Intermolecular effects on ^1H, ^{13}C, and ^{15}N nuclear magnetic shielding in HCN

Cynthia J. Jameson

Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680

A. Keith Jameson

Department of Chemistry, Loyola Univesity, Chicago, Illinois 60626

D. Oppusunggu and S. Wille

Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680

(Received 30 July 1981; accepted 15 September 1981)

We have observed the temperature dependence of the ^1H, ^{13}C, and ^{15}N NMR spectra in HCN in the liquid phase and also in the saturated vapor. Concentrations observed in 0.05 to 0.30 mol/l for the vapor and 21–27 mol/l for the liquid at temperatures ranging from 230 up to 380 K. The gas-to-liquid shifts and the chemical shift between the dimer and the monomer have been determined for ^1H, ^{13}C, and ^{15}N nuclei. A dichotomy in the ^{15}N shifts in nitrogen nuclear environments capable of hydrogen bonding is noted. ^{15}N in HCN appears to be an archetype of nitrogen nuclear environment which is in the same class as pyridine and acetonitrile (and which behaves in a manner opposite to that of ^{15}N in NH_3 and saturated amines), such that the effect of intermolecular interactions is to lead to an unusual increase rather than the usual decrease in shielding observed for all other nuclei.

INTRODUCTION

One approach to the study of intermolecular forces is observing the spectral behavior of a solute in various solvents. Variations in the NMR spectrum can be particularly informative, especially if more than one nucleus in the solute is observed. In this study, we observe the ^1H, ^{13}C, and ^{15}N nuclei in HCN molecule in the liquid and in the vapor phase in equilibrium with it, and follow the changes in nuclear shielding as a function of temperature.

The effects of intermolecular interactions on nuclear shielding have been observed as chemical shifts between the dilute gas and the liquid, shifts between the gas and the infinitely dilute solution, and shifts in gases with increasing density. In a dilute gas the nuclear shielding can be written as a virial expansion in density

$$\sigma(T,\rho)=\sigma_0(T)+\sigma_1(T)\rho+\sigma_2(T)\rho^2+\cdots .$$

σ_1 has been observed to be negative, that is, intermolecular interactions generally have a deshielding effect.[1,2] Thus, at a given temperature the nuclear resonance frequency increases with increasing density of the gas.

The theoretical interpretation of σ_1 with a binary collision model proposed by Raynes, Buckingham, and Bernstein[3] (RBB) has had varying success for different molecular systems.[1,4] While the solute parameters A and B of the original RBB theory have been found to be completely independent of neither the solvent molecule nor the temperature,[1] this theory still provides the basic understanding of the subject of intermolecular interactions on nuclear shielding in a dilute gas. This model of the second virial coefficient of nuclear shielding gives σ_1 as a sum of several contributions

$$\sigma_1=\sigma_{1b}+\sigma_{1a}+\sigma_w+\sigma_{1E}+\sigma_{1r}+\sigma_{1s} .$$

All terms are long-range interaction terms originally included in the theory except for σ_{1r} and σ_{1s}, with which we will denote the short range repulsive interactions and the specific interactions (such as complex or hydrogen bond formation).

The bulk susceptibility contribution to shielding has been shown by Dickinson[5] to be given by $\sigma_b=(\alpha-4\pi/3)\chi_V$, where χ_V is the volume susceptibility of the substance, and α is determined by sample geometry. Thus, the bulk susceptibility contribution to σ_1 is $\sigma_{1b}=(\alpha-4\pi/3)\chi_m$, where χ_m is the molar magnetizability. σ_{1b} is negative for diamagnetic samples observed in cylindrical or coaxial cylindrical tubes transverse to the field direction. σ_{1w} is negative according to the fluctuating electric field model which was incorporated into the RBB theory.[3] This may be the usual sign for this term, so long as it is interpreted to include only the effects of the dispersive interactions. The attractive nature of the dispersion forces normally leads to an expansion of the electron cloud about a resonant nucleus and hence deshields it. This qualitative picture holds strictly only for a monatomic molecule, however. It is not inconceivable that attractive intermolecular forces can lead to a greater shielding of a nucleus in a diatomic or polyatomic molecule. σ_{1E} can be of either sign and is an important term when the probe molecule has an intrinsic electric dipole moment.[3] σ_{1a} can be of either sign, depending on the shapes of the interacting molecules, and is appropriate to include when two molecules have preferred relative orientations (i.e., an anisotropic intermolecular potential function).[6] σ_{1r} has been explored by theoretical calculations. For Xe it has been found to be negative and large by Adrian.[7] Raynes has found it to be relatively small compared to the observed σ_1 values for nuclei in small molecules, such as for ^1H in H_2 interacting with He,[8] ^{13}C, ^{17}O, and ^3He in CO interacting with He,[9] and ^1H, in CH_4 interacting with He or CH_4.[10] Systems in which σ_{1s} is likely to be important have been largely ignored in gas phase studies. The observed σ_1 has been found to

0021-9606/82/010152-11$02.10

TABLE I. Intermolecular effects on ^{15}N shielding in two classes of nitrogen environments.[a]

