Nuclear Magnetic Resonance and Infrared Studies of N^{15}-Substituted Trimethylsilyl-, -germyl-, and -stannylanilines. A Test of $(p\rightarrow d)-\pi$ Interactions in Group IV Nitrogen Bonds[1]

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Abstract: Infrared and proton magnetic resonance spectra of the aniline-N^{14} and -N^{15} isotopomers and their N-trimethylsilyl, -germyl, and -stannyl derivatives have been measured and compared. Nmr assignments have been checked by comparisons of proton spectra at 60 and 100 Mcps; by proton–N^{15} heteronuclear experiments at 9400 G; and by observation of N^{15} satellites. The one-bond N^{15}–H couplings can be interpreted (on the assumption of a dominant Fermi spin–spin interaction, small radial variations for nitrogen wave functions, and equal distributions of s character in the σ bonds) in terms of pyramidal arrangements of bonds at nitrogen. The relation of the stereochemical situation at nitrogen to the question of $(p\rightarrow d)-\pi$ or $(p\rightarrow p)-\pi$ bonding involving nitrogen is discussed.

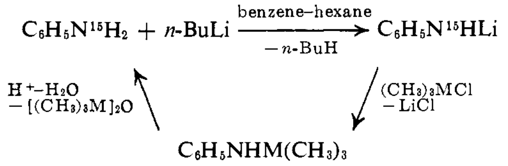
We have carried out experiments designed to test the hypothesis of $(p\rightarrow d)-\pi$ interactions in the bonds formed between nitrogen and the fourth group elements silicon, germanium, and tin. We report here the results of our study of the N-trimethylmethyl, silyl, germyl, and stannyl derivatives of aniline and aniline-N^{15} by nuclear magnetic resonance spectroscopy. Availability of the N^{14} and N^{15} isotopomers allowed in addition an infrared study.

Experimental Section

Apparatus. The nmr data were obtained on three types of instruments: the Varian A-60 spectrometer with temperature-regulating accessories, Hewlett-Packard audio oscillator (Model 200 AB), and electronic counter (Model 521 C); the Varian HA 100 spectrometer with a Varian C 1024 time-average computer; and a heteronuclear double-resonance spectrometer operating at 9400 G described previously.[3] The temperatures in the A-60 magnet gap were calculated from peak separations in the ethylene glycol or methanol samples using Varian calibration data.

Infrared spectra were recorded on a Perkin-Elmer Model 521 grating spectrometer and calibrated with polystyrene. Differential double-beam experiments utilizing the N^{14} and N^{15} isotopomeric pairs of compounds (as shown for N-trimethylsilylaniline-N^{14} and -N^{15} in Figure 1) afforded an indication of the bands which underwent a frequency change on N^{15} substitution. Compounds were examined as liquid smears.

Syntheses. Aniline-N^{15} (95%) was obtained from Merck Sharpe and Dohme of Canada, Ltd. and was used in the microsynthetic procedure depicted in eq 1. Lithioamination by the monolithium salt of aniline afforded the organometallic derivatives in better yield than the one-step synthesis known for silicon[4] while eliminating removal of half the aniline as the hydrochloride.



$$\begin{tikzcd}[column sep=small] C_6H_5N^{15}H_2 + n\text{-BuLi} \arrow[rr, "\text{benzene–hexane}", "-n\text{-BuH}"'] & & C_6H_5N^{15}HLi \arrow[dl, "(CH_3)_3MCl", "-LiCl"'] \\ & C_6H_5NHM(CH_3)_3 \arrow[ul, "H^+\text{–}H_2O", "-[(CH_3)_3M]_2O"'] & \end{tikzcd} \qquad (1)$$

N-Trimethylsilylaniline. *n*-Butyllithium and aniline (2.5 g, 0.0269 mole) in equimolar proportion were refluxed in benzene–hexane solution for 45 min until butane evolution ceased. The resulting yellow-green precipitate of monolithioaniline reacted with an equimolar amount of trimethylchlorosilane during 3 hr of reflux. Combined benzene extracts from the heavy lithium chloride precipitate allowed the product (bp 106–107° (24 mm)) to be collected in 83% yield. In practice runs on the N^{14} aniline isotopomer, monolithioaniline was found to be extremely sensitive to hydrolysis to aniline and to air oxidation to aniline-black and aniline-blue.

N-Trimethylgermylaniline. Preparation of trimethylchlorogermane proved an unexpected difficulty despite a variety of reported routes.[5] A synthetic procedure recently discovered by Mironov and Kravchenko[6] gave reproducible results from the following route.

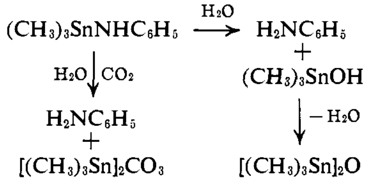
$$(CH_3)_4Ge + i\text{-}C_3H_7Cl \xrightarrow{AlCl_3} (CH_3)_3GeCl \qquad (2)$$

N-Trimethylgermylaniline (bp 85–86° (4 mm), 67–68° (1 mm)) was prepared as described above. *Anal.* Calcd for $C_9H_{15}NGe$: C, 51.5; H, 7.2; N, 6.7; Ge, 34.6; mol wt, 209.6. Found: C, 51.73; H, 7.31; N, 6.81; Ge, 31.34; mol wt, 230, 220.

