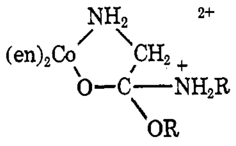
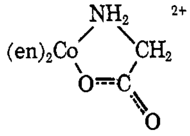
yield esters in acid solution and this is regarded as resulting from the preferential loss of $-NH_2R^+$ from the tetrahedral intermediate. Certainly the amine moiety in II will be fully protonated in the acidic conditions used ($pK_a \sim 7$)[19] and the products require that $-OC_3H_7$ and $-NH_2^+CH_2CO_2C_2H_5$ have similar leaving abilities from the tetrahedral carbon atoms. We do not understand the reason(s) for these differences but suggest that it may derive from effects similar to those giving rise to stabilization of the intermediate itself. Also the above is not an isolated example, as other studies in these laboratories demonstrate that approximately equal amounts of III and IV are formed in the intramolecular condensation of $(en)_2Co(H_2O)^{3+}NH_2CH_2CONHCH_2CO_2H$ at pH 0–2, presumably *via* a similar tetrahedral intermediate.


II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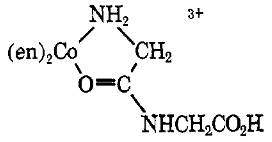
IV

Acknowledgment. The authors wish to thank the Microanalytical Unit for C, H, and N analyses and the referees for criticism and comments.

(19) Estimated from $K = 16\ M$ for mechanism II.

An ^{15}N–^{1}H Coupling Constant Study of the Bonding in Some N–P, N–As, N–S, and N–Si Compounds[1]

A. H. Cowley* and J. R. Schweiger

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received October 11, 1972*

Abstract: Fourteen ^{15}N-labeled aminophosphines, aminophosphoranes, aminoarsines, sulfenamides, and aminosilanes have been synthesized. The ^{15}N–^{1}H nmr coupling constants of these compounds have been determined in an attempt to test the validity of the $N \rightarrow P$ π-bonding hypothesis. It was found that it is unnecessary to employ the π-bonding model to explain the experimental data. The results are adequately dealt with by considering the redistribution of electrons within the σ frameworks of the molecules. The synthesis and characterization of the parent aminotetrafluorophosphorane, F_4PNH_2, are described.

Aminophosphines are of interest because they possess lone pair electrons on both the nitrogen and phosphorus atoms. Very early in the study of these compounds it became apparent that the phosphorus atom is more basic than the nitrogen atom. Thus, chemical and vibrational spectroscopic evidence indicate that it is the phosphorus atom which is quaternized in the $C_6H_5P[N(C_2H_5)_2]_2 \cdot CH_3I$[2] and $(CH_3)_2NP(CH_3)_2 \cdot CH_3I$[3] salts and that P–B bonding exists in the borane adducts $[(CH_3)_2N]_3PBH_3$,[4] $(H_2N)_3PBH_3$,[5] and $(CH_3)_2NPF_2 \cdot B_4H_8$.[6] Subsequent X-ray crystallographic studies[7,8] have confirmed that the phosphorus atom is the dative center in the last two compounds, and recent nmr and ir studies have established phosphorus donation when a variety of aminophosphines are treated with the Lewis acids CH_3^+,[9] alkylboranes,[10] PF_5,[11] and $(C_2H_5)_3Al$.[12] Similarly, the work of Sislers's group[13] indicates that chloramination always occurs at the phosphorus atom of aminophosphines. Furthermore, there is a substantial body of literature to the effect that the phosphorus atom is the donor atom when aminophosphines behave as ligands toward CuCl,[14] $RhCl_2$,[15] $CoBr_2$,[16] and a variety of metal carbonyl derivatives.[17] From the standpoint of the relative basicities of tertiary amines and the analogous tertiary phosphines, the

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(1) Abstracted from the Ph.D. Dissertation of J. R. Schweiger, The University of Texas at Austin, Austin, Texas, 1972. For a preliminary communication of this work see A. H. Cowley and J. R. Schweiger, *Chem. Commun.*, 1491 (1970).

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preferential phosphorus donor character of aminophosphines appears somewhat surprising. In view of this some authors have proposed a π-bonding model in which the P–N σ bond is supplemented by a dative π bond from a filled nitrogen 2p orbital to a vacant acceptor orbital on phosphorus.[18]

Before proceeding it is appropriate to point out that there is spectroscopic evidence for preferential nitrogen bonding in a few cases. Greenwood and Robinson[19] have suggested that BX_3 coordinates to the nitrogen atom of $RNHP(CF_3)_2$ on the basis of nmr evidence. More recently Fleming and Parry[20] and Fleming and coworkers[21] have obtained nmr and ir data which establish dative nitrogen bonding in the BF_3 adducts of $(CH_3)_2NPF_2$ and $CH_3\overline{NCH_2CH_2(CH_3)NP}F$, respectively. Nitrogen donation has also been invoked in the adduct $(CH_3)_2NPCl_2 \cdot AlCl_3$.[22] However, in contrast to this P–Al bonding has been claimed in the adducts of $[(CH_3)_2N]_3P$ and $[(CH_3)_2N]_2PCl$ with $AlCl_3$.[23] Initial attack at nitrogen has also been suggested in cases where decomposition products such as R_2NBX_2[24] ($X = F, Cl, CH_3$) have been isolated from complexation reactions.

