The Crystal Structure of a Spirocyclic Cyclophosphazene

N₃P₃(NMe₂)₄(NHCH₂CH₂NH) - Evidence for Intermolecular Hydrogen Bonding

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Z. Naturforsch. 33b, 588-589 (1978); received February 21, 1978

Tetrakis(dimethylamino)(ethylenediamino)cyclotriphosphazene, X-ray, Crystal Structure, Spirocyclic Structure, Envelope Conformation

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···N bond in the crystal which persists in solution.

Becke-Göhring and Boppel [1] studied the reaction of hexachlorocyclotriphosphazene, Na₃P₃Cl₆ with ethylenediamine and isolated the tetrachloro-(ethylenediamino) derivative, Na₃P₃Cl₆(NHCH₂CH₂NH) 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 ³¹P NMR data for its dimethylamino derivative, Na₃P₃(NMe₂)₄(NHCH₂CH₂NH) (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 cyclo-triphosphazene 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 (CH₂Cl₂ or benzene) slowly develop turbidity presumably because of a cross-linking reaction as reported for the bis(amin) derivative, Na₃P₃Cl₄[NH₂]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 Na₃P₃(NHCH₂CH₂NH)(NMe₂)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 CAD-4 diffractometer by the ω—2θ scan technique using monochromated Mo Ka radiation. Out of 2800 reflections measured up to 2θ = 45°, 1520 were above the threshold [I > 3σ(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, Na₃P₃(NMe₂)₄ [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 Na₃P₃Cl₄ 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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The e.s.d.'s for the bond distances (Å) are P–N ~0.01, N–C and C–C ~0.02 Å, for the angles they are ~1°.

N(1) is out of this plane by 0.18 Å. The spiro ring has an envelope conformation with N(6) displaced by 0.4 Å from the plane formed by the atoms P(2), N(7), C(5) and C(6). The mean planes through the phosphazene ring and spiro ring are nearly perpendicular to each other. The dimethylamino groups exhibit Type III conformation [8], the mean value of torsion angles with respect to the phosphazene ring being 57.1°.

There is a short intermolecular contact distance of 3.18 Å between N(2) of the phosphazene ring and N(6) of the spiro ring, which suggests a weak hydrogen bond. A similar feature has been observed in the crystal structure of gem-N₂P₂Cl₄(NHBuᵗ)₂ [9]. This N–H⋯N bond is apparently responsible for the deviation of N(6) from the plane of the spiro ring in compound 2. The presence of hydrogen bonding is supported by infra-red spectroscopic studies. The spectrum of the dimethylamino derivative (2) shows two bands attributable to N–H stretching vibrations at 3230 and 3355 cm⁻¹ in the solid and at 3230 and 3440 cm⁻¹ in benzene solution, compared to only one band at 3360 cm⁻¹ in the spectrum of the chloro precursor. These data suggest that hydrogen bonding probably persists in solution as well. The infrared spectrum of the bis-t-butylamino derivative, N₃P₃Cl₄(NHBuᵗ)₂ in the solid state shows two sharp closely spaced peaks at 3385 and 3420 cm⁻¹ and a broad band at 3275 cm⁻¹; in solution only one band at 3390 cm⁻¹ is observed. Evidently, in this case the hydrogen bonds present in the solid break up in solution. In aminocyclophosphazenes, the ring nitrogen atoms are quite basic as a result of conjugative electron flow from the exocyclic amino substituents [8, 10]. The electron density at the ring nitrogen atoms in compound 2 will be more than in the bis-t-butylamino derivative, N₃P₃Cl₄(NHBuᵗ)₂ reflecting the greater strength of the hydrogen bonding interaction in the former.

We thank Professors R. A. Shaw, A. R. Vasudeva Murthy and C. C. Patel for kind interest. Thanks are also due to U. G. C., New Delhi for support (S. S. K. and K. R.).