	Class I		Class II		
B	NH_3	Me_3N	HCN	CH_3CN	Pyridine
σ (neat liq.) $-\sigma_0$[b]	-20[e,i,f] at 300 K	-6.9[f] at 150 K -4.2 at 300 K	$+10.4$[t] at 346 K $\sim+12$[h] at 300 K	$+11.3$[i] at 227.5 K $+9.8$[i] at 300 K	$+6.3$[j] at 300 K
σ (soln in CCl_4) $-\sigma_0$	-17.9[g] (5% in CCl_4)	-7.3[l]		$+6.6$[c,i]	$+4.6$[j]
σ (soln in CH_3OH) $-\sigma_0$	-15.5[g]	-9.2[l]	reacts vigorously with alcohols	$+13.4$[c,i]	$+22.2$[j]
protonation shift[d] $\sigma_{BH+}-\sigma_B$	~-30[m]	~-30[m]	$\sim+108$[k,h]	$\sim+102$[k]	$\sim+122$[j]

[a] All numbers extrapolated to infinitely dilute solution and corrected for bulk susceptibility unless otherwise stated.

[b] Chemical shifts from the vapor at some low density are used in cases where $\sigma_0(T)$ and $\sigma_1(T)$ have not been determined.

[c] Reference 17, not corrected for bulk susceptibility.

[d] Not well-defined, usually $[\sigma(BH^+Cl^-\ soln)-\sigma(B,\ neat\ liq.)]$, but conditions are not comparable, so consider these numbers approximate (not corrected for bulk susceptibility).

[t] This work, not corrected for bulk susceptibility.

[e] Reference 44.

[f] Reference 22.

[g] Reference 45.

[h] Reference 46.

[i] Reference 11.

[j] Reference 19.

[k] Reference 20.

[l] Reference 15.

[m] Reference 16.

be negative in all the gas phase studies of which we are aware.[2] This may be due in part to the dominance of σ_{1_b} in some cases and of σ_{1_w} in others.

It should be noted that although the linear dependence of chemical shifts with density in the gas phase has been found to persist in the liquid phase in some compounds,[4] σ_1 is not defined for the liquid phase, where there must be simultaneous interactions between several molecules because of the small intermolecular separations. We shall refer to the density dependence of σ in liquids in terms of an "apparent σ_1." The nuclear resonance signal of the liquid usually appears at a higher frequency than the gas. The liquid resonance frequency also has been normally found to decrease with increasing temperature, accompanying the usual decrease in liquid density with increasing temperature at constant pressure.[1,11] Similarly, the nuclear resonance signal of a solute molecule in an infinitely dilute solution usually appears at a higher frequency than that in the dilute gas.[1] In other words, it is found in most cases that $(\sigma-\sigma_b)_{liq} < (\sigma-\sigma_b)_{gas}$, i.e., intermolecular interactions lead to decreased shielding. The exceptions to this general observation have usually been attributed to large positive σ_a contributions due to disk-shaped solvent molecules such as benzene with large magnetic anisotropies.[12] We report here additional exceptions to this general observation.

All other interactions that result in observed chemical shifts that are drastically different from those expected for perfect mixtures have generally been implied to be strong interactions which can result in the formation of molecular aggregates, e.g., donor–acceptor complexes. Hydrogen bonding shifts are usually reported as the chemical shift between the molecule in the neat liquid and in a solvent with which hydrogen bonding is proposed (or, for molecules capable of hydrogen bonding in the neat liquid, as the chemical shift between the neat liquid and the solution in an inert solvent). There is some ambiguity associated with the interpretation of this shielding difference between two condensed phases, as there are medium effects on shielding in each phase and only the difference is observed. A shielding difference which is more amenable to interpretation is the chemical shift between an infinitely dilute solution, or the neat liquid, and the zero-pressure gas at the same temperature [so that $\sigma_0(T)$ will effectively cancel]. The chemical shift between the neat liquid and its equilibrium vapor at a given temperature has been used by Litchman *et al.*[11] as a good approximation to the above, when vapor densities are small.

From compilations of chemical shifts in nitrogen NMR spectroscopy,[13,14] we find that nitrogen nuclear environments capable of hydrogen bonding can be generally classified into two classes, depending on their shifts upon protonation, self-association shifts, and shifts in the presence of solvent molecules which are proton donors or proton acceptors. Table I shows some examples. It must be assumed that members of these two classes actually form a continuum due to cancelling effects of various factors.

There are data obtained in the liquid phase, such as protonation shifts, or shifts between a solution in a proton donor and a solution in CCl_4, to indicate that the NH_3 type of behavior might also be observed in the following types of nitrogen sites: alkyl amines in general,[15,16] amides,[13] isonitriles,[17] and the pyrrole nitrogen in azoles.[18,19] Similarly, there is indication that HCN type of behavior might also be observed in the fol-

TABLE II. Temperature dependence of nuclear resonance in HCN.

