ON THE LARGE DIFFERENCE BETWEEN THE DIASTEREOMERIC ^{1}J(PP) VALUES
OF   1,2-bis TRIFLUOROMETHYLDIPHOSPHINE

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Recent theoretical and experimental studies concerned with the stereochemistry of

diphosphines have shown that their conformation may follow two different trends depending

primarily on the electronegativity of the substituents. Thus, on one hand, the studies of P_2H_4,

$P_2(CH_3)_4$ [1]   and $P_2(But)_4$ [2]   indicate that diphosphines substituted by weakly electro-

negative atoms or groups favour the *gauche* conformation, as a result of the stabilizing "gauche

effect" [3] between the adjacent lone pairs, while on the other hand the studies of P_2F_4 [4],

P_2Cl_4 [5] and $P_2(CF_3)_4$ [4] indicate in those compounds a preference for the *trans* conformation,

which can be attributed to electrostatic repulsions between the strongly electronegative atoms

or groups X and/or to stabilizing *gauche* interactions between the lone pairs and the polar P-X

bonds [3]

In the case of diphosphines $(R_1PR_2)_2$ which can exist in two diastereomeric forms, a

great difference in the electronegativity of R_1 and R_2 may result in a conflict between these

two trends which could be reflected by some differences in the properties of the two isomers

To illustrate such a case, we report here our observation and interpretation of the large differ-

ence between, and the temperature dependence of the ^{1}J(P-P) values in the *meso* and d,l dia-

stereomers of 1,2-bis-trifluoromethyl-diphosphine I [6]

The ^{19}F nmr spectrum of I (a+b) has been recently described [7] The ^{1}H[^{19}F] and ^{31}P

[^{19}F] nmr spectra display the expected AA'XX' spin systems (one for each diastereomer) The

spectra were temperature dependent , the parameters observed at 35°C and -100°C are given in table   The relative signs of the ^{1}J(P-H), ^{1}J(P-P) and ^{3}J(H,H) coupling constants were obtained by heteronuclear triple resonance experiments involving ^{19}F noise-decoupling, ^{31}P tickling and observation of the ^{1}H spectrum The absolute signs in the table are based son the reasonable assumption that ^{1}J(P-H) is positive [8]

Table   Chemical shifts (δ,ppm) and coupling constants (J,Hz) for the two isomers [c] of $(CF_3PH)_2$

Temp °C	Isomer	^{1}J(P-P)	^{1}J(P-H)	^{2}J(P,H)	^{3}J(H,H)	$\delta(^1H)$ [a]	$\delta(^{31}P)$ [b]
35	a	-135 2	+205 6	+3 2	+9 2	3 68	90 3
	b	-183 7	+213 9	+15 2	+3 0	3 82	92 0
-100	a	-114 8	+213 7	+1 8	+7 4	—	91 5
	b	-203 4	+223 2	+15 5	+0 5	—	95 1

a   to low-field of $(CH_3)_4$ Si   ,   b   to high-field of 85% H_3PO_4 ,   c   at both temperatures, the populations of the isomers are nearly equal

The most striking feature in the parameters is the large difference between the ^{1}J(P-P) values of Ia and Ib which amounts to 48 Hz at 35°C and increases to almost 90 Hz at -100°C

Two important factors can be considered to explain this difference, the influence of the relative orientation of the adjacent lone pairs on the phosphorus atoms [9] and the influence of the hybridization state of the phosphorus atoms [10,11]

In the present case, we believe that the latter factor has a minor influence   If the large difference observed in the ^{1}J(P-P) values was primarily due to hybridization changes, it should involve a larger ^{31}P chemical shift difference for the two diastereomers The difference here observed (less than 4 ppm) is quite comparable to the ones observed between the diastereomers of $(C_6H_5PH)_2$ [12] which do not show any difference in their ^{1}J(P-P)values, and between the isomers of $(C_6H_5PCH_3)_2$ [13] which show a relatively small difference of 19 Hz Thus, it seems more likely that the large difference observed in the ^{1}J(P-P) values for $(CF_3PH)_2$ is due to a difference in the lone pair orientation in the two isomers

By an INDO type calculation of ^{1}J(PP) in P_2H_4 [14], it was shown that this coupling is highly dependent upon the bond orientation around the phosphorus A recent study based on an *Ab initio* [15] calculation of P_2H_4 in four different conformations and using a method which has been shown to give satisfactory results for ^{1}J values [16] indicates that this coupling

increases as the dihedral angle $\emptyset$ between the directions assigned to the lone pair electron on

phosphorus increases from $0°$ (-283 Hz) to $180°$ (+11 Hz) This calculation includes the three

contributions(Fermi contact, dipolar and orbital) The angular variation depends mainly of the

Fermi contact term

The $^1J(PP)$ values obtained from the nmr spectral analysis of $(PCH_3)_5$ [17] and $(PCF_3)_5$ [9]

support the $^1J(PP)$ calculated trend It must however be pointed out that an opposite trend was

suggested in the case of $P(tBu)_4$ [10]

If one considers the rotamers of $(CF_3PH)_2$ (Figure) for the d,ℓ isomer, the *gauche*

rotamer g1 will be the most stable form since this rotamer fulfils all the factors, *gauche*

relationship of the lone pairs, *trans* relationship of the electronegative CF_3 groups, maximum

number of *gauche* interactions between the lone pairs and the polar P-C bonds which are consider-

ed to stabilize the conformation of diphosphines [1,5] The decrease in temperature will thus

increase the population of the *gauche* rotamer which will result in an increase in $|^1J(P-P)|$

Thus we assign diastereomer b to the d,ℓ isomer ($^1J(P-P)$ = 203 4 Hz at -100°) In the *meso*

isomer, the decrease in $|^1I(P-P)|$ is explained on the basis of the preference of the electro-

negative CF_3 groups to adopt the *trans* disposition and therefore to favour the *trans* conform-

ation

It is noteworthy that the $^2J(P,H)$ and $^3J(H,H)$ values are also markedly different in the

two diastereomers, but the angular dependence of these coupling constants is probably complicat-

ed by the presence of the phosphorus lone pairs and they are at present of little help for the

conformational assignment
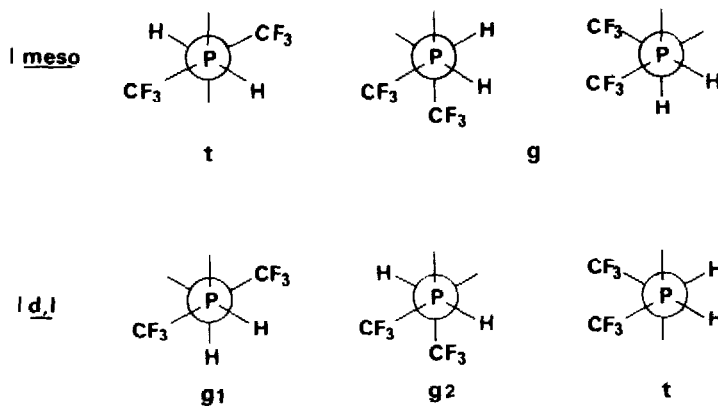
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