equation leads to a predicted ratio $k_{-1}/k_{-2} \cong 0.3$ to 0.5 for these hydrolyzing metals, $a_{11}/a_{22} < 1$ if θ/φ is less than approximately 2-3.3. If θ/φ exceeds this range and we are still observing the slower of two relaxation processes, then this slow process must correspond to a_{22} (since $a_{11}/a_{22} > 1$ implies $\tau_1^{-1} > \tau_2^{-1}$).

The results of this sort of analysis can then be summarized as

	$\phi/arphi$	Slow process
Iron(III)	19-61	a_{22}
Gallium(III)	5.2 - 6.7	a_{22}
Chromium(III)	1.8 - 3.4	?
Thorium(IV)	1.3 - 1.5	a_{i1}
Scandium(III)	1.0 - 1.7	a_{11}
Indium(III)	0.38-0.60	a_{11}

The chromium(III) case cannot be resolved by this argument although we see no reason to doubt our earlier assignment of specific rates based on a concordance of kinetic and thermodynamic equilibrium constants.⁵ On the other hand, our previous assignment of specific rates k_1 and k_{-1} in the case of aqueous gallium(III) hydrolysis was in error. We correctly determined that the slower of the two anticipated gallium(III) hydrolysis reactions was the one we could observe. However, we mistakenly assumed a_{11} to be the slow process.⁷ In the gallium(III) case as with iron(III) it is actually the second hydrolysis step (eq 2) that is slower. Thus the corrected specific rates for gallium(III) are $k_{-2} = 4.5 \times 10^9 M^{-1} \sec^{-1}$ and $k_2 = 1.7 \times 10^5 \sec^{-1}$ with $k_2/k_{-2} = 10^{-4.4}$, in rough agreement with the potentiometric¹⁷ * $K_2 = 10^{-3.5}$.

Acknowledgment. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant AF-AFOSR-69-1717-D.

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A Study of Nitrogen-15 Nuclear Magnetic Resonance Shifts in Pure

Methylamines and Pure CH₃C¹⁵N^{1a}

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The ¹⁵N liquid association shifts and temperature dependences of the ¹⁵N chemical shifts of ¹⁵NH₃, CH₃¹⁵NH₂, (CH₃)₂¹⁵NH, (CH₃)₃¹⁵N, and CH₃C¹⁵N are presented and discussed. In the order given above, the vapor chemical shifts are 0, -14.5, -26.1, -28.7, and -273.4 ppm, respectively. The liquid association shifts at the melting point are -22.6, -9.4, -3.2, -6.9, and +11.3 ppm, respectively, and the temperature coefficients are +4.3, +1.6, +0.5, +2.0, and -2.1 (all $\times 10^{-2}$ ppm/°C), respectively. The difference in the shift data between the amines and acetonitrile is attributed to the dominance of the diamagnetic term in the case of the amines compared to the dominance of the paramagnetic term in acetonitrile.

Introduction

In recent publications^{2a,b} we have demonstrated that the ¹⁷O resonance in pure liquid water and the ¹⁵N resonance in pure liquid ammonia are both considerably downfield of the resonances in their respective vaporphase molecules. The liquid-phase resonance also shifts, in each case, to lower field with decreasing temperature in linear fashion. Moreover, taking pure ¹⁵NH₃ as an example, the ¹⁵N shift between vapor and liquid and the temperature coefficient of the ¹⁵N shift in the liquid are both more than ten times as large as the corresponding parameters for the NH₃ proton resonance. It is thus possible for the ¹⁵N resonance to be a sensitive probe for study of liquid-phase intermolecular interactions traditionally studied by proton resonance measurements. We have, in fact, more recently shown^{3,4}

 ⁽a) Work supported by the U. S. Atomic Energy Commission;
 (b) AWU Faculty Research Participant at Los Alamos Scientific Laboratory.

