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Cyclen Phosphine Oxide: Hydrogen Bonding and Transannular N → P Interaction

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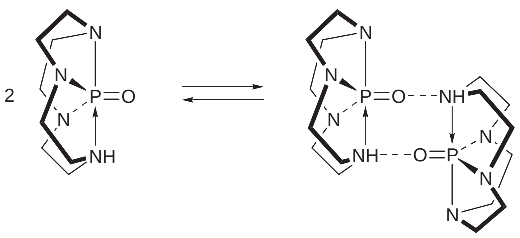
The crystal structure of cyclen phosphine oxide demonstrates the existence of an N → P interaction in the crystalline state.

In previous papers[1,2] we proposed a stoichiometric triprotection of tetraazamacrocycles, involving phosphoryl, thiophosphoryl and selenophosphoryl groups in order to mono-N-alkylate the ring. Compared to higher homologues, cyclen phosphine chalcogenides are known to possess unique properties[2,3] interpreted as the consequence of a transannular interaction. Furthermore, for the cyclen phosphine oxide **1a**, ^{31}P NMR observations have led one to suspect a monomer–dimer equilibrium in solution[4] (Scheme 1). Consequently, we wondered whether the monomeric form, **1a**, or the dimeric one, **2**, was responsible for this interaction. One of the best indications of such an interaction is the measurement of the N–P distance on the basis of the crystal structure of cyclen phosphine oxide.



1a **2**

Scheme 1

The X-ray analysis showed a dimeric structure in the crystal lattice with four water molecules; the dimeric entity is held by two intramolecular hydrogen bonds in a fairly rigid conformation (Fig. 1). In the dimer the transannular distances for each cyclen phosphine oxide moiety are 2.110 and 2.116 Å, respectively. These distances are, first, longer than single bonds between a pyramidal phosphorus and a tetrahedral nitrogen (*i.e.* 1.870 Å) and secondly, noticeably shorter than the sum of the van der Waals radii (3.41 Å): so, they clearly demonstrate a strong transannular interaction between the phosphorus and the free pseudoaxial nitrogen in the dimer.

However, in dilute $CDCl_3$ solutions, the ^{31}P chemical shift measured for the cyclen phosphine oxide monomer (δ 6.5) indicates a still noteworthy N → P interaction.

Finally, *ab initio* calculations helped us to grade the strength of this interaction. As they showed a shorter N–P distance in the dimer than in the monomer the interaction in the former is stronger. Moreover, the water molecules included in the dimeric structure are responsible for its stability, and consequently hydrogen bonding enhances the transannular interaction.

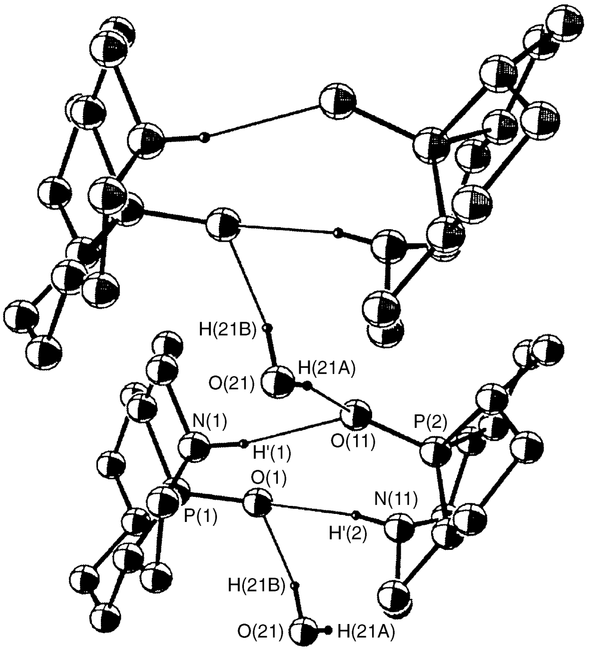


Fig. 1 View of the crystal structure along the [100] direction

Crystal Data.—$2C_8H_{17}NO_4P \cdot 4H_2O$, triclinic, space group $P\bar{1}$, $a = 7.739(10)$, $b = 8.706(10)$, $c = 20.918(4)$ Å, $\alpha = 85.64(8)$, $\beta = 79.88(6)$, $\gamma = 63.87(5)°$, $V = 1246(2)$ Å^3, $Z = 2$, $D_x = 1.345$ g cm^{-3}, $\mu = 2.22$ cm^{-1}; $F(000) = 544$; $T = 294$ K. Ranges of *h, k, l:* 0, 9; −10, 10; −24, 24. The sample was studied on a CAD 4 Nonius diffractometer with graphite monochromatized Mo-Kα radiation. Data collection gave 4744 reflections 4385 of which were independent ($R_{int} = 0.013$) with $I > 2\sigma(I)$. The data were corrected for Lorentzs-polarization effects. The structure was solved by direct methods (SIR 97) and refined by full matrix least-squares techniques based on 4385 observations and 392 variables which gave $R = 0.044$ and $R_w = 0.118$.

Techniques used: ^{31}P NMR, MS, X-ray diffraction, *ab initio* calculations

Fig. 1: ORTEP view of dimeric cyclen phosphine oxide

Fig. 2: View of the crystal structure along the [100] direction

Table 1: O–H···O(P) contacts involving water molecules

Table 2: Selected bond lengths (Å) and angles (°)

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Table 3: Transannular N–P distances calculated at HF/6-31G* level

Tables 4–6: Atomic coordinates, anisotropic displacement parameters, hydrogen coordinates

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