N-Trimethylstannylaniline[7] (bp 77° (0.05 mm)) was prepared as described above in 78% yield.

Decomposition of the compounds by acid hydrolysis was as shown in eq 1. Aniline was freed from the hydrochloride by addition of base and repeated extraction with ether.

The nature of the products of hydrolysis of $C_6H_5N^{15}HM(CH_3)_3$ in the M = Sn case is not as simple as shown and is moreover dependent upon reaction conditions. Possible products of hydrolysis in air include trimethyltin carbonate[8] and hydroxide,[9] each of which can be produced from N-trimethylstannylaniline.



$$\begin{tikzcd} (CH_3)_3SnNHC_6H_5 \arrow[r, "H_2O"] \arrow[d, "H_2O"', "CO_2"] & H_2NC_6H_5 + (CH_3)_3SnOH \arrow[d, "-H_2O"] \\ H_2NC_6H_5 + [(CH_3)_3Sn]_2CO_3 & {[(CH_3)_3Sn]_2O} \end{tikzcd} \qquad (3)$$

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[1] Portions of this investigation have already appeared: (a) E. W. Randall, J. J. Ellner, and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 622 (1966); (b) *Inorg. Nucl. Chem. Letters*, **1**, 109 (1966); (c) Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; (d) E. W. Randall and J. J. Zuckerman, *Chem. Commun.*, 732 (1966); (e) Abstracts, 3rd International Symposium on Organometallic Chemistry, Munich, Aug 1967.

[2] Department of Chemistry, Queen Mary College, London, E.1, England.

[3] D. G. Gillies and E. W. Randall, *J. Sci. Instr.*, **43**, 466 (1966).

[4] H. H. Anderson, *J. Am. Chem. Soc.*, **73**, 5802 (1951); R. C. Osthoff and S. W. Kantor, *Inorg. Syn.*, **5**, 55 (1957).

[5] E. G. Rochow, *J. Am. Chem. Soc.*, **70**, 436 (1948); M. Schmidt and I. Ruidisch, *Z. Anorg. Allgem. Chem.*, **311**, 331 (1961).

[6] V. F. Mironov and A. L. Kravchenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 988 (1965).

[7] K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 358 (1962); *J. Chem. Soc.*, 1944 (1965).

[8] K. Sisido and S. Kozima, *J. Org. Chem.*, **27**, 4051 (1962); H. Sato, *Bull. Chem. Soc. Japan*, **40**, 410 (1967).

[9] R. Okawara and K. Yasuda, *J. Organometal. Chem.* (Amsterdam), **1**, 356 (1964).

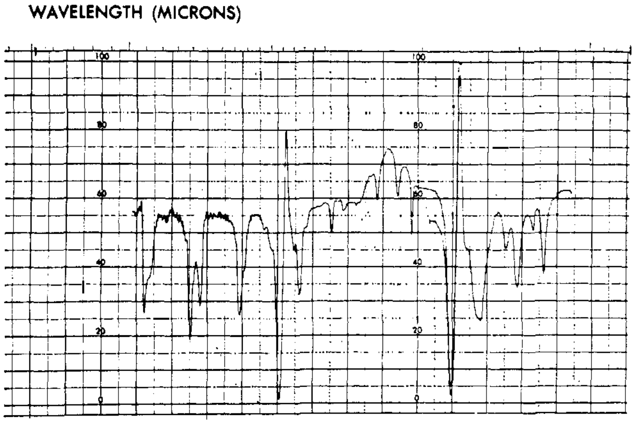

Figure 1. Differential double-beam infrared spectrum of N-trimethylsilylaniline-N^{14} and -N^{15} isotopomeric pairs with the N^{14} compound in the sample beam and the N^{15} compound (smaller quantity) in the reference beam.

The nmr assignments (detailed below) were checked by observation at 100 Mcps of N^{15} satellites in natural abundance for the silyl case (using the time-average computer) and the germyl case (using high receiver gain, slow sweep, and a long time constant). The assignment of trimethylstannylaniline-N^{15} was facilitated by the presence of Sn^{117} and Sn^{119} satellites.

The phenyl proton regions were not analyzed.

