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 exceptions occur,¹ 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 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-dioxaphosphorinan-2-ones:

\[
\begin{align*}
\Delta \nu_l &= K(3 \cos^2 \phi_l - 1) R_1^{-3} \\
\end{align*}
\]

where \( K \) is a constant, \( \Delta \nu_l \) is the chemical shift induced in proton \( H_l \) on complexation of the substrate with the shift reagent, \( R_1 \) the distance between the proton \( H_l \) and the lanthanide in the complex, and \( \phi_l \) the angle between the vector \( R_1 \) and the principal axis of the complex.

According to eqn. 1, the chemical shifts induced in 1 on complexation at the phosphoryl-oxygen will depend on the relative contributions from conformers 1a and 1b. 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.³

On this background, the derivatives listed in Table 1 have been prepared, and their chemical shifts, \( \nu_l \), measured as a function of mol fraction, \( x \), of the shift reagent Eu(fod)₃.⁴ In all experiments the substrate concentration was kept constant equal to 0.100 M.

The effect of adding Eu(fod)₃ to CCl₄ solutions of compounds 1a and 1d is illustrated in Fig. 1. As for the other derivatives studied, there is a linear \( \nu/x \)-dependence in the low concentration range of the shift reagent. The \( \nu/x \)-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 1a—1e generate qualitatively very similar \( \nu/x \)-
Table 1. Eu(fod)_2 NMR data for compounds Ia-Id and II.

| Compound | Solvent | \( k \) (Hz/mol fraction shift reagent) \( (\text{CH}_3)_A \) | \( (\text{CH}_3)_B \) | \( H_A \) | \( H_B \) | \( r \) | \( J(\text{POCH}_A) \) \( x=0 \) | \( J(\text{POCH}_A) \) \( x=1 \) | \( J(\text{POCH}_B) \) \( x=0 \) | \( J(\text{POCH}_B) \) \( x=1 \) |
|----------|---------|----------------|----------------|------|------|-------|--------------|--------------|--------------|--------------|--------------|
| R=CH₃    | CCl₄    | 85  | 155 | 205 | 435 | 2.1  | 17  | 20  | 6  | 3  |
| Ia       | CDCl₃   | 55  | 115 | 145 | 295 | 2.0  | 15  | 19  | 8  | 3  |
| R=CH₄Ph  | CCl₄    | 70  | 110 | 150 | 310 | 2.1  | 17  | 20  | 5  | 2  |
| Ib       | CDCl₃   | 50  | 100 | 130 | 250 | 1.9  | 15  | 19  | 7  | 3  |
| R=Ph     | CCl₄    | 110 | 190 | 220 | 600 | 2.7  | 17  | 20  | 6  | 3  |
| Ic       | CDCl₃   | 35  | 135 | 145 | 315 | 2.2  | 13  | 19  | 10 | 5  |
| R=Cl     | CCl₄    | 110 | 160 | 230 | 260 | 1.2  | 27  | 27  | 3  | 3  |
| Id       | CDCl₃   | 95  | 135 | 160 | 210 | 1.3  | 27  | 27  | 3  | 2  |
| II       | CCl₄    | 160 | 230 | 340 | 770 | 2.3  |

\( a \) A and B denote, respectively, the highfield and lowfield signals.

\( b \) \( x=0.30 \).

\( c \) \( x=0.22 \).

Fig. 1. \( \nu/\text{x} \)-plots (CCl₄) 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, 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 1a — Ic. Additional support for this conclusion is obtained when observing the Eu(fod)$_3$ induced shifts in 1,2-dimethyl-1,3-propanediol cyclic sulfite (II), a compound for which the axial preference of the SO-$\gamma$-oxygen seems to be established. The $r/s$-plot obtained for II, Fig. 1, is qualitatively similar to the plots for 1a — 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 1a — Ic is also consistent with the relative large difference between the axial POCH coupling constants, indicating the dominance of either Iax or 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 1a — 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$_3$)$_2$P=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 Ic 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 $r/s$-curves in CCl$_4$ show that the contribution from Iax cannot be significant. Consequently, as far as only chair forms are considered, the conformation of Ic must be a chair with the P=O bond equatorial.

8. For references see Corio, P. L., Smith, S. L. and Wasson, J. R. Anal. Chem. 44 (1972) 413 R.

Received July 14, 1972.