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that when ${}^{15}NH_3$ or $Me_3{}^{15}N$ is dissolved in a solvent the ${}^{15}N$ resonance undergoes a shift which may be correlated with the types of interactions which can occur between the amine and the given solvent.

In the present work, we report results of a study of the ¹⁵N resonance in the pure compounds ¹⁵NH₃, CH₃¹⁵NH₂, (CH₃)₂¹⁵NH, and (CH₃)₃¹⁵N. We were primarily interested in measuring the shift of the ¹⁵N resonance in the pure liquid relative to the pure vapor and comparing this "liquid-association shift" with the temperature dependence of the ¹⁵N shift in the pure liquid for a series of structurally related compounds. For compounds which are monomolecular in the gas phase, the liquid-association shift is presumably produced by intermolecular interactions in the liquid and since the variation with temperature of the ¹⁵N shift in the liquid is almost surely due to some sort of thermal perturbation of these interactions, we felt there might be some correlation between these two nmr parameters.

In previous work,³ we observed that protonation or dilution with H₂O produces strong *downfield* shifts of the ¹⁵N resonance in the ¹⁵NH₃ molecule. For the CH₃CN molecule, on the other hand, Lowenstein and Margalit⁵ have reported that the ¹⁴N resonance shifts *upfield* on dilution with H₂O or methanol and Olah and Kiovsky⁶ have reported a strong *upfield* shift of the ¹⁵N resonance on protonation. We have therefore also measured the ¹⁵N liquid-association shift and the temperature dependence of the ¹⁵N shift in the liquid for pure CH₃C¹⁵N to determine whether or not these shifts also differ in direction from those for the amines.

Experimental Section

1. Synthesis of ¹⁵N-Labeled Compounds. The original source of ¹⁵N for this work was nitric oxide gas, isotopically enriched by low-temperature distillation.⁷ The following sequence of reactions was used to convert this material to isotopically enriched ¹⁵NH₈ or ¹⁵NH₄Cl.

¹⁵NO + H₂
$$\xrightarrow{\text{Ni catalyst}}_{300^{\circ}}$$

¹/₂ ¹⁵N₂ + H₂O
 $\xrightarrow{\text{[Ca metal]}}_{700^{\circ}}$ Ca₃¹⁵N₂ $\xrightarrow{\text{H}_2\text{O}}$ ¹⁵NH₃ $\xrightarrow{\text{aqueous HCl}}$ ¹⁵NH₄Cl

Starting material containing essentially 100%¹⁵N was available to us and was occasionally used for preparing vapor samples where the low density of nuclei makes signal detection more difficult. For liquid samples, material containing $\sim 50\%$ ¹⁵N generally gave adequate nmr signals.

a. ${}^{15}NH_3$. This material was prepared as indicated above. ${}^{15}NH_3$ stored in a stainless steel cylinder attached to a Pyrex vacuum system through a stainless steel valve could be measured out and transferred by standard techniques either for nmr sample preparation or for use in other syntheses. b. $CH_3^{15}NH_2$. This material was prepared by the sequence of steps listed below.



The above steps are a combination of two published syntheses with obvious minor modifications.⁸

c. $(CH_3)_2$ ¹⁵NH. This compound was prepared by the following sequence of reactions.



The above synthesis is a slight modification of a published procedure.⁹

d. $(CH_3)_3^{15}N$. $(CH_3)_3^{15}N \cdot HCl$ was prepared by refluxing ¹⁵NH₄Cl in an aqueous solution of formic acid and formaldehyde according to a published procedure.¹⁰ The procedure reports a yield of 75.4% of Me₃¹⁵N · HCl, but we found that carrying out the reaction exactly as directed resulted in a product containing significant quantities of Me¹⁵NH₂·HCl and Me₂¹⁵NH·HCl. By doubling the ratio of formaldehyde to ¹⁵NH₄Cl and refluxing for 16–24 hr instead of the indicated 10 hr, we were able to obtain pure Me₃¹⁵N·HCl in over 90%

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⁽⁷⁾ We are indebted to Dr. B. B. McInteer and Mr. R. M. Potter of this laboratory for supplying us with this material.

