

## Synthesis, N.M.R. Spectra, and X-Ray Crystal Structure of 2-*trans*-4-Diamino-2,4,6,6-tetra-*n*-propoxycyclotriphosphazatriene. The First Example of a Geminal to *trans*-Nongeminal Amino-group Migration in Phosphazene Chemistry

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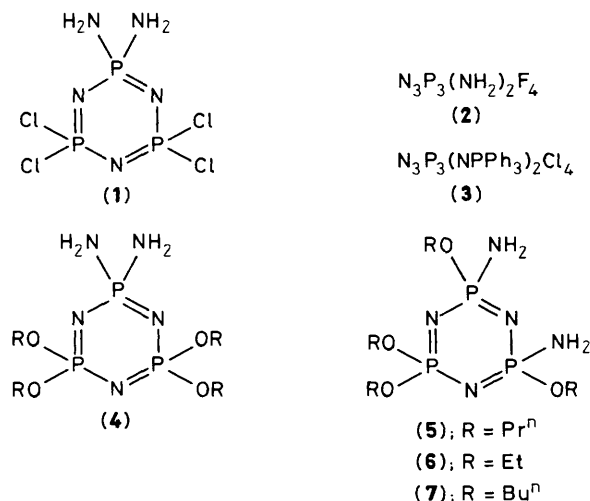
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X-Ray crystallographic and n.m.r. spectroscopic investigations show that the geminal amino derivative  $N_3P_3Cl_4(NH_2)_2$  on treatment with sodium *n*-propoxide in *n*-propanol gives the *trans*-compound,  $N_3P_3(NH_2)_2(OPr^n)_4$ , this being the first example of a rearrangement of this type in phosphazene chemistry.

The O → N alkyl group migration in alkoxyphosphazenes to yield oxophosphazanes is well established,<sup>1</sup> as are the *cis* ⇌ *trans* rearrangements in nongeminal aminochlorocyclotriphosphazatrienes.<sup>2</sup> We now report the first example of a geminal → *trans*-nongeminal migration of an amino (NH<sub>2</sub>) group.

Although no crystal structure is to date available for the diaminotetrachlorocyclotriphosphazatriene  $N_3P_3(NH_2)_2Cl_4$  (**1**), little doubt exists about its geminal nature, as two derivatives,  $N_3P_3(NH_2)_2F_4$ <sup>3</sup> (**2**) and  $N_3P_3(NPPh_3)_2Cl_4$ <sup>4</sup> (**3**), have been investigated by X-ray crystallography and were shown to have a geminal disposition of the two nitrogenous



substituents. The same geminal structure is deduced by  $^{31}P$  n.m.r. spectroscopy for the diamino compound (1).<sup>5</sup> Whilst proton coupling is not apparent at room temperature, the B part of the  $A_2B$   $^{31}P$  n.m.r. spectrum in acetone at  $\delta_B$  8.0 p.p.m. broadens at  $-85^\circ C$ .

Treatment of compound (1) with an excess of sodium *n*-propoxide in *n*-propanol at room temperature for 4 h, or at reflux for 1 h, gave a diaminotetra-*n*-propoxy derivative,  $N_3P_3(NH_2)_2(OPr^n)_4$ , of m.p.  $124^\circ C$ . This is not the expected geminal derivative (4) (R = Pr<sup>n</sup>), but has a nongeminal structure (5) as shown by a single-crystal *X*-ray structure determination.<sup>†</sup>

Its  $^{31}P$  n.m.r. spectrum ( $CDCl_3$ ) is of the  $A_2B$  type,  $\delta_A$  21.4,  $\delta_B$  16.5 p.p.m.,  $^2J(AB)$  66.4 Hz. The  $^1H$  n.m.r. spectrum ( $CDCl_3$ ) is very complex. The  $OCH_2$  region of the spectrum with  $^{31}P$  heteronuclear decoupling is shown in Figure 1. An initial spectrum suggested three environments (and hence a *cis*-structure) but following the *X*-ray crystallographic structure determination (see below), a longer accumulation time showed low intensity peaks (Figure 1), indicating that the apparent two low-field environments of the *n*-propoxy groups were the central two lines of an AB quartet, owing to the intrinsic asymmetry of the  $OCH_2$  protons. Both *n*-propoxy environments [ $P(OPr^n)_2$  and  $P(OPr^n)(NH_2)$ ] have this intrinsic

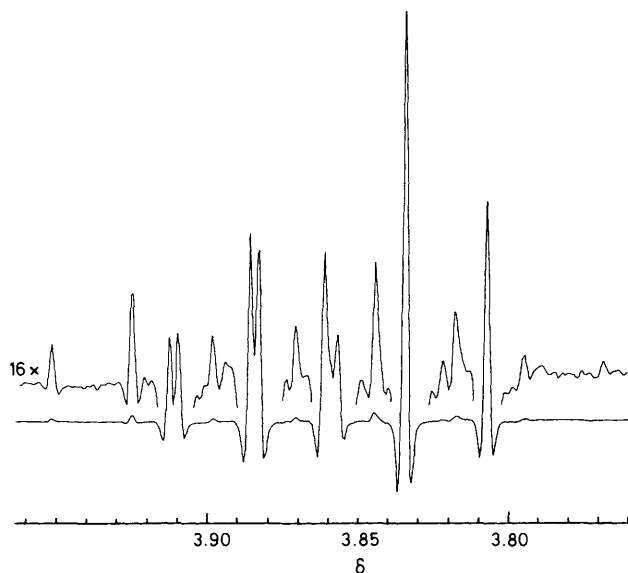


Figure 1.  $^1H$ -( $^{31}P$ ) N.m.r. spectrum of compound (5) showing the  $OCH_2$  region.