Trimethylsilylaniline. The complete spectrum at 60 Mcps for the N^{15} isotopomer is shown in Figure 2. The NH regions of the N^{14} and N^{15} samples are compared in Figure 3. The N^{14}–H proton line is broadened by electric quadrupole effects of the N^{14} nucleus. The doublet of small intensity in the N^{15} case (Figure 3b) arises from a small amount of aniline-N^{15}. The resulting value of 78.5 cps for $J(N^{15}–H)$ in aniline is obtained also at 100 Mcps and falls in the range of 78–81 cps found for solutions of aniline-N^{15} in various solvents.[13]

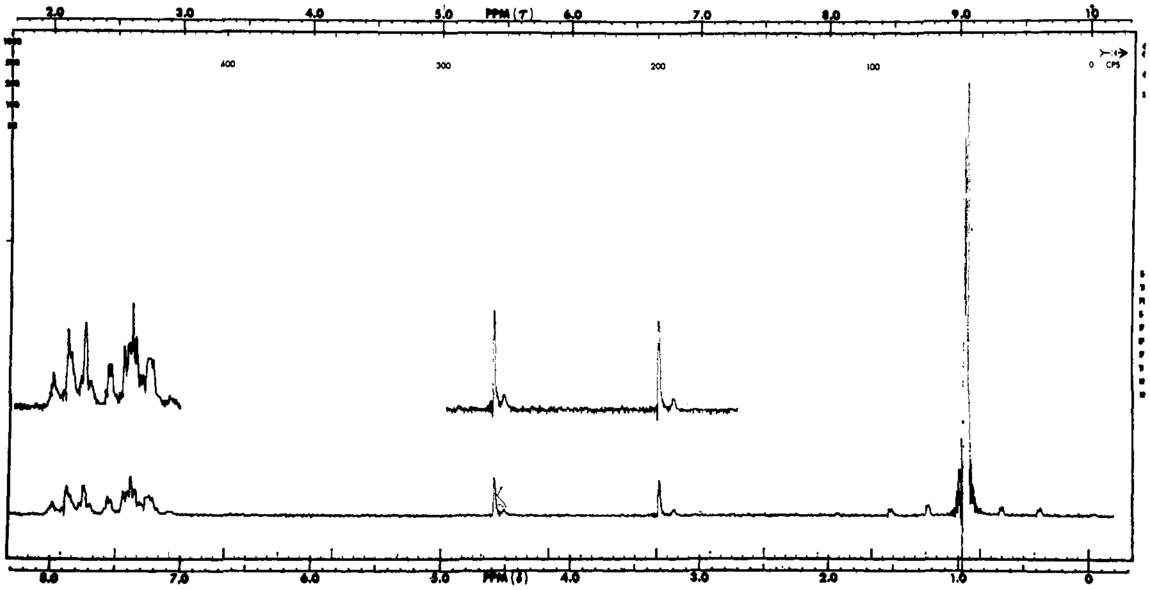

Figure 2. Complete proton magnetic resonance spectrum at 60 Mcps and 35° of N-trimethylsilylaniline-N^{15}.

N-*t*-Butylaniline. Preparation from the following route

$$t\text{-BuX} + C_6H_5NH_2 \longrightarrow t\text{-BuNHC}_6H_5 + C_6H_5NH_3X \quad (4)$$

involves the side reaction

$$t\text{-BuX} + C_6H_5NH_2 \longrightarrow (CH_3)_2C{=}CH_2 + C_6H_5NH_3X \quad (5)$$

The procedure of Hickinbottom,[10] suitably modified for eq 4, where X = Br, by Verkade[11] and by Girault-Vexlearschi[12] was applied. A 2:1 molar ratio of aniline and *t*-butyl bromide was refluxed for 6 hr at 50°. Isobutylene gradually evolved. Precipitation of anilinium bromide resulted in a solidified orange-brown mass which was treated with NaOH and extracted with ether. The collected ether extracts were distilled to give the product (bp 52–56° (9 mm); 93° (19 mm), 203–206° (750 mm)) in 20% yield.

Results and Assignments

The N^{14} and N^{15} isotopomeric pairs were examined for aniline and its N-trimethylsilyl, -germyl, and -stannyl derivatives as an aid to assignment both of the proton resonance spectra and the infrared spectra.

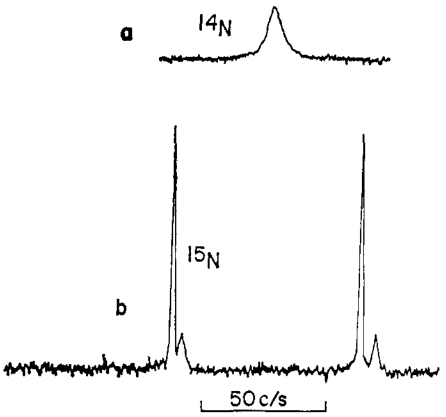

Figure 3. The N–H regions of the proton magnetic resonance spectra of (a) the N^{14} and (b) the N^{15} isotopomers of N-trimethylsilylaniline at 60 Mcps. The small doublet in (b) is attributed to aniline-N^{15}.

The N^{15}–H proton doublet is collapsed to a single line by irradiation at a frequency of 4,053,483.6 ± 3 cps for a

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(10) W. T. Hickinbottom, *J. Chem. Soc.*, 946 (1933).

(11) P. E. Verkade, *Rec. Trav. Chem.*, 77, 559 (1959); personal communication, 1964.

(12) G. Girault-Vexlearschi, *Bull. Soc. Chim. France*, 582 (1956).