The second area where multiple bonding has been suggested concerns the stereochemistry of aminophosphines. Dynamical nmr studies[25] have established that many aminophosphines exhibit P–N torsional barriers in the range $\Delta G^{\ddagger} = 8$–12 kcal/mol. In considering the contributors to the barriers' magnitudes, certain features were not explicable on the basis of lone pair–lone pair repulsion or steric effects and were, therefore, ascribed to multiple bonding effects within the P–N linkage. First, it was noted that unsymmetrical aminophosphines[26] of the type R_2NPXY possess P–N rotational barriers which are 25–30% higher than the corresponding symmetrical compounds R_2NPX_2 or R_2NPY_2. This was attributed to p_π–d_π bonding effects in the following way. If P (3d) orbitals are of low enough energy to be used, they must contribute to both the σ and π bonding. In an unsymmetrical aminophosphine the σ bonding requirements for 3d orbitals in the P–X and P–Y bonds presumably differ. This, in turn, causes an angular dependence of the p_π–d_π bonding in the P–N linkage. A second argument for a p_π–d_π interaction is provided by the work of Goldwhite and Rowsell[27] who noted that compounds with widely differing phosphorus substituents such as $CHCl_2CF_2P(Cl)N(CH_3)_2$ and $(CH_3)_2CHP(Cl)N(CH_3)_2$ had very similar nmr coalescence temperatures. If the barriers were due to lone pair repulsions, the coalescence temperatures would be expected to vary because the substituents should affect the phosphorus lone pair electrons to differing extents.

Thirdly, certain structural information has been published which could be indicative of multiple bonding in the P–N bond. Thus, in $(CH_3)_2NPF_2$[8] and H_2NPF_2[28] X-ray and microwave studies, respectively, indicate that the P–N bond distance is somewhat short for the P–N single bond and that the nitrogen atom adopts a trigonal planar geometry. In contrast to this work, electron diffraction studies of the same molecules indicate that the nitrogen atom deviates from planarity.[29] However, this is a surprising result in view of recent vibrational spectroscopic studies[30] which indicate that $(CH_3)_2NPF_2$ exists in only one conformation in the gaseous, liquid, and solid states.

Dative N→P π bonding has also invoked in regard to pentacoordinate phosphorus compounds. For instance, dynamical nmr studies reveal that alkylaminotetrafluorophosphoranes,[31] R_2NPF_4 (and alkylthiotetrafluorophosphoranes,[32] $RSPF_4$), exhibit higher intramolecular fluorine atom permutational barriers than other XPF_4 species. Since P–N rotation must be rapid to achieve fluorine atom equivalence, it is assumed that much of the observed 6–12 kcal/mol barrier is due to P–N bond torsion and *ergo* to multiple bonding effects.[33] In the case of $(H_2N)_2PF_3$ the P–N torsional barrier was estimated to be 11.15 kcal/mol and this barrier was attributed entirely to dative N→P π bonding.[34] Recently symmetry consideration, together with semiempirical molecular orbital calculations,[35] have been employed to support the hypothesis of substantial equatorial planar N→P π bonding in the model compound H_2NPF_4.

At the outset the present work was concerned with the ^1H nmr spectra of a series of ^{15}N labeled aminophosphines and aminofluorophosphoranes bearing NH or NH_2 groups, the principal objective being to determine whether the ^{15}N–^1H coupling constant trends were interpretable within the framework of the π bonding model described above. Subsequently it became apparent that the interpretation could be set within a broader context if comparable data were available for other ^{15}N-heteroatom systems, such as aminoarsines, sulfenamides, and aminosilanes.[36]

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(18) Most discussions of π bonding have related to the use of vacant 3d orbitals of, *e.g.*, P or S. However, derived valence-state ionization potential data indicate that for neutral atoms the 4p and 3d orbitals are very close in energy. Consequently $2p_\pi$–$4p_\pi$ bonding may be as important as $2p_\pi$–$3d_\pi$ bonding; see L. C. Cusachs and J. R. Linn, *J. Chem. Phys.*, 46, 2919 (1967).

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Experimental Section

Materials. $^{15}NH_3$ (96.5% enriched) was purchased from Bio-Rad Laboratories and used without subsequent purification. The ^{15}N labeled compounds $(CF_3)_2P^{15}NH_2$,[37] $[(CF_3)_2P]_2{}^{15}NH$,[38] $(CH_3)(CF_3)P^{15}NH_2$,[39] $[(CH_3)(CF_3)P]_2{}^{15}NH$,[39] $F_2P^{15}NH_2$,[40,41] $F_3P(^{15}NH_2)_2$,[42] $(CF_3)_2As^{15}NH_2$,[43] $[(CF_3)_2As]_2{}^{15}NH$,[43] $CF_3S^{15}NH_2$,[44] $(CF_3S)_2{}^{15}NH$,[44] $[(CH_3)_3Si]_2{}^{15}NH$,[45] and $(SiH_3)_2{}^{15}NH$[46] were prepared by substituting 96.5% enriched $^{15}NH_3$ for $^{14}NH_3$ in the original preparation. The compound $(C_2F_5)_2P^{15}NH_2$ was synthesized by substituting $(C_2F_5)_2PCl$[47] for $(CF_3)_2PCl$ in the procedure of Harris.[37] It was, however, necessary to conduct the reactions in a closed vessel (*vide infra*); furthermore the relatively high cost of the ^{15}N label made it desirable to develop methods for recovery of $^{15}NH_3$.[48] Since F_4PNH_2 is a new compound its synthesis is described in more detail.[49]

