present results do not constitute a direct contradiction[5] or corroboration[1] of the work of previous authors, since identical conditions of solvent (benzene) and concentration (infinite dilution) can never be attained. Experiments with other aromatic solvents are being undertaken with the hope of resolving this discrepancy.

We have analyzed the temperature dependence of the nmr spectra of I–III according to the method of Alexander.[14] The ring-inversion processes of I–III were characterized by activation energies on the order of 15 kcal/mole. Detailed consideration of the rate processes will be deferred to the complete paper. This work is being expanded to include the oxygen, sulfur, sulfoxide, silicon, and remaining group V heterocycles.

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(p → d)–π Interactions in the Silicon–Nitrogen Bond. An Experimental Test

Sir:

We have tested the hypothesis of (p → d)–π interaction in the silicon–nitrogen bond by the synthesis and study of systems suitable for the application of nmr techniques. It has been shown recently that nitrogen–proton coupling constants are useful parameters for the examination of nitrogen atom hybridization, provided the dominant coupling mechanism is by the Fermi contact term (other necessary conditions have been discussed).[1,2] In this event the magnitude of the coupling J(N–H) between directly bonded atoms is proportional to the s character of the nitrogen orbital directed toward the hydrogen. The amount of s character in the nitrogen hybrid should increase with (p → d)–π bonding between nitrogen and silicon since this interaction requires the use of a nitrogen orbital with large, perhaps pure, p character. Thus the N–H coupling should provide a measure of this interaction in Si–N–H systems.

We have accordingly synthesized the isotopic isomers (for which we have coined the word "isotopomers"[3]) N-trimethylsilylaniline-N^{14} and -N^{15}, the isotopic substitution being effected because of the more favorable nmr spectral behavior of N^{15} compared with quadrupolar N^{14}. N-Trimethylsilylaniline[4] (I) was obtained by the action of trimethylchlorosilane on the yellow monolithio salt of aniline in benzene–hexane solution. This novel route, although requiring first the *in situ* preparation of the lithium salt from *n*-butyllithium, gave I in better yield (80%) than previously reported for the one-step synthesis[5] since no aniline hydrochloride is produced.

The nmr spectral parameters measured on a Varian A-60 using audio side-band calibration are: $J(\mathrm{N}^{15}\text{–H}) = 76.0 \pm 0.2$ cps; $\tau(\mathrm{N}^{15}\text{–H})$ 6.853 ± 0.003 cps; $J(\mathrm{CH_3}\text{–}\mathrm{N}^{15}) = 1.0 \pm 0.1$ cps; $\tau(\mathrm{CH_3})$ 8.567 ± 0.003 cps.

The bonding situation at the nitrogen apparently differs little from (I)-N^{15} to the sp^3-hybridized ammonium-N^{15} ion [$J(\mathrm{N}^{15}\text{–H}) = 73.7$ cps;[6] 73.2 cps[2]], whereas the results for both of these compounds differ markedly from the values of 98.7[1] and 90.5[2] cps for the sp^2-hybridized pyridinium ion. We deduce on the hypothesis outlined above that there is little (p → d)–π interaction in I.

We have observed the N^{15}–H coupling in aniline-N^{15} [$J(\mathrm{N}^{15}\text{–H}) = 78.5 \pm 0.2$ cps] in solutions of I, where the silicon compound acts as a drying agent, releasing aniline-N^{15} on hydrolysis. The observation of this coupling indicates lack of the proton exchange which is normally found in insufficiently dried samples of aniline-N^{15} and which causes collapse of the N^{15}–H doublet.[7] The magnitude of this coupling is consistent with a pyramidal stereochemical arrangement around nitrogen in aniline as deduced from dipole moment studies.[8]

These results clearly show that the hypothesis outlined above for coupling constants is incompatible with the hypothesis that there is considerable π interaction either in I or in aniline. The coupling constant hypothesis has ignored the effect of variations in the radial portions of the wave functions which may change according to the effective nuclear charge on nitrogen. Grant and Lichtman have recently cautioned use of directly bonded C^{13}–H couplings to deduce s character on the grounds that $J(\mathrm{C}^{13}\text{–H})$ depends on the effective nuclear charge of carbon.[9] Use of this factor alone for the N–H systems cannot explain the differences between $\mathrm{NH_4^+}$ and pyridinium ion without recourse to the other factors previously enumerated.[1,2]

The observation of $J(\mathrm{CH_3}\text{–}\mathrm{N}^{15})$ in (I)-N^{15} and of separate resonances for aniline-N^{15} (τ 6.947 ± 0.002 cps) and (I)-N^{15} in mixtures of the two shows that any exchange of trimethylsilyl group occurs at a rate slower than about 1 sec^{-1}, despite the ease of transamination reactions involving silicon.[10] No change in the spectrum of (I)-N^{15} was observed on heating to 120°.

Experiments are in progress to test the (p → d)–π bonding hypothesis in other group IV–nitrogen bonds.

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