(13) E. D. Becker, personal communication, 1965.

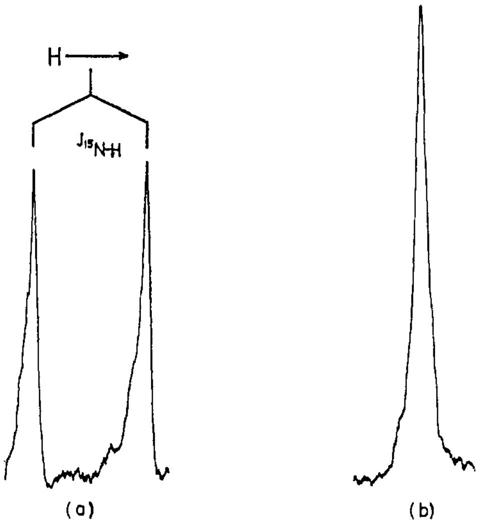

Figure 4. The N-H regions of the proton magnetic resonance spectrum of N-trimethylsilylaniline-N^{15} at 40 Mcps (a) without and (b) with irradiation at 4,053,483.6 ± 3 cps.

basic proton frequency of 40,000,052.1 cps as shown in Figure 4.

The trimethylsilyl protons are a singlet for the N^{14} case and a 1.1-cps doublet (at 60 and 100 Mcps) for the N^{15} isotopomer. The doublet is perturbed by irradiation of the N^{15} sample with a low power second radiofrequency field (a process referred to as "tickling") at 4,053,533.2 ± 0.5 and 4,053,456.4 ± 0.5 cps as shown in Figure 5. The difference between these frequencies is 76.8 cps, the doublet line separation in the ^{15}N region. The coupling is thus a three-bond, H-C-Si-N^{15} coupling.

Trimethylgermylaniline. The N^{15}–H coupling constant was determined from observation of satellites on the N^{14}–H line in the compound with nitrogen in a natural distribution of isotope abundances. The value thus obtained could be checked against the N^{15}–H coupling constant obtained from the N^{15} isotopomer. This compound contained aniline-N^{15} starting material which allowed measurement of its $J(N^{15}–H)$ value in solution of the germanium amine (79.4 cps). In addition to the 1.1-cps $J(N^{15}–H)$ doublet in the trimethylgermyl region, a lower intensity 1.0-cps doublet was observed due to a second species containing the H–C–Ge–N^{15} grouping, possibly $[(H_3C)_3Ge]_2N^{15}C_6H_5$.

Trimethylstannylaniline. The N^{14} sample gave a single peak in the N–H proton region as for the germyl and silyl analogs.

The preparation of the N^{15} isotopomer gave a sample containing some aniline–N^{15} (Figure 6). The Sn–N^{15}–H proton lines were identified by the presence of satellites due to Sn^{117} and Sn^{119}. The Sn^{117} and Sn^{119} components were not separated. The mean coupling is 20 cps. The Me_3Sn line was a singlet of line width <1.5 cps.

The Sn–N^{15} doublet was collapsed by strong perturbation with a second radiofrequency of 4,053,290.8 cps. The aniline-N^{15} doublet was collapsed at 4,053,326.5 cps. These results were confirmed by "tickling" experiments.

Aniline-N^{15}. The N^{15}–H coupling constant for aniline, unlike the N–H chemical shifts, was largely invariant with changes in solvent.

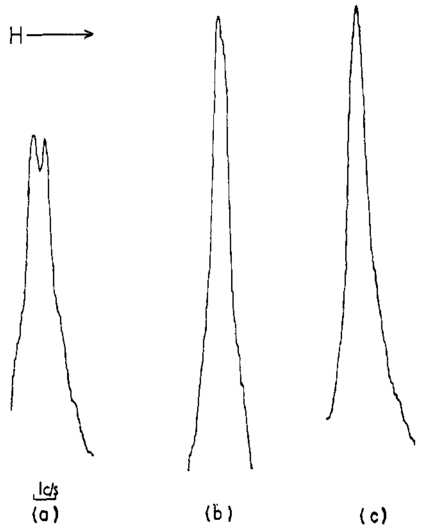

Figure 5. The methyl proton regions of the proton magnetic resonance spectrum of N-trimethylsilylaniline-N^{15} at 40 Mcps (a) without irradiation, (b) with irradiation at 4,053,533.2 ± 0.5 cps, and (c) with irradiation at 4,053,456.4 ± 0.5 cps.

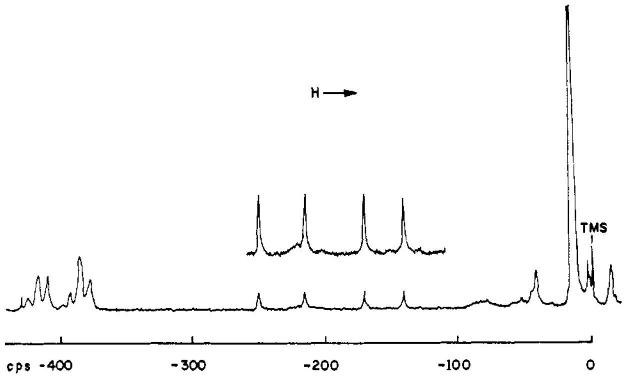

Figure 6. The proton magnetic resonance spectrum of N-trimethylstannylaniline-N^{15} with aniline-N^{15} present.

