

# Nitrogen-15 Nuclear Magnetic Resonance Shifts in $\text{Me}_3^{15}\text{N}$ -Solvent Systems<sup>1a</sup>

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Received February 12, 1970

**Abstract:** A model previously used to interpret  $^{15}\text{N}$  nmr shifts for the  $^{15}\text{NH}_3$  molecule in a series of liquid solvents has been applied to the  $^{15}\text{N}$  shifts for  $\text{Me}_3^{15}\text{N}$  in the same solvents. The results are in accord with the predictions of the model and serve to confirm the conclusion that the  $^{15}\text{N}$  shifts are principally determined by intermolecular interactions involving the nitrogen lone-pair electrons. It also seems increasingly clear that intermolecular interactions other than formation of the generally accepted types of hydrogen bonds can make significant contributions to the  $^{15}\text{N}$  shift in amines.

We recently demonstrated<sup>2</sup> that the  $^{15}\text{N}$  nmr shift relative to gaseous  $^{15}\text{NH}_3$ , for the  $^{15}\text{NH}_3$  molecule at "infinite dilution" in a number of liquid solvents at room temperature, is adequately explained in terms of an empirical model which assumes that the observed shift is a simple sum of contributions due to two general types of interactions: (1) the interaction of the  $^{15}\text{NH}_3$  nitrogen lone-pair electrons with solvent molecule protons or hydrocarbon groups and (2) the interaction of solvent molecule unshared electron pairs with the  $^{15}\text{NH}_3$  protons. Based on this model and a number of assumptions, we concluded that interactions of the first type made much larger contributions to the  $^{15}\text{NH}_3$  shifts than did interactions of the second type.

In an effort to test the general validity of the model and assumptions used in the above-mentioned work, we have undertaken a study of the  $^{15}\text{N}$  nmr shifts for the  $\text{Me}_3^{15}\text{N}$  molecule at infinite dilution in the same solvents used in the  $^{15}\text{NH}_3$  work. Since the  $\text{Me}_3^{15}\text{N}$  molecule has no protons directly bonded to the  $^{15}\text{N}$  nucleus, we would expect interactions of the second type to make negligible contributions to the  $^{15}\text{N}$  shift in  $\text{Me}_3^{15}\text{N}$ . The  $^{15}\text{N}$  shifts in  $\text{Me}_3^{15}\text{N}$  would therefore be expected to be determined almost entirely by the interactions of the nitrogen lone-pair electrons.

In a recently reported study<sup>3</sup> of  $^{17}\text{O}$  shifts for  $\text{H}_2^{17}\text{O}$  in the solvents acetone, ammonia, and trimethylamine, we concluded that the dominant contribution to the observed shifts resulted from interaction of water oxygen lone-pair electrons with the solvent molecule. As mentioned earlier, the subsequent study of  $^{15}\text{NH}_3$  in a number of solvents led to a similar conclusion for the  $^{15}\text{N}$  shifts. This suggests the generality that when, in molecules like  $\text{NH}_3$  or  $\text{H}_2\text{O}$ , atoms such as N or O serve as both electron-pair donors (proton acceptors) and proton donors in hydrogen-bonded systems, the electron-pair donation makes the dominant contribution to the nmr shift of the atom relative to its resonance in the isolated molecule. However, Reuben<sup>4</sup> has re-

cently inferred, from  $^{17}\text{O}$  nmr shifts for  $\text{H}_2^{17}\text{O}$  in a number of solvents, that proton donation contributes roughly twice as much as to the shift as does electron-pair donation. This is in direct contradiction to our conclusion. The disagreement arises principally from use of differing sets of initial assumptions and demonstrates the need for a wide experimental base and more critical evaluation of models and assumptions used in correlating nmr shifts with intermolecular interactions.

Two preparations of  $\text{Me}_3^{15}\text{N}$  were used in this work, one enriched to 50% and the other to 100% in  $^{15}\text{N}$ . The  $^{15}\text{NH}_4\text{Cl}$  used in preparation of the  $\text{Me}_3^{15}\text{N}$  was derived from isotopically enriched  $^{15}\text{NO}$  as described previously.<sup>2</sup>

$\text{Me}_3^{15}\text{N}$ -solvent mixtures were prepared by distilling or pipetting measured amounts of materials directly into standard 5-mm o.d., 0.4-mm wall Pyrex nmr sample tubes. A small amount of TMS was condensed into each sample to help determine bulk susceptibility corrections. The contents of the sample tube were held at liquid  $\text{N}_2$  temperature while the tube was sealed off under vacuum.