	^{1}H	^{13}C	^{15}N
σ (liq., T) $-$ σ (liq., 300),[a] ppm	$+5.947 \pm 10^{-3}$ $(T-300)$	$+7.296 \times 10^{-3}$ $(T-300)$	-2.1775×10^{-2} $(T-300)$
	$+2.3538 \times 10^{-5}$ $(T-300)^2$	-1.70922×10^{-4} $(T-300)^2$	-5.508×10^{-5} $(T-300)^2$
	(265–360 K)	(230–325 K)	(265–340 K)
$(d\sigma/dT)$[a] equil vapor	-2.734×10^{-3}	-2.652×10^{-2}	$+2.8097 \times 10^{-2}$
ppm/deg	(300–370 K)	(325–370 K)	(340–376 K)

[a]These are the results of least-squares fitting of the data in Figs. 1–3 to a polynomial in T.

lowing types of nitrogen sites: imines,[13] azines,[13] and pyridine-type N in azoles.[18,19] The opposite behavior of the solvent shifts for the two classes of N environments were observed earlier in protonation shifts,[20,21] in gas to liquid shifts,[11] in shifts between neat liquids and solutions in CCl_4,[17] and solutions in a proton donor.[17–19] However, because of the many factors that affect these shifts, the dichotomy was not immediately obvious as it is in Table I when comparisons with the gas or isolated molecules can be made. Perhaps the most convincing evidence of a dichotomy is the comparison of the shifts between the isolated molecule and the solution in CCl_4, since specific interactions are not likely to play a role in these.

We have already reported the temperature and density dependence of ^{1}H and ^{15}N nuclear shielding in NH_3,[22] an archetype of nitrogen environment class I. In this paper, we report our studies on the ^{1}H, ^{13}C, and ^{15}N nuclear shielding in HCN, an archetype of nitrogen environment class II.

EXPERIMENTAL

In our gas phase studies, we normally prepare samples of known density within a range of density values which are less than the equilibrium vapor density over some reasonably wide range of temperatures (50–150 deg). To observe HCN gas at temperatures easily accessible with our variable temperature system (200–380 K) this would mean preparing samples of 5 amagat or less, covering at least a fivefold change in density. It is possible to do this, but HCN is known to polymerize to azulmic acid on long standing[23] and if any polymerization occurs, the sample density will not stay constant over the period of time that it takes to acquire precise data in samples of such low densities over at least a 50 deg temperature range. However, if we study the equilibrium vapor, the vapor density will remain constant and known at a given temperature, so long as there is some liquid HCN present, even with some polymerization. (We are neglecting the effects of the polymer on the vapor pressure of liquid HCN.)

Samples were prepared from potassium cyanide (in separate batches, 95% ^{15}N KCN, 95% ^{13}C KCN from Stohler Isotopes, normal KCN from Merck) treated with dilute sulfuric acid.[24] The hydrogen cyanide was liberated into a section of the vacuum line where it was cooled to liquid nitrogen temperature and degassed. Previously calibrated sample tubes of 2.2 mm i.d., 3.9 mm o.d., and about 5 cm long were filled and sealed off as previously described.[25] These samples fit into standard 5 mm o.d. NMR tubes with enough annular space for the toluene-d_8 liquid, which was used as a lock substance. The small sample tube which we use for variable temperature studies is especially important in this study. It is necessary to have a known uniform temperature throughout the sample since the vapor density depends on the temperature. By proper positioning of the NMR sample tube in the insert, both the vapor and the liquid or just the liquid could be observed, even with samples containing a very small amount of liquid.

In this study, we observed ^{1}H in liquid HCN at 265–360 K, ^{1}H in HC^{15}N vapor in equilibrium with liquid at 300–370 K, ^{15}N in liquid HC^{15}N (265–340 K) and its equilibrium vapor (340–376 K), ^{13}C in liquid H^{13}CN (230–325 K) and its equilibrium vapor (325–370 K). FTNMR spectra were obtained at 21.1 kG on a Bruker HFX90 variable frequency spectrometer with a Bruker B-KF 322s pulsed NMR spectrometer providing gated rf power amplification, a NIC293 controller as a pulse programmer and a Nicolet 1080 data system. ^{1}H spectra were acquired at 89.998 MHz, ^{13}C spectra at 22.633 MHz, and ^{15}N spectra at 9.121 MHz. Pulse repetition times of 0.55 s were used for ^{1}H and ^{15}N, 1.5 s for ^{13}C. Sweep widths of 1000 and 2000 Hz were used and 1 to 4 K data points were taken, zero filling to 8 K. Spectrometer and lock frequencies were monitored with a Fluke counter and all data were corrected for any variation in the lock frequency.