The proton chemical shifts are summarized in Table I and the N^{15}–H coupling constants in Table II. The double-irradiation experiments allow evaluation of the N^{15} shifts after corrections are made for the small field

Table I. Proton Chemical Shifts[a] for $(H_3C)_3MNHC_6H_5$ and Aniline

M		$(H_3C)_3M$	NH	Aniline-N^{15}
Si	N^{14}	8.5	187.5	
	N^{15}	*b*	188.8	183.2
Ge	N^{14}	17.5	174.2	
	N^{15}	*b*	178.4	194.4
Sn	N^{14}	12.5	165	
	N^{15}	*b*	177	209

[a] Cycles per second at 60 Mcps downfield from tetramethylsilane.
[b] Assumed the same as in the N^{14} isotopomer.

Table II. N^{15}–H Coupling Constants (cps ± 0.3 cps) for $(H_3C)_3MN^{15}HC_6H_5$ Containing Aniline-N^{15}

M	$J(N^{15}–H)$	$J(N^{15}MCH)$	Aniline
Si	76.0	1.1	78.5
Ge	77.1	1.1	79.4
Sn	73.8	*a*	79.2

[a] Not observed.

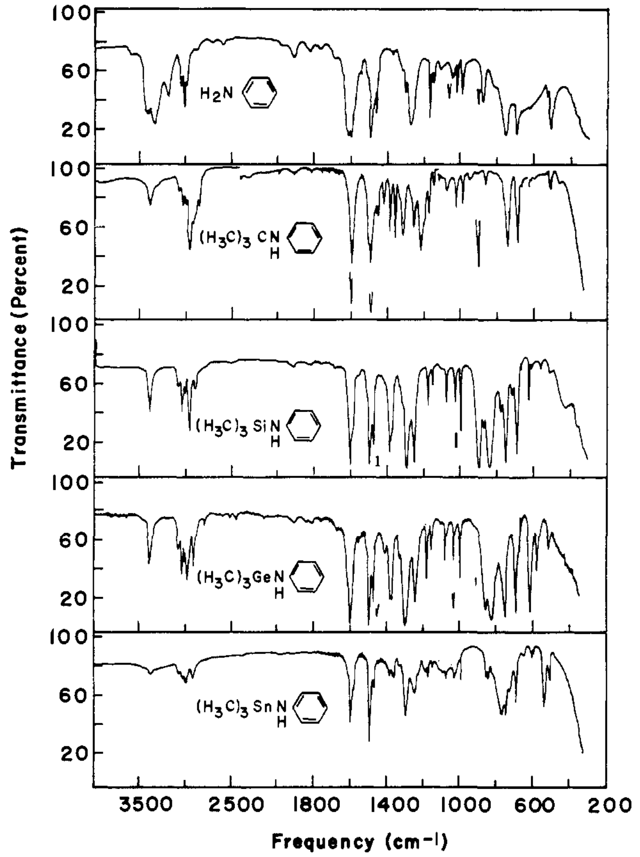

Figure 7. Infrared spectra of the N-trimethylmethyl, -silyl, -germyl, and -stannyl derivatives of aniline.

differences between the different irradiation experiments. The N^{15} shift results are given in Table III. The chemical shift variations for the N–H protons from one isotopomer to another and for aniline in different solvents is evidence of some hydrogen bonding effect, which may also account for the disparity in the nitrogen shifts for aniline.

Table III. N^{15} Chemical Shifts (ppm downfield from $N^{15}H_4^+$)

$(CH_3)_3SiNHC_6H_5$	45.0 ± 0.4
$(CH_3)_3GeNHC_6H_5$ (I)	43.0 ± 0.4
$(CH_3)_3SnNHC_6H_5$ (II)	35.9 ± 0.4
Aniline in I	44.8 ± 1.5
Aniline in II	45.2 ± 0.4
Aniline (neat)[a]	35 ± 0.4

[a] J. B. Lambert, G. Binsch, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **51**, 735 (1964).

