Conformations of Saturated Six-membered Ring Phosphorus Heterocycles. Non-chair Conformation for *cis*-2,5-Di-t-butyl-1,3,2-dioxaphosphorinan-2-one

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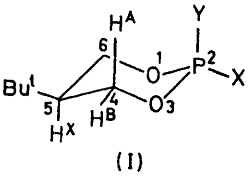
Summary Results of ^1H n.m.r. analyses indicate that the free-energy difference between certain chair and boat conformations of the *cis*-2,5-di-t-butyl-1,3,2-dioxaphosphorinan-2-one ring system is unusually low, perhaps 1 kcal/mol or less.

BOAT and twist forms of common six-membered saturated rings such as cyclohexane[1] and 1,3-dioxan[2] are normally 5—6 kcal/mol higher in free energy (ΔG°_{25}) than the corresponding chair conformations. ΔH° (chair → boat) for these systems is roughly that estimated from the rotational barriers in propane[3] and dimethyl ether.[4] For other heterocycles it is expected that ΔG°_{25} (chair → boat) may be more or less than 5—6 kcal/mol depending primarily on as yet unknown rotational barriers and to a lesser degree on non-bonded interactions.

We report here the interesting and perhaps surprising finding that for certain 1,3,2-dioxaphosphorinan-2-one ring systems the energy of a boat or twist conformation is unusually close to that of the corresponding chair. This conclusion rests on the following evidence.



(I)

a; $Y = OMe$ $X = O$
b; $Y = O$ $X = OMe$
c; $Y = Me$ $X = O$
d; $Y = O$ $X = Me$
e; $Y = Bu^t$ $X = O$
f; $Y = O$ $X = Bu^t$

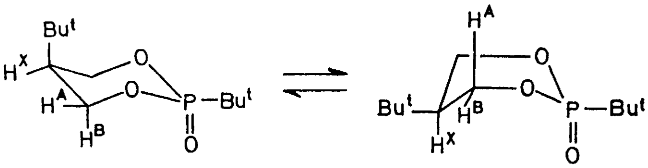
Previous work[5] had shown that for the series (Ia)—(Id), chair conformers with the 5-t-butyl group equatorial predominate. ^{1}H N.m.r. parameters for (Ie) and (If) in which phosphorus carries a bulky t-butyl group appear in the Table. Those for the *trans*-isomer (If) are as expected[5,6] for a chair conformer with both t-butyl groups equatorial. For the *cis*-isomer (Ie) the values of J_{AX} and J_{BX} are again consistent with a structure which has the 5-t-butyl oriented predominantly equatorial (or pseudoequatorial). However, J_{AP} and J_{BP} are now equal indicating a drastic change in the ring conformation at the phosphorus end of the molecule. The simplest explanation of these parameters is that (Ie) exists in solution in a boat conformation (II) ($\angle$ H^{A}COP = $\angle$H^{B}COP = *ca.* 120°).

TABLE. ^{1}H *N.m.r. parameters* (If) *and* (Ie)[a]

Compound	Coupling constants (J/Hz)[b]					Chemical shifts (δ)[c]		
	J_{AB}	J_{AX}	J_{BX}	J_{AP}	J_{BP}	H^X	H_A	H_B
(If)	−11	11	4·3	1·2	19	1·98	4·43	4·25
(Ie)	−10	10	5·0	10	10	2·46	4·11	4·49

[a] From inspection of first-order spectra taken in $CDCl_3$ at 220 MHz. Values were cross-checked by simulation of the 60 MHz spectra using the LAOCN3 program and plotting routine but were not iterated. [b] Absolute values reported except for J_{AB}, assumed negative. [c] In p.p.m. downfield from internal Me_4Si.

Evidently the *syn–axial* nonbonded interactions imposed on the chair conformation (Ie) by the axial 2-t-butyl are relieved by inversion of the phosphorus end of the ring to give (II). Alternatively, such strain could be relieved by complete ring inversion to give (III). That (III) is not present in major amounts is shown by the J_{AX} and J_{BX} values.



(III) (II)

For the equilibrium (III) ⇌ (II), ΔG°(III → II), may be broken up into two contributing terms: that for the axial → equatorial reorientation of the 5-t-butyl, $\Delta G^\circ(a \rightarrow e)$; and that for the chair → boat interconversion, ΔG°(c → b).

$$\Delta G^\circ(\mathrm{III} \rightarrow \mathrm{II}) = \Delta G^\circ(a \rightarrow e) + \Delta G^\circ(\mathrm{c} \rightarrow \mathrm{b}) \qquad (1)$$

From the values of J_{AX} and J_{BX} in the Table, a reasonable estimate of the lower limit of the ratio of (II) to (III) at ambient n.m.r. probe temperature would be 4:1. Thus, ΔG°(III → II) *ca.* −0·8 kcal/mol. Measurements of ΔG°-$(a \rightarrow e)$ in analogous 5-t-butyl-1,3-dioxans[7] and certain cyclic sulphites[8] are in the range −1·5 to −1·8 kcal/mol at temperatures of 25—40°. Thus, from equation (1), ΔG°-(c → b) is estimated to be *ca.* 1 kcal/mol.

The possibility that undetermined percentages of non-chair conformers might be present with some 1,3,2-dioxaphosphorinans had been suggested previously.[6a,9] However, the above data on compounds (Ie) and (If) provide the first clear spectral evidence for this as well as an estimate of ΔG°(chair → boat) at ambient temperature. It must be strongly emphasised that *cis*-2,5-di-t-butyl-1,3,2-dioxaphosphorinan-2-one may well represent a special case. ΔG°-$(a \rightarrow e)$ in equation (1) may be considerably more negative than indicated as molecular models suggest than in (III) expected flattening of the ring about phosphorus could give rise to steric interaction between the 2- and 5-t-butyl groups.

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