Synthesis of Aminotetrafluorophosphorane, F_4PNH_2. The gas-phase reaction of PF_4Cl with NH_3 was conducted in the apparatus shown in Figure 1. Prior to use a ₸ 7/25 stopper was inserted in joint D, and the reaction vessel was flamed several times over a 24-hr period after connection to the vacuum system. In a typical reaction 4.36 mmol of NH_3 was condensed into bulb B and allowed to volatilize completely after closing stopcock G. Tetrafluorochlorophosphorane[50] (2.18 mmol) was then condensed into bulb A and allowed to assume ambient temperature after closure of stopcock F. Stopcock G was then opened carefully so that a controlled gas phase reaction ensued in bulb A. As soon as the deposition of NH_4Cl had ceased the volatiles were transferred to the vacuum line and distilled through a series of U-traps held at −64, −90, and −196°. A virtually quantitative yield of F_4PNH_2 condensed in the −90° trap. The relative instability of F_4PNH_2 in the liquid state was evident from the presence of a residue which remained following each distillation. However, the compound showed no evidence of decomposition in the vapor phase on the basis of ir spectroscopy.

The limited stability of the new compound precluded a conventional elemental analysis. However, unequivocal identification of the compound may be made on the basis of its mass spectrum (Table I). Although no parent peak is present a significant abundance of the P − 1 peak, PF_4NH^+, is observed and the anticipated fragments at *m/e* values corresponding to $PF_4{}^+$ and $F_3PNH_2{}^+$ clearly establish the structure of the compound as F_4PNH_2.

Table I. Mass Spectrum of $F_4P^{14}NH_2$

m/e	Assignment	% rel abundance
31	P^+	0.9
50	PF^+	4.5
69	$PF_2{}^+$	17.2
83	PF_2N^+	2.7
84	PF_2NH^+	44.0
85	$PF_2NH_2{}^+$	13.6
88	$PF_3{}^+$	10.9
103	PF_3NH^+	17.7
104	$PF_3NH_2{}^+$	100
107	$PF_4{}^+$	77.6
122	PF_4NH^+	2.3

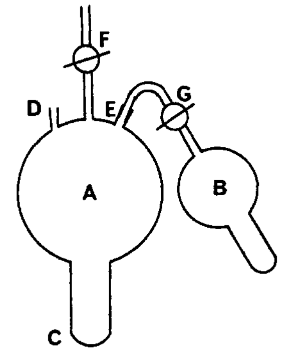

Figure 1. Reactor for the synthesis of ^{15}N labeled compounds.

Table II. Vapor-Phase Ir Spectrum of $F_4P^{15}NH_2$

Freq, cm^{-1}	Intensity[a]	Tentative assignment[b]
3575	m	N-H str
3465	m	
1570	m	N-H bend
1445	w	
1058	ms	P–F_{ax} str
1039	s	
1030	sh	
977	s	
967	s	
858	ms	P–F_{eq} str
850	s	
840	sh	
544	m	Unassigned
533	ms	
527	m	
505	m	
451	m	
432	sh	
412	s	

[a] s = strong, m = medium, w = weak, sh = shoulder. [b] These assignments are based on ref 41; A. J. Downs and R. Schmutzler, *Spectrochim. Acta*, **21**, 1927 (1965); D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc. A*, 171 (1966); D. H. Brown, K. D. Crosbie, J. J. Darragh, D. S. Ross, and D. W. A. Sharp, *ibid.*, 914 (1970); and G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 1903 (1967).

The vapor-phase infrared spectrum of $F_4P^{15}NH_2$ (Table II) also displayed the features which are expected for this formulation, namely N-H stretching at 3465 and 3575 cm^{-1}, P–F_{axial} stretching at 967, 977, 1030, 1039, and 1058 cm^{-1}, and P–$F_{equatorial}$ stretching at 840 (shoulder), 850, and 858 cm^{-1}.

Spectroscopic Measurements. (a) Ir Spectra. All ir spectra were measured in the vapor phase on a Perkin-Elmer Model 337 grating spectrophotometer. A 100-mm path length cell with KBr optics was used for all spectra.

(b) Mass Spectra. Mass spectra were obtained with a Consolidated Electrodynamics Corporation CEC 21-102 spectrometer applying an ionization voltage of 70 eV.

(c) Nmr Spectra. Most of the ^1H spectra were recorded on a Varian Associates A-60 spectrometer. In the cases of $(H_3Si)_2{}^{15}NH$, $F_2P^{15}NH_2$, and $F_4P^{15}NH_2$ it was necessary to employ temperatures of −50, −50, and −45°, respectively, due to the thermal instability of these compounds. The low-temperature ^1H spectra and all the ^{19}F spectra were recorded on a Varian Associates HA-100 spectrometer operating at 100 and 94.1 MHz, respectively. Probe temperatures were calibrated as described in the Varian Users Manual. Proton chemical shifts are reported in τ units with respect to $(CH_3)_4Si$ as internal standard.