The infrared assignments listed in Table IV are predicated on the basis that isotopomeric shifts arise from normal modes in which large N displacements occur and upon the assumption that one such normal mode is mainly the M–N stretch (M = C, Si, Ge, or Sn). The spectra are shown as Figure 7 for comparison. Bands thus assigned to the Si–, Ge–, and Sn–N stretches are absent in the spectrum of N-t-butylaniline and aniline itself. A small shift to lower frequencies was observed in the N–H deformation mode of aniline-N^{15}. Studies on N-deuterioaniline indicate that this frequency (1620 cm⁻¹) is coupled to the C–N stretch.[14]

Table IV. Infrared (cm⁻¹)

C–N stretch in		
Aniline	N^{14}	1276 ± 1
	N^{15}	1266 ± 2
$(CH_3)_3SiNHC_6H_5$	N^{14}	1294 ± 1
	N^{15}	1287 ± 1
$(CH_3)_3GeNHC_6H_5$	N^{14}	1295 ± 1
	N^{15}	1287 ± 1
$(CH_3)_3SnNHC_6H_5$	N^{14}	1292 ± 1
	N^{15}	1284 ± 1
Si–N stretch in		
$(CH_3)_3SiNHC_6H_5$	N^{14}	899 ± 1[a]
	N^{15}	890 ± 1
Ge–N stretch in		
$(CH_3)_3GeNHC_6H_5$	N^{14}	855 ± 1
	N^{15}	845 ± 1
Sn–N stretch in		
$(CH_3)_3SnNHC_6H_5$	N^{14}	843 ± 1
	N^{15}	835 ± 1

[a] NOTE ADDED IN PROOF. The recent observation of a shift in this frequency on N-deuteration [H. Bürger and V. Goetze, *Monatsch. Chem.*, **99**, 155 (1968)] suggests some coupling with ν(N–H).

Our assignment of the Si–N and aromatic C–N stretching frequencies in these compounds corroborates those in the literature[14,15] and of the Ge–N stretch is consistent with a study from this laboratory of fourth-group *gem*-diamines.[16] In the case of the Sn–N stretch we initially sought to test the three hypotheses in the literature and to resolve the controversy over the assignment of ν_{asym}(Sn–N). A band at 510 cm⁻¹ in the spectrum of N′,N′-dimethyl-N-phenylureidotin trimethyl has been assigned to ν(Sn–N) on the basis of the similarity of mass of the Sn–N and Sn–C groups in four-coordinate tin compounds.[17] Infrared spectra of tris(tri-n-alkyltin)amines containing methyl, ethyl, and propyl groups yielded an assignment of ν_{asym}(Sn–N) at 728, 712, and 712 cm⁻¹, respectively.[18] Infrared and Raman spectra of tris(trimethyltin)amine and tetrakis(dimethylamino)tin yielded assignments of ν_{asym}(Sn_3–N) at 514, ν_{asym}(Sn_3–N) at 672, and ν_{asym}(Sn–N_4) at 538 cm⁻¹ in the two compounds.[19] The N^{14} isotopomer of our compound contains bands in each of these regions (at 723, 688, 535, and 508 cm⁻¹).

We find that none of these bands shifts on isotopic nitrogen substitution. A band at 843 cm⁻¹ alone shifts to lower frequencies in the N^{15} isotopomer, and the assignment of ν_{asym}(Sn–N) in dimethylbis(diethylamino)stannane[16] at 880 cm⁻¹ corroborates our assignment of this band as ν(Sn–N).

The intensity of the band at 508 cm⁻¹ does decrease, however, along with the intensity of the 843-cm⁻¹ band on hydrolysis. We interpret this as evidence for assignment of the 508-cm⁻¹ absorption to the trimethyltin symmetric stretching mode with ν_{asym}(Sn–C) at

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(14) D. Hadzi and M. Skrbljak, *J. Chem. Soc.*, 843 (1957).

(15) R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 360 (1961); U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964).

(16) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **5**, 2055 (1966).

(17) T. A. George, K. Jones, and M. F. Lappert, *J. Chem. Soc.*, 2157 (1965).

(18) K. Sisido and S. Kojima, *J. Org. Chem.*, **29**, 907 (1964).

(19) R. E. Hester and K. Jones, *Chem. Commun.*, 317 (1966); see also H. Bürger and W. Sawodry, *Inorg. Nucl. Chem. Letters*, **2**, 209 (1966), who assign ν_{asym}(Sn–N_4) at 535 cm⁻¹ in tetrakis(dimethylamino)tin.

535 ± 1 cm^{-1} in our compound. The ratio of these peaks changes on hydrolysis, and their frequencies shift slightly as well. The former change is probably associated with a change in geometry of the trimethyltin group leading to a more planar arrangement of groups about tin in the product of hydrolysis. The small shift to lower frequencies observed in the 508-cm^{-1} band probably arises from the presence of a band in aniline itself at 503 cm^{-1}. Thus the change in relative absorption intensities of this band is not an accurate measure of the degree of hydrolysis. The asymmetric Sn-C stretching mode also undergoes a small shift (but to higher frequencies) on hydrolysis.

As mentioned above, among the products of hydrolysis of organotin amines in air is the corresponding organotin carbonate. These compounds possess a characteristic frequency at 840 cm^{-1}.[8] We have thus cautioned the use of ν_{asym}(Sn–N) as a diagnostic test for the Sn–N bond because of the action of air on these systems to produce carbonates.[1b]

Discussion

The one-bond N^{15}–H coupling in the aniline derivatives reported here is of some importance since it is related to the stereochemical situation at nitrogen which reflects in turn the nature of the bonds nitrogen exerts. When the bonded groups are silyl, germyl, and stannyl, the question of (p→d)–π bonding is of interest.

