was produced in an exothermic reaction which commenced near −78°. The mixture was allowed to stand at room temperature for 15 min and the volatile products were removed. Noncondensable gas (about 0.03 mmol) and 0.090 mmol of diborane (identified by its infrared spectrum) were obtained. Thus the stoichiometry was $1:BH_3 = 1.07$. The adduct was sublimed under high vacuum at 80–100° to give 43.4 mg of white crystalline solid, mp 106–109.5°. *Anal.* Calcd for $(CH_3)_3NBH_2CH_2N(CH_3)_2BH_3$: C, 50.1; H, 15.4. Found: C, 49.4; H, 15.0. The hydrolytic hydrogen value found, 3.43×10^{-2} mmol/mg, also agreed well with the calculated value of 3.47×10^{-2} mmol/mg.

The adduct from another preparation was sublimed with 74% recovery.

Titration of $(CH_3)_3NBH_2CH_2N(CH_3)_2H^+PF_6^-$.—A 43.7-mg sample was dissolved in 20.0 ml of water and titrated with 0.0975 N sodium hydroxide under nitrogen using a glass electrode standardized at pH 9 and a Beckman expanded-scale pH meter. A blank containing 20.0 ml of deionized water was similarly titrated. Estimation of pK_b was made from the titrant volume difference between the salt solution and blanks at pH 9.5, 10.0, and 10.5. The equation employed was $K_b = K_w(V_{ep} - \Delta V)/10^{-pH}\Delta V$, where V_{ep} is the theoretical volume of 1 equiv of base. Values obtained were 17×10^{-3}, 8×10^{-3}, and 5×10^{-3}. Similar results were obtained using 0.02 N sodium hydroxide.

It was found that 1 could be extracted into hexane from 0.1–1 N base. The distribution coefficient in 1 N base at 25.0° was determined as 2.2 ± 0.1, $D = [1]_{aqueous}/[1]_{hexane}$. A solution of 1 in hexane was prepared by extracting a solution of the conjugate acid of 1 in 1 N base. The concentration of the resulting hexane solution was determined by stirring an aliquot vigorously with deionized water and titrating under nitrogen. A 5.00-ml aliquot of the hexane solution was equilibrated with 1.00 ml of 1 N sodium hydroxide and the concentration of 1 in hexane was again determined. The decrease of 1 in the hexane phase was used to calculate the concentration of 1 in the aqueous phase. In experiments without the borane salt it was established that hexane by itself carries no basic material after shaking with 1 N sodium hydroxide and separating.

In several titrations of solutions of 1 in water with 0.02 N hydrochloric acid, differential titration curves, $\Delta pH/\Delta V$ *vs*. volume, exhibited maxima near pH 7.0.

$(CH_3)_3NBH_2CH_2N(CH_3)_2CH_2CO_2C_2H_5^+PF_6^-$.—A mixture of 0.26 g of 1 and 0.22 ml of ethyl bromoacetate in 5 ml of ether rapidly became cloudy, precipitating a clear oil which slowly crystallized. The bromide salt so obtained was dissolved in water and converted to the hexafluorophosphate by addition of excess ammonium hexafluorophosphate. The slightly soluble hexafluorophosphate was recrystallized from hot water; 0.33 g of white crystals, 46% yield; mp 70–74°. *Anal.* Calcd for $(CH_3)_3NBH_2CH_2N(CH_3)_2CH_2CO_2C_2H_5^+PF_6^-$: C, 33.2; H, 7.2; N, 7.7; B, 3.0. Found: C, 34.0; H, 7.2; N, 7.8; B, 2.2.

$(CH_3)_3NBH_2CH_2N(CH_3)_2BH_2N(CH_3)_3^+PF_6^-$ and $(CH_3)_3NBH_2CH_2N(CH_3)_2BH_2P(CH_3)_3^+PF_6^-$.—To a stirred solution of 311 mg (2.12 mmol) of $(CH_3)_3NBH_2CH_2N(CH_3)_2BH_3$ in 5 ml of dry chloroform was added dropwise a solution of 269 mg (1.06 mmol) of I_2 in 20 ml of chloroform. The mixture was stirred 15 min more after hydrogen evolution ceased. Then 2.11 mmol of trimethylamine was added and the clear solution was allowed to stand overnight. Solvent was removed and the resulting oil (iodide salt) was converted to the hexafluorophosphate salt; 490 mg, 80% yield. Recrystallization from hot water (10 mg/ml) gave white crystals, mp 103–104°. *Anal.* Calcd for $(CH_3)_3NBH_2CH_2N(CH_3)_2BH_2N(CH_3)_3^+PF_6^-$: C, 31.2; H, 8.7; N, 12.1; B, 6.2. Found: C, 31.5; H, 8.5; N, 12.0; B, 6.1.

