The Sign of the ^{15}N–^{31}P Coupling Constant

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Summary The sign of the directly bonded ^{31}P–^{15}N coupling constant in ^{15}N-labelled $(CF_3)_2PNH_2$ has been determined.

THE signs and magnitudes of the nuclear spin coupling constants of directly bonded nuclei are of importance in relation to developing the appropriate theory for such interactions.[1,2] Spin–spin coupling between Group V nuclei is of particular interest because this is the region of the Periodic Table where sign inversions occur.[2,3] We present the first information concerning the sign and magnitude of the ^{15}N–^{31}P coupling constant.

Nitrogen-15 labelled $(CF_3)_2PNH_2$ was prepared by a modification of Harris' method[4] in which $^{14}NH_3$ was replaced by 96·5% enriched $^{15}NH_3$. The relative sign information is based on spin tickling[5] (ST), nuclear Overhauser effect[6] (NOE), localised saturation effect[7] (LS), and selective decoupling of multiplets[8] (SDC) experiments as summarised in Table 1. Since the ^{15}N nucleus has a negative magnetogyric ratio it is convenient to express the data both in terms of the usual coupling constant, J_{AB}, and the reduced coupling constant, K_{AB}, which is defined by the equation[1]

$$K_{AB} = \frac{2\pi}{\hbar\gamma_A\gamma_B} J_{AB}$$

The sign and magnitude data which are presented in Table 2 are based on the assumption that $K(^{15}NP)$ is positive.

This assumption is reasonable on both theoretical[1] and experimental grounds.

TABLE 1

Summary of double resonance experiments on $(CF_3)_2P^{15}NH_2$

Experiment	Determined relative signs	Type of double resonance[a]
^1H–[^{19}F]	$J(^{15}NH)$ same sign $J(^{15}NPCF)$	SDC
	$J(PCF)$ same sign $J(PNH)$	SDC
^{31}P–[^1H]	$J(^{15}NH)$ diff. sign $J(^{15}NP)$	NOE,ST
	$J(FCPNH)$ same sign $J(PCF)$	NOE,ST,SDC
^{31}P–[^{19}F]	$J(^{15}NP)$ diff. sign $J(^{15}NPCF)$	NOE,LS
	$J(HNP)$ same sign $J(FCPNH)$	LS
^{31}P–[^{15}N]	$J(PNH)$ same sign $J(^{15}NH)$	ST
	$J(PCF)$ same sign $J(^{15}NPCF)$	ST

[a] See text for abbreviations.

The finding that $K(^{15}NP)$ is negative is not in accord with the model of Schaefer and Yaris[10] which predicts that directly bonded coupling constants will be positive if the electronegativity difference between the coupled atoms is less than 1·5. From the standpoint of Jameson and Gutowsky's model[2] the negative sign for $K(^{15}NP)$ means that the coupling mechanism is dominated by the core polarisation term. Presumably, this is due to appreciable *p*-character in the phosphorus bonding orbitals since the ^{15}N-^1H coupling constant of 85·64 Hz indicates that the nitrogen is approximately sp^2-hybridised.[11] Another way of interpreting the data is to take the view that ^{15}N resembles tervalent ^{31}P in its pattern of coupling constants.

TABLE 2

Relative signs and magnitudes of the coupling constants of $(CF_3)_2P^{15}NH_2$

Coupling	J(Hz)	K[a] (10^{20} cm^{-3})
^{31}P–^{15}N	+52·60	−106·75
^{15}N–^1H	−85·64	+70·36
^{15}N–P–C–^{19}F	−1·53	+1·34
^{31}P–N–^1H	−14·21	−2·92
^{31}P–C^{19}F	−81·33	−17·78
^{19}F–C–P–N–^1H	−0·055	−0·0049

[a] See text for definition.

Thus, $K(^{15}NP)$ is the same sign as $K(PP)$ for P^{III}–P^{III} compounds,[12] and the positive sign for $K(^{15}NPCF)$ agrees with that found[13] for the *P*–P–C–*F* coupling in $(CH_3)_2PP(CF_3)_2$ and $(CH_3)_3PPCF_3$. An obvious exception to this generalisation is the fact that $K(P^{15}NH)$ and $K(PPH)$ are of opposite sign. However, it is well known[3] that two bond couplings are sensitive to many factors such as the bond angle and the nature of the substituents on the coupled nuclei and the intervening atom.

We thank the National Science Foundation and the National Aeronautics and Space Administration for financial support.

(*Received, September 7th*, 1970; *Com.* 1512.)

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