THE CONFORMATION AND REACTIVITY OF 1,3,2-DIOXAPHOSPHORINANES

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The conformation of alicyclic molecules is determined mainly by non-bonded interactions, as expressed in the theory of conformational analysis[1]. In the case of heterocyclic molecules however, electronic factors are important, and steric factors are *generally* small for dioxaphosphorinanes[2] (Table 1). A summary of some significant results of recent conformational studies on these molecules is given in Table 1.

Table 1.   The preferred conformations of some dioxaphosphorinanes[3]

| (I) | X—P⟨O...O⟩ | (II) | O=P with X and ⟨O...O⟩ |
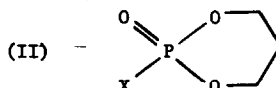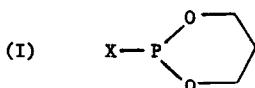
Axial   MeO (a); Cl (b); Me (c);   **Axial**   MeO (h); Cl (j); H (k)

Pr^1 (d); Ph (e)   **Equatorial** Me (ℓ); Ph (m); Me$_2$N (n)

Equatorial Me$_2$N (f); MeNH (g)

In this note we advance a general explanation of the conformational preference based on the main interactions of the lone pairs on the 1,3 oxygen atoms of a dioxaphosphorinane, with adjacent groups. Oxygen with local C_{2v} symmetry has lone pairs in b_1 and a_1 orbitals as shown by photoelectron spectroscopy[4] (e.g. on H_2O). Since the orbital of higher energy (b_1) is largely non-bonding, 2p, we shall assume this to be the important interacting orbital (termed n_0).

The main interactions involve repulsion between oxygen and phosphorus lone pairs ($n_0 - n_p$), between n_0 and the electrons in the PX bond ($n_0 - \sigma_{PX}$), and a hyperconjugative attraction ($n_0 - \sigma_{PX}^*$) involving the antibonding orbital of the P-X bond, similar to that which has been proposed to account for the axial conformation of some 1-substituted pyranoses (sometimes referred to as the *anomeric effect*[5]).

In addition, a secondary repulsion originating from the interaction of lone pairs on bonded atoms, e.g. oxygen and nitrogen, has to be considered. These perturbations are

shown diagrammatically in Fig. 1(i) - (v) and are greater when the appropriate orbital on phos-
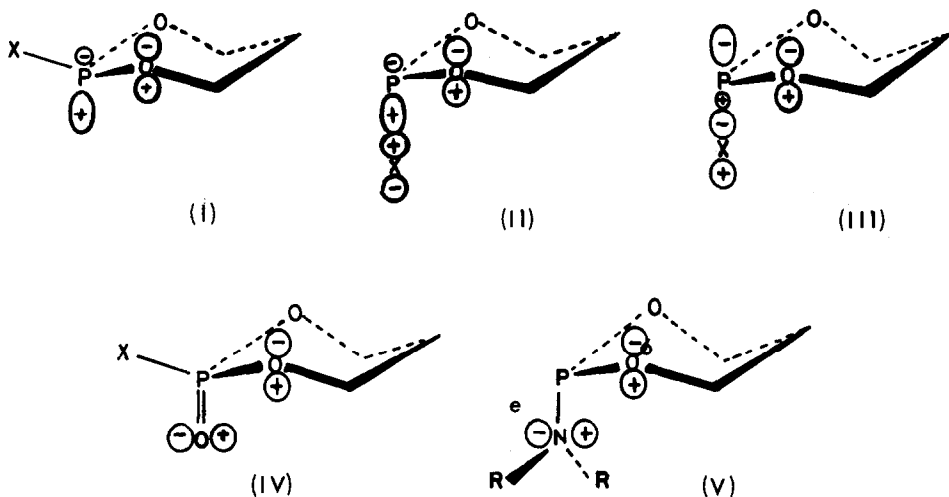phorus is in the axial position.

Fig. 1. Major interactions determining the conformation of 1,3,2-dioxaphosphorinanes

For tervalent phosphorus compounds the substituent on phosphorus *normally* adopts the axial
conformation in order to reduce $(n_O - n_P)$. When the phosphorus lone pair (n_P) is made to adopt
the axial position by the introduction of locking Me groups in the 4-and 6-positions (of I(a))
orbital splitting[6] occurs, raising the energy of the n_O- n_P orbital. This increases the
reactivity towards methyl iodide[7], and the basicity towards BH₃ as shown by the decrease in
B-H stretching frequency[8] from 2393 to 2382 cm^{-1}).

The equatorial conformation of the N-substituted phosphorinanes (f) and (g) may be due to
a dominant n_O-n_N interaction (Fig. 1(v)) involving the lone pair on nitrogen, since the iso-
propyl group (compound (d)) adopts the axial conformation.