Results and Discussion

^{15}N–^1H Coupling Constants. All of the proton spectra except that of $F_4P^{15}NH_2$ were first order at either 60 or 100 MHz spectrometer frequency; hence both the ^{15}N–^1H coupling constant and proton chemical shift

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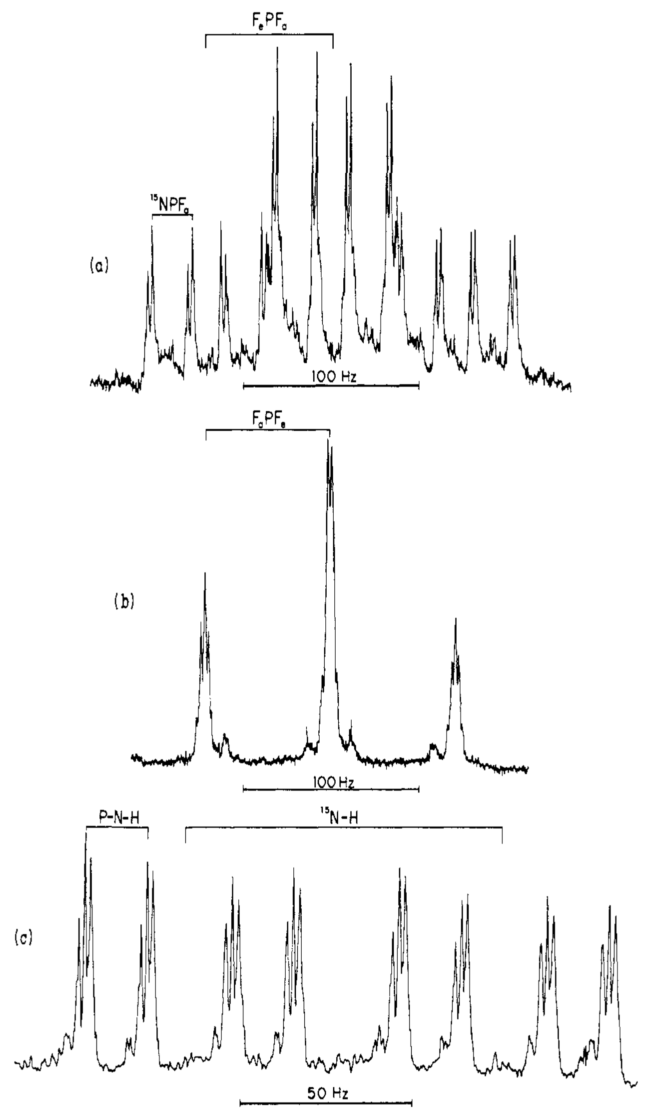

Figure 2. Nmr spectra of $F_4P^{15}NH_2$ in $HCCl_2F$ solution: (a) upfield half of 94.1-MHz ^{19}F spectrum of the axial fluorines, (b) upfield half of 94.1-MHz ^{19}F spectrum of the equatorial fluorines, and (c) 100-MHz ^1H spectrum.

data which are presented in Table III were obtained directly from the recorded spectral traces. In the case of $F_4P^{15}NH_2$ second-order effects are clearly apparent in the proton spectrum (Figure 2c). It was, however, possible to recognize the $^{15}N-^1H$ coupling constant on a first-order basis, and the proton chemical shift was taken to be the center of the complex but symmetrical resonance.

Nmr data have, in fact, been puslished previously for $F_2P^{15}NH_2$. However, there appears to be some discrepancy regarding the ^1H spectrum of this compound. One group[28] reported a doublet while Rankin[41] observed additional doublet and triplet splittings due to the ^{31}P and ^{19}F nuclei, respectively. Our spectral data ($J_{^{15}NH} = 82.7$, $J_{P-N-H} = 19.8$, and $J_{F-P-N-H} = 13.3$ Hz) are in excellent agreement with those of Rankin.[41]

It will be noted that $(CH_3)(CF_3)P^{15}NH_2$ and $[(CF_3)(CH_3)P]_2{}^{15}NH$ possess chiral centers at the phosphorus atoms. This should result in chemical shift nonequivalence for the NH_2 and NH protons in these compounds (Table III). In the case of $(CF_3)(CH_3)P^{15}NH_2$ the amino group is prochiral; hence the amino protons should exhibit chemical shift nonequivalence provided that the phosphorus pyramid is stable on the nmr time scale.[51] However, the observed spectrum indicates that the NH_2 protons in $(CF_3)(CH_3)P^{15}NH_2$ are equivalent. Since it is unlikely that the phosphorus atom is undergoing rapid inversion at ambient temperature (phosphorus inversional barriers are generally > 30 kcal/mol),[52] it is assumed that the amino protons are accidentally chemical shift equivalent. The compound $[(CF_3)(CH_3)P]_2{}^{15}NH$ possesses two chiral centers which results in the formation of meso and racemate forms.

