Synthesis and Structure of the First Example of a Borazinylcyclotriphosphazene

Mark F. Welker, Ian Manners, Masood Parvez, and Harry R. Allcock*

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, U.S.A.

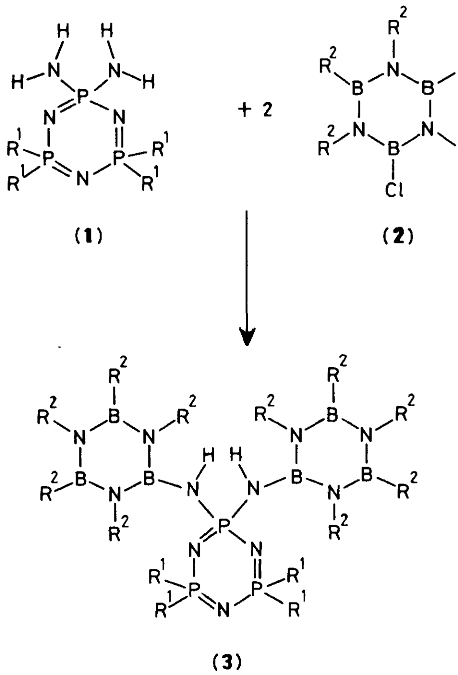
The first example of a borazinyl-phosphazene, *gem*-$N_3P_3(NMe_2)_4(NH\text{-}B_3N_3Me_5)_2$, has been prepared and its structure determined by single crystal *X*-ray diffraction.

Cyclic and high polymeric phosphazenes are known with a wide variety of organic, inorganic, and organometallic side groups.[1—3] However, to the best of our knowledge, no examples of phosphazenes with borazinyl side groups have been reported. Species of this type are of considerable interest both as possible polymerization 'monomers'[4] and as pyrolytic precursors to novel non-oxide ceramic materials.[5] Indeed, pyrolysis of oligomeric aminoborazines has recently been used to synthesize boron nitride.[6] Recent work in our laboratory has shown that aminopolyphosphazenes are prospective pyrolytic precursors to new ceramic materials.[7] We report here the synthesis and structure of the first borazinylcyclotriphosphazene. In a later paper, we will describe the extension of this work to the macromolecular level and the results of subsequent pyrolysis studies.

Reaction of the aminophosphazene (**1**)[8] with *B*-chloropentamethylborazine (**2**)[9] [tetrahydrofuran (THF), 67 °C, 3 h] in the presence of triethylamine as hydrogen halide acceptor followed by filtration, removal of the solvent, extraction of the residue with hexane, and cooling to −15 °C, afforded colourless, air- and moisture-sensitive crystals of the *gem*-bis(borazinylamino)tetrakis(dimethylamino)cyclotriphosphazene (**3**)

Table 1. Selected bond lengths (Å) and angles (deg.) with estimated standard deviations in parentheses for the two independent molecules (**3A**) and (**3B**).

	(**3A**)	(**3B**)		(**3A**)	(**3B**)
P(1)–N(1)	1.601(4)	1.568(6)	P(3)–N(3)	1.614(6)	1.590(6)
P(1)–N(3)	1.618(7)	1.568(6)	P(3)–N(6)	1.726(9)	1.613(7)
P(1)–N(4)	1.644(6)	1.683(6)	P(3)–N(7)	1.623(9)	1.617(6)
P(1)–N(5)	1.667(5)	1.664(6)	B(1)–N(4)	1.38(1)	1.54(1)
P(2)–N(1)	1.604(6)	1.547(7)	B(1)–N(10)	1.42(1)	1.47(2)
P(2)–N(2)	1.595(8)	1.556(6)	B(1)–N(12)	1.56(1)	1.32(1)
P(2)–N(6)	1.695(6)	1.587(9)	B(4)–N(5)	1.48(1)	1.43(1)
P(2)–N(7)	1.681(7)	1.672(9)	B(4)–N(13)	1.39(1)	1.45(2)
P(3)–N(2)	1.632(6)	1.608(7)	B(4)–N(15)	1.46(1)	1.42(1)
N(4)–P(1)–N(5)	106.3(3)	105.5(3)	P(2)–N(2)–P(3)	117.9(5)	123.8(3)
N(1)–P(1)–N(3)	116.9(3)	113.5(3)	P(1)–N(3)–P(3)	120.6(3)	123.1(4)
N(1)–P(2)–N(2)	119.2(3)	114.1(3)	P(1)–N(4)–B(1)	139.4(4)	130.3(4)
N(2)–P(3)–N(3)	119.3(3)	114.1(3)	P(1)–N(5)–B(4)	134.4(5)	140.6(5)
P(1)–N(1)–P(2)	120.7(4)	127.4(3)			



Scheme 1. $R^1 = NMe_2$, $R^2 = Me$.

