Carbon-13 Nuclear Magnetic Resonance of 1,3,2-Dioxaphosphorinan-2-ones

By A. A. Borisenko,* N. M. Sergeyev, E. Ye. Nifant'ev, and Yu. A. Ustynyuk
(*N.M.R. Laboratory, Department of Chemistry, Moscow State University, Moscow, U.S.S.R.*)

Summary The $^3J(^{13}C\ldots{}^{31}P)$ coupling constants in some 1,3,2-dioxaphosphorinan-2-ones have been shown to depend upon the POCC dihedral angle and the orientation of the P...O bond.

Determination of the ^{13}C–^{31}P coupling constants of organophosphorus compounds is useful for structural assignments.[1] However, the dependence of ^{13}C–^{31}P coupling constants on the stereochemistry has not been previously reported.

The proton decoupled ^{13}C n.m.r. spectra of a number of 1,3,2-dioxaphosphorinan-2-ones are given in Tables 1 and 2.

It has been shown by n.m.r. and magnetic dipole data[2] that in (**1a**) the P=O and Me groups are *cis* and equatorial and that the molecule is in the chair form, and in (**1b**) the P=O and Me groups are *trans* and the P=O group is axial.

TABLE 1

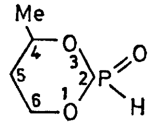
^{13}C *chemical shifts* (*relative to* Me_4Si), ±0·2 *p.p.m.*

Compounds	C-4	C-5	C-6	4-Me^{eq}	5-Me^{ax}	5-Me^{eq}	6-Me^{ax}	6-Me^{eq}
(1a)	74·4	33·7	65·9	22·9				
(1b)	74·8	32·7	64·6	22·4				
(2a)	71·8	45·1	83·3	32·3			27·0	32·6
(2b)	73·1	44·1	82·7	23·3			28·7	31·8
(3)	76·6	32·5	76·6		22·2	20·5		

TABLE 2

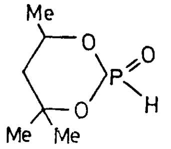
^{13}C–^{31}P *coupling constants*, ±0·2 Hz

Compounds	^2J C-4	^3J C-5	^2J C-6	^3J 4-Me^{eq}	^4J 5-Me^{ax}	^4J 5-Me^{eq}	^3J 6-Me^{ax}	^3J 6-Me^{eq}
(1a)	5·9	6·1	5·3	8·9				
(1b)	7·2	9·9	6·8	4·8				
(2a)	5·3	5·9	7·1	9·1			1·8	5·9
(2b)	6·4	11·0	7·1	6·0			<0·6	4·5
(3)	5·6	6·3	5·6		<0·3	1·0		



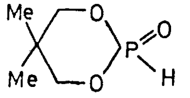
(1a) Me and P=O *cis*

(1b) Me and P=O *trans*



(2a) 4-Me and P=O *cis*

(2b) 4-Me and P=O *trans*



(3)

The configurations of (**2a**) and (**2b**) have similarly been determined.

The signals in the ^{13}C spectra were assigned on the basis of the general trends for ^{13}C chemical shifts[3] and by off-resonance partial proton decoupling.

The 5-methyl signals in the spectrum of compound (**3**) were assigned by selective ^{13}C–{^{1}H} decoupling.[4]

Tables 1 and 2 show the difference between the ^{13}C n.m.r. data of isomers (**1a**) and (**1b**) and (**2a**) and (**2b**), especially the ^{13}C–^{31}P vicinal coupling constants, where the effect of the spatial arrangement of the P=O bond can be observed. Similar differences have recently been observed for *cis*- and *trans*-2-methyl-5-t-butyl-1,3,2-dioxaphosphorinans.[5] The $^{13}CH_3(6)$–^{31}P constants demonstrate the dependence of the ^{13}C–^{31}P vicinal constants on the POCC dihedral angle. The constants are much higher for the equatorial methyls (dihedral angle, *ca.* 180°) than they are for the axial methyl (dihedral angle *ca.* 60°). This resembles the dependence of the ^{31}P–H vicinal constants upon the dihedral angle in 1,3,2-dioxaphosphorinans.[6]

For compound (**3**), it is noteworthy that the long-range coupling constant $^4J(^{13}C\ldots^{31}P)$ is observed only for the carbon of the equatorial methyl. Thus, as with the H–H coupling constants, the ^{13}C–^{31}P long-range coupling constants are greater when the interacting nuclei are W arranged (W rule).

(*Received*, 18*th January* 1972; *Com.* 073.)

---

[1] G. A. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 2132 and references therein.

[2] E. Ye. Nifant'ev, A. A. Borisenko, I. S. Nasonovsky, and E. I. Matrosov, *Dokl. Acad. Nauk U.S.S.R.*, 1971, **196**, 121.

[3] E. F. Mooney and P. H. Winson, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 153.

[4] K. D. Bartle, R. S. Edmundson, and D. W. Jones, *Tetrahedron*, 1967, **23**, 1701.

[5] W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *J. Amer. Chem. Soc.*, 1971, **93**, 797.

[6] D. W. White and J. G. Verkade, *J. Magn. Resonance*, 1970, **3**, 111.