Table III. ^{15}N-H Coupling Constants, Calculated Per Cent 2s Character at Nitrogen and ^{1}H Chemical Shifts

Compound	$J_{^{15}NH}$	% 2s (N)	τ N-H
$(CF_3)_2P^{15}NH_2$	85.6	30.8	7.48
$(C_2F_5)_2P^{15}NH_2$	85.8	30.9	7.57
$[(CF_3)_2P]_2{}^{15}NH$	81.9	29.2	5.84
$(CH_3)(CF_3)P^{15}NH_2$	79.9	28.3	8.00
$[(CH_3)(CF_3)P]_2{}^{15}NH$	77.5, 78.7[a]	27.3, 27.8	7.25, 7.30
$F_2P^{15}NH_2$	82.7	29.6	6.21
$F_3P(^{15}NH_2)_2$	87.5	31.6	7.08
$F_4P^{15}NH_2$	90.3	32.8	6.62
$(CF_3)_2As^{15}NH_2$	73.4	25.6	7.67
$[(CF_3)_2As]_2{}^{15}NH$	79.0	28.0	6.60
$(CF_3)S^{15}NH_2$	80.6	28.7	7.03
$[(CF_3)S]_2{}^{15}NH$	99.1	36.6	5.53
$[(CH_3)_3Si]_2{}^{15}NH$	66.5	22.6	9.49
$(SiH_3)_2{}^{15}NH$	71.4	24.7	10.15
$H_3B_3N_3H_3$	78.0[b]	27.5	

[a] Due to phosphorus chiral centers. [b] E. Burows, private comunication.

Since Paolillo and Becker[53] have found that the $^{15}N-^1H$ coupling constant of aniline is quite sensitive to the nature of the solvent, it was decided to investigate the effects of changing the solvent and solute concentrations of the two representative compounds $(CF_3)_2P^{15}NH_2$ and $[(CF_3)_2P]_2{}^{15}NH$. These studies (Table IV) show that the magnitude of the $^{15}N-^1H$ coupling differs by less than 0.1% in the solvents $(CH_3)_4Si$, $HCCl_2F$, and toluene-d_8. Furthermore, changing the concentration of the solute from 0.1 to 7.0 *M* also produces less than a 0.1% change in $J_{^{15}NH}$.

Table IV. Solution Studies on $(CF_3)_2P^{15}NH_2$ and $[(CF_3)_2P]_2{}^{15}NH$

Solute	Solvent	Molarity	$J_{^{15}NH}$, Hz
$(CF_3)_2P^{15}NH_2$	$(CH_3)_4Si$	0.160	85.6
		6.640	85.6
	$HCCl_2F$	0.250	85.5
		7.440	85.6
	Toluene-d_8	4.840	85.5
		6.10	85.5
$[(CF_3)_2P]_2{}^{15}NH$	$(CH_3)_4Si$	0.138	81.9
		5.690	81.0
	$HCCl_2F$	0.217	81.9
		4.55	82.0
	Toluene-d_8	0.214	81.5
		0.353	81.0

A number of attempts have been made to correlate the magnitude of a directly bonded coupling constant

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(51) See, for example, K. Mislow and M. Raban, *Top. Stereochem.*, 1, 23 (1967).

(52) A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 93, 6507 (1971).

(53) L. Paolillo and E. D. Becker, *J. Magn. Resonance*, 2, 168 (1970).

with the nature of the bond hybridization.[54] In establishing such relationships it is generally assumed that the Fermi contact term represents the predominant coupling mechanism, an assumption which is particularly reasonable if one of the coupled nuclei is a proton.[55] In the case of the ^{15}N nucleus two groups[56,57] arrived independently at an empirical relationship between the directly bonded ^{15}N–^{1}H coupling constant, $J_{^{15}\mathrm{NH}}$, and the 2s character in the nitrogen bonding orbitals. The phenomenological equation of Binsch, *et al.*,[56] is presented in eq 1. Although this equation

$$s = 0.43J_{^{15}\mathrm{NH}} - 6 \qquad (1)$$

was established originally on the basis of tetrahedral and trigonal-planar nitrogen geometries, it has since been shown[58] to be valid for linear nitrogeneous species such as $HCNH^+$ and CH_3CNH^+. The main objective of the present work was to probe the nature of the nitrogen geometry by determining the magnitude of $J_{^{15}\mathrm{NH}}$ in a series of aminophosphines and related compounds. In turn it was hoped that this would provide information concerning the nature of the nitrogen–heteroatom bond. For example a one bond coupling of ~75 Hz would be indicative of a tetrahedrally hybridized nitrogen on the basis of eq 1. This would infer that the nitrogen lone pair resides in a sp^3 hybrid orbital and that very little dative N→heteroatom π bonding would take place, *i.e.*, the N–heteroatom bond would be essentially a pure σ bond.[59] On the other hand an ^{15}N–^{1}H coupling constant of ~95 Hz would indicate that the nitrogen atom employs sp^2 hybrid orbitals in its σ framework. In this situation the nitrogen lone pair would reside in a pure 2p orbital and very strong nitrogen→heteroatom dative π bonding could be inferred.[60] The foregoing arguments are, of course, based on the assumption that the sign of the ^{15}N–^{1}H coupling constant does not change. Such an assumption appears to be reasonable on both theoretical and experimental grounds.[61]