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(9) See ref 8, Part I, p 598.

⁽¹⁰⁾ See ref 8, Part II, p 1837.

yield.¹¹ The free amine was liberated from this salt by adding concentrated aqueous NaOH.

e. $CH_3C^{15}N$. This material was prepared by initially reacting ¹⁵NH₃ with excess CH_3COCl at Dry Ice temperature to form a mixture of $CH_3CO^{15}NH_2$ and ¹⁵NH₄Cl. After pumping off the excess CH_3COCl , the $CH_3CO^{15}NH_2$ was separated from the ¹⁶NH₄Cl by a low-temperature (50–75°) sublimation in a stream of Ar. The $CH_3(O=)C^{15}NH_2$ was mixed with an excess of P_2O_5 and the mixture heated to $\sim 100^\circ$ in a distillation apparatus which was continually flushed with dry Ar. The overall yield of $CH_3C^{15}N$ was 40-50%.

2. Nmr Measurements. The nmr measurements were made on a Varian DP-60A instrument in which the external lock-on mechanism was utilized to fix the magnetic field so that H_2O protons resonated at exactly 60 MHz. The ¹⁵N resonances were then observed by using a General Radio Co. digital frequency synthesizer and the ramp voltage of a Varian C-1024-time-averaging computer to sweep the working frequency in the region of 6.08 MHz.

The liquid amine samples were sealed in Pyrex tubes of $\sim 8 \text{ mm}$ o.d. diameter. A thin-walled glass thermocouple well was sealed into the tube so that the tip of the well was immersed several millimeters at the top of the liquid sample. Sample volumes were ~ 1 cc. The temperature of the sample, was varied by flowing hot or cold N₂ around the sample tube. The temperature was read on a thermocouple inserted in the thermocouple well.

Gas samples were generally prepared by sealing $\sim 1 \text{ mmol of liquid in an ampoule } \sim 35 \text{ mm long prepared from 15-mm o.d. standard-wall Pyrex tubing. Vaporization of the entire liquid sample would thus produce vapor pressures of the order of 5 atm. The vapor resonance was easily observed under these conditions by using the Varian C-1024 time-averaging computer.$

Results and Discussion

The principal experimental results are listed in Table I. The temperature coefficient of ¹⁵N shift in each pure liquid is derived from the plot of ¹⁵N shift vs. temperature for that liquid (cf. Figures 1 and 2). In every case, the dependence of shift on temperature showed no significant departure from linearity over the temperature range studied (in the case of $CH_3C^{15}N$, nearly the entire liquid range). The vapor resonances, on the other hand, were not measurably shifted by temperature changes of 40 to 50°, indicating no significant degree of vapor-phase association for any of the compounds studied.

The first two rows of Table I list parameters derived from the vapor resonances. They display some interesting features which we think are noteworthy. Confining our attention to the amine data, the J_{18N-H} values demonstrate that the coupling between ¹⁵N and directly

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Figure 1. Temperature coefficient for ¹⁵N shift in pure liquid amines.



Figure 2. ¹⁵N shifts for CH₃C¹⁵N liquid and vapor.

(11) It was convenient to follow the reaction by periodically taking a few drops of the reaction mixture and examining its pur spectrum. The methyl proton resonances for the species $(CH_3)_3NH^+$ (doublet), $(CH_3)_2NH_2^+$ (1:2:1 triplet), and $CH_3NH_3^+$ (1:3:3:1 quartet) are easily differentiated.

