Magnetic Double Resonance Studies of Silylaminodifluorophosphine and Some Related Amines

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Homonuclear and heteronuclear double resonance techniques have been used to determine the relative signs of coupling constants involving ^{1}H, ^{15}N, ^{19}F, ^{29}Si, and ^{31}P in ^{15}N-enriched aminodifluorophosphine, silylaminodifluorophosphine, disilylamine, and trisilylamine. The magnitudes of coupling constants not observable in ^{1}H or ^{19}F spectra, and ^{15}N, ^{29}Si, and ^{31}P chemical shifts, have also been determined in these experiments. Assuming ^{1}K(NH) and ^{1}K(SiH) to be positive, and ^{1}K(PF) to be negative, the absolute signs of the coupling constants have been deduced.

ALTHOUGH very many n.m.r. studies of compounds containing phosphorus–fluorine bonds have been reported, only one determination of the value of a directly bonded phosphorus–nitrogen coupling constant has been published.[1] As yet, therefore, there is no information about how this coupling varies with the nature of the phosphorus and nitrogen substituents. The recently reported aminofluorophosphine [2] and silylaminodifluorophosphine [3] are, when substituted with ^{15}N, good subjects for double resonance studies, having first order spectra with few overlapping lines. We report here the results of studies of these compounds, and of disilylamine and trisilylamine.

EXPERIMENTAL

Aminodifluorophosphine was prepared by the gas phase reaction of ammonia and bromodifluorophosphine.[2] Reaction of the product with silyl bromide in the liquid phase gave silylaminodifluorophosphine.[3] Disilylamine and trisilylamine were both prepared by the gas phase reaction of ammonia and silyl chloride. After a short reaction time a mixture of products was obtained, and disilylamine and trisilylamine could be separated by fractional condensation *in vacuo*. Purities of products were checked by i.r. and n.m.r. spectroscopy.

N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer operating at 100 MHz (^{1}H) or 94·075 MHz (^{19}F). The probes of this instrument were double tuned to accept a second radiofrequency, provided by a Schlumberger FS 30 frequency synthesizer.[4] The relative frequencies of the independent crystal sources of the spectrometer and synthesizer were checked before and after each experiment, so that measured irradiation frequencies should be correct to at least one part in 10^{7}. ^{15}N, ^{29}Si, or ^{31}P Chemical shifts could therefore be determined by comparison of decoupling frequencies required for different compounds containing the same nucleus.

For homonuclear double resonance experiments sidebands of the spectrometer frequency, generated by a Muirhead decade oscillator, were used.

Spectra were run at room temperature (*ca.* 300 K) on samples containing between 0·2 and 0·3 mmol of compound in *ca.* 0·7 ml of solvent. Solvents used were C_6H_6 (for disilylamine), Me_4Si (for trisilylamine), and $Me_4Si–CCl_3F$ (for fluorophosphine derivatives).

RESULTS

The Figure is a representation of the ^{1}H, ^{15}N, ^{19}F, and ^{31}P spectra of silylaminodifluorophosphine. All these spectra are first order, but overlapping lines lead to apparently complex intensity distributions. The origins of these are shown in the Figure. The spectra of the other amines are similar, but somewhat simpler.

Table 1 lists all the double resonance experiments that were performed, and the information about relative signs of reduced coupling constants that was deduced from them. The experiments provide more than enough information to relate all the coupling constants observed, and the results are all fully self-consistent. These experiments also enabled the magnitudes of coupling constants involving

TABLE 1

Double resonance experiments

Compound	Experiment	Coupling constants related		Relative signs
$PF_2{}^{15}NH_2$	H–{N}	^{3}K(FH)	^{2}K(FN)	Equal
		^{2}K(PH)	^{1}K(PN)	Opposite
	H–{F}	^{1}K(NH)	^{2}K(FN)	Equal
		^{2}K(PH)	^{1}K(PF)	Opposite
	H–{P}	^{1}K(NH)	^{1}K(PN)	Opposite
		^{3}K(FH)	^{1}K(PF)	Opposite
	F–{H}	^{2}K(FN)	^{1}K(NH)	Equal
	F–{N}	^{3}K(FH)	^{1}K(NH)	Equal
		^{1}K(PF)	^{1}K(PN)	Equal
	F–{P}	^{3}K(FH)	^{2}K(PH)	Equal
		^{2}K(FN)	^{1}K(PN)	Opposite
$PF_2{}^{15}NHSiH'_3$	H–{N}	^{2}K(PH)	^{1}K(PN)	Opposite
	H–{F}	^{3}K(HH′)	^{4}K(FH′)	Equal
		^{2}K(PH)	^{1}K(PF)	Opposite
	H–{P}	^{3}K(HH′)	^{3}K(PH′)	Equal
		^{1}K(NH)	^{1}K(PN)	Opposite
		^{3}K(FH)	^{1}K(PF)	Opposite
	H′–{H}	^{2}K(NH′)	^{1}K(NH)	Equal
		^{4}K(FH′)	^{3}K(FH)	Equal
		^{3}K(PH′)	^{2}K(PH)	Equal
	F–{H}	^{2}K(FN)	^{1}K(NH)	Equal
	F–{H′}	^{3}K(FH)	^{3}K(HH′)	Equal
		^{2}K(FN)	^{2}K(NH′)	Equal
	F–{N}	^{3}K(FH)	^{1}K(NH)	Equal
		^{1}K(PF)	^{1}K(PN)	Equal
	F–{P}	^{3}K(FH)	^{2}K(PH)	Equal
		^{2}K(FN)	^{1}K(PN)	Opposite
$(SiH'_3)_2{}^{15}NH$	H–{H′}	^{1}K(NH)	^{2}K(NH′)	Equal
	H–{N}	^{3}K(HH′)	^{2}K(NH′)	Equal
	H′–{H}	^{2}K(NH′)	^{1}K(NH)	Equal
	H′–{N}	^{3}K(HH′)	^{1}K(NH)	Equal
$^{29}SiH'_3{}^{15}N(^{28}SiH_3)_2$	H′–{N}	^{1}K(SiH′)	^{1}K(SiN)	Equal
	H′–{Si}	^{2}K(NH′)	^{1}K(SiN)	Equal

