Synthesis and Structural Investigation of an Unusual Double Hydrogen-Bridged Dimeric Cyclophosphazene Derivative

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Cyclotriphosphazadiene, ^{1}H NMR, X-ray, Crystal Structure, Double hydrogen-bonded tricycle

The formation, ^{1}H NMR spectroscopic and X-ray crystallographic investigations of a double hydrogen-bridged tricyclic system of a cyclotriphosphazadiene derivative, $[N_3HP_3(O)Cl_2(NEt_2)_3]_2$ are described and discussed. This is the first neutral molecule having both cyclophosphazene and cyclophosphazane character to be structurally investigated.

Aminolysis[1] and alcoholysis[2] reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (**1**), are sometimes complicated by competitive solvolysis reactions.

$N_3P_3Cl_6$ (**1**) reacts with eight mol. equivalents of diethylamine in benzene to give a small quantity of a compound of empirical formula, $C_{12}H_{31}Cl_2N_6OP_3$ *(**2**), m.p. 167.5 °C. Addition of water to the reaction solvent enhances the yield of compound **2**. The mass spectrum shows peaks at $m/e = 438$ and 402, which correspond to the molecular ion $[C_{12}H_{31}{}^{35}Cl_2N_6OP_3]^+$ and to $(M\text{-}36)^+$, *i.e.*, elimination of HCl.

* After completion of this work, a compound of this composition was reported[5]; its structure was not investigated.

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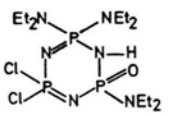
The ^{1}H NMR spectrum of compound **2** (100 MHz, CCl_4) shows a complex multiplet $-N(CH_2CH_3)_2$ and three overlapping triplets $-N(CH_2CH_3)_2$ indicating distinct chemical environments for the three diethylamino-groups. The spectrum also contains a broad resonance peak at $\delta = 9.2$ (1 proton) which disappears after the compound has been shaken with deuterium oxide. The IR spectrum has a band at 2670 cm^{-1} and a number of bands in the region 1160–1240 cm^{-1} (*cf.* ref. [2]).

The spectroscopic evidence suggests that compound **2** is 2,2-dichloro-4,4,6-trisdiethylamino-6-oxocyclotriphosphazadiene, $N_3HP_3(O)Cl_2(NEt_2)_3$.



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The molecular weight of compound **2** in benzene solution (osmometry) is *ca.* 815 and does not vary significantly with concentration. This value indicates a strong tendency for compound **2** to exist as a dimer in solution. An X-ray crystallographic investigation was undertaken to clarify the bonding.

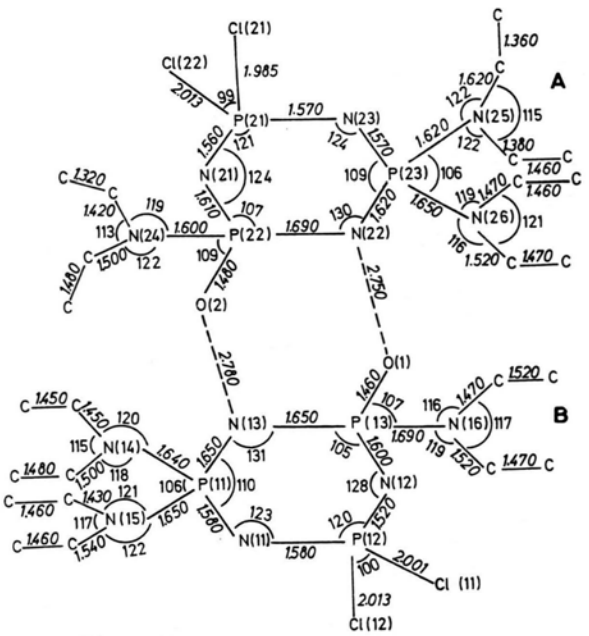

Fig. 1. Bond lengths and bond angles of $[N_3HP_3(O)Cl_2(NEt_2)_3]_2$.