The percentage 2s characters in the nitrogen bonding orbitals which are indicated in Table III were calculated on the basis of eq 1. These data suggest that the nitrogen atom is approximately trigonal planar in the compounds $(CF_3)_2PNH_2$, $(C_2F_5)_2PNH_2$, $F_3P(NH_2)_2$, and F_4PNH_2. On the other hand an approximately tetrahedral nitrogen geometry is indicated for such compounds as $(CF_3)(CH_3)PNH_2$, $(CF_3)_2AsNH_2$, and CF_3SNH_2. At this point two factors seem to determine the nitrogen atom geometry. First, increasing the electronegativity of the substituents on phosphorus leads to an increase in the per cent of 2s character in the nitrogen orbitals and therefore to an increase in N→P dative π bonding. This is obvious in comparing the $J_{^{15}\mathrm{NH}}$ values of $(CF_3)(CH_3)PNH_2$ and $(CF_3)_2PNH_2$ and also from the increase of $J_{^{15}\mathrm{NH}}$ along the series F_2PNH_2, $F_3P(NH_2)_2$, and F_4PNH_2. The second feature is that replacing phosphorus by arsenic results in a decrease in the per cent of 2s character at nitrogen. This follows from comparison of the $J_{^{15}\mathrm{NH}}$ values of $(CF_3)_2PNH_2$ with $(CF_3)_2AsNH_2$ or $[(CF_3)_2P]_2NH$ with $[(CF_3)_2As]_2NH$. Both of these trends are consistent with the π-bonding model in the sense that the attachment of electronegative groups to phosphorus contracts and lowers the energies of the acceptor 3d or 4p orbitals, thus facilitating N→P dative π bonding and the adoption of a trigonal-planar nitrogen geometry. Furthermore, dative π bonding should not be as effective for aminoarsines because the 4d and 5p orbitals are considerably more diffuse than the corresponding acceptor orbitals of phosphorus.

When an attempt is made to extend this approach to other nitrogen–heteroatom bonds, it is obvious that it meets with difficulties. Consider the silylamines, $[(CH_3)_3Si]_2NH$, and $(SiH_3)_2NH$. On the basis of eq 1 these compounds possess 22.6 and 24.7% 2s character in their nitrogen bonding orbitals. However, electron diffraction studies indicate that the Si–N–Si bond angles are 125.5 ± 1.8 and 127.9 ± 0.2° in $[(CH_3)_3Si]_2NH$ and $(SiH_3)_2NH$, respectively.[62] Despite the fact that the imino proton was not detected and the possibility that the N–H bond is distorted from the heavy-atom plane, the structural data are in accord with the nitrogen per cent 2s character being much nearer to 33.3% than 25%. In the case of borazine structural studies establish that the nitrogen is definitely trigonal planar.[63] Again it will be noticed that eq 1 breaks down since the scalar ^{15}N–^{1}H coupling constant of 78 Hz[64] indicates that the per cent of 2s character in the nitrogen bonding orbitals is only 27.5%. It would, therefore, appear that eq 1, which is based on a series of organonitrogen compounds, is not applicable to cases where the electronegativity of the heteroatom is markedly different from that of carbon. Accordingly we turned our attention to an alternative explanation of the ^{15}N–^{1}H coupling constant data.

By employing the Pople and Santry approach[55] it is possible to derive the following simplified expression for the Fermi contact contribution of the one bond ^{15}N–^{1}H coupling constant

$$J_{^{15}\mathrm{NH}} \propto \gamma_{^{15}\mathrm{N}}\gamma_{\mathrm{H}}(\Delta E)^{-1}\alpha_{\mathrm{N}}^{2}\alpha_{\mathrm{H}}^{2}|\psi_{\mathrm{N(2s)}}(0)|^{2}|\psi_{\mathrm{H(1s)}}(0)|^{2} \qquad (2)$$

Here $\gamma_{^{15}\mathrm{N}}$ and γ_{H} are the magnetogyric ratios of the coupled nuclei, ΔE is the average excitation energy, α_{N}^2 and α_{H}^2 are the s characters of the hybrid orbitals which make up the N–H bond, and the $|\psi(0)|^2$ terms represent the magnitudes of the indicated s orbitals at the appropriate nuclei. Two assumptions will be made at this point: (i) ΔE will be regarded as a constant and (ii) that changes in the groups bonded to nitrogen will not affect α_{H}^2 and $|\psi_{\mathrm{H(1s)}}(0)|^2$. The basis of assumption (i) is the work of Inglefield and Reeves[65] which shows that consistent results are obtained if ΔE is treated as a

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(54) The most widely recognized correlation is that between the ^{13}C–^{1}H coupling constant and 2s character in the carbon bonding orbitals. See N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 31, 768 (1959).

(55) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(56) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, 86, 5564 (1964).

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(59) See, however, E. A. V. Ebsworth, *Chem. Commun.*, 530 (1966).

(60) M. J. S. Dewar and P. Rona, *J. Amer. Chem. Soc.*, **91**, 2259 (1969).

(61) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, **51**, 2790 (1969).