Table I: ¹⁵ N Nmr Parameters f	for Sin	aple Amines	and ($CH_{3}C$	^{15}N
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	¹⁵ N H ₈	CH315NH2	(CH ₈) ₂ ¹⁸ NH	(CH ₈) ₈ ¹⁵ N	CH ₃ C ¹⁵ N
J_{15N-H} , vapor ^a	61.2	64.5	67.0		
¹⁵ N shift, vapor ⁵	(0)	-14.5	-26.1	-28.7	-273.4
¹⁵ N shift, liquid ^c , d	-22.6(-77.7)	-23.9(-93.5)	-29.3(-96)	-35.6(-117)	-262.1(-45.7)
Liquid-assoc shift	-22.6	-9.4	-3.2	-6.9	+11.3
Temp coeff of ¹⁵ N shift,	$4.3 imes 10^{-2}$	$1.6 imes10^{-2}$	$0.5 imes10^{-2}$	$2.0 imes10^{-2}$	$-2.1 imes 10^{-2}$
liquide					

^a Units are Hz. Uncertainty = ± 0.3 Hz. ^b Units are ppm relative to ${}^{15}NH_8(v)$. Uncertainty = ± 0.2 ppm. Negative sign indicates shift is downfield. ^c Shifts, in ppm relative to ${}^{15}NH_8(v)$, are for the ${}^{15}N$ resonance at the melting point (listed in °C in parentheses). These are obtained by extrapolating data in Figures 1 and 2. Volume susceptibility corrections between vapor and liquid at $\sim 30^{\circ}$ have been made but changes in susceptibility due to changes in liquid density with temperature have been ignored. The trend in these data between CH₃¹⁵NH₂ and (CH₃)s¹⁵N follows very closely that reported by Witanowski and Januszewski^d for the ¹⁴N shifts in these same compounds but their shifts are all 1–2 ppm farther downfield than ours when both sets of data are referred to the same reference. ^d M. Witanowski and H. Januszewski, *Can. J. Chem.*, 47, 1321 (1969). ^e Units are ppm/°C. Uncertainty = $\pm 0.2 \times 10^{-2}$ ppm/°C.

bonded hydrogen increases with increasing methyl substitution. Roberts, et al.,12 have suggested a linear relationship between s character of the ¹⁵NH bond and the ¹⁵NH coupling constant provided, among other things, that the mean electronic excitation energy remains constant throughout a given series. Using the equation proposed by these authors, an increase in s character from 20.3% to 22.8% would account for the increase in J_{15N-H} in going from ${}^{15}NH_3$ to $(CH_3)_2{}^{15}NH$. The bond angle data¹³ for the series NH₃, CH₃NH₂, and $(CH_3)_2NH$ are not sufficiently precise to provide any independent evidence with regard to such small changes in hybridization. Thus, a small increase in s character of the ¹⁵NH bond might reasonably explain the observed increase in $J_{^{16}N-H}$. However, Tannenbaum, Coffin, and Harrison¹⁴ have shown that the absorption bands in the region of $50,000 \text{ cm}^{-1}$ undergo appreciable shifts to lower frequency with methyl substitution in the series NH₃, CH₃NH₂, (CH₃)₂NH, and $(CH_3)_3N$. This result is consistent with a decrease in electronic excitation energy but it is not completely clear which electronic excitation is involved. If the uv absorption is due to excitation of an electron in the lone-pair orbital, there may be no necessary correlation between the uv and $J_{\text{BN-H}}$ data. However, if the excitation energy for an electron in the ¹⁵N⁻H bond were being lowered, then the $1/\Delta E$ dependence of the coupling constant might lead to the observed increase in $J_{^{18}N-H}$. In addition, calculations utilizing the principle of "bond-effective nuclear charge"¹⁵ can account for the observed trend in $J_{^{16}N-H}$. Following the same procedure for ${}^{15}NH_3$ as for ${}^{13}CH_4$, the value of 0.29 for the charge transfer, $Q_{\rm NH}$, in the NH bond satisfactorily determines the couplings. The lone-pair charge transfer, while taken to be zero, is not greatly significant in this calculation. The value of 0.29 for $Q_{\rm NH}$ is slightly larger than the Q_{CH} found in the methane case but is reasonable considering the electronegativities of the two atoms. As a result, since most of the parts of the

contact term of the directly bonded coupling constant expression can individually account for the observed changes in coupling, relying on any one of them in a specific case is highly suspect.