RESULTS

The results of observing ^{1}H, ^{13}C, and ^{15}N NMR spectra in the liquid and the equilibrium vapor in hydrogen cyanide are shown in Figs. 1–3 and Table II. The ^{1}H and ^{15}N data are plotted as $\nu \pm \frac{1}{2}J_{av}(^1\mathrm{H}-^{15}\mathrm{N})$, in order to superimpose the data from both members of the doublets. The ^{1}H–^{15}N coupling constant did not show any consistent change with temperature outside of experimental error. The absolute value of $^2J_{NH}$ is 7.0 ± 1 Hz, to be compared with 8.7 ± 0.1 Hz reported earlier for liquid HCN.[26] The ^{1}H–^{13}C coupling constants are plotted separately in Fig. 4. They agree with the value of 267.3 ± 0.10 Hz reported recently for liquid HCN.[27] It is seen in Fig. 4 that the coupling constant $^1J_{CH}$ in HCN has a measurable concentration and temperature dependence, which we can express approximately as: $J(T,\rho) = J_0(T) + J_1(T)\rho + \cdots$. As for $^1J_{BF}$ in $^{11}BF_3$,[28] the C–H coupling constant in

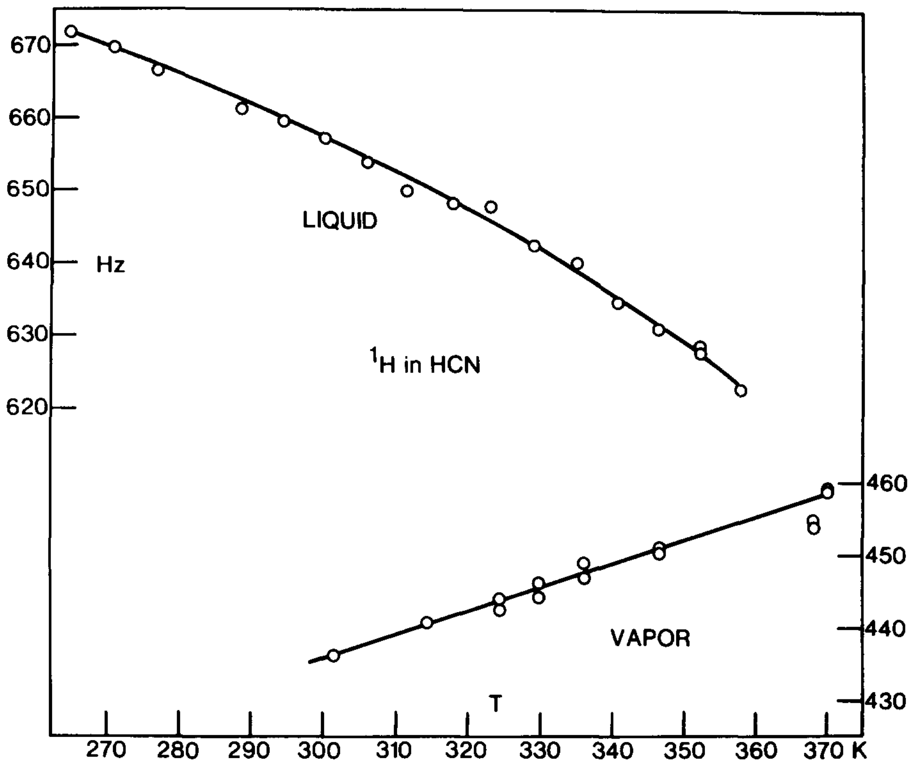


FIG. 1. Temperature dependence of the ^{1}H NMR frequencies observed in liquid HCN and in the vapor in equilibrium with the liquid.

liquid HCN has a greater magnitude than that in the vapor. In this case, however, we are presently unable to get values of dJ_0/dT and $J_1(T)$ separately. From the gas–liquid shift in the coupling constant at 336.6 K, we estimate J_1 to be 2.5×10^{-2} Hz/amagat.

Gas to liquid shifts for HCN were measured by observing both liquid and vapor in the same spectrum at a given temperature. The results are shown in Table III.

ANALYSIS

There have been many computational techniques used for the NMR study of hydrogen bonding in solution.[12] However, none of them have taken into consideration intramolecular dynamic effects (temperature dependence due to rovibrational averaging) and nonspecific intermolecular effects. Let us consider only dimer formation and include these medium and dynamic effects. Consider a dimer-forming system such as

$$2\,\mathrm{HCN} \rightleftharpoons \mathrm{H{-}C{\equiv}N}_A \cdots \mathrm{H{-}C{\equiv}N}_B$$

at a given temperature T. Let σ_m, σ_A, σ_B, be the absolute shielding of the nitrogen (or other) nucleus in the monomer site and the dimer sites, respectively. Let the association shift be defined as $\delta(T)=[\sigma_A(T)+\sigma_B(T)]/2-\sigma_m(T)$. Let α be the degree of association which de-