The  $^{15}\text{N}$  resonances were recorded by holding the magnetic field constant and sweeping the frequency as described previously.<sup>2</sup>  $^{15}\text{N}$  shifts were measured at  $29.6 \pm 0.5^\circ$  and are reported relative to gaseous  $\text{Me}_3^{15}\text{N}$ , whose  $^{15}\text{N}$  resonance was observed in a sample of  $\text{Me}_3^{15}\text{N}$  vapor in equilibrium with  $\text{Me}_3^{15}\text{N}$  liquid at  $29.6$  or  $73^\circ$ . (The vapor resonance is 4.22 ppm upfield of the liquid resonance at  $29.6^\circ$  and the absolute position of the vapor resonance at  $73^\circ$  is the same as it is at  $29.6^\circ$ .) Susceptibility corrections were made by measuring the volume susceptibilities of all samples and applying the correction for cylindrical geometry.<sup>5</sup> The overall uncertainty in the shift measurements is less than  $\pm 0.2$  ppm.

The relatively long relaxation time for  $^{15}\text{N}$  in the  $\text{Me}_3^{15}\text{N}$  molecule in liquid  $\text{Me}_3\text{N}$  and in most of the solvents used requires that care be taken not to saturate the resonance. The observed  $^{15}\text{N}$  resonances were relatively broad but well-defined singlets (2–3 Hz wide at half-height). The broadness is probably due to unresolved splitting by the methyl protons.

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, 1959, p 81.

(1) (a) Work supported by the U. S. Atomic Energy Commission; (b) Los Alamos Scientific Laboratory; (c) University of New Mexico; Associated Western Universities Research Participant at Los Alamos Scientific Laboratory.

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(4) J. Reuben, *J. Amer. Chem. Soc.*, **91**, 5725 (1969).

Table I.  $^{15}\text{N}$  Solvent Shifts in Ppm Relative to  $\text{Me}_3^{15}\text{N}(\text{g})$ 

Solvent	Mol % $\text{Me}_3^{15}\text{N}$						
	50	30	10	5	1	0.1	0 <sup>a</sup>
$\text{NH}_3$	-4.85	-4.92	-5.21	-5.26	-5.48		-5.4
$\text{MeNH}_2$	-4.59	-4.81	-4.92	-5.05			-5.1
$\text{Me}_2\text{NH}$	-4.59	-4.73	-4.96	-4.88			-5.0
$\text{H}_2\text{O}$	-7.71	-9.10	-10.52	-10.67	-11.01	-11.09	-11.1
$\text{MeOH}$	-6.61	-7.74	-8.85	-8.80			-9.2
$\text{Me}_2\text{O}$	-4.16	-4.03	-4.01	-4.00			-4.0
$\text{Me}_3\text{N}$							-4.2
$\text{Me}_4\text{C}$	-4.25	-4.12	-4.19	-4.22			-4.2
$\text{EtOH}$	-6.61	-7.50	-8.43	-8.67			-8.9
$\text{Et}_2\text{O}$	-4.44	-4.50	-4.58	-4.51	-4.46		-4.6
$\text{EtNH}_2$	-4.81	-4.81	-4.95	-4.97			-5.1
$\text{Et}_2\text{NH}$	-4.72	-4.90	-4.77	-4.83			-5.0
$\text{Et}_3\text{N}$	-4.39	-4.47	-4.58	-4.55			-4.6
$\text{Et}_4\text{C}$	-4.41	-4.44	-4.43				-4.5
$\text{CCl}_4$	-5.94	-6.49	-6.85				-7.3

<sup>a</sup> The extrapolated value.

## Results and Discussion

Table I lists the observed  $^{15}\text{N}$  shifts for  $\text{Me}_3^{15}\text{N}$  as a function of mol %  $\text{Me}_3^{15}\text{N}$  in a number of solvents. These data are plotted in Figure 1. Since the plots are linear within experimental uncertainty, we assume that they may be extrapolated to zero  $\text{Me}_3^{15}\text{N}$  concentration to yield an "infinite dilution shift" for  $\text{Me}_3^{15}\text{N}$  in each of the solvents used. These infinite dilution shifts are listed under 0 mol %  $\text{Me}_3^{15}\text{N}$  in Table I.

