The Signs and Magnitudes of Spin-coupling Constants in a Polycyclic Molecule

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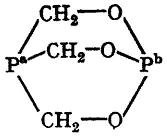
The magnitude and, in some cases, the signs of the spin–spin coupling constants between directly bound ^{31}P-nuclei in a variety of compounds are now known.[1] However, data for the coupling between phosphorus nuclei which are separated by more than one bond are scarce, and no sign information appears to be available. Our knowledge of the signs and magnitudes of ^{31}P–H and ^{31}P–^{13}C coupling constants is reasonably comprehensive,[2] but in most of the systems studied there has been a high degree of conformational mobility, and the observed coupling constants have been averages. We have therefore studied the rigid polycyclic molecule 2,6,7-tri-oxa-1,4-diphosphabicyclo[2,2,2]-octane (I) in which the steric relationships are fixed.[3]



Heteronuclear double-resonance experiments were performed on a JEOL spectrometer with a modified probe at a frequency of 60 MHz. The compound was examined both as a neat liquid at 80° and as a solution in dichloromethane at 25°. No significant differences between the coupling constants in the two samples were noticed. The Table gives the results and the particular experiments used

N.m.r. parameters in $P(CH_2O)_3P$

	Hz.	Irradiated nucleus
$^1J(^{13}C\text{–}H)$	$+153{\cdot}4\pm0{\cdot}4$	$^{31}P^a$
$^1J(^{13}C\text{–}^{31}P^a)$	-24 ± 4	^{13}C
$^2J(^{31}P^a\cdots H)$	$+9{\cdot}3\pm0{\cdot}1$	$^{31}P^b$
$^3J(^{31}P^b\cdots{}^{31}P^a)$	$-38{\cdot}1\pm0{\cdot}4$	$^{31}P^a$
$^3J(^{31}P^b\cdots H)$	$+2{\cdot}7\pm0{\cdot}1$	
$^2J(^{31}P^b\cdots{}^{13}C)$	$\leqslant10$	$^{31}P^b$
$^4J(H\cdots H)$	$\pm1{\cdot}3\pm0{\cdot}4$	
$\Xi\ (^{31}P^a)$	$40{,}478{,}050\pm4$	
$\Xi\ (^{31}P^b)$	$40{,}484{,}395\pm4$	
$\Xi\ (^{13}C)$	$15{,}087{,}676\pm4$	

to obtain them: the Ξ values[2] are the appropriate resonant frequencies corrected to a polarizing magnetic-field strength at which tetramethylsilane would give a proton resonance of exactly 100 MHz.

The ^{31}P chemical-shift difference (156·8 p.p.m.) found here agrees well with that previously obtained by direct ^{31}P resonance,[3] and the double-resonance experiments also confirmed unequivocally that the original assignment of the numerically larger of the two $^{31}P \cdots H$ coupling constants to $^{2}J(^{31}P \cdots H)$ was correct. The values of $^{2}J(^{31}P \cdots H)$ in trialkyl phosphines are normally within a few Hz of zero, although larger values can arise when bulky groups are present. Quaternization of phosphorus is accompanied by a change in this coupling constant to a more negative value,[4] and this is thought to be due to greater *s*-character in the P–C bonds in the quaternary compound. This view is supported by the changes in the bond angles at the phosphorus atom which occur simultaneously. The original explanation[3] for the large value of $^{2}J(^{31}P \cdots H)$ in (I) ignored the signs of coupling constants, and the situation was taken to be analogous to that in a P^{V} compound, so that phosphorus hybridization close to sp^3 was suggested. Our work shows that this is not so, and it seems more likely that the hybridization of P^a is close to p^3, with correspondingly small interbond angles at phosphorus. It is difficult to form an estimate of the angles at P^a from inspection of a model without knowing the angles at the carbon and oxygen atoms, but the relatively large negative value of $^{1}J(^{31}P-^{13}C)$ supports our view. (Compare values of $-13·6$ and $+55·5$ Hz for this coupling in (Me_3P and $Me_4P^+I^-$ respectively.[2])

The value for $^{3}J(^{31}P \cdots {}^{31}P)$ implies that a pair of phosphorus nuclei connected by a single CH_2–O fragment should give a coupling constant of *ca.* $-$ 13 Hz, for zero dihedral angle between the P–C (O) bonds. This assumes that there is no direct interaction between the two ^{31}P nuclei, (*i.e.* no "through space" coupling) and the rather short $P \cdots P$ distance of *ca.* 2·8 Å suggests that this may not be so. Indeed, repulsion between the two phosphorus atoms may distort the molecule in such a way as to give unusually small interbond angles at phosphorus and hence the anomolous values for $^{2}J(^{31}P \cdots H)$ and $^{1}J(^{31}P-^{13}C)$.

We thank the S.R.C. for funds for the spectrometer, and the Governors of Sir John Cass College for a research assistantship (to J.A.N.).

(*Received, December 4th,* 1968; *Com.* 1661.)

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