Similarly, from 319 mg of $(CH_3)_3NBH_2CH_2N(CH_3)_2BH_3$, 218 mg of iodine, and 2.28 mmol of trimethylphosphine, after workup, was obtained 537 mg of crude $(CH_3)_3NBH_2CH_2N(CH_3)_2BH_2P(CH_3)_3^+PF_6^-$. Recrystallization from hot water gave 267 mg of pure material, mp 123–124°. *Anal.* Calcd for $(CH_3)_3NBH_2CH_2N(CH_3)_2BH_2P(CH_3)_3^+PF_6^-$: C, 29.7; H, 8.3; N, 7.7; B, 5.9; P, 17.0. Found: C, 29.8; H, 8.6; N, 7.9; B, 5.8; P, 16.9.

A Study of the Bonding in Group IV Amines

BY JOHN MACK AND CLAUDE H. YODER[1]

N-Methyl C^{13}–H coupling constants and relative basicities were measured for the compounds $(CH_3)_3MN(CH_3)_2$ and $M[N(CH_3)_2]_4$, where M = C, Si, Ge, and Sn. The coupling constants for the trimethyl series varied in the order Si > Ge = C > Sn and for the tetrakis series in the order Si > C > Ge > Sn. The relative basicities in both series varied in the order Ge > Si. The trends are interpreted as indicative of a decrease in $(p-d)\pi$ overlap from silicon to tin, with the major change occurring between silicon and germanium.

The bonding in silylamines has been a subject of considerable concern and numerous publications ever since the discovery of the planarity and low basicity of trisilylamine. Although there has been a recent flourish of experiments resulting in agnostic interpreta-

tion,[2] it is generally conceded that the chemical and physical peculiarities of silylamines as compared to organic amines are a result of $(p-d)\pi$ bonding. The bonding in other group IV amines has received much

less consideration. In fact, the matter of the variation in π bonding down group IV in general has received relatively little attention.

With the exception of some of the early work by Benkeser, *et al.*,[3] most of the evidence to date points to a decrease in π overlap from silicon to tin.[4] Guidance from theoretical quarters is limited primarily to the classic document of Craig, Maccoll, Nyholm, Orgel, and Sutton, where it was concluded that "when the d orbital is considerably more diffuse than the p orbital, the overlap is better than when they are commensurate; but conditions are not critical."[5] These workers also indicated, however, that the ratio of the diffuseness of the two interacting orbitals can in certain cases be prohibitive and that electronegative substituents may cause contraction of the d orbitals and thereby increase overlap.[6]

The present work is an attempt to evaluate the existence and variation of π bonding in some group IV amines. The choice of amines for study was dictated by considerations of simplicity and availability of carbon homologs. Thus, the compounds $(CH_3)_3MN(CH_3)_2$ and $M[N(CH_3)_2]_4$ were prepared where $M = C$, Si, Ge, or Sn.

The parameters measured—N-methyl C^{13}–H coupling constants and relative hydrogen-bonding basicities—were chosen because of their dependence on the nature of the M–N bonding.

Experimental Section

Syntheses.—All group IV halides, except trimethylbromogermane, used as starting materials were commercial products. Trimethylbromogermane was prepared by bromination of tetramethylgermane in 2-bromopropane.[7] Dimethylamine was dried over Linde Type 4A Molecular Seives. Solvents were dried by refluxing over calcium hydride. All operations were carried out in oven-dried glassware and under a nitrogen atmosphere. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

t-Butyldimethylamine was prepared by methylation of *t*-butylamine with formaldehyde and formic acid following the procedure of Spialter and Pappalardo.[8]

Trimethyldimethylaminosilane was obtained by amination of trimethylchlorosilane with excess dimethylamine in ether. The product distilled at 81–84° (740 mm) (lit.[9] 86° (760 mm)).