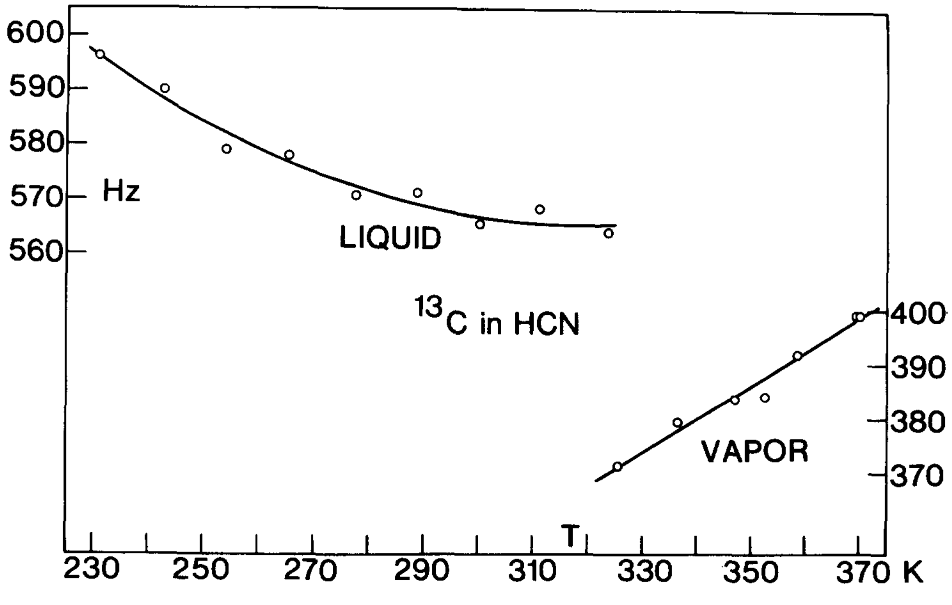


FIG. 2. Temperature dependence of the ^{13}C NMR frequencies observed in liquid HCN and in the vapor in equilibrium with the liquid.

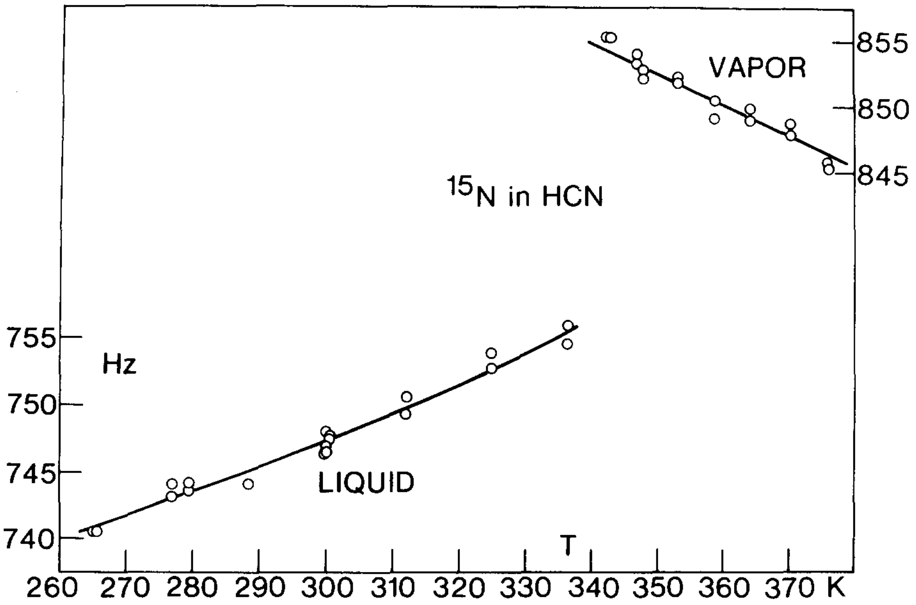


FIG. 3. Temperature dependence of the ^{15}N NMR frequencies observed in liquid HCN and in the vapor in equilibrium with the liquid.

pends on the concentration C and the temperature T. $C(1-\alpha)$ is the concentration of monomer and $\alpha C/2$ the dimer, such that the association equilibrium constant K equals $\alpha/2(1-\alpha)^2C$ and $\alpha \simeq 2KC$ for $\alpha \ll 1$. Under conditions of fast exchange between the bound and the free chemical species, we consider the average shielding which will be observed.

A. Without medium effects

Assuming only monomers and dimers with no medium effects, with fast exchange, only the average shielding will be observed

$$\begin{aligned}\sigma_{\text{av}}(T,C) &= (1-\alpha)\sigma_m + \alpha(\sigma_A+\sigma_B)/2 \\ &= \sigma_m + \alpha[(\sigma_A+\sigma_B)/2 - \sigma_m] ,\end{aligned} \tag{1}$$

or

$$\nu_{\text{av}}(T,C) = (1-\alpha)\nu_m + \alpha(\nu_A+\nu_B)/2 . \tag{2}$$

For equilibrium vapor data, a plot of $\nu(T,C)$ vs $\alpha(T,C)$ would yield

$$\begin{aligned}-\frac{1}{\nu_0}\frac{\partial\nu(T,C)}{\partial\alpha(T,C)} &= \left(\frac{\partial\sigma}{\partial\alpha}\right)_T \\ &= \tfrac{1}{2}[\sigma_A(T)+\sigma_B(T)] - \sigma_m(T) = \delta(T) ,\end{aligned} \tag{3}$$

TABLE III. Parameters obtained from the temperature dependence of the nuclear resonance in liquid HCN and its equilibrium vapor.

nucleus	σ (liq., T) $-\sigma$(equil vap, T) (ppm)	δ_{av}(ppm)[a] estimate
^{1}H	-2.00 at 346.6 K	$-$ 1.440
^{13}C	-7.68 at 336.6 K	-13.630
^{15}N	$+10.4$ at 346.7 K	+ 14.080

[a]The association shift $(\sigma_A+\sigma_B)/2-\sigma_m$ was calculated using Eq. (3), i.e., neglecting nonspecific medium effects and rovibrational averaging.

which is the association shift. $\alpha(T,C)$ can be calculated from the temperature dependence of the equilibrium vapor pressure of liquid HCN[29] and the equilibrium constant for dimer formation,[30] assuming only monomer and dimer coexist in the vapor phase.

