

NMR AND STEREOCHEMICAL STUDIES OF NON AROMATIC HETEROCYCLIC COMPOUNDS

PART III* : $^{31}\text{P}\dots^{13}\text{C}$ COUPLING CONSTANTS : EFFECT OF PHOSPHORUS LONE PAIR ORIENTATION ON

$$^2J_{^{31}\text{P}-\text{O}-^{13}\text{C}}$$

M. Haemers**, R. Ottinger, D. Zimmermann and J. Reisse.

Laboratoire de Chimie Organique, Faculté des Sciences Appliquées, Université Libre de Bruxelles, 50, avenue F.D. Roosevelt, 1050 Bruxelles, Belgium.

(Received in UK 5 April 1973; accepted for publication 19 April 1973)

Although the problem of $^{31}\text{P}\dots^{13}\text{C}$ nuclear spin coupling has been the subject of several investigations (1), the stereochemical dependance of these coupling constants was pointed out only recently (2-6). In particular, it has been shown that the two bond P-C-C (3) and P-N-C (4) coupling constants are very sensitive to the orientation of the lone pair on phosphorus. This prompts us to report some preliminary experimental results on $^{31}\text{P}\dots^{13}\text{C}$ coupling constants in cyclic phosphites. It will be shown that the two bond P-O-C coupling follows a similar angular dependance as $^2J_{\text{P}-\text{C}-\text{C}}$ and $^2J_{\text{P}-\text{N}-\text{C}}$. The data discussed in this paper are given in Table I. Details about synthesis, spectra recording and ^{13}C signal assignments will be published elsewhere (7).

It is presently established that the 1,3,2-dioxaphosphorinane derivatives exist in a chair conformation with the substituent on phosphorus (Cl, OCH_3 , CH_3) in the preferred axial orientation (8 and ref. given). As it was shown in previous work (8a), the isomers called A and B of VI and VII differ essentially in the orientation of the methoxy substituent on P^{III}. These compounds are thus particularly well suited to study the influence of phosphorus lone pair orientation on $^{31}\text{P}\dots^{13}\text{C}$ coupling constants.

For a methoxy group in the axial position as in II to V, VIA and VIIA, the most populated rotamers should be those presenting the methyl "outside" i.e. the O- CH_3 bond cis[†] to the phosphorus lone pair. $^2J_{\text{P}-\text{O}-\text{C}}^{\text{cis}}$ is thus c.a 18 Hz (cf. table I). This value is probably positive on the basis of magnitude and sign of $^2J_{\text{P}-\text{O}-\text{C}}$ in trimethyl- (+ 10.0 Hz \pm 0.2) and triethylphosphites (+ 11.3 Hz \pm 0.2) (1a).

For an equatorial OCH_3 group (VIB and VIIB), different rotamers can exist : the

* Part I and Part II : see references (8a) and (7)

** Chargée de Recherches du Fonds National de la Recherche Scientifique Belge.

† Cis is relative to the mutual orientations of the C-O bond and the phosphorus lone pair. The dihedral angle for the "methyl outside" rotamer being probably lower than 20° (9), the term "cis" seems preferable to the term "gauche" which is associated with a dihedral angle of the order of 60°.

two "methyl up" and the "methyl down". In the former, the O-CH₃ bond is cis to the phosphorus lone pair, as for an axial OCH₃ group, and, in the latter, the O-CH₃ bond is trans to the lone pair. We can estimate the approximate value of $^2J_{P-O-C}^{trans}$ (dihedral angle near 180°), taking into account that in the compounds with an axial methoxy group, the C₄-O₃ and the C₆-O₁ bonds are trans to the phosphorus lone pair.

Table I : $^{31}P...^{13}C$ coupling constants (Hz) in 1,3,2-dioxaphosphorinanes^a.

Derivatives	$^2J_{C_4...P}$	$^2J_{C_6...P}$	$^2J_{CH_3-O-P}$	$^3J_{C_5:...P}^b$
I 	2.4	2.4	-	5.2
II 	1.3	1.3	18.0	5.2
III 	1.5	1.5	18.3	5.4
IV 	1.3	1.3	18.7	4.7
V 	1.7	2.2	18.3	4.6
VIA 	2.7	2.7	18.2	4.2
VIB 	1.8	1.8	10.7	13.5
VIIA 	1.8	2.1	18.7	4.7
VIIIB 	1.7	2.2	12.0	14.0

a. The coupling constants between phosphorus and carbon atoms of methyl ring-substituents are as follow : 1.5 Hz (III), 1.2 Hz (IV : eq. CH₃), < 1 Hz (IV : ax. CH₃), 3.3 Hz (V), 3.2 Hz (VIA) and 1.6 Hz (VIB)

b. The stereochemical dependance of $^3J_{P-O-C}$ relative to the phosphorus configuration has been discussed in some details elsewhere (7).

As we can see in table I, for the cyclic carbon atoms C_4 and C_6 , the values of ${}^2J_{P-O-C_{4,6}}^{trans}$ are small, in the range $|1.3|$ to $|2.7|$ Hz*. If we postulate that the ${}^2J_{P-O-C}^{trans}$ coupling constant for a cyclic carbon atom is similar to the ${}^2J_{P-O-C}^{trans}$ coupling constant for an exocyclic OCH_3 group, it is possible to rationalise the small ${}^2J_{P-O-CH_3}$ observed for the compounds with an equatorial OCH_3 group. This coupling constant corresponds to an averaged value between a large positive ${}^2J^{cis}$ value, corresponding to the two "methyl up" rotamers, and a small (positive or negative) ${}^2J^{trans}$ value. Without any precise knowledge about the rotamers' populations and the exact ${}^2J^{cis}$ and ${}^2J^{trans}$ values, it is impossible to determine the sign of ${}^2J^{trans}$ by the method previously described (10).