The magnitude of the one-bond N^{15}–H coupling has been discussed previously[20,21] in terms of a dominant Fermi contact interaction (approximation I) following more extensive work on the C^{13}–H couplings. A second approximation (II) inherent in assuming equal distribution of s character among the σ bonds around nitrogen has been explicitly pointed out for N^{15}–H.[21]

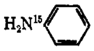
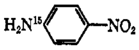
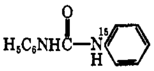
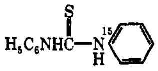
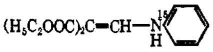
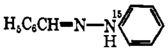
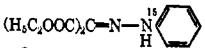
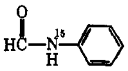
On these assumptions the only clearly anomalous cases in relating structure to N^{15}–H coupling are pyrrole[21] and diphenylketimine.[20] The latest results on pyrrole largely remove this anomaly.[22]

More recently Grant and Litchman[23] have recalled attention to radial terms affecting the s electron density at a nucleus. They have been able to rationalize a large number of C^{13}–H couplings without invoking angular variations in wave functions. Neglect of the radial terms constitutes approximation III. Nevertheless, their approach alone seems incapable of accounting for the following sequence of N^{15}–H results: NH$_3$ (64.0 ± 2.0 cps),[24] NH$_4^+$ (73.7,[25] 73.2[20] cps), aniline (78–81 cps),[1a,13] amides (88.0–92.6 cps),[21] and the pyridinium ion (90.5[20] or 98.7[21] cps). It seems reasonable then to discuss the results of this study employing approximations I–III noted above.

The magnitude of the N^{15}–H couplings for aniline is considerably lower than the value associated with sp^2 hybridization (33% s character for the N–H bonds). This result for aniline has found recent confirmation in microwave work which establishes the nonplanarity of the molecule, with ∠HNH = 113° 54′.[26]

The magnitudes of the N^{15}–H coupling constants for aniline and its derivatives are shown in Table V.[26a]

Table V. J(N^{15}–H) Values (cps)

	78–81[a]
	88[b]
	89.7[c]
	89.8[c]
	91.4[c]
	92.7[c]
	94.7[c] 96.1
	91.2[d]

[a] References 13 and 1a. [b] M. R. Bramwell and E. W. Randall, unpublished results. [c] Reference 28. [d] Reference 27.

N substitution by unsaturated groups such as –C(=O)H,[27] –C(=O)NHC$_6$H$_5$, –C(=S)NHC$_6$H$_5$, –CH=C(COOC$_2$H$_5$)$_2$, –N=CHC$_6$H$_5$, and –N=C(COOC$_2$H$_5$)$_2$[28] capable of conjugation with the nitrogen lone pair leads to a marked increase in the value of J(N^{14}–H), from 79–81 cps in aniline itself to 89.7–96.1 cps in these derivatives. Other effects of this (p→p)–π overlap include restricted rotation about the C–N bond[29] and high force constant[30,31] and shortening of this bond.[32]

For aniline and other substituted benzenes there is a wealth of other information to support the contention that (p→π)–π bonding between the nitrogen lone pair and the phenyl ring is important. Since the nitrogen in aniline is nonplanar, we may conclude that this (p→π)–π overlap may be considerable for sp^3 nitrogen. The overlap may be expected to increase, however, as the hybridization approaches sp^2 and the lone-pair orbital approaches pure p character. This possibility has been tested by comparison of the stereochemistry at nitrogen as examined through the N^{15}–H coupling for p-nitroaniline-1-N^{15}. The p-nitro derivative has a

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

(21) A. J. R. Bourn and E. W. Randall, *Mol. Phys.*, **8**, 567 (1964).

(22) Professor J. D. Roberts has recently communicated a redetermination of the N^{15}–H coupling in pyrrole amounting to approximately 100 cps, which was obtained by spectrum accumulation of N^{15} satellites in natural abundance.

(23) D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc.*, **87**, 3994 (1965). See also J. E. Huheey, *J. Chem. Phys.*, **45**, 405 (1966); and A. Saika, *ibid.*, **45**, 2715 (1966).

(24) R. A. Ogg and J. D. Ray, *ibid.*, **26**, 1515 (1957).

(25) J. D. Baldeschwieler, *ibid.*, **36**, 152 (1962).

(26) D. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966).

(26a) NOTE ADDED IN PROOF: We have recently measured J(N^{15}–H^1) for the unique nitrogen in B-aminoborazine, the boron-nitrogen analog of aniline, to be 79.1 cps (D. E. Fenton, R. F. Porter, E. S. Yeung, and J. J. Zuckerman, unpublished results). Current electron-diffraction data for this compound are best interpreted assuming that the amino hydrogens are not coplanar with the ring atoms. However, the magnitudes of the bond angles around this nitrogen can be estimated within large error limits only (W. Harshbarger and S. H. Bauer, private communication, 1968).