Figure 5 shows for the equilibrium vapor, $\sigma(T,C)$ vs $\alpha(T,C)$ for ^{1}H, ^{13}C, and ^{15}N. If we neglect nonspecific medium effects and the temperature dependence due to rovibrational averaging, the slopes of the curves in Fig. 5 yield the association shift δ according to Eq. (3). These values are -1.44 ppm for ^{1}H, -13.63 ppm for ^{13}C, and $+14.08$ ppm for ^{15}N.

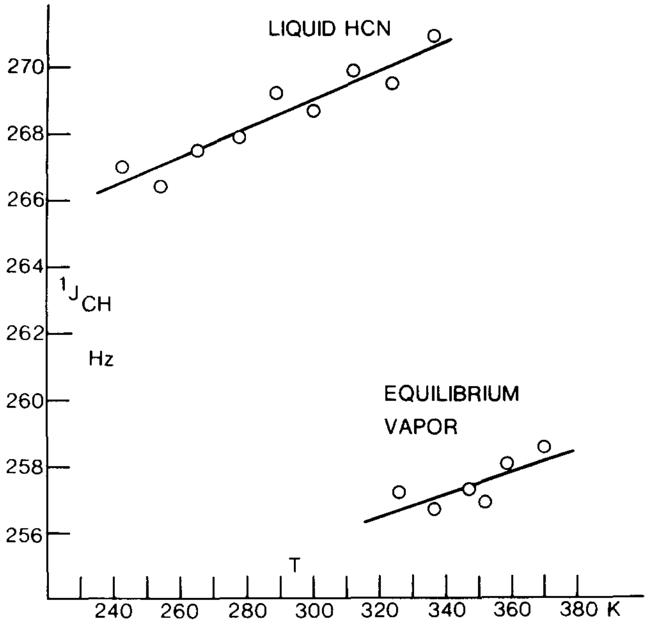


FIG. 4. Temperature dependence of the $^1J_{\text{CH}}$ coupling constant in HCN. For the liquid a least-squares fit to the straight line gives $^1J_{\text{CH}}$ (liquid) $= 269.06 + 4.405\times10^{-2}$ $(T-300\text{ K})$ Hz. For the equilibrium vapor, $^1J_{\text{CH}}$ (equil. vapor) $= 255.77 + 3.519\times10^{-2}$ $(T-300\text{ K})$ Hz.

B. With medium effects

To include medium effects, we replace σ_m by the virial expansion

$$\sigma_m + \sigma_1(m,m)C(1-\alpha) + \sigma_1(m,AB)C\alpha/2 + \cdots$$

at low densities, replace σ_A by

$$\sigma_A + \sigma_1(A,m)C(1-\alpha) + \sigma_1(A,AB)C\alpha/2 + \cdots ,$$

and σ_B by

$$\sigma_B + \sigma_1(B,m)C(1-\alpha) + \sigma_1(B,AB)C\alpha/2 + \cdots ,$$

so that

$$\sigma(T,C) = (1-\alpha)[\sigma_m(T) + \sigma_1(m,m)C(1-\alpha) + \sigma_1(m,AB)C\alpha/2] + \tfrac{1}{2}\alpha\{\sigma_A + \sigma_B + [\sigma_1(A,m) + \sigma_1(B,m)]C(1-\alpha) + \tfrac{1}{2}[\sigma_1(A,AB) + \sigma_1(B,AB)]C\alpha\} + \cdots . \tag{4}$$

Collecting terms in α and replacing $(\sigma_A + \sigma_B)/2 - \sigma_m$ by $\delta(T)$

$$\sigma(T,C) = \sigma_m(T) + \sigma_1(m,m)C + \alpha\{\delta(T) - 2\sigma_1(m,m)C + [\sigma_1(m,AB) + \sigma_1(A,m) + \sigma_1(B,m)]C/2\} + \alpha^2 C\{\sigma_1(m,m) - \tfrac{1}{2}\sigma_1(m,AB) - \tfrac{1}{2}[\sigma_1(A,m) + \sigma_1(B,m)] + \tfrac{1}{4}[\sigma_1(A,AB) + \sigma_1(B,AB)]\} \cdots . \tag{5}$$

If we neglect terms in α^2 and higher powers

$$\sigma(T,C) \simeq \sigma_0(T) + \sigma_1 C + \alpha\delta(T) + \tfrac{1}{2}\alpha C\Delta\sigma_1 , \tag{6}$$

where $\sigma_0(T) = \sigma_m(T)$, since σ_0 is the shielding in the limit of the isolated molecule, $\sigma_1 = \sigma_1(m,m)$ due to nonspecific interactions between monomers, and

$$\Delta\sigma_1 = [\sigma_1(m,AB) + \sigma_1(A,m) + \sigma_1(B,m) - 4\sigma_1(m,m)] .$$

From Eq. (6), the limiting slope as vapor density goes to zero is

$$\lim_{C\to 0}(\partial\sigma/\partial C)_T \simeq \sigma_1 + 2K(T)\delta(T) .$$

This includes the usual medium effect due to nonspecific interactions between HCN molecules in the form of σ_1, as well as a measure of the association shift δ. Thus, for a dimer-forming system, the "apparent σ_1" may be considerably larger than or even opposite in sign to that for a system involving only van der Waals interactions.