In compounds VIB and VIIB, which have an equatorial OCH_3 group, the $O-C_{4,6}$ bond and the phosphorus lone pair are gauche to each other ($\theta \approx 60^\circ$). The sign of the small ${}^2J_{P-O-C_{4,6}}^{gauche}$ coupling constants reported in Table I is yet unknown. Nevertheless, we can already conclude that the angular dependance of ${}^2J_{P-O-C}$ presents a steep variation between $\theta = 0^\circ$ (${}^2J_{P-O-C}^{cis}$) and $\theta = 60^\circ$ (${}^2J_{P-O-C}^{gauche}$), the absolute value of ${}^2J_{P-O-C}^{trans}$ being of the same order of magnitude as ${}^2J_{P-O-C}^{gauche}$.

In summary, our results can be considered as a demonstration of the strong dependance of the ${}^2J_{P^{III}-O-C}$ coupling constant toward the dihedral angle between the lone pair on phosphorus and the O-C bond. ${}^2J_{P^{III}-O-C}$ is large (and positive) for the cis orientation and small (with a yet unknown sign) for the trans orientation. This behaviour is qualitatively similar to the angular dependance described in the literature for ${}^2J_{P^{III}-N-C}$ (4) and ${}^2J_{P^{III}-C-C}$ (3).

An explanation for the lone pair orientation effect on coupling constants has been proposed recently (11). Nevertheless, it seems to us that no firm conclusion can be drawn presently in the case of ${}^2J_{P^{III}-X-C}$ coupling constants. Indeed, variations of the ${}^2J_{P-X-C}$ coupling constant ($X = O, C$) with the phosphorus configuration have also been observed in tetracoordinated phosphorus compounds (thus without lone pair on the phosphorus atom) (3b, 5). These variations seem smaller than in the analogous P^{III} compounds (3b, c) but, until now, only the absolute values of the coupling constants were considered. The determination of the signs of some ${}^2J_{P-O-C}$ coupling constants will constitute the next step of this study.

* There seems to be a small effect of $C_{4,6}$ substituents on $|{}^2J_{P-O-C}|$ but not always in the same direction (compare compounds V and VIA_{4,6} to II).

Acknowledgments: The authors are indebted to Professor Chiurdoglu for his interest and to the "Fonds de la Recherche Fondamentale Collective" for his financial support.

REFERENCES

- (1) a. W. Mc FARLANE, Proc. Roy. Soc., Ser. A, 306, 185 (1968)
b. J.P. ALBRAND and D. GAGNAIRE, Chem. Comm., 874 (1970)
c. C. SCHUMANN and H. DREESKAMP, *ibid.*, 619 and 671 (1970)
d. G.C. LEVY and J.D. CARGIOLI, *ibid.*, 1663 (1970)
e. G.A. GRAY, J. Am. Chem. Soc., 93, 2132 (1971) and ref. cited
f. H.J. JAKOBSEN and O. MANSCHER, Acta Chem. Scand., 25, 680 (1971);
T. BUNDEGAARD and H.J. JAKOBSEN, Tet. Letters, 3353 (1972);
H.J. JAKOBSEN, T. BUNDEGAARD and R.S. HANSEN, Mol. Phys. 23, 197 (1972)
g. M.P. SIMONNIN, R.M. LEQUAN and F.W. WEHRLI, Tet. Letters, 1559 (1972)
- (2) G.A. GRAY et S.E. CREMER, Tet. Letters, 3061 (1971)
- (3) a. *ibid.*, Chem. Comm., 367 (1972); b. *ibid.*, J. Org. Chem. 37, 3458 and 3470 (1972)
c. J.J. BREEN, S.I. FEATHERMAN, L.D. QUIN and R.C. STOCKS, Chem. Comm., 657 (1972)
d. S. SORENSEN, R.S. HANSEN and H.J. JAKOBSEN, J. Am. Chem. Soc., 94, 5900 (1972)
- (4) M.P. SIMONNIN and R.M. LEQUAN, Chem. Comm., 1204 (1972)
- (5) A.A. BORISENKO, N.M. SERGEYEV, E. Ye. NIFANT'EV and YU. A. USTYNYUK, *ibid.*, 406 (1972)
- (6) R.D. LAPPER, H.H. MANTSCH and I.C.P. SMITH, J. Am. Chem. Soc., 94, 6243 (1972)
- (7) M. HAEMERS, R. OTTINGER, D. ZIMMERMANN and J. REISSE, Tetrahedron, *in press*.
- (8) a. *ibid.*, Tet. Letters, 461 (1971)
b. W.G. BENTRUDE, K.C. YEE, R.D. BERTRAND and D.M. GRANT, J. Am. Chem. Soc., 93, 797 (1971)
- (9) V.A. NAUMOV, N.M. ZARIPOV and V.G. DASHEVSKII, Zhurn. Strukt. Khim., 12, 156 (1971)
- (10) C. CUVELIER, R. OTTINGER and J. REISSE, Tet. Letters, 277 (1972)
- (11) W.B. JENNINGS, D.R. BOYD, C.G. WATSON, E.D. BECKER, R.B. BRADLEY and D.M. JERINA, J. Am. Chem. Soc., 94, 8501 (1972)