The situation is more complex in the case of the 2-substituted 1,3,2-dioxaphosphorinane-
2-oxides (II). Here the differential interaction of the two groups substituted on phosphorus
with the oxygen lone pairs must be considered. Thus in the general case, the interactions (ii)
(iv) in Fig. 1 are relevant. For the full structures of these compounds, 1(ii) - 1(iii)
should be read to contain the equatorial P=O group. We shall analyse the problem by a simple

perturbation argument of the kind developed extensively elsewhere[9]. In order to limit the discussion we shall consider molecules II j and ℓ only as similar arguments can be applied to the other systems in Table 1. Comparing j and ℓ, the interactions 1(ii) and 1(iii) are important with X in the axial position.

Since the magnitude of a perturbation increases *inter alia* with an increase in the coefficient of an interacting atom, and with a decrease in the energy separation of the interacting orbitals, $\epsilon_1' > \epsilon_2'$; on the other hand, $\epsilon_1 > \epsilon_2$ since ϵ_1 and ϵ_2 are negative energies. Hence $(\epsilon_1 + \epsilon_1') > (\epsilon_2 + \epsilon_2')$, i.e. preference for the axial position is greater for a chlorine atom than for a carbon atom.
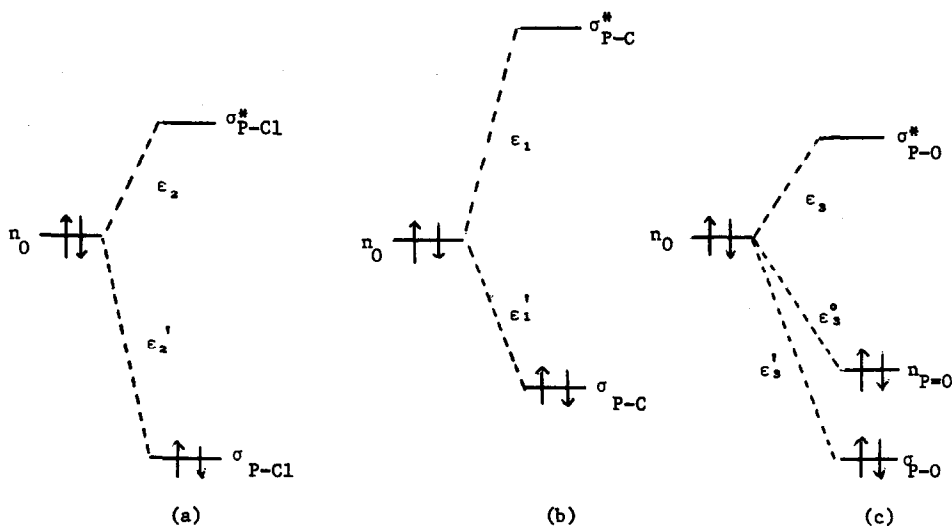

Fig. 2. Perturbations involving the cyclic oxygen 2p orbital (n) with axial bonds at phosphorus (a) chlorine (b) carbon (c) oxygen (P=O).

These interactions have to be compared with corresponding ones involving the axial P=O bond (Fig. 2(c)). To a first approximation we may assume that $(\epsilon_2' + \epsilon_2) \simeq (\epsilon_3' + \epsilon_3)$ since P-O and P-Cl bonds are of comparable polarity. This implies equal energies for conformations with Cl and O in the axial position. In addition however, a secondary interaction involving lone pairs n_{PO} on the phosphoryl oxygen atom and n_0 must be considered (see Fig. 1(iv)). This additional perturbation, ϵ_3°, increases the repulsion energy of the conformer with axial oxygen, and hence the conformer with chlorine axial is the more stable, i.e. $(\epsilon_3' + \epsilon_3^\circ + \epsilon_3) > (\epsilon_2 + \epsilon_2)$. With carbon in the axial position (Fig. 2(b)), the reverse is the case, i.e. $(\epsilon_1' + \epsilon_1) > (\epsilon_3' + \epsilon_3^\circ + \epsilon_3)$. We propose to call this general concept *orbital balance*.

The conformation of IIk may be examined in a similar manner. Here the situation is similar, although $(\epsilon_1' + \epsilon_1)$ is smaller for a P-H bond than for a P-CH₃ bond. The orbital balance is therefore changed so that $(\epsilon_3' + \epsilon_3^\circ + \epsilon_3) > (\epsilon_1' + \epsilon_1)_H$ where ϵ_1' and ϵ_1 refer to perturbations between n_0 and σ and σ^* orbitals of the P-H bond. A classical treatment of

course leads to the same conclusion in this case. The increased repulsion $(\epsilon'_s + \epsilon''_s)$ with axial P=O explains the increased basicity of the conformer of IIk with the P=O group locked in the unfavourable axial position by 4,6 substituents[3k]. Orbital splitting raises the energy of the lone pair on the phosphoryl oxygen atom which increases the interaction with the OH group of a phenol, as shown by the change in the vibrational frequency[3k] ($\Delta\nu_{OH}$ changes from 315 cm^{-1} to 345 cm^{-1} with a change from equatorial to axial oxygen). A detailed account of this and related work will appear shortly[10].

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