6. Bugge, A., Gestblom, B. and Hartmann, O. *Acta Chem. Scand.* **24** (1970) 105.
7. Bugge, A., Gestblom, B. and Hartmann, O. *Acta Chem. Scand.* **24** (1970) 1953.
8. Bugge, A. *Acta Chem. Scand.* **25** (1971) 27.
9. Wright, Jr., W. B. *J. Heterocycl. Chem.* **9** (1972) 879.
10. Mikailovic, M. L. J. and Tot, M. *J. Org. Chem.* **22** (1957) 652.
11. King, W. J. and Nord, F. F. *J. Org. Chem.* **14** (1949) 405.
12. Paulmier, C. and Pastour, P. *Compt. Rend.* **C 265** (1967) 926.
13. Yur'ev, Yu. K., Magdesieva, N. N. and Monakhova, A. T. *Khim. Geterotsikl. Soedin.* **4** (1968) 645.
14. Gronowitz, S. and Michael, U. *Arkiv Kemi* **32** (1970) 283.

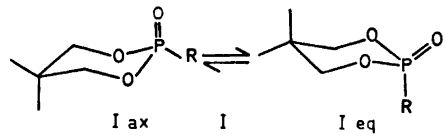
Received August 29, 1972.

Lanthanide Induced Chemical Shifts in 5,5-Dimethyl-1,3,2-dioxaphosphorinan-2-ones with Respect to the Conformational Preference of the 2-Substituent

A. J. DALE

Chemical Institute, University of Bergen, N-5000 Bergen, Norway

Although exeptions occur,[1,2] the majority of work considering configuration/conformation in substituted or unsubstituted 1,3,2-dioxaphosphorinan-2-ones shows that the geometrical arrangement which gives the thermodynamically most stable molecule, is a chair-like structure, presumably flattened at the phosphorus end of the ring.[2-7] The stereochemistry around the phosphorus atom, that is, whether the 2-substituent is axially or equatorially oriented, is, however, open to question. In cases where crystal structures have been determined, the P=O bond is uniformly oriented equatorially. This need not be the situation in solution. Generally, an equilibrium between two conformers, having the P=O bond axial and equatorial, respectively, should be considered, *i.e.*, for 5,5-dimethyl-1,3,2-dioxaphosphophorinan-2-ones:



I ax I I eq

The potential of lanthanide NMR shift reagents for assignment of protons in complex molecules is now well documented.[8] In principle, these applications are based on the equation:

$$\Delta\nu_i = K(3\cos^2\phi_i - 1)R_i^{-3} \qquad (1)$$

where K is a constant, $\Delta\nu_i$ is the chemical shift induced in proton H_i on complexation of the substrate with the shift reagent, R_i the distance between the proton H_i and the lanthanide in the complex, and ϕ_i the angle between the vector R_i and the principal axis of the complex.

According to eqn. 1, the chemical shifts induced in I on complexation at the phosphoryl-oxygen will depend on the relative contributions from conformers Ia and Ib. Thus there is the possibility of obtaining information with respect to the axial/equatorial preference of the P=O bond in this type of compounds, as proposed by Yee and Bentrude in an article reporting the use of Eu(dpm) for simplifying the NMR spectrum of *trans*-2-methyl-5-*tert*-butyl-1,3,2-dioxaphosphorinan-2-one.[9]

On this background, the derivatives listed in Table 1 have been prepared, and their chemical shifts, ν_i, measured as a function of mol fraction, x, of the shift reagent Eu(fod)$_3$.[10] In all experiments the substrate concentration was kept constant equal to 0.100 M.

The effect of adding Eu(fod)$_3$ to CCl_4 solutions of compounds Ia and Id is illustrated in Fig. 1. As for the other derivatives studied, there is a linear ν/x-dependence in the low concentration range of the shift reagent. The ν/x-slope in this region of x can therefore be taken as a quantitative measure for the changes in chemical shifts caused by complexation with Eu(fod)$_3$. These slopes, the k-values, are listed in Table 1, together with the POCH coupling constants.