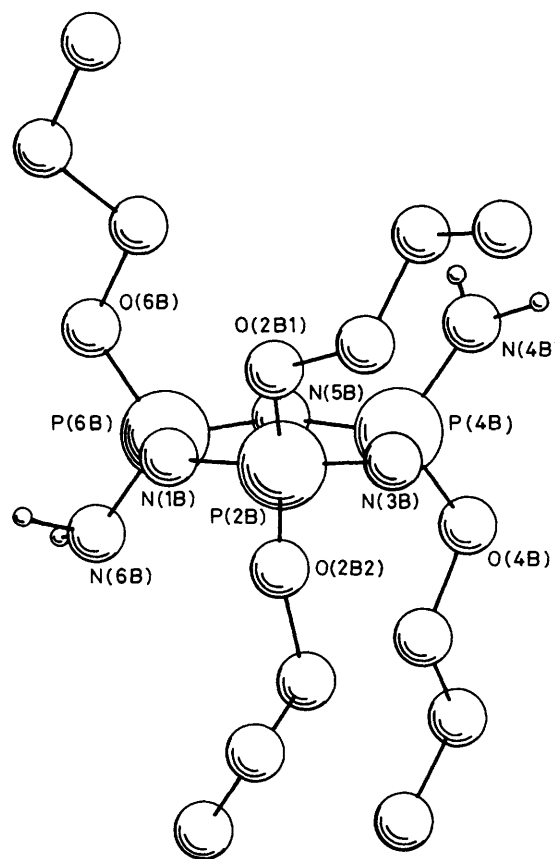


Figure 2. Molecular structure of compound (5) (only one molecule, of the two in the asymmetric unit is shown).

<sup>†</sup> Crystal data:  $N_3P_3(NH_2)_2(OPr^n)_4$  (5),  $M = 403.34$ ,  $F(000) = 3456$ , monoclinic, space group  $C2/c$ ,  $a = 27.842(4)$ ,  $b = 14.730(3)$ ,  $c = 21.912(5)$  Å,  $\beta = 94.36(2)^\circ$ ,  $U = 8960.52$  Å<sup>3</sup>,  $Z = 16$ ,  $D_c = 1.196$  g/cm<sup>3</sup>,  $\lambda(Mo-K\alpha) = 0.71069$  Å,  $\mu = 2.44$  cm<sup>-1</sup>,  $R = 0.10$  for 3263 unique reflections with  $I > 1.5\sigma(I)$ . The intensities were measured on an Enraf-Nonius CAD-4 diffractometer in the manner described elsewhere<sup>6</sup> using graphite-monochromatized  $Mo-K\alpha$  radiation in an  $\omega/2\theta$  scan mode with  $\theta$  in the range  $1.5$ – $25^\circ$ . The structure was solved by direct methods applying SHELX-84<sup>7</sup> and refined by least-squares. There are two crystallographically independent molecules in the asymmetric unit, both having *trans*-nongeminal arrangements of the  $NH_2$  groups. There are no significant structural differences between the two molecules. Hydrogen atoms of the  $NH_2$  groups were located experimentally and included with individual  $U_{iso}$  values (where N–H distances are fixed at 1.01 Å), but those on carbon atoms have not been included, since all the carbon atoms have high thermal parameters. All the non-carbon atoms were refined anisotropically and the carbon atoms isotropically with O–C and C–C distances fixed at 1.461 and 1.500 Å respectively. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

asymmetry, but only the one of the former has to date been observed [ $OCH_2$   $\delta$  3.89, 3.88 (intrinsic asymmetry), 3.84;  $CCH_2$  1.69, 1.68,  $CH_3$  0.95, 0.94]. The  $^{13}C$  n.m.r. spectrum ( $CDCl_3$ ) shows two environments [ $OCH_2$  67.05 (d), 66.46 (t);  $CCH_2$  24.03 (d), 24.08 (t);  $CH_3$  10.51, 10.46].

The structure of compound (5) is shown in Figure 2.<sup>8</sup>

Because of the thermal motion of the n-propoxy groups e.s.d.s are rather high. Nevertheless we can make the following statements. The ring P–N bond lengths are in the usual range (1.56–1.60 Å) for cyclophosphazenes. The exocyclic P–N bonds are longer (1.60–1.64 Å) and possibly significantly different from each other, as they are involved in a complex hydrogen-bonded system (which will be discussed elsewhere).

The above is thus the first recorded example in phosphazene chemistry in which a geminal P(NH<sub>2</sub>)<sub>2</sub> group rearranges to give two *trans*-nongeminal groupings P(NH<sub>2</sub>)(OPr<sup>n</sup>).

A similar reaction of the diamino compound (**1**) with sodium ethoxide in ethanol and with sodium n-butoxide in n-butanol gave predominantly the analogues (**6**) and (**7**) respectively of compound (**5**).

At present we have no evidence as to the mechanism of this rearrangement.

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