

Isolation, N.M.R. Spectra, and X-Ray Crystal Structures of two Isomeric $N_3P_3Cl_2[O(CH_2)_3O]_2$ Derivatives. The First Example of Dispiro/Spiro-Ansa Isomerism in Phosphazene Chemistry

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From the reaction of $N_3P_3Cl_6$ with 1,3-dihydroxypropane two isomeric $N_3P_3Cl_2[O(CH_2)_3O]_2$ derivatives were isolated, whose n.m.r. spectra suggest, and crystal structures prove, that they represent an example of dispiro/spiro-ansa isomerism, the first of its kind in phosphazene chemistry.

The reactions of difunctional reagents with cyclophosphazenes can give rise in principle to four types of structures:^{1,2} (i) spiro (both functional groups of reagent attached to the same phosphorus atom), (ii) ansa (the two functional groups attached to different phosphorus atoms in the same molecule), (iii) cross-linking (each functional group attached to different phosphazene rings) to give small units or polymers, (iv) only one functionality attached, the other free.

Spiro derivatives are now well documented synthetically,²⁻⁸ spectroscopically,²⁻⁸ and crystallographically.⁶⁻¹¹ Examples of cross-linking have been reported, e.g. $N_3P_3Cl_5[NH(CH_2)_4NH]N_3P_3Cl_5$,¹² as have cases of monofunctionality, e.g. $N_3P_3Ph_2(MeNCH_2CH_2OH)Cl_3$ and $N_3P_3Ph_2(MeNCH_2CH_2OH)_2Cl_2$.^{2,4}

Ansa structures had been ascribed erroneously¹³ to the products, $N_3P_3Cl_4[NH(CH_2)_nNH]$ ($n = 2,3,4$), of the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (1) with primary diamines, $H_2N(CH_2)_nNH_2$, ($n = 2,3,4$).¹³ These were later proven to be spiro structures,²⁻⁴ and this was subsequently confirmed by X-ray crystallography.⁹⁻¹¹

Authentic ansa structures proved to be elusive. A complicated three step synthesis was recently reported¹⁴ to yield $N_3P_3Cl_3Me[NH(CH_2)_3O]$ to which an ansa structure was ascribed. Structural details, were, however, not reported.

We now report two isomeric derivatives, $N_3P_3Cl_2[O(CH_2)_3O]_2$, obtained from the reaction of (1) with 1,3-dihydroxypropane. The compounds had different m.p.s., but identical mass spectrometric molecular weights (353) (calc. for $N_3P_3(^{35}Cl)_2O_4C_6H_{12}$ 353). Both compounds had ³¹P n.m.r. spectra (in $CDCl_3$, 85% H_3PO_4 as reference) of the A₂B type [(2) δ_A 8.3, δ_B 25.7 p.p.m., $|J_{AB}|$ 70.5 Hz; (3) δ_A 30.1, δ_B 9.1 p.p.m., $|J_{AB}|$ 73.7 Hz]. Both isomers had very complex ¹H n.m.r. spectra. Observation of the CCH₂ protons with

homonuclear decoupling of the OCH₂ protons gave a four-line AB pattern (δ_A 1.90, δ_B 2.09, $|J_{AB}|$ 14.3 Hz) for compound (2), Figure 1(a), and a similar four line AB pattern (δ_A 1.96, δ_B 2.19, $|J_{AB}|$ 16.0 Hz) together with an intense singlet (δ 1.90) for compound (3), Figure 1(b). (In both compounds further fine splitting due to ⁴J_{PH} was observed). The above data suggested a dispiro structure for compound (2) and a spiro-ansa one for compound (3), and confirmed the usefulness of the spiro protons for structural assignments.⁶ An X-ray structure analysis has confirmed the above.[†]

Compound (2) has a dispiro structure (Figure 2)¹⁸ with both phosphate rings in chair conformations. As in the monospiro

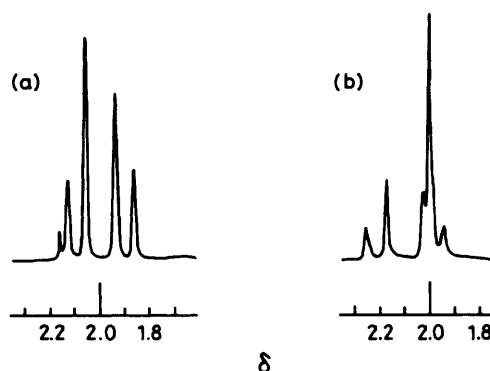
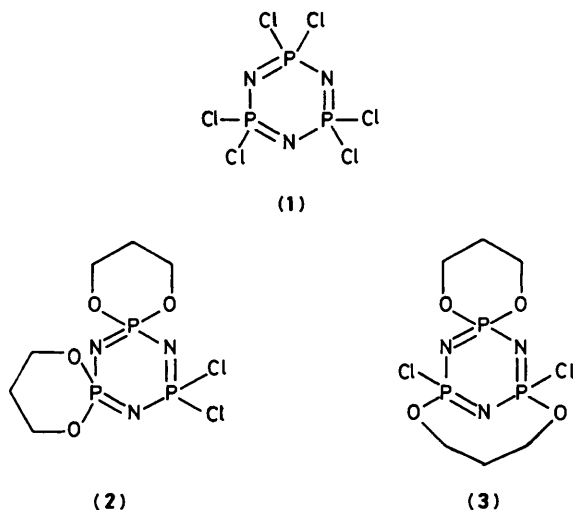


Figure 1. The ¹H n.m.r. (199.5 MHz, $CDCl_3$ solution, Me_4Si as reference) spectra of the CCH₂ groups (with homonuclear decoupling of the OCH₂ protons) of (a) the dispiro, (b) the spiro-ansa isomers of $N_3P_3Cl_2[O(CH_2)_3O]_2$.



