# Effect of Chiral Solvents on $^{31}$P Nuclear Magnetic Resonance Spectra of Diastereoisomeric Pyrophosphoramides

By Melvin D. Joesten,*† Howard E. Smith, and Vernon A. Vix, jun.
*(Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235)*

*Summary* The sensitivity of $^{31}$P n.m.r. to differences in magnetic environment caused by association of a chiral solvent with enantiomeric pyrophosphoramides is demonstrated.

$^1$H Nuclear magnetic resonance is useful in distinguishing enantiomers with asymmetrically substituted carbon or nitrogen atoms.[1,2] However, no report has appeared on the use of n.m.r. to examine the effect of chiral solvents on the resonances of an asymmetric atom.

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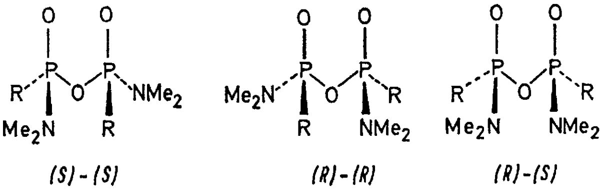
† On leave during 1972—1973 at Trinity College, Dublin, Ireland.

We reported previously that the proton-decoupled $^{31}P$ n.m.r. spectrum of *PP'*-di-isopropyl-*NNN'N'*-tetramethylpyrophosphoramide (I) as the neat liquid consists of two sharp singlets of about equal intensity separated by 18 Hz.[3] These were assigned, respectively, to the racemic modification [(*S*,*S*)-(I) and (*R*,*R*)-(I)] and to the *meso* form [(*S*,*R*)-(I)].



(I) R = Pr$^{i}$
(II) R = Et
(III) R = OEt

In the present work the effect of chiral solvents on the proton-decoupled $^{31}P$ n.m.r. spectrum of (I) has been examined. When racemic 2,2,2-trifluoro-1-phenylethanol[4] is used as the solvent, the two signals are separated by 7 Hz (Figure).‡ The use of either (*S*)-(+)- or (*R*)-(−)-2,2,2-trifluoro-1-phenylethanol[2,4] causes a 1 Hz splitting of the higher field signal (Figure). Theoretically a splitting of both $^{31}P$ signals would be expected since, for example, association of (*R*)-(+)-2,2,2-trifluoro-1-phenylethanol with each asymmetric phosphoryl site would give *R* ··· *S*–*S* ··· *R* and *R* ··· *R*–*R* ··· *R* for the racemic pair and *R* ··· *R*–*S* ··· *R* for the *meso* form. The main difference between the two would be the additional possibility of coupling of the nonequivalent phosphorus atoms in the *meso* form. This possibility was checked by obtaining Fourier transform n.m.r. spectra of (I) in racemic and in optically active 2,2,2-trifluoro-1-phenylethanol. The spectra were identical with those illustrated in the Figure, and there was no evidence of the AB doublet of doubles expected if coupling were present in the *meso* form.

The effects of the R group in (I) and of the chiral solvent were also investigated. The Fourier transform n.m.r. spectrum of (II) in optically active 2,2,2-trifluoro-1-phenylethanol gives a splitting of the high-field signal of 0·4 Hz while no splitting of the high-field signal was observed for (III) in this same solvent. When (*S*)-(−)-α-phenylethylamine is used as the solvent, both $^{31}P$ signals of (I) remain as sharp singlets. Thus the steric influence or basicity of the R group and the acidity of the solvent affect the splitting pattern.

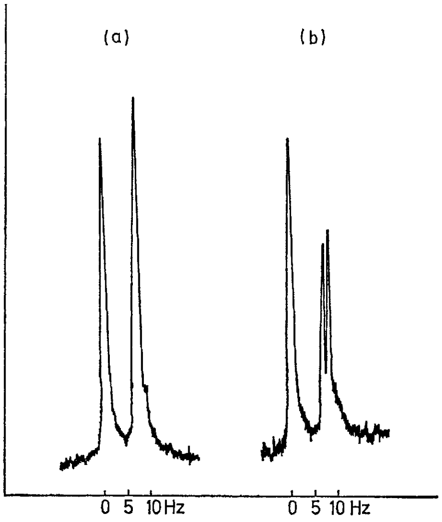


FIGURE. (a) *Proton-decoupled* $^{31}P$ *n.m.r. spectrum at* ca. 45° *of* PP'-*di-isopropyl*-NNN'N'-*tetramethylpyrophosphoramide mixed with racemic* 2,2,2-*trifluoro*-1-*phenylethanol* (1 : 10 *mol ratio*). δ *relative to* 85% $H_3PO_4$, −36·27 *and* −36·44. (b) *Proton-decoupled* $^{31}P$ *n.m.r. spectrum at* 45° *of* PP'-*di-isopropyl*-NNN'N'-*tetramethylpyrophosphoramide mixed with* (R)-(−)-2,2,2-*trifluoro*-1-*phenylethanol* (1 : 15 *mol ratio*). δ *relative to* 85% $H_3PO_4$, −36·31, −36·33, *and* −36·52.

The present work demonstrates the sensitivity of $^{31}P$ n.m.r. to differences in magnetic environment caused by the association of an optically active solvent with phosphoryl donor sites. This can be viewed as a hydrogen-bonding interaction in which the acidity of the solvent and the basicity of the phosphoryl site influence the splitting pattern. Although the definite assignment of the high-field doublet in the Figure is still not possible, we favour assigning it to the racemic pair since there is no evidence for the complex AB doublet of doubles expected for the *meso* form.

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‡ $^{31}P$ n.m.r. spectra were obtained with a Varian XL-100-15 spectrometer at 40·5 MHz. The sample was contained in a 5 mm precision-bore tube centred in a 12 mm precision-bore tube. The space between the tubes contained $(CD_3)_2CO$. All protons were decoupled using "white noise."

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[4] W. H. Pirkle, S. D. Beare, and T. G. Burlingame, *J. Org. Chem.*, 1969, **34**, 470.