Using the same model and assumptions previously employed in the  $^{15}\text{NH}_3$  study,<sup>2</sup> we assume the  $^{15}\text{N}$  shift of the  $\text{Me}_3^{15}\text{N}$  molecule at infinite dilution in a particular solvent is given by a summation of shift contributions of two general types: (1) contributions due to interaction of the  $\text{Me}_3^{15}\text{N}$  nitrogen lone-pair electrons with solvent protons or hydrocarbon groups ( $\sigma_{A_x}$  terms) and (2) contributions due to interaction of solvent molecule unshared electron pairs with the  $\text{Me}_3^{15}\text{N}$  methyl groups ( $\sigma_{B_y}$  terms). Assuming each contribution depends only upon the kind of solvent molecule atom or group involved and is independent of the overall composition of the solvent molecule, the observed infinite dilution shifts in all solvents except  $\text{CCl}_4$  should be given by an appropriate summation of only six different "shift parameters" defined as follows: (1) shift contribution due to interaction of the  $\text{Me}_3^{15}\text{N}$  nitrogen lone-pair electrons with a

$$\left. \begin{aligned} \text{solvent molecule OH proton} &= \sigma_{A_{\text{OH}}} \\ \text{solvent molecule NH proton} &= \sigma_{A_{\text{NH}}} \\ \text{solvent molecule methyl group} &= \sigma_{A_{\text{Me}}} \\ \text{solvent molecule ethyl group} &= \sigma_{A_{\text{Et}}} \end{aligned} \right\} \sigma_{A_x}$$

and (2) shift contribution due to interaction of the  $\text{Me}_3^{15}\text{N}$  methyl groups with

$$\left. \begin{aligned} \text{solvent oxygen lone-pair electrons} &= \sigma_{B_{\text{O}}} \\ \text{solvent nitrogen lone-pair electrons} &= \sigma_{B_{\text{N}}} \end{aligned} \right\} \sigma_{B_y}$$

The observed infinite dilution shift in a given solvent should then be given by a summation of the sort

$$\delta_{\text{solvent}} = \sum_x C_x \sigma_{A_x} + \sum_y C_y \sigma_{B_y}$$

where  $x$  runs over the four subscripts OH, NH, Me, and Et,  $y$  is either O or N, and  $C_y$  is either 0 or 1. To evaluate the coefficients  $C_x$ , we assume that in a solvent which has more than one site capable of interacting

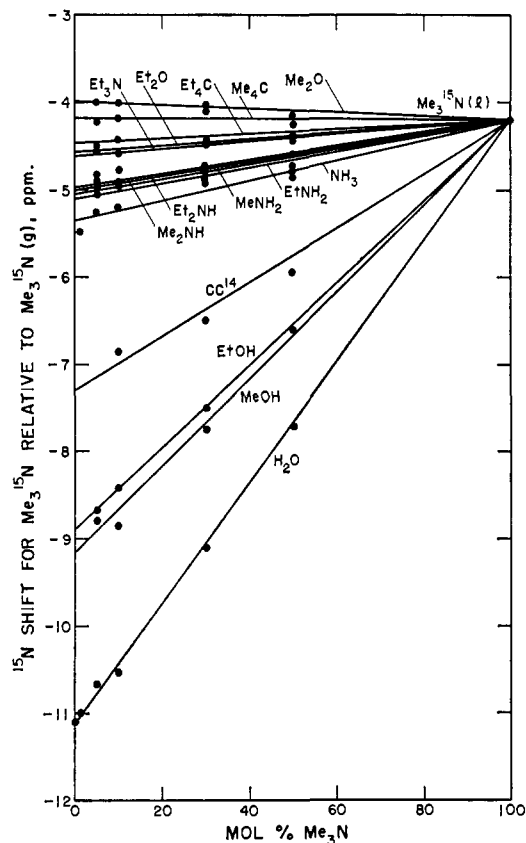


Figure 1.  $^{15}\text{N}$  nmr shifts for  $\text{Me}_3^{15}\text{N}$  in a number of liquid solvents.

with a  $\text{Me}_3^{15}\text{N}$  nitrogen lone pair, the probability of interaction with a given solvent site will be simply directly proportional to its relative abundance in the solvent molecule. Thus, for example, the infinite dilution shift for  $\text{Me}_3^{15}\text{N}$  in  $\text{EtNH}_2$  as solvent is given as

$$\delta_{\text{EtNH}_2} = \frac{2}{3}\sigma_{A_{\text{NH}}} + \frac{1}{3}\sigma_{A_{\text{Et}}} + \sigma_{B_{\text{N}}}$$