The shift of the ¹⁵N resonance in the amine vapor to progressively lower field with increasing methyl substitution (*cf.* second row of Table I) is roughly in accord with the uv absorption data cited above. A decrease in mean excitation energy should lead to an increase in the paramagnetic contribution to the shift. However, the results of Tannenbaum, *et al.*,¹⁴ indicate that if Δ is the total decrease in excitation energy between NH₃ and (CH₃)₃N, the decrease between NH₃ and CH₃NH₂ is ~2/3 Δ and between NH₃ and (CH₃)₂NH, ~7/8 Δ . If the change in ΔE were the only factor influencing the ¹⁵N shifts, one would expect the shifts to follow the same pattern. Since the shifts depart significantly from this pattern it is likely that other factors are also involved.

The ¹⁵N liquid-association shifts listed in the fourth row of Table I represent the downfield shift of the ¹⁵N resonance in the liquid at its melting point relative to the gas-phase resonance whose position, within the experimental uncertainty, is independent of temperature. Thus, for each compound, this shift is assumed to be the result of changing the ¹⁵N environment from that in the free molecule to that in the most highly structured liquid. We note that the ¹⁵N liquid-association shifts for all the amines are downfield (liquid resonance downfield of vapor resonance) but of varying magnitude. Since we had concluded from our previous

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studies^{3,4} that the interaction of the amine nitrogen lone-pair electrons with an N-H proton (hydrogen-bond formation) makes a larger contribution to the ¹⁵N shift than does interaction of the nitrogen lone-pair electrons with solvent methyl groups, we anticipated that the liquid-association shifts for the amines in Table I would *decrease* in magnitude on replacement of protons by methyl groups. This does indeed occur as we go from ¹⁵NH₃ to $(CH_3)_2^{15}NH$. The *increase* in magnitude of the liquid-association shift on replacing the proton of $(CH_3)_2^{15}NH$ with another methyl group to form $(CH_3)_3^{15}N$ was unexpected.

The temperature coefficient of nmr shift for the proton resonance in hydrogen-bonded liquids is generally believed to arise from thermal perturbation of the hydrogen-bonded structure either by altering the ratio of hydrogen-bonded to nonhydrogen-bonded species16 or by changing the degree of excitation of the hydrogenbond-stretching vibrational mode.¹⁷ In liquid primary and secondary amines, one would expect these types of thermal perturbations to also influence the shift of the ¹⁵N nucleus since the nitrogen lone-pair electrons are involved in any hydrogen-bonds which are present. In addition, our previous studies^{3,4} of the ¹⁵N shifts for ${}^{15}\mathrm{NH_3}$ or $(\mathrm{CH_3})_3{}^{15}\mathrm{N}$ in a number of solvents indicate that interaction of the nitrogen lone-pair electrons with solvent molecule methyl or ethyl groups contributes significantly to the ¹⁵N shift. Thermal perturbation of this type of interaction might also cause the ¹⁵N resonance to shift with temperature. The plots in Figure 1 demonstrate that in the liquid amines the ¹⁵N shift has a significant temperature dependence not only in the hydrogen-bonding liquids ${}^{15}NH_3$, HC_3NH_2 , and $(CH_3)_2NH$, but also for $(CH_3)_3{}^{15}N$. Thus, as Hindman, et al.,¹⁸ have previously shown for proton NMR shifts, the ¹⁵N resonance can shift appreciably with temperature in systems which would not generally be considered as "hydrogen-bonded." It is also interesting to note that for all the liquid amines in Figure 1. (1) the ¹⁵N resonance shifts to lower field with decreasing temperature and (2) the shift, within experimental uncertainty, is a linear function of the temperature. The first observation is consistent with the expectation that lowering the temperature strengthens the intermolecular interactions in the liquid and therefore causes the liquid-association shift to increase in magnitude. The linearity of the temperature dependence of the ¹⁵N shift seems, at first glance, to be inconsistent with the models proposed for explaining temperature dependences of nmr shifts in liquids. Thus, for example, if we assume that lowering the temperature increases the fraction of ¹⁵N atoms in hydrogen bonds, the simplest shift expression is