[†] Crystal data, $N_3P_3Cl_2[O(CH_2)_3O]_2$: (2) [m.p. 227 °C (decomp.)], $M = 354.01$, $F(000) = 720$, orthorhombic, space group $Pnma$, $a = 10.316(2)$, $b = 13.752(3)$, $c = 9.670(3)$ Å, $U = 1371.9$ Å³, $Z = 4$, $D_c = 1.713$ g/cm³, $\lambda(Mo-K_\alpha) = 0.71069$ Å, $\mu = 8.3$ cm⁻¹, $R = 0.036$ for 962 unique reflections with $I \geq 1.5\sigma(I)$; (3) [m.p. 166–168 °C], $M = 354.01$, $F(000) = 720$, monoclinic, space group $P2_1/c$, $a = 10.096(1)$, $b = 8.692(1)$, $c = 15.778(3)$ Å, $\beta = 93.79(1)^\circ$, $U = 1381.7$ Å³, $Z = 4$, $D_c = 1.701$ g/cm³, $\lambda(Cu-K_\alpha) = 1.54178$ Å, $\mu = 73.95$ cm⁻¹, $R = 0.056$ for 2154 unique reflections with $I \geq 1.5\sigma(I)$. The intensities were measured on an Enraf-Nonius CAD-4 diffractometer in the manner described elsewhere¹⁵ using graphite monochromatized $Mo-K_\alpha$ and Ni-monochromatized $Cu-K_\alpha$ radiations in an $\omega/2\theta$ scan mode in the range θ 1.5–25 and θ 3–70° for the compounds (2) and (3) respectively. The structures were solved by direct methods applying SHELX-84¹⁶ and refined by least-squares. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms, located from difference maps, isotropically. An absorption correction was applied for (3).¹⁷

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.

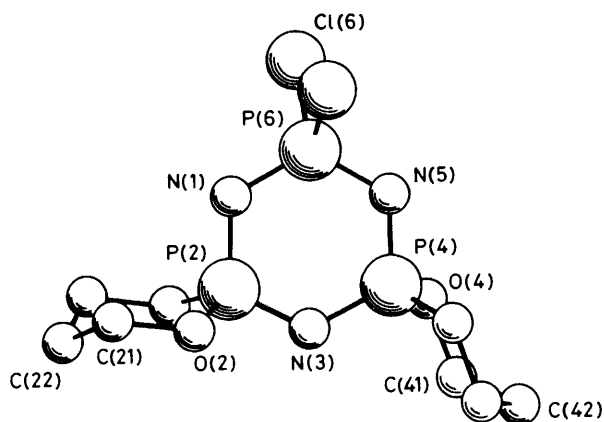


Figure 2. Molecular structure of the dispiro isomer (2).

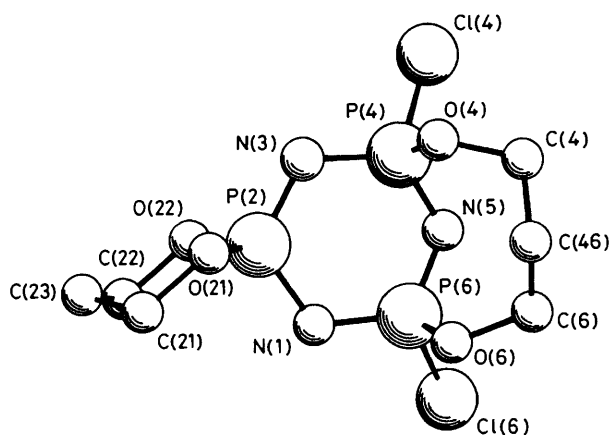


Figure 3. Molecular structure of the spiro-ansa isomer (3).

derivative, $N_3P_3Cl_4[O(CH_2)_3O]$,^{7,19} the P–N bond in the segment P(spiro)–N–P Cl_2 is longer at the spiro atom than that at the P Cl_2 centre.

Compound (3) has one dioxopropane moiety (at P-2) in a spiro chair conformation, the other as part of an eight-membered ring spanning P-4 and P-6 (Figure 3). The latter ring has a boat-chair conformation with the NP $_2$ O $_2$ C $_2$ moiety as the boat portion. This nitrogen atom (N-5) lies 0.523 Å below the plane of the other five atoms of the cyclotriphosphazatriene ring. The angle P-4–N-5–P-6 is small, 112.7(2)°, indeed the smallest endo nitrogen angle in a cyclotriphosphazene so far reported. By contrast the angle at N-3 in compound (2) is 124.2°, near the maximum value for P–N–P angles in cyclotriphosphazatrienes. The P–O bond distances in the spiro and ansa rings of compound (3) are the same

[1.579(2) and 1.568(3) Å respectively], but the P–O–C bond angles in the six-membered ring is considerably smaller [118.3(2)°] than the one in the eight-membered ring [121.9(2)°], the latter resembling the analogous angle in the seven-membered ring of $N_3P_3Cl_4[O(CH_2)_3O]$.^{7,19} Other crystallographic and spectroscopic details will be discussed elsewhere.

Compounds (2) and (3) represent the first authentic example of a spiro-ansa isomerism in phosphazene chemistry.

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