Trimethyldimethylaminogermane.—A 1.6 *M* solution of butyllithium (Foote Mineral) in hexane (95 ml, 0.15 mol) was added dropwise with stirring to dimethylamine (6.6 g, 0.15 mol) in 100 ml of benzene at 0°. The mixture was allowed to warm to room temperature and then trimethylbromogermane (24.5 g, 0.15 mol) in 30 ml of benzene was added dropwise at room tempera-

ture. After 20 hr of refluxing the mixture was cooled several days in a refrigerator to make the precipitation of lithium bromide as complete as possible. The mother liquor was then decanted and concentrated by distillation at atmospheric pressure. Fractional distillation of the residue on a 6-in. column filled with glass beads afforded *ca.* 5 g (20% yield) of a colorless liquid boiling at 98–107° (740 mm). The product of another preparation was purified on an annular spinning-band column and a fraction at 100–101° was obtained. *Anal.* Calcd for $C_5H_{15}NGe$: C, 37.11; H, 9.34; N, 8.66; Ge, 44.86. Found: C, 36.33; H, 8.97; N, 7.70; Ge, 44.30.

Tetrakis(dimethylamino)methane was obtained from the reaction of tetramethylformamidinium chloride with the lithium salt of dimethylamine following the procedure of Weingarten and White.[10] The product had a melting point of 119–122.5° (lit.[10] 122.5–124.5°). It was found to react rapidly with chloroform.

Tetrakis(dimethylamino)silane was prepared by amination of silicon tetrachloride with dimethylamine in benzene. The product distilled at 59.5–60.5° (16 mm) (lit.[11] 72–75° (13 mm)).

Tetrakis(dimethylamino)germane was secured by treatment of germanium tetrachloride with excess dimethylamine in petroleum ether (bp 30–60°) at −60°. The product distilled at 72° (8 mm) (lit.[11] 87–89° (15 mm)).

Tetrakis(dimethylamino)stannane was obtained by lithioamination of tin tetrachloride. The boiling point of the product was 89° (0.5 mm) (lit.[12] 51° (0.15 mm)).

Trimethyldimethylaminostannane was a gift of Dr. M. F. Lappert.

The nmr and ir spectra of all of the above preparations were completely consistent with the proposed structures. Nmr chemical shifts are given in Table I.

TABLE I
CHEMICAL SHIFTS (± 0.6 cps)[a]

| | (CH₃)₃MN(CH₃)₂ | | | | M[N(CH₃)₂]₄ | |
| | M(CH₃)₃ | | N(CH₃)₂ | | N(CH₃)₂ | |
	Neat	50% CHCl₃	Neat	50% CHCl₃	Neat	50% CHCl₃
C	48.8	...	117.8	...	153.9	154.7
Si	0.0	0.0	144.5	144.3	155.6	156.4
Ge	10.0	13.1	146.4	147.2	164.4	...

[a] All values are in cycles per second relative to TMS at 60 Mcps.

Nmr spectra were obtained on Varian A-60 and A-60A spectrometers operating at 38 ± 3°. N-Methyl coupling constants were measured by the standard side-banding technique using a Hewlett-Packard 200 CD audio oscillator and a 521 C or 522 B electronic counter. Each value is the average of at least three tracings. Chloroform coupling constants were obtained at 250-cps sweep width and are averages of at least three tracings.

Chloroform and deuteriochloroform used in spectral studies were shaken three times with alumina to remove ethanol and stored in stoppered brown bottles for no more than 1 day.

Infrared basicity work was carried out on a Perkin-Elmer 257 spectrometer operating at 10-fold scale expansion in the 2400–2100-cm⁻¹ region. Deuteriochloroform solutions of the compounds (*ca.* 1:10 mole ratio) were examined in sodium chloride solution cells. Spectra were calibrated with benzene absorption peaks at 2326 and 2208 cm⁻¹.[13] Shifts in ν(C–D) were determined relative to the value reported for gaseous deuteriochloroform.[13]

Results and Discussion

N-Methyl C^{13}–H coupling constants are presented in Table II. The constants were determined from the

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(5) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332, 354 (1954).

(6) See also D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956).

(7) V. F. Mironov and A. L. Kravchenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1026 (1967).

(8) L. Spialter and J. A. Pappalardo, *J. Org. Chem.*, **22**, 840 (1957).

(9) E. A. V. Ebsworth and H. J. Emeléus, *J. Chem. Soc.*, 2150 (1958).

(10) H. Weingarten and W. A. White, *J. Am. Chem. Soc.*, **88**, 2885 (1966).

(11) H. H. Anderson, *ibid.*, **74**, 1421 (1952).