$$\delta = \frac{\delta_2 K_0 e^{-\Delta H/RT}}{1 + K_0 e^{-\Delta H/RT}} \tag{1}$$

where δ_2 is the shift of the ¹⁵N resonance in the hydro-

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gen-bonded environment relative to its position in a liquid-phase "monomeric" or nonhydrogen-bonded species, K_0 is a constant of integration, and ΔH is the enthalpy difference between the hydrogen-bonded and monomeric species.

Equation 1 clearly will not generally yield a linear variation of shift with temperature. Thus, if the proposed model is to be consistent with the experimentally observed linearity, it must be demonstrated that for a reasonable set of values for the parameters δ_2 , K_0 , and ΔH , eq 1 will fit the experimental observations within experimental uncertainty. We therefore attempted to fit eq 1 to the ¹⁵N shift vs. temperature data for liquid ¹⁵NH₃ (cf. Figure 1) using a nonlinear least-squares computer program to find best values for the parameters δ_2 , K_0 , and ΔH . The results are $\delta_2 = -24.5 \pm 0.7$ ppm, $K_0 = 0.22 \pm 0.05$, and $\Delta H = -1.5 \pm 0.2$ kcal/ mol. With these best parameter values, eq 1 duplicates the experimental data to well within the experimental uncertainty. Moreover, the best parameter values seem reasonable. Thus, accepting the model on which the parameters are based, we consider the ¹⁵N in liquid ¹⁵NH₃ as rapidly exchanging between two environments in equilibrium with each other. In the hydrogen-bonded environment, the ¹⁵N resonance is shifted 24.5 ppm downfield of its position in the monomeric environment, and the enthalpy of stabilization of the hydrogen-bonded with respect to the monomeric species is -1.5 kcal. Taking all three parameter values together we calculate that liquid ammonia is 91% hydrogen bonded (*i.e.*, 91% of the N atoms are involved in hydrogen bonding) at its melting point and 83% hydrogen bonded at its boiling point. None of these conclusions seems untenable except perhaps the value of -1.5 kcal/mol for the enthalpy of hydrogen-bond formation in liquid NH₃. This value seems rather low compared with the heat of vaporization of \sim 5.5 kcal/ mol for liquid NH₃¹⁹ or the enthalpy of formation of -4.4 kcal/mol reported²⁰ for a hydrogen-bonded gasphase ammonia dimer. However, we know of no directly measured values of the hydrogen bond strength in liquid NH₃ and therefore cannot rule out the value of -1.5 kcal/mol. It thus appears that the model is reasonably consistent with the experimental observations although we do not wish to imply that it is the only model which adequately interprets the data.

Whatever the exact source of the variation of ¹⁵N shift with temperature in the liquid amines, the linear dependence yields a temperature coefficient which is

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constant over a rather wide temperature range. A comparison of these temperature coefficients (5th row of Table I) with the liquid association shifts (fourth row of Table I) for the amines shows a striking similarity in behavior of these two parameters. Thus, for the series ¹⁵NH₃, CH₃¹⁵NH₂, and (CH₃)₂¹⁵NH, both parameters progressively decrease in magnitude with the ratio between them remaining approximately constant. Both parameters increase in magnitude in going from $(CH_3)_2^{15}NH$ to $(CH_3)_3^{15}N$. These results are clearly consistent with the view that the variation of shift in the liquid is due to thermal perturbation of the intermolecular interactions responsible for the liquidassociation shift. However, the minimum in both parameters at $(CH_3)_2$ ¹⁵NH suggests that even for a series of structurally related compounds in which the electronic environment is not grossly altered from one molecule to the next, relatively subtle changes in bond hybridization or in the anisotropy of the electronic distribution about the nitrogen may obscure any correlation between the magnitudes of the ¹⁵N shift parameters and the types and/or strengths of the liquid phase interactions involving the nitrogen.