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(63) E. K. Mellon, Jr., and J. J. Lagowski, *Advan. Inorg. Chem. Radiochem.*, **5**, 259 (1963), and references therein.

(64) E. Burows, private communication. The authors are grateful to Dr. Burows for this datum.

(65) P. T. Inglefield and L. W. Reeves, *J. Chem. Phys.*, 40, 2424 (1964).

constant for a series of similar compounds. The validity of assumption (ii) has been discussed previously in relation to metal–phosphorus couplings.[66] This means that the changes in $J_{^{15}\mathrm{NH}}$ are assumed to be dominated by changes in α^2_{N} and $|\psi_{\mathrm{N(2s)}}(0)|^2$ in the following manner. The so-called isovalent hybridization hypothesis[67] states that s character concentrates in the bonds which are directed toward electropositive substituents. For structures of the general types XNH_2 and X_2NH this means that, *e.g.*, as the electronegativity of X increases that nitrogen 2s character is progressively diverted into the N–H bonds. In turn this causes increases in α^2_{N} and $|\psi_{\mathrm{N(2s)}}(0)|^2$ which result in an increase in $J_{^{15}\mathrm{NH}}$. There is, in fact, a very good correlation between $J_{^{15}\mathrm{NH}}$ and the electronegativity of the heteroatom which is attached to nitrogen (Table V). In Table VI it is apparent that there is also a good correlation between the group electronegativity[68] and the magnitude of the one-bond ^{15}N–^1H coupling. No electronegativity values are available for the $-PF_3$ and $-PF_4$ moieties; however, the PF_4 group is anticipated to be more electronegative than the PF_3 group and the $J_{^{15}\mathrm{NH}}$ values are in the expected order. The only abnormality relates the $J_{^{15}\mathrm{NH}}$ value for $[(CF_3)_2P]_2{}^{15}NH$. In all the other cases studied the one-bond ^{15}N–^1H coupling constant increases in proceeding from the XNH_2 to the X_2NH compound. Evidently this abnormality is not due to a solvent effect since the solution studies (*vide supra*) reveal insignificant changes in $J_{^{15}\mathrm{NH}}$ when either the solute concentration or the solvent is changed.

Table V. Pauling Electronegativities for XNH_2 and X_2NH

Atom X, electronegativity	$J_{^{15}\mathrm{NH}}$, Hz	Atom X, electronegativity	$J_{^{15}\mathrm{NH}}$, Hz
Si, 1.8	65–72	P, 2.1	80–86
As, 2.0	73–80	S, 2.5	80–100
B, 2.0	78		

Table VI. Group Electronegativities[a] for XNH_2 and X_2NH

Group X	Electronegativity	$J_{^{15}\mathrm{NH}}$, Hz
$-SiH_3$	2.21	71.4
$-Si(CH_3)_3$	2.27	66.5
$-P(CF_3)(CH_3)$	2.80	77.5–79.9
$-As(CF_3)_2$	3.22	73.4–79.0
$-PF_2$	3.29	82.7
$-P(CF_3)_2$	3.30	81.9–85.6
$-SCF_3$	3.38	80.6–99.1
$-PF_3$	*b*	87.5
$-PF_4$	*b*	90.3

[a] Reference 68. [b] No electronegativity values available.

While the correlation between $J_{^{15}\mathrm{NH}}$ and the substituent electronegativity of XNH_2 and X_2NH compounds does not preclude the presence of a π component in the nitrogen–heteroatom linkage, it is clear that it is unnecessary to invoke the p_π–d_π bonding in order to explain the present nmr data. This view is consonant with the following theoretical and experimental observations.

(i) *Ab initio* SCF-MO calculations[69] on the parent aminophosphine, H_2NPH_2, indicate that the nitrogen atom adopts a trigonal planar geometry as a consequence of the inductive transfer of electron density from the PH_2 to the NH_2 moiety. It is now well established[70] that electron release to a tricoordinate atom causes relative stabilization of the planar structure. Note that a p_π–d_π bond would result in an electron transfer from nitrogen to phosphorus. Moreover it was found that the nitrogen atom of H_2NPH_2 is computed to be trigonal planar regardless of the presence or absence of d-type functions in the basis set. In fact the role of such functions appears to be one of increasing the mathematical flexibility of the basis set.[71]

(ii) Harrison, Ulrich, and Zuckerman[72] have recently found that in the series of heteroatom-substituted phosphines $C_6H_5PHX(CH_3)_3$; X = Si, Ge, and Sn that $J_{^{31}\mathrm{PH}}$ is smaller than in $C_6H_5PH_2$ or $C_6H_5PHC(CH_3)_3$. If (p→d) π conjugation were important the substitution of silicon, germanium, or tin for hydrogen should raise the $J_{^{31}\mathrm{PH}}$ value. Furthermore, the substitution of a second group which is capable of d-orbital conjugation, *e.g.*, $[(CH_3)_3Si]_2PH$ lowered the $J_{^{31}\mathrm{PH}}$ value even more. Furthermore the ^{31}P–^1H coupling constants in $(CH_3)_3MPH_2$, where M = Si or Sn are lower than in phosphine itself. These authors concluded that their results are inconsistent with a π-bonding model but were best interpreted from the standpoint of σ-effects alone.

