The Crystal Structure of a Spirocyclic Cyclophosphazene $N_3P_3(NMe_2)_4(NHCH_2CH_2NH)$ – Evidence for Intermolecular Hydrogen Bonding

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An X-ray crystal structure analysis of tetrakis(dimethylamino)(ethylenediamino)cyclotriphosphazene reveals a novel spirocyclic structure with the spiro ring having an envelope conformation. There is evidence for an intermolecular $N-H \cdots N$ bond in the crystal which persists in solution.

Becke-Göhring and Boppel [1] studied the reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ with ethylenediamine and isolated the tetrachloro(ethylenediamino) derivative,

to which an *ansa* type structure (chlorine atoms replaced from two phosphorus atoms) was assigned [2, 3]. A reinvestigation of the reaction has been reported recently [4] and a spirocyclic structure (1) (chlorine atoms replaced from the same phosphorus atom) has been assigned on the basis of ^1H and ^{31}P NMR data for its dimethylamino derivative, $N_3P_3(NMe_2)_4(NHCH_2CH_2NH)$ (2). In order to confirm the structural assignment, an X-ray crystallographic study of compound (2) has been carried out, the results of which are reported in this paper. Compound 2 represents the first example of a cyclotriphosphazene derivative containing mixed amino substituents to be studied by X-ray crystallography.

Compound 1 is highly susceptible to hydrolysis by atmospheric moisture. Furthermore, solutions of the compound even in dry organic solvents (CH_2Cl_2 or benzene) slowly develop turbidity presumably because of a cross-linking reaction as reported for the bis(amino) derivative, $N_3P_3Cl_4(NH_2)_2$ [5]. Therefore crystals of compound 1 suitable for crystallographic

studies could not be obtained. On the other hand, the dimethylamino derivative (2) is nonhygroscopic and stable in solution. Crystals of compound 2 were grown from light petroleum (40–60 °C) – methylene chloride (2:1).

The compound $N_3P_3(NHCH_2CH_2NH)(NMe_2)_4$ crystallises in the orthorhombic space group *Pbcn* with $a = 15.11$, $b = 13.57$, $c = 18.71$ Å and $Z = 8$. Intensity data were collected on a *CAT-4* diffractometer by the $\omega-2\theta$ scan technique using monochromated *MoK α* radiation. Out of 2800 reflections measured upto $2\theta = 45^\circ$, 1520 were above the threshold [$I \geq 3\sigma(I)$]. The structure has been solved by direct methods using *Multan* [6] and refined by least squares to an *R*-index of 0.062 using anisotropic temperature factors. Hydrogen atoms have not been included in the calculations.

The molecular structure with bond parameters is shown in the Figure. As expected from chemical studies, the compound has a spirocyclic structure with the atoms P(2), N(6), C(5), C(6) and N(7) forming the spiro ring. All the P–N bond distances within the phosphazene ring are equal and the average P–N distance (1.59 Å) is identical with the mean P–N bond length (1.588 Å) in the hexakis-(dimethylamino) derivative, $N_3P_3(NMe_2)_6$ [7]. Furthermore the endocyclic angles also have closely similar values. The mean P–N and N–C bond distances (1.68 and 1.48 Å respectively) in the spiro ring are equal to the corresponding mean distances in the $\equiv P(NMe_2)_2$ groups. However considering the NPN angles, we find that N(7) P(2) N(6) is significantly smaller than the corresponding angles at P(1) and P(3), probably due to ring formation.

The phosphazene ring is nonplanar. The atoms P(1), P(2), P(3), N(2) and N(3) are in a plane, the maximum deviation from planarity being 0.02 Å.

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There is a short intermolecular contact distance of 3.18 Å between N(2) of the phosphazene ring and

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