nitrogen lone pair of electrons is equivalent in each case. Although extended-Hückel calculations support the transfer of nitrogen lone-pair electron density to silicon 3*d* orbitals in $NMe_2(SiMe_3)$,[20] the strongly electron withdrawing[1] P^V centre in (**1**) is a better π acceptor than the Si^{IV} centre and the long silicon–nitrogen bond lengths reflects a decreased transfer of π electron density to the silicon atom. Competition for nitrogen lone-pair electrons between phosphorus and acyl centres has also been investigated by structural studies.[21] A rough correlation between short silicon–nitrogen bond lengths and increased percentage *s* character has been noted.[17] If this effect were operative in (**1**), the more electronegative P^V would direct more *p* character to the P(2)–N(3) bond hence causing increased *s* character in the N(3)–Si bond.[22] Since a long, rather than a short, silicon-nitrogen bond is observed, it appears reasonable to ascribe the variations in exocyclic nitrogen lone-pair delocalization described above as being reasonable for the long silicon-nitrogen bond length.

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