Although it is common practice to relate the variations in nuclear spin coupling constants to hybridization effects, it should be borne in mind that the Fermi contact interaction also depends on the cube of the effective nuclear charges of the coupled atoms.[73] This effect has been demonstrated experimentally for both the ^{13}C–^1H and ^{31}P–^1H directly bonded couplings.[73,74] Our results are also consistent with this approach since increasing the electronegativity of the groups attached to nitrogen should increase the effective nuclear charge at nitrogen which would, in turn, increase $J_{^{15}\mathrm{NH}}$.

The variations in the ^1H chemical shifts in Table III conform to expectation in the same sense that the amino or imino proton resonance experiences a progressively downfield shift as the group electronegativity of the nitrogen substituent is increased. There is not, however, a linear relationship between $J_{^{15}\mathrm{NH}}$ and the chemical shift of the NH_2 or NH group.

Synthesis and Stereochemistry of F_4PNH_2. In view of the recent interest in the synthesis and stereochemistry of aminotetrafluorophosphoranes[31,33–35,42,75] it seemed appropriate to prepare F_4PNH_2, the parent member of this class of compound. Aminotetrafluorophos-

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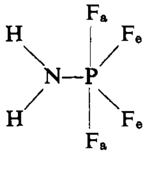
phorane is readily synthesized by the gas-phase reaction of PF_4Cl with NH_3. The establishment of the formulation F_4PNH_2 lies principally on mass spectral evidence (see Experimental Section). The observation of ^{19}F resonances of equal integrated intensity at -24.3 (F_a) and -1.33 ppm (F_e) (relative to internal $HCCl_2F$) is consistent with a trigonal bipyramidal structure in which the amino group occupies an equatorial site.



The complex appearance of the ^{19}F and ^{1}H nmr spectra (Figure 2) is ascribed to the fact that the molecule appears to constitute an $A_2KK'PTXX'$ spin system. The only satisfactory manner of extracting all the spin coupling parameters will be to perform iterative calculations and spectral simulations. At the present time, therefore, only approximate values are available for the coupling constants $J_{F_aPF_e}$ ($\sim$71 Hz), J_{F_aPNH} ($\sim$42 Hz), and J_{F_ePNH} ($\sim$1.6 Hz). However, the couplings $J_{PF_e} = 936$, $J_{PF_a} = 760$, $J_{^{15}NH} = 90.3$, $J_{^{15}NPF_a} = 22.8$, and $J_{PNH} = 17.7$ Hz can be recognized on a first order basis. The observation that the axial fluorines and amino protons are chemical shift equivalent (but spin coupling nonequivalent) implies that these nuclei are symmetrically disposed with respect to each other. Presumably the ground-state geometry of F_4PNH_2 involves a coplanar arrangement of the amino hydrogens and axial fluorine atoms since this would permit maximum F···H–N intramolecular hydrogen bonding. This suggestion is also in accord with the high barrier to intramolecular ligand exchange in F_4PNH_2. Although broadened, separate F_{axial} and $F_{equatorial}$ resonances are still discernible at 30°, thus placing $\Delta G^{\ddagger}$ in excess of 15 kcal/mol. Such an increase in barrier over, *e.g.*, $(CH_3)_2NPF_4$ (where $\Delta G^{\ddagger} \sim 9.0$ kcal/mol[34,75]), is presumably a consequence of intramolecular hydrogen bonding.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP 28634) and the Robert A. Welch Foundation for generous financial support. Several stimulating discussions with Professor John W. Gilje are also appreciated.

Computer-Aided Interpretation of Mass Spectra. III. A Self-Training Interpretive and Retrieval System[1,2]

Kain-Sze Kwok,[3] Rengachari Venkataraghavan, and F. W. McLafferty*

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received October 26, 1972*

Abstract: A self-training system is described for computer interpretation of mass spectra which utilizes directly data of all available reference spectra, and does not require prior spectra–structure correlations of these data either by human or computer effort. The computer selects different classes of data known to have high structural significance, such as characteristic ions, series of ions, and masses of neutrals lost, from the unknown mass spectrum, and matches these against the corresponding data of all the reference spectra. The reference compounds of closest match in each data class are examined for common structural features; criteria have been determined so that such features can be identified with approximately 95% reliability. Tests with 110 "unknowns" not represented in the reference file showed that extensive to complete structural information can be obtained if spectra of related compounds are present in the reference file.

Compared to other spectroscopic methods commonly employed, a mass spectrum is unique in the large quantity of data it contains; the spectrum of a complex molecule can have hundreds of peaks, each discrete in mass. In sharp contrast to other methods, however, the chemist usually makes use of only a small percentage of these data for structure elucidation of an unknown. Although there has been substantial progress in mechanistic and empirical correlation of mass spectral data with molecular structure,[4,5] the large quantity of data itself apparently is a deterrent both to further progress by mass spectrometrists and to the acquiring of present knowledge by chemists with applicable problems. The average spectrum in our laboratory reference file representing 13,000 compounds contains over 100 peaks; searching such a data base for detailed similarities to an unknown spectrum is obviously a complex task. The rapidly growing utilization of gas chromatography–mass spectrometry, which can produce scores of mass spectra per hour, has greatly increased the need for such capabilities.

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