It is seen from Table 1 (but more clearly from diagrams) that derivatives Ia–Ic generate qualitatively very similar ν/x-

Table 1. Eu(fod)$_3$ NMR data [a] for compounds Ia-Id and II.

Compound	Solvent	k(Hz/mol fract. shift reagent)					J(POCH$_A$)		J(POCH$_B$)	
		$(CH_3)_A$	$(CH_3)_B$	H_A	H_B	r	$x=0$	$x=1$	$x=0$	$x=1$
R=CH_3	CCl_4	85	155	205	435	2.1	17	20	6	3
Ia	$CDCl_3$	55	115	145	295	2.0	15	19	8	3
R=CH_2Ph	CCl_4	70	110	150	310	2.1	17	20	5	2
Ib	$CDCl_3$	50	100	130	250	1.9	15	19	7	3
R=Ph	CCl_4	110	190	220	600	2.7	17	20	6	3
Ic	$CDCl_3$	35	135	145	315	2.2	13	19	10	5
R=Cl	CCl_4	110	160	230	260	1.2	27 [b]	27	3 [b]	3
Id	$CDCl_3$	95	135	160	210	1.3	27 [c]	27	3 [c]	2
II	CCl_4	160	230	340	770	2.3				

[a] A and B denote, respectively, the higfield and lowfield signals.
[b] $x=0.30$.
[c] $x=0.22$.

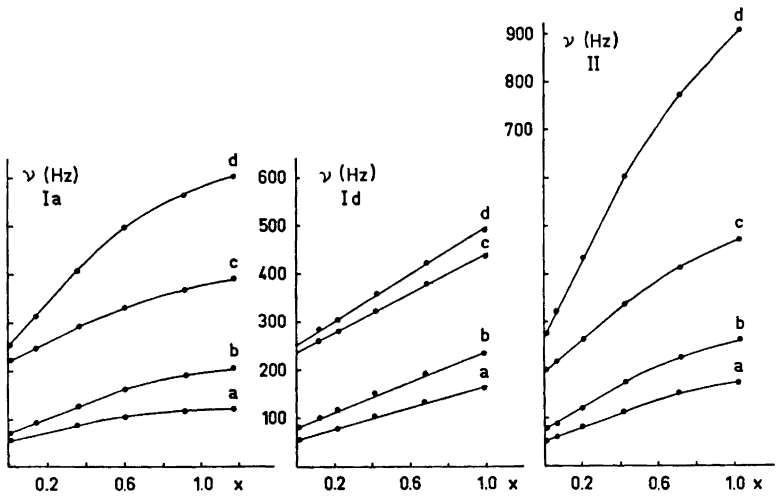


Fig. 1. ν/x-plots (CCl_4) for compounds Ia, Id, and II. a: high field methyl group. b: low field methyl group. c: high field methylene proton. d: low field methylene proton.
Chemical shifts (Hz) are downfield from internal TMS, and were measured by means of a JEOL JNM-C-60H spectrometer operating at 60 MHz.

plots. Tentatively this would mean that the type of contributing conformers are the same for these compounds. Considering chair forms only, eqn. 1 applied to a molecular model shows that a much greater differentiation of the shifts induced in the methylene protons on $Eu(fod)_3$ complexation is to be expected when the P=O bond is oriented axially as compared to the alternative equatorial orientation. More quantitatively, this differentiation can be expressed by the ratio of the k-values for the methylene protons, the r-value, Table 1. On this basis, the obtained results indicate that Iax is the main contributing conformer in derivatives Ia–Ic. Additional support for this conclusion is obtained when observing the $Eu(fod)_3$ induced shifts in 2,2-dimethyl-1,3-propanediol cyclic sulfite (II), a compound for which the axial preference of the SO-oxygen seems to be established.[11–13] The v/x-plot obtained for II, Fig. 1, is qualitatively similar to the plots for Ia–Ic, an observation which provides strong evidence for analogous conformation in these two classes of compounds.