Compound **2**, $N_3HP_3Cl_2(O)(NEt_2)_3$, m.p. 167.5 °C, crystallised in the orthorhombic space group $P2_12_12_1$ with $a = 18.78$ (1), $b = 17.56$ (1), $c = 13.49$ (1) Å; $V = 4449$ Å^3, $D_{calc} = 1.31$ g/cm^3 for $Z = 8$, $D_{exp} = 1.29$ g/cm^3, MW = 439.25; 1870 independent reflections with statistically significant intensities were measured by diffractometer using Cu Kα radiation. The structure was solved by weighted multisolution

tangent refinement and Fourier techniques. Least-squares refinement has proceeded to $R = 0.077$.

The crystallographic investigation confirmed the spectroscopic findings. The molecule consists of two trimer units **A** and **B**, whose gross structures are superimposable; hence the compound is not the meso-form. Units **A** and **B** are held together by two N–H···O hydrogen-bonds, giving rise to a tricycle.

Figure 1 shows the bond lengths and bond angles of the molecule, Figure 2 is a view of unit **A**. Unit **A** has a twist boat form with P(22) and N(23) above the mean plane of the ring by 0.12 and 0.09 Å respectively and P(21) and N(22) below this mean plane by 0.10 and 0.15 Å respectively. Unit **B** has a boat form with P(13) and N(11) above the base of the boat by 0.23 and 0.11 Å respectively. The ring bond lengths of the Cl_2P–N–$P(NEt_2)_2$ segment are typical of phosphazenes[3] and those of the $(Et_2N)_2P$–NH–$P(O)(NEt_2)$ segment of phosphazanes[4]. In the Cl_2P–N–$P(O)NEt_2$ segment both P–N bonds are relatively short, with the one adjacent to the $\equiv PCl_2$ group the shorter. The bond angles at $N\hat{P}(Cl_2)N$ are normal for trimeric phosphazenes[3] but the adjacent $P\hat{N}P$ angles are somewhat larger. The ring angle at the nitrogen atom involved in hydrogen-bonding is the largest. At the phosphoryl phosphorus, the ring angle is small as it is in phosphazanes[4].

This structure represents the first one in which a neutral molecule displays mixed phosphazene-phosphazane character.

Experimental

Wet diethylamine (0.45 mole) was added slowly to a stirred solution of $N_3P_3Cl_6$ (0.057 mole) in benzene. The mixture was boiled (20 h). Diethylamine hydrochloride was filtered off and the filtrate evaporated to dryness. The resultant oil was dissolved in light petroleum (b.p. 40–60 °C) and the solution maintained at 0 °C (48 h). Colourless crystals of 2,2-dichloro-4,4,6-trisdiethylamino-6-oxocyclotriphosphazadiene, m.p. 167.5 °C (9% yield) were deposited.

$C_{12}H_{31}N_6OP_3Cl_2$

Calcd	C 32.8	H 7.1	N 19.1	P 21.2	Cl 16.2,
Found	C 33.0	H 7.0	N 19.1	P 21.4	Cl 16.3.

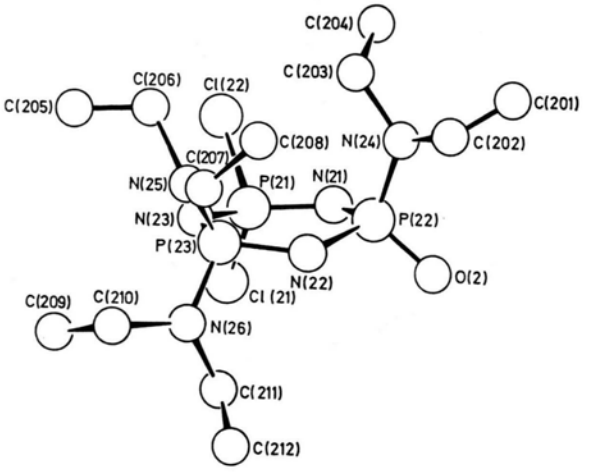

Fig. 2. $N_3HP_3(O)Cl_2(NEt_2)_3$: Unit **A**.

P. E. D. thanks the S. R. C. for a studentship.

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