(12) K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1944 (1965).

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neat compounds and as 50% (v/v) solutions in chloroform. Tin amines are known to react with chloroform[14] (tetrakis(dimethylamino)methane was found to be just as reactive), and therefore constants for the two stannylamines were obtained from the neat compounds while the solid methane was run in benzene.

TABLE II

N-METHYL C^{13}–H COUPLING CONSTANTS (± 0.3 CPS)

| | $(CH_3)_3MN(CH_3)_2$ | | $M[N(CH_3)_2]_4$ | |
	Neat	50% CHCl₃	Neat	50% CHCl₃
C	131.4	132.0	133.4[b]	
Si	132.2	132.6	135.0	135.4
Ge	131.4	132.0	132.4	132.6
Sn	130.2[a]		132.0[a]	

[a] Deviation ± 0.6 cps.   [b] *Ca.* 50% in benzene; ± 0.6 cps.

Carbon-13–proton coupling constants are generally believed to be some function of the polarity and hybridization in the C–H bond. A recent discussion[15] based on a dominant contact coupling mechanism showed that the constant in a substituted methane should be proportional to a bond normalization constant,[16] the average excitation energy of the C–H bonds, the third power of the effective nuclear charge on carbon, and the amount of s character in the C–H bonds. Assuming the first two parameters to remain constant, it is clear that $J(C^{13}$–H) should be related to the effective nuclear charge and the s character in the C–H bonds. Experimentally, this conclusion appears to be valid, at least in similar or homologous series.[17]

How, then, will (p–d)π bonding affect the magnitude of the coupling constant? An increase in effective electronegativity of X in a group XCH_3 will increase both the effective nuclear charge of carbon and the amount of s character in the C–H bonds (according to isovalent hybridization arguments[18]) and will result, therefore, in an increase in the coupling constant. The effective electronegativity of nitrogen in the group $MNCH_3$ will depend upon the σ electronegativity of M (electron release through σ bonds) and any (p–d)π delocalization which may occur.

On the basis of the above arguments, $J(C^{13}$–H) should decrease from M = carbon to silicon and remain relatively constant or perhaps decrease slightly from silicon to tin, if there is no (p–d)π overlap in the compounds examined. That is, in the event of no π overlap, the constants are determined by the variation in σ electronegativity of M and all scales agree that silicon, germanium, and tin are less electronegative than carbon. The order actually observed in Table II, Si > C = Ge > Sn for the trimethyl series and Si > C > Ge $\gtrless$ Sn for the tetrakis series, must be

ascribed, then, to (p–d)π delocalization in the silicon derivatives. The order, C = Ge, in the trimethyl series may be indicative of a small amount of π overlap in the germanium derivatives. This assumes, of course, the absence of π interaction in the carbon compound.

Table III contains the shift, $\Delta\nu$(C–D), in the C–D stretching frequency of deuteriochloroform in a 1:10 mole ratio mixture with the amines relative to the stretching frequency in gaseous $CDCl_3$ and the C^{13}–H coupling constants of chloroform in solutions of various concentrations with the amines. Both parameters are related to the basicity of the amines with respect to hydrogen bonding.

TABLE III

RELATIVE BASICITIES TOWARD CHLOROFORM

| | $\Delta\nu$(C–D) (± 5), cm⁻¹ | $J(C^{13}$–H) for CHCl₃ (± 0.5), cps | | |
		1:5[a]	2:5[a]	5:5[a]
		$(CH_3)_3MN(CH_3)_2$		
C	96	211.9[b]	211.3[c]	211.1
Si	61	210.2	210.1	209.7
Ge	76	211.4	211.1	210.0
		$M[N(CH_3)_2]_4$		
Si	10	209.4	209.4	209.5
Ge	60	209.7	209.6	209.6

[a] Volume of chloroform:volume of compound.   [b] 2:7.   [c] 4:7.

The relationship between stretching frequency and energy of hydrogen bond was first recognized by Badger and Bauer in a study of alcohol–donor systems.[19] The linearity of this relationship has been verified for the interaction of phenol with various bases[20] and a theoretical rationalization has been presented for its existence.[21] Although the validity of this relationship has been questioned by some workers,[22] it seems reasonable to assume that $\Delta\nu$ will be roughly proportional to the strength of the hydrogen bond at least in homologous series where both atoms interacting with hydrogen are the same.