The data for $CH_3C^{15}N$ (cf. Figure 2 and column 5 of Table I), when compared with corresponding data for the amines, clearly demonstrates the difference in behavior which may be brought about by gross alteration of the electronic structure around the nitrogen. For $CH_3C^{15}N$ condensation from vapor to liquid leads to an *upfield* shift of the ¹⁵N resonance. Moreover the ¹⁵N shift in the liquid continues to move to *higher* field with *decreasing* temperature. Thus the data for $CH_3C^{15}N$ remain consistent with the premise that the temperature variation of shift in the liquid is due to thermal perturbation of the interactions responsible for the liquid-association shift. However, $CH_3C^{15}N$ appears to differ consistently from the simple aliphatic amines in the direction of ¹⁵N shift produced by similar types of changes in the nitrogen environment. We suggest that this is due to dominance of the paramagnetic term in the ¹⁵N chemical shift for $CH_3C^{15}N$ while the ¹⁵N shifts in the amines are dominated by the diamagnetic term. Thus, in the gaseous molecules, the ¹⁵N resonance in $CH_3C^{15}N$ is strongly shifted paramagnetically (273.4 ppm downfield) relative to ¹⁵NH₃. This is consistent with the large increase in anisotropy of the electron distribution about the nitrogen in $CH_3C^{15}N$

crease in the average value of r. The rather good constancy of the ratio of ¹⁵N liquidassociation shift to temperature coefficient of $^{15}\mathrm{N}$ shift in all the liquids studied here (ratio $\simeq -500 \pm 100$) prompted us to compile a larger list of liquids and nuclei for which these parameters had been measured. Table II is a compilation of such data that we were able to find readily in the literature. As anticipated, the ratio of liquid association shift at the melting point to the temperature coefficient of shift in the liquid does not vary greatly over the entire table. Thus, from a purely empirical point of view, one could get a quite good approximation to the temperature coefficient of shift for a particular nucleus in any of these liquids by taking $-\frac{1}{500}$ of the liquid-association shift for that nucleus. It is interesting that the ratio of the enthalpy change on

relative to ¹⁵NH₃. If the paramagnetic term dominates, any intermolecular interactions which tend to

displace electrons away from the ¹⁵N nucleus would,

through the $(1/r^3)$ dependence of the paramagnetic

term, lead to a decrease in the paramagnetic term or an upfield shift of the ¹⁵N resonance. For ammonia or

the methylamines on the other hand, dominance of the

diamagnetic term would, through its (1/r) dependence, lead to a downfield shift of the ¹⁵N resonance for an in-

Table II: Corr	elation o	f Lia	uid-Association	Shifts v	vith (Other	Data
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Compd	Nucleus	Liquid-assoc shift, S, ppm	Temp coeff of shift in liquid, dS/dT, ppm/°C	$rac{S}{\partial S/\partial T}$	$\left(\frac{\Delta H}{\Delta C_p}\right)_{evap}$
$^{15}\mathrm{NH}_3$	^{15}N	-22.6	$4.3 imes 10^{-2}$	-525	-587'
$\rm NH_3$	чH	-1.05^{a}	$2.7 imes 10^{-3^e}$	-389	-587'
$\mathrm{CH}_{8}^{15}\mathrm{NH}_{2}$	$^{15}\mathrm{N}$	-9.4	$1.6 imes 10^{-2}$	-587	
$(CH_3)_{2}^{15}NH$	15 N	-3.2	$0.5 imes10^{-2}$	-640	-370''
(CH ₃) ₃ ¹⁵ N	^{15}N	-6.9	$2.0 imes10^{-2}$	-345	
CH ₃ C ¹⁶ N	^{15}N	+11.3	$-2.1 imes 10^{-2}$	-538	-810^{h}
$H_{2}^{17}O$	17O	-36^{b}	$4.8 imes 10^{-2^{b}}$	-743	$-1000^{f_{ij}}$
H_2O	۱H	-4.66°	$9.9 imes10^{-3^c}$	-471	$-1000^{f,i}$
H_2S	$^{1}\mathrm{H}$	-1.46^{d}	$4.2 imes10^{-3d}$	-349	
H_2Se	$^{1}\mathrm{H}$	-1.85^{d}	$4.6 imes 10^{-3^{d}}$	-402	
H ₂ Te	۱H	-3.29^{d}	6.6×10^{-3d}	-500	