Proceeding in this fashion and excluding for the moment the solvents  $\text{CCl}_4$  and  $\text{Et}_4\text{C}$ , we may write 13 such equa-

**Table II.** Scheme of Coefficients

Solvent	$C_x$				$C_y$	
	$\sigma_{A_{Me}}$	$\sigma_{A_{Et}}$	$\sigma_{A_{NH}}$	$\sigma_{A_{OH}}$	$\sigma_{B_N}$	$\sigma_{B_O}$
H <sub>2</sub> O				1		1
Me <sub>2</sub> O	1					1
Me <sub>3</sub> N	1				1	
Me <sub>4</sub> C	1					
MeNH <sub>2</sub>	1/3		2/3		1	
MeOH	1/2			1/2		1
EtOH		1/2		1/2		1
Me <sub>2</sub> NH	2/3		1/3		1	
EtNH <sub>2</sub>		1/3	2/3		1	
Et <sub>2</sub> O		1				1
Et <sub>3</sub> N		1			1	
Et <sub>2</sub> NH		2/3	1/3		1	
NH <sub>3</sub>			1		1	

tions with the coefficients for each solvent listed in Table II. We then used a least-squares computer program to determine the six shift-parameter values which give the best fit between the experimentally observed infinite dilution shifts and those calculated from the equations indicated above. Although such a procedure produced shift-parameter values which gave a very good fit between calculated and experimental infinite dilution shifts (sum of squares of deviations = 2.4), the derived values for  $\sigma_{B_O}$  and  $\sigma_{B_N}$  were comparable in magnitude with the experimental uncertainty in the shift measurements ( $\pm 0.2$  ppm). We therefore neglected the  $\sigma_{B_y}$  parameters and attempted a least-squares fit using only the four  $\sigma_{A_x}$  parameters. The results are shown in Table III. The sum of the squares of the deviations

**Table III.** Values of Parameters and Calculated Results

Best parameter values	Infinite dilution shifts			
	Solvent	Exptl	Calcd	Diff
$\sigma_{A_{OH}} = -11.9$	H <sub>2</sub> O	-11.1	-11.9	-0.8
$\sigma_{A_{NH}} = -5.4$	Me <sub>2</sub> O	-4.0	-4.4	-0.4
	Me <sub>3</sub> N	-4.2	-4.4	-0.2
$\sigma_{A_{Et}} = -4.7$	Me <sub>4</sub> C	-4.2	-4.4	-0.2
	MeNH <sub>2</sub>	-5.1	-5.1	0
$\sigma_{A_{Me}} = -4.4$	MeOH	-9.2	-8.1	+1.1
	EtOH	-8.9	-8.3	+0.6
	Me <sub>2</sub> NH	-5.0	-4.7	+0.3
	EtNH <sub>2</sub>	-5.1	-5.2	-0.1
	Et <sub>2</sub> O	-4.6	-4.7	-0.1
	Et <sub>3</sub> N	-4.6	-4.7	-0.1
	Et <sub>2</sub> NH	-5.0	-5.0	0
	NH <sub>3</sub>	-5.4	-5.4	0

between calculated and experimental shifts in Table III is 2.4 indicating that the fit here is just as good as that obtained by including the  $\sigma_{B_y}$  parameters. We therefore conclude that within the experimental uncertainties of this work, the  $\sigma_{B_y}$  shift contributions are completely negligible.

With regard to the best parameter values in Table III we note that the value of  $\sigma_{A_{Et}}$  derived from the solvents listed is in very good agreement with the experimentally determined value of the infinite dilution shift for Me<sub>3</sub><sup>15</sup>N in tetraethylmethane (*cf.* Table I). This is consistent with the proposed model which assumes  $\sigma_{A_{Et}}$  to be the only shift contribution for Me<sub>3</sub><sup>15</sup>N at infinite dilution in Et<sub>4</sub>C.