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[2] D. W. H. Rankin, *J. Chem. Soc. (A)*, 1971, 783.

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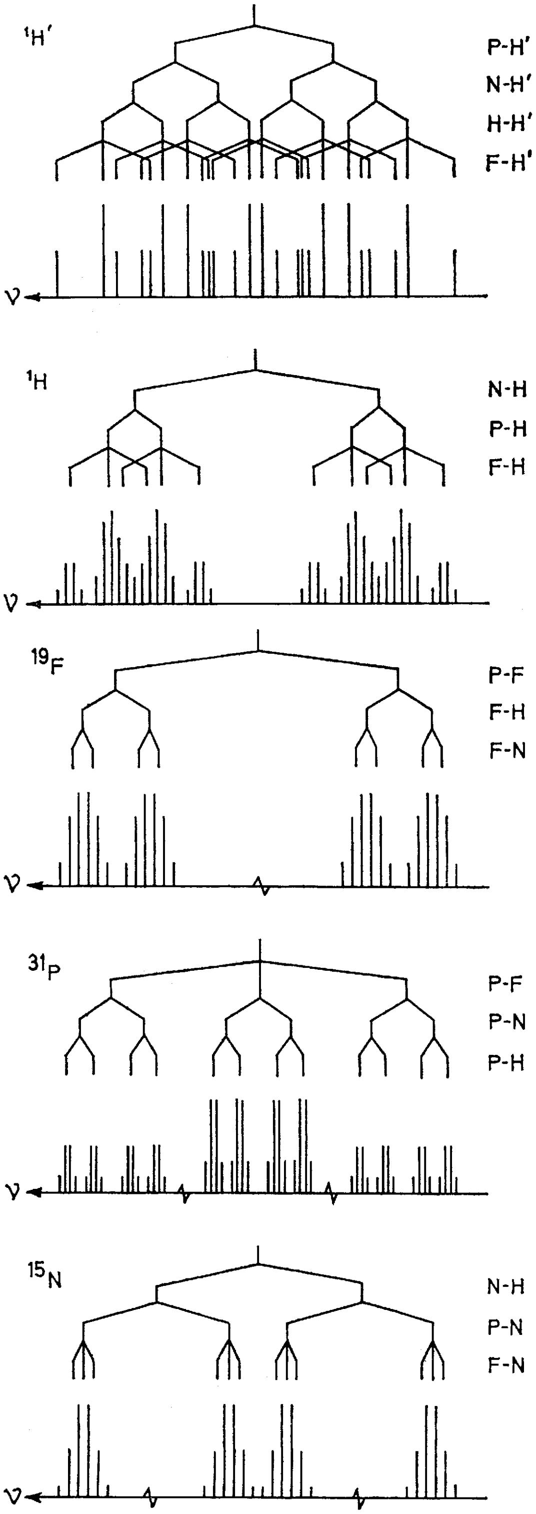
nuclei other than ^{1}H and ^{19}F to be determined. All measured coupling constants are listed in Table 2: the **absolute signs given there are based on the assumptions** that ^{1}K(PF) is always negative,[5,6] but that ^{1}K(NH) and ^{1}K(SiH) are positive.[7–9]



N.m.r. spectra (not to scale) of PF$_2$^{15}NHSiH'$_3$. The origins of the small quartet splittings, due to coupling with the H' protons, are not shown

^{1}H, ^{15}N, ^{19}F, ^{29}Si, and ^{31}P Chemical shifts for the amines studied are given in Table 3. ^{1}H and ^{19}F Shifts were measured directly, and the others were derived from irradiation frequencies required to perturb ^{1}H or ^{19}F spectra.