The postulated axial preference of the P=O bond for Ia–Ic is also consistent with the relative large difference between the vicinal POCH coupling constants, indicating the dominance of either Iax of Ieq.

When changing the solvent from CCl_4 to $CDCl_3$, there is generally a decrease in the r-value, indicating a displacement of the conformational equilibrium towards Ieq. Such a change in the conformer ratio should be reflected in a convergence of the POCH couplings, an expectation which is born out, Table 1.

A comparison of the POCH coupling constants for compounds Ia–Ic at $x=0$ and $x=1$ shows that the addition of $Eu(fod)_3$ causes the difference between them to increase. This trend is observed in CCl_4 as well as in $CDCl_3$, and must be interpreted in terms of a displacement of the conformational equilibrium towards Iax. This interpretation is strongly supported by the fact that the POCH coupling constant for a 0.1 M solution of $(CH_3O)_3P$=O in CCl_4 is virtually unaffected by the presence of $Eu(fod)_3$.

The change in the coupling constants above can therefore not be explained as a result of a contact contribution caused by complexation. Regardless of this somewhat unfavourable result, that the addition of $Eu(fod)_3$ to some extent distorts the equilibrium under investigation, the conclusions considering the conformational preference of the P=O bond should still be valid. The ability of $Eu(fod)_3$ to influence the conformational equilibrium has very recently been demonstrated for the *trans* isomers of 2-R-5-*tert*-butyl-1,3,2-dioxaphosphorinan-2-one (R=Ph, CH_3).[14]

The very different POCH couplings found for Id indicate the presence of a single conformer. This conclusion is further supported by the invariance of these coupling constants on changing the solvent from CCl_4 to $CDCl_3$ or on adding $Eu(fod)_3$ in either of these solvents. On the other hand, the v/x-curves in CCl_4 show that the contribution from Iax cannot be significant. Consequently, as fas as only chair forms are considered, the conformation of Id must be a chair with the P=O bond equatorial.

1. Bentrude, W. G. and Yee, K. C. *Chem. Commun.* **1972** 169.
2. White, D. W., McEven, G. K., Bertrand, R. D. and Verkade, J. G. *J. Chem. Soc.* **B 1971** 1454.
3. Kainosho, M. and Shimozawa, T. *Tetrahedron Letters* **1969** 865.
4. Katritzky, A. R., Nesbit, M. R., Michalski, J., Tulimowski, Z. and Zwierzak, A. *J. Chem. Soc.* **B 1970** 140.
5. Bentrude, W. G. and Hargis, J. H. *Chem. Commun.* **1969** 1113.
6. Majoral, J. P., Pujol, R., Navech, J. and Mathis, F. *Tetrahedron Letters* **1971** 3755.
7. Majoral, J. P., Pujol, R. and Navech, J. *Bull. Soc. Chim. France* **1972** 606.
8. For references, see Corio, P. L., Smith, S. L. and Wasson, J. R. *Anal. Chem.* **44** (1972) 413 R.
9. Yee, K. C. and Bentrude, W. G. *Tetrahedron Letters* **1971** 2775.
10. Rondeau, R. E. and Sievers, E. R. *J. Am. Chem. Soc.* **93** (1971) 1522.
11. Edmundson, R. S. *Tetrahedron Letters* **1965** 1649.
12. Green, C. H. and Hellier, D. G. *J. Chem. Soc. Perkin Trans. 2* **1972** 458.
13. Van Woerden, H. F. and Havinga, E. *Rec. Trav. Chim.* **86** (1967) 341.
14. Bentrude, W. G., Tan, H. W. and Yee K. C. *J. Am. Chem. Soc.* **94** (1972) 3264.

Received July 14, 1972.