The temperature dependence of the nuclear shielding in the vapor in equilibrium with the liquid is

$$\frac{d\sigma}{dT} = \frac{d\sigma_0}{dT} + \alpha\frac{d\delta}{dT} + \frac{\alpha C d\Delta\sigma_1}{dT} + \frac{C d\sigma_1}{dT} + \frac{dC}{dT}\left[\sigma_1 + (\delta + \tfrac{1}{2}\Delta\sigma_1 C)\frac{\partial\alpha}{\partial C} + \tfrac{1}{2}\Delta\sigma_1\alpha\right] + \frac{dK}{dT}[\delta + \tfrac{1}{2}\Delta\sigma_1 C]\frac{\partial\alpha}{\partial K} . \tag{7}$$

If we assume that δ, $\Delta\sigma_1$, and σ_1 are approximately temperature independent over the range of temperatures in which the equilibrium vapor was observed

$$\frac{d\sigma(C,T)}{dT} \simeq \frac{d\sigma_0(T)}{dT} + [\delta + \tfrac{1}{2}C\Delta\sigma_1]\frac{d\alpha}{dT} + [\sigma_1 + \tfrac{1}{2}\alpha\Delta\sigma_1]\frac{dC}{dT} . \tag{8}$$

Further, neglecting $\tfrac{1}{2}\alpha\Delta\sigma_1$ relative to σ_1 and $\tfrac{1}{2}C\Delta\sigma_1$ relative to δ

$$\frac{d\sigma(C,T)}{dT} \simeq \frac{d\sigma_0}{dT} + \frac{\delta d\alpha}{dT} + \frac{\sigma_1 dC}{dT} . \tag{9}$$

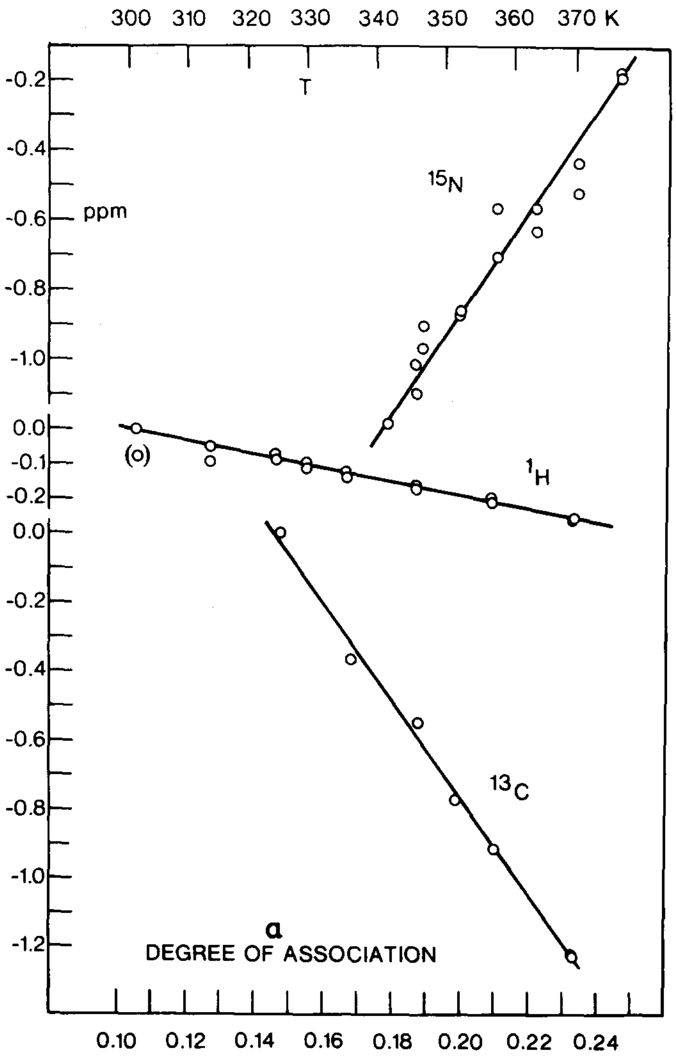


FIG. 5. Variation of ^{1}H, ^{13}C, and ^{15}N nuclear shielding in HCN vapor (in equilibrium with the liquid) with the degree of association. In the absence of nonspecific medium effects and temperature dependence due to rovibrational averaging of the shielding, the slope is the association shift for each nucleus.

We see that the temperature dependence observed in the equilibrium vapor is only partly due to $\delta d\alpha/dT$. Thus, the values of δ obtained from Fig. 5 are only approximate.