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evaporation to the difference in specific heat between liquid and vapor, $(\Delta H/\Delta C_p)_{\rm evap}$, is also of this order of magnitude for a number of liquids. There is a crude rationale for this similarity if one assumes that the liquid association shift, S, is proportional to the heat of evaporation. Thus, if $S \propto \Delta H_{\rm evap}$, then $(\partial S/\partial T) \propto$ $(\partial \Delta H_{\rm evap}/\partial T) \propto (\Delta C_p)_{\rm evap}$ or $[S/(\partial S/\partial T)] \cong (\Delta H/$ $\Delta C_p)_{\rm evap}$. This is obviously an oversimplification since the thermodynamic properties are influenced by energy changes in all the degrees of freedom of the systems involved while the shifts may be primarily determined by the energies of interactions along certain bonds or directions. However, if this type of model, applied to those interactions which influence the shift, is valid, the temperature dependence of shift in the liquid would be considered as simply due to increasing strength of interaction with decreasing temperature and the linearity of the temperature dependence of shift in the liquid would be attributed to the near constancy of the rate of change of this interaction energy with temperature. Thus, since this "continuum" model could probably fit the nmr observations as well as the "two-statemodel" represented by eq 1, the nmr evidence alone cannot rule out either possibility.

Self-Association of Butylamines¹

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An iterative matrix technique is described for solving the quasichemical equations. The method is then applied to interpret the amino proton dilution chemical shift of four butylamines in cyclohexane. Comparison of the results with equilibrium calculations indicates that the best stoichiometry for butylamine self-association is the formation of noncyclic trimers.

In the course of other work,² it became desirable for us to learn something about the strength and extent of hydrogen bonding in the four isomeric primary butylamines. We therefore studied their proton magnetic resonance spectra upon dilution with the inert solvent, cyclohexane, and sought a model to describe the data over the entire concentration range. The data were successfully interpreted both by a simple monomer*n*-mer equilibrium model and in terms of the quasichemical approximation.³⁻⁵ Comparison of the two sets of results leads to the conclusion that the best selfassociation model is the formation of noncyclic trimers.

The amines were the best grades available from Fisher and Eastman Kodak. They were further purified by distilling twice or more over potassium hydroxide pellets using a Vigreux reflux column; the last distillation of each amine was carried out immediately before its use. Experiments were done using both Fisher Certified cyclohexane which was refluxed overnight over calcium hydride and then fractionated⁶ and Fisher spectrograde cyclohexane without further purification. No differences were observed between these two solvents. Tetramethylsilane (TMS) from NMR Specialties was used as an internal standard.

All glassware was thoroughly dried and was flushed with dry nitrogen gas just before use. Samples were prepared by pipetting and the nmr sample tubes were degassed and sealed under vacuum. The chemical shift measurements were obtained with a Jeolco Model C-60H (60 MHz) spectrometer employing external locking and running in the frequency-sweep mode. The frequency of the sweep oscillator was measured with a Hewlett-Packard Model SRC counter. Chemical shifts were determined by the difference between the frequency at the proton of interest and that at the TMS

⁽¹⁾ Supported by a grant from the National Science Foundation.

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