Structure of 2,2,4,4-Tetrachloro-6-phenyl-6-(2′,2′,2′-triphenylphosphazen-1′-yl)-cyclotriphosphazatriene—an Example of a Cyclophosphazene with a Phosphazenyl Side-chain

By MALCOLM BIDDLESTONE,† GRAHAM J. BULLEN,*‡ PETER E. DANN,‡ and ROBERT A. SHAW*†

(† *Department of Chemistry, Birkbeck College, University of London, Malet Street, London* WC1E 7HX and ‡ *Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex*)

Summary An *X*-ray crystallographic investigation of the title compound reveals very short and equal exocyclic P–N bonds, which are in fact shorter than the endocyclic P–N bonds at the point where the triphenylphosphazenyl substituent is attached.

THE reaction of octachlorocyclotetraphosphazatetraene with phenylmagnesium bromide yields two compounds of composition $N_4P_4Ph_4Cl_4$,[1,2] to which incorrect structures were originally assigned.[1] We have shown elsewhere that the compound of m.p. 212·5° is 2,2,6,6-tetrachloro-4,4,8,8-tetraphenylcyclotetraphosphazatetraene,[3] and also deduced that the compound, m.p. 181°, is a ring contracted isomer, 2,-2,4,4-tetrachloro-6-phenyl-6-(2′,2′,2′ -triphenylphosphazen-1′-yl)cyclotriphosphazatriene.[2,4] The high basicities of triphenylphosphazenylcyclophosphazenes[5] towards perchloric acid in nitrobenzene and the absence of detailed structural data on compounds where phosphorus is linked to three phosphazenyl nitrogen atoms prompted us to carry out an *X*-ray crystallographic investigation.

$N_3P_3Cl_4Ph(NPPh_3)$, (m.p. 181°), $M = 630{\cdot}16$, monoclinic, $a = 8{\cdot}95$, $b = 14{\cdot}35$, $c = 21{\cdot}63$ Å, $\beta = 90{\cdot}5°$, $U = 2776$ Å^3, $Z = 4$, $D_c = 1{\cdot}51$, $D_m = 1{\cdot}50$ g cm^{-3}, space group $P2_1/n$.

X-Ray intensities were measured by diffractometer with Mo-K_α radiation. 4901 Independent reflexions with statistically significant intensities were obtained. The structure was solved by direct methods with use of weighted multi-solution tangent refinement. Least-squares refinement with use of anisotropic temperature factors for all atoms except hydrogen has proceeded to $R = 0{\cdot}071$ and refinement continues. The hydrogen atoms have been included in the calculations by placing them at positions estimated from the molecular geometry.

The bond lengths and angles are shown in the Figure. The phosphazene ring shows considerable deviations from planarity. These deviations cannot be summarised simply but to a first approximation atoms P(1), N(1), P(2), and N(2) are coplanar, with N(3) out of their mean plane by 0·1 Å on one side and P(3) by 0·15 Å on the other. The conformation of the Ph_3PN substituent is such that atoms C(1), P(3), N(4), and P(4) are almost coplanar, with P(4)–N(4)···C(1) approximately colinear.

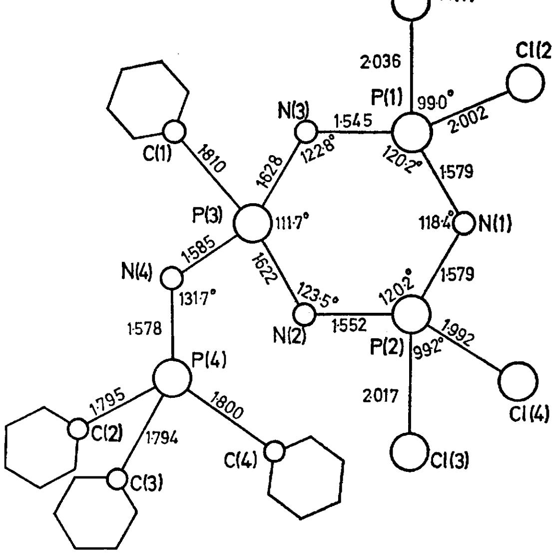

FIGURE. Bond lengths (Å) and bond angles. E.s.d.s: for the lengths P–Cl 0·003, P–N 0·005—0·007, P–C 0·006 Å; for the angles Cl–P–Cl 0·1, N–P–N 0·3, P–N–P 0·4°.

Other salient features are: (i) The two exocyclic P–N bond lengths are equal, indicating extensive delocalisation of the bonding electrons, and short (of similar length to the *endo* P–N bonds in the Cl_2P–N–PCl_2 segment of the molecule); an analogous situation occurs in $Ph_3P{=}N\text{-}SO_2\text{-}p\text{-tol}$.[6] Further, the *endo* P–N bonds at the Ph_3PN substituted phosphorus atom, such as P(3)–N(2), are longer than the *exo* P–N bonds. Adjacent to these longer *endo* P–N bonds in a 'three-centre P–N–P island' are short *endo* P–N bonds, *e.g.*, P(2)-N(2), as in *gem*-$N_3P_3Ph_2Cl_4$.[7] (ii) The phenyl group bonded to P(3) is eclipsed with atom N(4), a conformation which is different from that known for $\geqslant$PPhCl[8] or $\geqslant PPh_2$[7,9] groupings though it occurs for >P(:S)Ph in cyclic thiodiphosphazanes.[10] (iii) In each $\geqslant PCl_2$ group one P–Cl bond is significantly longer than the other. Unequal P–Cl bonds were observed in *gem*-$N_3P_3Ph_2Cl_4$,[7] but the differences are even larger in the structure reported here.

(iv) The torsion angles P(4)–N(4)–P(3)–N(2) and P(4)–N(4)–P(3)–N(3) are 60 and 67°, respectively, as compared to a P–N–S–O torsion angle of 38° in $Ph_3P{=}N\text{-}SO_2\text{-}p\text{-tol}$.[6] Hitherto torsion angles observed in such ylides have been either 0 or 30—40° (*cf.* ref. 6).

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