It is interesting to compare the best shift parameters for the Me<sub>3</sub><sup>15</sup>N-solvent systems with those previously obtained for <sup>15</sup>NH<sub>3</sub> in the same solvents. These are compared in Table IV. Apart from the anticipated

**Table IV.** Best Shift-Parameter Values

	Me <sub>3</sub> <sup>15</sup> N	<sup>15</sup> NH <sub>3</sub> <sup>a</sup>
$\sigma_{A_{OH}}$	-11.9	-25.2
$\sigma_{A_{NH}}$	-5.4	-19.1
$\sigma_{A_{Et}}$	-4.7	-16.5
$\sigma_{A_{Me}}$	-4.4	-13.2
$\sigma_{B_O}$	0	+3.3
$\sigma_{B_N}$	0	+2.1

<sup>a</sup> The  $\sigma_A$  values in this list are all 2.1 ppm larger in magnitude than those listed in ref 2. In that work, the value for the <sup>15</sup>N shift between <sup>15</sup>NH<sub>3</sub> vapor and <sup>15</sup>NH<sub>3</sub> liquid was erroneously taken as -15.9 ppm owing to incorrect application of a volume susceptibility correction. The correct value is  $-18.0 \pm 0.2$  ppm. As a result of this error, the infinite dilution shifts and  $\sigma_A$  parameters for <sup>15</sup>NH<sub>3</sub> given in ref 2 are all too small in absolute magnitude by 2.1 ppm. The  $\sigma_B$  parameters are unaffected. This change does not alter the principal conclusions of that work.

result that the  $\sigma_{B_y}$  shift contributions are relatively much more important for <sup>15</sup>NH<sub>3</sub> than for Me<sub>3</sub><sup>15</sup>N, Table IV also demonstrates that the  $\sigma_{A_x}$  parameters for Me<sub>3</sub><sup>15</sup>N, though smaller in absolute magnitude, are in the same direction relative to the gas-phase resonance (paramagnetic) and show the same trend in relative magnitudes (*i.e.*,  $\sigma_{A_{OH}} > \sigma_{A_{NH}} > \sigma_{A_{Et}} > \sigma_{A_{Me}}$ ) as the corresponding parameters for <sup>15</sup>NH<sub>3</sub>. This suggests that, at least for simple amines, interactions of the nitrogen lone-pair electrons will, in general, lead to a downfield shift of the <sup>15</sup>N resonance relative to the gaseous molecule. Moreover, for both Me<sub>3</sub><sup>15</sup>N and <sup>15</sup>NH<sub>3</sub>, shift contributions due to interactions not generally considered to be hydrogen bonding ( $\sigma_{A_{Et}}$  and  $\sigma_{A_{Me}}$ ), although somewhat smaller than the hydrogen-bonding contributions ( $\sigma_{A_{OH}}$  and  $\sigma_{A_{NH}}$ ), are by no means negligible in comparison. In the H<sub>2</sub><sup>17</sup>O study of Reuben,<sup>4</sup> referred to in the introduction, oxygen lone-pair interactions other than hydrogen-bond formation are tacitly assumed to contribute nothing to the <sup>17</sup>O shift. In the light of our <sup>15</sup>N results in amine systems, we feel that such an assumption may lead to serious errors in interpretation.

With regard to the <sup>15</sup>N infinite dilution shift for Me<sub>3</sub><sup>15</sup>N in CCl<sub>4</sub>, the comparatively large paramagnetic nature of the shift suggests a strong interaction between the nitrogen lone-pair electrons of Me<sub>3</sub><sup>15</sup>N and the CCl<sub>4</sub> molecule. In the <sup>15</sup>NH<sub>3</sub> work previously referred to we also observed a large downfield shift of the <sup>15</sup>N resonance for <sup>15</sup>NH<sub>3</sub> at infinite dilution in CCl<sub>4</sub>. The exact nature of the interaction between these amines and CCl<sub>4</sub> is not known. However, Stevenson and Coppinger,<sup>6</sup> on the basis of ultraviolet absorption measurements, conclude that triethylamine and CCl<sub>4</sub> form a 1:1 complex and that, in general, "the halomethanes constitute a hitherto unrecognized class of "acceptors" (albeit weak) for strong donors of the amine type." This suggestion that donation of the amine nitrogen lone pair is involved in formation of the complex would be completely consistent, from our point of view, with the strong downfield shift of <sup>15</sup>N resonance.

**Acknowledgment.** The authors are indebted to Dr. B. B. McIner and Mr. R. M. Potter of this laboratory for providing us with the <sup>15</sup>N-enriched NO from which the Me<sub>3</sub><sup>15</sup>N was derived.

(6) D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, **84**, 149 (1962).