(yield, 81%).† Compound (**3**) was characterized by ^{31}P and ^{11}B n.m.r. spectroscopy,‡ mass spectrometry, and satisfactory elemental analysis. The ^{31}P n.m.r. spectrum of (**3**) was characteristic of an A_2B spin system (δ_A 24.9, δ_B 12.9, J_{PNP} = 47.5 Hz). The ^{11}B n.m.r. spectrum contained two broad resonances (at 35.2 and 27.7 p.p.m.) assigned to boron atoms bonded to methyl groups and amino groups, respectively. The electron impact mass spectrum of (**3**) showed the expected molecular ion at m/z 640. Additional characterization was obtained by X-ray diffraction analysis of a single crystal of (**3**) grown by cooling a saturated hexane solution to −15 °C.

The single crystal X-ray diffraction analysis confirmed the structure of (**3**) and indicated the presence of two independent molecules, (**3A**) and (**3B**), within the unit cell.§ The structure of (**3A**) is shown in Figure 1 and the important molecular dimensions of (**3A**) and (**3B**) are summarized in Table 1. Although (**3A**) and (**3B**) possess two significantly different molecular geometries, both molecules show several common characteristics. The mean exocyclic B–N bond length (1.46 Å) is comparable to the mean endocyclic B–N bond length (1.44 Å), which indicates a bond order greater than unity. The mean exocyclic P–N(borazinylamino) bond length (1.66 Å) is also shorter than that of a P(sp^3)–N(sp^3) single bond (1.77 Å),[10] indicating some π-character.[11] These observations indicate significant delocalization of the borazinylamino nitrogen lone pair, principally into the borazinyl ring rather than into the phosphazene ring. The borazinyl rings of each molecule are planar and nearly parallel [dihedral angles of 15.5(6)° for (**3A**) and 13.9(7)° for (**3B**)]. Both phosphazene rings have slight twist-boat conformations. The distinctions between (**3A**) and (**3B**) can be seen by examination of Table 1. The endocyclic bond angles of (**3B**) are more distorted than those of (**3A**), but are comparable to those for species such as *gem*-$N_3P_3(NH_2)_2(OMe)_4$,[12] *gem*-$N_3P_3Cl_2(NHPr^i)_4$,[13] and $N_3P_3(NMe_2)_6$.[14] The endocyclic P–N bonds and the exocyclic P–N(dimethylamino) bonds of (**3a**) are significantly longer than the corresponding bonds of (**3B**), whereas the exocyclic P–N(borazinylamino) bonds of (**3A**) are shorter.

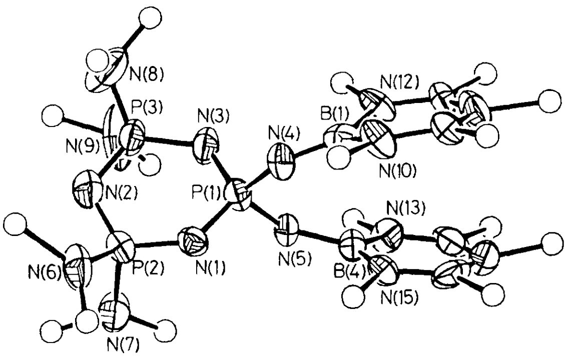


Figure 1. ORTEP representation of the structure of (**3A**), showing 50% probability anisotropic thermal ellipsoids for P, N, and B. The C atoms are assigned arbitrary radii, and the H atoms omitted for clarity.

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† *gem*-$N_3P_3Cl_4(NH\text{-}B_3N_3Me_5)_2$ and *gem*-$N_3P_3(OPh)_4(NH\text{-}B_3N_3Me_5)_2$ have also been prepared by similar methods.

‡ ^{31}P and ^{11}B N.m.r. data are referenced to 85% H_3PO_4 and $BF_3{\cdot}Et_2O$, respectively.

§ *Crystal data*: $C_{18}H_{56}B_6N_{15}P_3$, M = 640.54, triclinic, space group $P1$, a = 9.424(2), b = 13.841(1), c = 14.570(4) Å, α = 79.40(1), β = 83.44(2), γ = 73.99(1)°, V = 1791.5 Å^3, Z = 2, D_c = 1.187 g cm^{-3}, Mo-K_α radiation, λ = 0.71073 Å, μ = 0.196 mm^{-1}. R = 0.066 for 754 parameters and 4412 observed reflections with $I > 3\sigma(I)$, measured on an Enraf-Nonius CAD4 diffractometer at 293 K. Initial attempts to solve the structure in the centrosymmetric space group, $P\bar{1}$, showed a disordered phosphazene (P_3N_3) group with two P_3N_3 moieties separated by 1.5 Å. This indicated $P1$ as the alternative space group, requiring two independent molecules in the asymmetric unit. Therefore, the structure was solved by direct methods and successfully refined in the space group $P1$ by full-matrix least-squares calculations allowing anisotropic thermal parameters for the non-hydrogen atoms. A few carbon atoms of the dimethylamino groups show large thermal motions and the possibility of disorder cannot be ruled out. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.