With this as an operating principle, the $\Delta\nu$(C–D) data in Table III clearly indicate that the silyl derivative in each series forms the weakest hydrogen bond. This observation can be explained, as it has been in other systems,[13,23] as a result of π delocalization in the Si–N bond. The fact that $\Delta\nu$ for trimethyldimethylaminogermane is lower than $\Delta\nu$ for the carbon analog, even though the lower electronegativity of germanium should make it more basic, probably indicates the presence of some π overlap in the Ge–N bond as well.

(14) C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 2170 (1966)

(15) D. M. Grant and W. M. Litchman, *ibid.*, **87**, 3994 (1965).

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(23) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press Inc., New York N. Y., 1963.

The relationship of the C^{13}–H coupling constant of chloroform in a chloroform–donor mixture to the basicity of the donor was apparently first noticed by Evans.[24] This relationship is somewhat more complex than the $\Delta\nu$–ΔH one above, because exchange between unassociated and associated chloroform results in a coupling constant which is a weighted average of the constant in pure chloroform and the constant in the base-associated chloroform. Thus, $J(C^{13}$–H) for chloroform–base mixtures depends not only on ΔH for the hydrogen bond but also on K for the reaction

$$B + HCCl_3 \rightleftharpoons B\cdots HCCl_3$$

The $J(C^{13}$–H) data in Table III for the trimethyl series parallel the $\Delta\nu$ data in suggesting that the silyl derivative is the least basic and the carbon derivative the most basic. The carbon and germanium derivative values have a greater concentration dependence than the silicon compound and this may also be evidence for their greater basicity.

To a first approximation, one might expect basicity to be some function of the effective electronegativity of nitrogen in compounds with very similar steric requirements (for reaction with the reference acid). Comparison of the data in Tables II and III indicates that within a given series the higher the N-methyl

(24) D. F. Evans, *J. Chem. Soc.*, 5575 (1963).

C^{13}–H constants, the lower the basicity as measured by $\Delta\nu$. This is obviously a crude generalization, however, as the similar $J(C^{13}$–H) but differing $\Delta\nu$ values for the trimethylsilyl and -germyl compounds would indicate.

In conclusion, then, the bulk of the data indicates that nitrogen in the silicon derivatives has the highest effective electronegativity and that these compounds are also the least basic. The effective electronegativities vary in the order M = Si > Ge = C > Sn for the trimethyl series and Si > C > Ge $\geqslant$ Sn for the tetrakis series. The chloroform shift data indicate that the basicities toward chloroform as a reference acid vary in the order C > Ge > Si in the trimethyl series and Ge > Si in the tetrakis series.

We believe that these trends can best be rationalized by $(p-d)\pi$ bonding in the silyl derivatives, a considerably smaller amount in the germanium derivatives (at least in trimethyldimethylaminogermane), and probably none in the tin compounds.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

The Synthesis and Properties of Difluorodithiophosphoric Acid

BY T. L. CHARLTON AND R. G. CAVELL

Difluorodithiophosphoric acid, a volatile monomeric compound (bp 72°), has been synthesized by either (1) reaction of iodothiophosphoryl difluoride with hydrogen sulfide or (2) reaction of hydrothiophosphoryl difluoride with sulfur. The acid is slowly hydrolyzed by water and it reacts with chlorine and hydrogen iodide but not with iodine, air, methyl mercaptan, or iodothiophosphoryl difluoride. Amines form salt-like adducts from which the acid is not displaced by hydrogen chloride indicating that the acid is a strong one. Nmr spectra indicate rapid proton exchange in solution. Infrared spectra and mass spectra are reported.

Introduction

Following the recent synthesis of bis(trifluoromethyl)-dithiophosphinic acid, $(CF_3)_2PS_2H$, both in our laboratory[1] and by Gosling and Burg,[2] it was of interest to synthesize and study the analogous difluoro acid, difluorodithiophosphoric acid. The salts[3a,b] and the hydrated form[3a] of this acid have only recently been

reported. A recent brief communication[3c] mentioned anhydrous difluorodithiophosphoric acid but no preparative details were given. In contrast, the oxygen analog, difluorophosphoric acid,[4] and organic dithiophosphinic acids[5] are well known and have been extensively studied.

Experimental Section

Standard vacuum techniques using a Pyrex-glass apparatus were employed. Stopcocks were lubricated with Apiezon N grease. Infrared spectra were measured with a Beckman IR-12 (4000–300 cm^{-1}) and mass spectra with an AEI MS-9 double-

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