

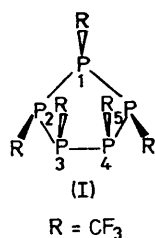
Stereochemical Dependence and Substituent Effects on the $^1J(\text{PP})$ N.m.r. Spin-spin Coupling in Cyclopentaphosphines $(\text{PR})_5$

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Summary The $^1J(\text{PP})$ n.m.r. couplings obtained for $(\text{PCF}_3)_5$ are compared with the values previously obtained for $(\text{PMe})_5$ and the results are discussed in terms of bond orientation and substituent effects.

ALTHOUGH an increasing number of $^1J(\text{PP})$ spin coupling values, in a wide variety of polyphosphorus compounds have become available in the last few years, attempts to rationalise these values in terms of substituent effects have only been moderately successful.^{1,2} It has been suggested from calculations of $^1J(\text{PP})$ in P_2H_4 and P_2F_4 that the coupling might depend upon the angle of internal rotation.³ This prediction has already received some experimental support.^{4,5} In particular, the $^1J(\text{PP})$ values, in the cyclophosphine $(\text{PMe})_5$,⁵ differ by more than 60 Hz, depending upon the *cis* or *trans* relationship of the methyl substituents



attached to the coupled phosphorus atoms. We now report¹ $J(\text{PP})$ values of the cyclophosphine $(\text{CF}_3\text{P})_5$ (I)⁶ which further substantiate the stereochemical dependence of $^1J(\text{PP})$ noted in $(\text{MeP})_5$.

The fluorine-noise-decoupled 40 MHz ^{31}P spectrum of (I) shows a well resolved AA'BB'C system spread over 1000 Hz. The spectrum was analysed, as described for $(\text{MeP})_5$,⁵ using a thorough set of homonuclear ^{31}P - ^{31}P tickling experiments. The results are given in the Table.

X-Ray diffraction studies of $(\text{PCF}_3)_5$,⁷ have shown that his molecule adopts an asymmetric conformation in the solid state with the *cis-trans* disposition of the CF_3 groups as in (I).

Temperature dependent changes have been observed in the ^{19}F n.m.r. spectrum of (I).⁸ The ^{31}P - ^{19}F spectrum recorded at *ca.* 40° (AA'BB'C system) shows that compound (I) has a rigid C_s symmetry, or that a conformational change, fast on the n.m.r. time scale, occurs to produce an average C_s symmetry. According to the X-ray structural data⁷ the latter hypothesis seems more likely.

The $^1J(\text{PP})$ coupling values in $(\text{PCF}_3)_5$ (Table) show the same trend as previously observed in $(\text{PMe})_5$.⁵ The difference between the *cis*-($J_{3,4}$) and the *trans* couplings ($J_{1,2}$, $J_{1,5}$, $J_{2,3}$, $J_{4,5}$) is even greater (> 100 Hz) in the case of $(\text{PCF}_3)_5$. The $^2J(\text{PP})$ values observed in $(\text{CF}_3\text{P})_5$ are also consistent with the ones observed in $(\text{MeP})_5$ and it seems that a 1,3-*cis* arrangement of the lone pairs on the coupled nuclei make this coupling more positive.

As previously explained in the case of $(\text{PMe})_5$ ⁵ it seems reasonable to assume that the $^1J(\text{PP})$ values obtained in $(\text{PCF}_3)_5$ are negative. Comparison of the $^1J(\text{PP})$ values in $(\text{MeP})_5$ and $(\text{CF}_3\text{P})_5$ allows the effect of substituent electronegativity in two closely related geometries to be investigated. The observed changes are not in the same direction for the J_{cis} and J_{trans} values since J_{cis} is more negative in $(\text{CF}_3\text{P})_5$ than in $(\text{MeP})_5$ by *ca.* 30 Hz ($|J_{cis}(\text{PCF}_3)_5| > |J_{cis}(\text{PMe})_5|$) while the J_{trans} values are more positive in $(\text{CF}_3\text{P})_5$ by the same amount ($|J_{trans}(\text{PCF}_3)_5| < |J_{trans}(\text{PMe})_5|$). These opposite variations show that, as far as three-co-ordinate phosphorus atoms are concerned, any explanation of the influence of substituent electronegativity on $^1J(\text{PP})$ must take into account the stereochemical dependence of this spin coupling. It is apparent from our results that eclipsing the lone-pairs on the coupled phosphorus atoms would favour large negative values of $^1J(\text{PP})$ but no clear indication has emerged yet for other lone-pair

TABLE. ^{31}P chemical shifts (p.p.m.)^a and $J(\text{PP})$ coupling constants (Hz) of $(\text{CF}_3\text{P})_5$.

$\delta(\text{P}_1)$	$\delta(\text{P}_2)$	$\delta(\text{P}_3)$	$J_{1,2}$	$J_{1,3}$	$J_{2,5}$	$J_{2,4}$	$J_{2,3}$	$J_{3,4}$
-7.5	-10.0	+1.1	∓ 214.5	± 36.9	± 0.8	∓ 5.3	∓ 223.3	∓ 343.2

^a Negative values are downfield from external 85% H_3PO_4 .

relationships and more $^1J(\text{PP})$ values, in a variety of geometries are needed before any comprehensive picture can be drawn.

We thank Professor D. Gagnaire for helpful discussions and Mr. R. Nardin for his technical assistance in the n.m.r.

experiments. $(\text{CF}_3\text{P})_5$ was prepared at California State University, Los Angeles, and we are grateful to Professor H. Goldwhite for expert advice on handling this compound.

(Received, 10th May 1974; Com. 534.)

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