TABLE 3

Chemical shifts

Compound	PF$_2$NH$_2$	PF$_2$NHSiH'$_3$	(SiH'$_3$)$_2$NH	(SiH'$_3$)$_3$N
τ(^{1}H)	+6·77(2)	+7·19(2)	+10·86(2)	
τ(^{1}H')		+5·65(2)	+5·64(1)	+5·58(1)
δ(^{15}N) [a]	+21·4(2)	+14·1(5)	−69·0(2)	−79·9(1)
δ(^{19}F) [b]	−58·1(2)	−55·2(3)		
δ(^{29}Si) [c]		n.o.	n.o.	−39·9(2)
δ(^{31}P) [d]	+145·9(2)	+150·4(5)		

[a] P.p.m. to high frequency of external Me$_4$N$^+$I$^-$. [b] P.p.m. to high frequency of internal CCl$_3$F. [c] P.p.m. to high frequency of external Me$_4$Si. [d] P.p.m. to high frequency of external 85% H$_3$PO$_4$. Estimated standard deviations are given in parentheses. n.o. = Not observed.

DISCUSSION

It is to be expected that when the magnitudes of coupling constants of one type in a number of compounds are similar, the signs will be the same. The results of the present study (Table 2) show that this is so for each type of coupling that has been investigated. This consistency provides further evidence that the relative signs of ^{1}K(NH), ^{1}K(SiH), and ^{1}K(PF), the three standards used, are as assumed.

The consistency in magnitudes of coupling constants in different molecules makes the negative value of ^{2}K(PH) reported for aminobis(trifluoromethyl)phosphine[1] surprising. However, in the same study ^{2}K(PF) was found to be negative, whereas in other very similar compounds this coupling had been shown to be positive.[10,11] It seems that these results have been obtained by use of double resonance experiments to relate signs of coupling constants, whereas it is signs of reduced coupling constants that are related by this method. The study of aminobis(trifluoromethyl)phosphine contains the only report to date of a phosphorus–nitrogen coupling constant. The value of +52·6 Hz is fairly close to those found for silylaminodifluorophosphine and aminodifluorophosphine (+69 and +73·0 Hz), but all three compounds are similar derivatives of phosphorus(III) and nitrogen(III).

Interpretation of coupling constants over more than one bond is always difficult: the presence of atoms such as phosphorus, nitrogen, and fluorine makes it more so. Positive reduced constants for three-bond couplings

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of three different types accord with the simple alternating rule based on Fermi contact alone: positive over odd numbers of bonds, negative over even numbers. However, all the two- and four-bond reduced coupling constants are also positive. The positive value for ${}^4K$(FH′) in silylaminodifluorophosphine may well be due to direct (*i.e.* through space) interaction between the coupled nuclei; such interaction seems from other evidence to be important for this compound in the gas phase.[3] The similarity of the absolute values of ${}^4K$(FH′) and ${}^3K$(PH′) in this amine and the compounds MH_3YPF_2 (M = Si or Ge; Y = S, Se, or Te) [12] suggests that the coupling mechanisms are similar, and therefore that some form of hydrogen bonding occurs between the silyl or germyl groups and the fluorine atoms in the group VI compounds also. The SiH′ coupling constant in silylaminodifluorophosphine is consistent with this hypothesis.

TABLE 2

Coupling constants

Coupling	No. of bonds	$PF_2{}^{15}NH_2$		$PF_2{}^{15}NHSiH'_3$		$(SiH'_3)_2{}^{15}NH$		$(SiH'_3)_3{}^{15}N$	
		J	*K*	*J*	*K*	*J*	*K*	*J*	*K*
NH	1	−80·4(4)	+66·2	−73·1(3)	+60·2	−71·3(2)	+58·7		
PN	1	+73·0(5)	−148	+69(1)	−140				
PF	1	−1207(1)	−264·1	−1215(5)	−265·8				
SiH′	1			−224(4)	+94	−211(1)	+88	−212(1)	+89
SiN	1			n.o.	n.o.	n.o.	n.o.	+6(1)	+25
PH	2	+18·6(3)	+3·83	+18·8(2)	+3·87				
NH′	2			−4·1(1)	+3·4	−4·3(1)	+3·6	−4·2(1)	+3·5
FN	2	−6·4(4)	+5·6	+4·2(2)	+3·7				
HH′	3			+3·1(1)	+0·26	+3·4(1)	+0·29		
FH	3	+12·8(4)	+1·14	+14·0(2)	+1·24				
PH′	3			+8·0(2)	+1·65				
FH′	4			+2·1(1)	+0·19				

Note: Values of *J* are given in Hz. Estimated standard deviations are quoted in parentheses. Reduced coupling constants, *K*, are in units of 10^{19} N A^{-2} m^{-3}. n.o. = Not observed.

Of the chemical shifts in Table 3, only those for ^{15}N nuclei, and for hydrogens bonded to nitrogen, require special comment. The ^1H shifts are obviously very sensitive to the nature of other substituents at nitrogen, with difluorophosphine groups moving the resonance to high frequency. The ^1H shifts correlate with the associated ^{15}N shifts, for silylaminodifluorophosphine resonates slightly to low frequency of aminodifluorophosphine, but considerably to high frequency of disilylamine. The exceptionally low ^{15}N shift of trisilylamine is to be expected, for the ^{19}F, ^{31}P, ^{77}Se, or ^{125}Te chemical shifts of the silyl derivatives of these elements are all among the lowest known for the respective nuclei.[12–14]

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