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$Eu(fod)_3$ Induced ${}^3J_{HP}$ Variation and Conformational Changes in Seven-membered-ring Phosphates

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Summary A conformational equilibrium between the two chair forms, (2a) and (2b), has been established for the 3-substituted 1,5-dihydro-2,4,3-benzodioxaphosphepin 3-oxides (1) with the aid of Eu(fod)₃, which caused a large variation of ${}^{3}J_{\rm HP}$ attributable to the increase of the axial phosphoryl conformer.

MANY studies of six-membered-ring phosphorus heterocycles have been reported, but larger homologues have received little attention. While carrying out a conformational analysis of the 3-substituted 1,5-dihydro-2,4,3benzodioxaphosphepin 3-oxides (1)[†] we observed a variation of ${}^{3}J_{\rm HP}$ on addition of the lanthanide shift reagent, from which conformational aspects of this mobile system were deduced.

¹H N.m.r. data are shown in the Table. Coupling constants were determined from the AB part of an ABX (X=P) pattern. Spectra are simplified to an AMX type with the Eu or Pr reagent which co-ordinates at the phosphoryl oxygen. Plots of chemical shifts vs. [shift reagent]/ [1] are linear.



While the geminal coupling constant, J_{AB} , remains constant, the two sets of ${}^{3}J_{HP}$ vary greatly and in a comple-

 $^{+}$ 3-Chloro-1,5-dihydro-2,4,3-benzodioxaphosphorepin 3-oxide (1a), m.p. 135—139°, was prepared from phthalyl alcohol and phosphorus oxychloride. Treatment of (1a) with methanol or phenol gave methyl (1b), m.p. 126·5—128°, and phenyl phosphates (1c), m.p. 96—97°. Satisfactory analytical and spectral data were obtained for these compounds.

mentary manner. This is not expected from a consideration of substituent effects¹ and suggests perturbation to the conformational equilibrium.²

The stable conformation of the cycloheptenes and their benzologues is the chair form.³ Our results (Table) show an equilibrium between the two chair forms, (2a) and (2b), following from a Karplus-like correlation⁴ between ${}^{3}J$ (POCH) and the dihedral angles (\angle POCH_{ax} 30°, \angle POCH_{eq} 150°).

Compound (1c) exists predominantly in the chair form (2a; X=OPh). This is supported by $v_{P=0}$ (1320 cm⁻¹ in possibly reflecting a greater stability of the conformer (2a)and a decreased basicity of the phosphoryl oxygen due to the electronegative chlorine atom.

The methyl ester (1b) shows $v_{P=0}$ at 1285 cm⁻¹ as a broad peak, indicating conformational mixtures. Without the shift reagent, the ${}^{3}J_{\rm HP}$ values are similar. That this is not due to other conformers such as twist-boat, but is caused by the presence of two chair forms in nearly equal amounts, can be proved by Eu(fod)₃ addition. The shifted spectrum shows the presence of a greater proportion of (2b; X =OMe).§

Compound	[Eu(fod) ₃]/[substrate]	$J_{{ m AB}}$	J_{AP}	J_{BP}	δ	$\delta_{\mathbf{B}}$	$\delta_{\mathbf{B}} - \delta_{\mathbf{A}}$
(1 a)	0	13.3	10.6	29.6	5.45	5.07	-22.4
	0.2	13.4	10.2	28.9			-24.2
	0.4	13.3	11.2	28.7			-16.3
	0.6	a	a	<u>a</u>			-11
(1b	0 ^b	13.7	15.0	16.7	5.]	15	0
	0.2	13.6	15.8	16.3			42.1
	0.4	13.8	17.1	15.6			81.5
	0.8	13.8	18.5	13.8			151.5
(1c)	0	$13 \cdot 2$	10.0	23.3	5.31	5.20	-6.6
	0.2	13.3	14.7	17.7			39.1
	0.45	13.7	16.3	16.0			103.5
	0.66	13.7a.c	a	14.6d			143
	0.83	13.7a.c	a	13·7ª			182

TABLE.	Chemical	shifts	and	coupling	constants	in	CDCl ₃
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^a Obscured by phenyl protons. ^b A small amount of Eu(fod)_a was added to determine J's. ^c Estimated. ^d JAB was assumed to be 13.7 Hz.

 CCl_4 , eq-P=O) and the constancy of the ${}^{3}J_{HP}$ values even at -60° . Eu(fod)₃ addition shifts the equilibrium to the (2b; X = OPh) side.[‡] Increase of (2b) should result in an averaging of ${}^{3}J_{\text{HP}}$ and a greater downfield shift of the axial proton H_B than for H_A . This is found to be the case. Equatorial co-ordination would not be expected to show such a large $\Delta \delta_{AB}$.

General trends are followed with (1a, $v_{P=0}$ 1306 cm⁻¹) but the equilibrium appears not to be seriously perturbed,

Saturated seven-membered-ring phosphates undergo pseudo-rotation between twist-boat forms, as indicated by the time-averaged coupling constants found for 2-methoxy-(b.p. 92—93.5°/0.5 mm, J_{AB} 12.0, J_{AP} 16.8, J_{BP} 16.2 Hz) and 2-phenoxy-1,3,2-dioxaphosphepan 2-oxides (b.p. 146- $148^{\circ}/0.2$ mm, J_{AB} 11.9, J_{AP} 16.5, J_{BP} 16.8 Hz).

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 \ddagger An equilibrium point is determined by the equatorial preference of the P=O group and the steric effects of a substituent on phosphorus. The geometrical preference of P=O appears to be lost by complexation with the Eu reagent, which modifies the nature of P=0 bonding.

In support of the axial phosphoryl preference on Eu(fod)₃ addition, a constant value for J_{HP} was reported for a six-membered-ring phosphonate in which the phosphoryl group is axially oriented in the stable form (K.C. Yee and W. G. Bentrude, *Tetrahedron* Letters, 1971, 2775).

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