(27) A. J. R. Bourn, D. G. Gillies, and E. W. Randall, *Tetrahedron*, **20**, 1811 (1964).

(28) A. K. Bose and I. Kugajevsky, *ibid.*, **23**, 1489 (1967).

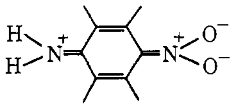
(29) A. J. R. Bourn, D. G. Gillies, and E. W. Randall, *ibid.*, **22**, 1825 (1966), and references therein.

(30) S. I. Mizushima, T. Simanouti, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba, and O. Fujioka, *J. Am. Chem. Soc.*, **72**, 3940 (1950).

(31) D. E. DeGraff and G. B. B. M. Sutherland, *J. Chem. Phys.*, **26**, 716 (1957).

(32) C. C. Costain and J. M. Dowling, *ibid.*, **32**, 158 (1960).

larger interaction dipole moment than does aniline itself[33] because of the importance in valence bond formulation of canonical forms such as



The nitrogen pyramid is thus expected to be flattened relative to aniline. In agreement with this, the coupling constant is found to increase from 78–81 to 88 cps.[34] Thus we can conclude that the utilization of the nitrogen lone pair in (p→p)–π and (p→π)–π interactions has the effect of increasing markedly the magnitude of the N^{15}–H coupling constant.

A third type of change it is possible to work upon aniline is N substitution by a group capable of (p→d)–π conjugation with the nitrogen lone pair. It is generally agreed that the extent of (p→d)–π bonding for nitrogen should be maximal when the nitrogen lone pair occupies a pure p orbital and the σ bonds about nitrogen are planar. The planarity of the N σ skeleton of trisilylamine is usually rationalized in this way. The magnitudes of the N^{15}–H coupling constants where trimethylsilyl, trimethylgermyl, and trimethylethylstannyl groups have substituted at nitrogen are given in Table II. These substituted anilines give lower values of $J(N^{15}\text{–H})$ than does aniline itself and so are probably more pyramidal. The value in the N-stannyl case is little different from the value of the ammonium ion (25% s character). We may conclude from our results that there is no stereochemical evidence for (p→d)–π bonding in these compounds.[34a]

N substitution by *two* groups, each of which is capable of conjugation with the nitrogen lone pair, deserves comment. Studies of the N^{15} isotopomers in a series of substituted formamides [$HCONH_2$ (92.0 cps); $HCONHCH_3$ (92.6 cps); $HCONHC_6H_5$ (91.2 cps)][27] indicate that substitution by the N-phenyl group [(p→π)–π interaction] has little effect on the conjugation of HC(=O)– with the nitrogen lone pair [(p→p)–π conjugation]. There is thus a *prima facie* case for believing that the (p→π)–π interaction would not affect any (p→d)–π bonding in the trimethylsilyl, -germyl, and -stannyl derivatives of aniline.[35] Placing a second trimethylsilyl group at nitrogen in place of the phenyl ring may be used as a test of the consistency of this approach since such (p→π)–π complications are absent in bis(trimethylsilyl)amine. Recent work with bis(trimethylsilyl)amine-N^{15} shows that the N^{15}–H coupling is reduced to 66.5 ± 0.5 cps,[36] a value which is very close to that for ammonia itself, and which we take to be consistent with a pyramidal nitrogen. Had there been greater utilization of the nitrogen lone pair in (p→d)–π bonding, the s character of the N–H bond, and hence $J(N^{15}\text{–H})$, should have increased, which is not the case.

An alternative approach in the bissilyl derivative is to reject assumption III and, presuming that all molecules have a planar M_2NH skeleton, to calculate the bond angles from $J(N^{15}\text{–H})$ using the correlation between it and s character.[37] This proposal has the merit of providing data testable by structural studies without requiring determination of a bond angle involving hydrogen.

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(33) J. W. Smith, "Electric Dipole Moments," Butterworth & Co. Ltd., London, 1955.

(34) M. R. Bramwell and E. W. Randall, unpublished results.

(34a) NOTE ADDED IN PROOF. Corroboration for these conclusions has come from studies of *o-p*-fluorine coupling constants *vs. p*-fluorine chemical shifts in N-trimethylsilyl- and N-trimethylstannylperfluorophenylanilines [M. G. Hogben, A. J. Oliver, and W. A. G. Graham, *Chem. Commun.*, 1183 (1967)] and from uv spectra of N-silyl-substituted anilines (C. G. Pitt, private communication, 1968).

(35) It has been argued that the effect of the trimethylsilyl group on the (p→π)–π overlap between nitrogen and the phenyl group may obscure the comparison between N-trimethylsilylaniline and aniline itself [P. G. Perkins, *Chem. Commun.*, 258 (1967)].

(36) E. A. V. Ebsworth, personal communication, 1966; R. S. Bailyn and J. J. Zuckerman, unpublished results.

(37) E. A. V. Ebsworth, Proceedings of the 1st International Symposium on Organosilicon Chemistry, Prague, 1965; *Pure Appl. Chem.*, 13, 189 (1966); personal communication, 1966.