Thus, we have in Eq. (9) a description of the observed temperature dependence for the vapor in Figs. 1–3. The unknown functions of temperature are $d\sigma_0/dT$, δ, and σ_1. If we further assume that the temperature dependence of the isolated molecule is a linear one and that the temperature dependence of δ and σ_1 is slight, then for each nucleus in HCN we have three unknown numbers to be determined from the experimental curves: (1) the temperature coefficient of nuclear resonance in the isolated molecule due to rovibrational averaging $d\sigma_0/dT$; (2) the association shift $\delta = (\sigma_A + \sigma_B)/2 - \sigma_m$; (3) the virial coefficient σ_1 for effects of nonspecific intermolecular interactions on chemical shielding. Since $\sigma(C, T)$ is nearly linear over the temperature range for which our vapor data have been measured, and since $d\alpha/dT$ is nearly constant for this same range of temperatures, it is not possible to determine all three parameters. Of course, the neglect of both $d\sigma_0/dT$ and σ_1 reduces the analysis to that of Eqs. (1)–(3), which yields δ, as in Eq. (3). If we neglect the last term in Eq. (9), we can obtain a better estimate of δ than that of Eq. (3). For the equilibrium vapor, Eq. (9) will reduce to

$$(d\sigma/dT)_{\text{eq. vap.}} = d\sigma_0/dT + \delta(d\alpha/dT)_{\text{eq.vap.}} , \tag{10}$$

whereas for the gas at a constant density at temperatures above saturation

$$(d\sigma/dT)_C = d\sigma_0/dT + \delta(d\alpha/dT)_C . \tag{11}$$

Since both $(d\alpha/dT)_{\text{eq.vap.}}$ and $(d\alpha/dT)_C$ are known, a better estimate of the association shift δ would be

$$\delta = [(d\sigma/dT)_{\text{eq.vap.}} - (d\sigma/dT)_C]/ [(d\alpha/dT)_{\text{eq. vap.}} - (d\alpha/dT)_C] , \tag{12}$$

and at the same time, an estimate of $d\sigma_0/dT$ can be obtained

$$d\sigma_0/dT = \tfrac{1}{2}\{(d\sigma/dT)_{\text{eq.vap.}} + (d\sigma/dT)_C - \delta[(d\alpha/dT)_{\text{eq.vap.}} + (d\alpha/dT)_C]\} . \tag{13}$$

The results of this analysis for all three nuclei in HCN are shown in Table III. The gas-to-liquid shifts at the boiling points have previously been used as measures of the association shift δ.[11] Since we have values for gas-to-liquid shifts as well as association shifts for all three nuclei in HCN, we compare them in Table III. We see that the gas-to-liquid shifts are of the same order of magnitude as, but not equal to, the association shifts estimated using Eq. (3).

The analysis of the liquid data is much more involved. In liquid HCN, it is known that n mers of various lengths are present[30] so that the average shielding in the liquid may be written as[12]

$$\sigma_{\text{av}}(T) = \frac{\sigma_m M_1 + 2K_2(T)M_1^2\sigma_{AB} + 3K_3(T)M_1^3\sigma_{ABC} + \cdots}{M_1 + 2K_2(T)M_1^2 + 3K_3(T)M_1^3 + \cdots} , \tag{14}$$

where M_1 is the concentration of the monomer, $\sigma_{AB} = (\sigma_A + \sigma_B)/2$ is the average chemical shielding in the dimer, $\sigma_{ABC} = (\sigma_A + \sigma_B + \sigma_C)/3$ is the average chemical shielding in the trimer, ... and K_2, K_3 ... are the equilibrium constants for n mer formation. Although there exist estimates of the equilibrium constants for the formation of the higher n mers, K_3, etc.,[30] we do not have any independent information about the parameters σ_{ABC}, etc., the nuclear shielding in the higher n mer species. Note that Eq. (14) holds only if the monomer is the dominant species. That the coupling constants $^1J_{\text{CH}}$ and $^2J_{\text{NH}}$ are observed in both the vapor and liquid phase is consistent with the formation of linear n mers, maintaining the integrity of the monomeric unit in the forming and breaking of long chains (unlike HF).

From the known temperature dependence of the vapor and liquid density of hydrogen cyanide,[29] we have plotted the variation of the nuclear shielding with the total concentration of HCN. These are shown in Fig. 6. The temperature dependence of the resonance frequencies due to rovibrational motion have not been removed. These curves will be described by Eq. (14) only if the monomer continues to be the dominant species even in the liquid phase. It appears that a single equilibrium in which the associated species are dominated by a particular n mer, does not apply here.[30] If this were the case, an analysis similar to that used for Fig. 5 would be applicable.

In the analysis of the liquid data, evaluation of the parameters requires a preliminary hypothesis on the nature of self-association in the liquid, that is, which of the dimeric, trimeric, etc., polymeric structures predominate. Even in the vapor phase there is evidence for long chains in hydrogen cyanide.[30] Since we have data on all three nuclei, although the nuclear parameters differ, we should obtain the same information about the nature of liquid HCN from each of ^{1}H, ^{13}C, and ^{15}N shielding behavior in the liquid. In an attempt to interpret our shielding data in the liquid, we take the approach that charge redistribution is related to chemical shifts. It has been generally found that in linear polymers (such as in the linear hexamer of HF[31]), there is little excess charge on the middle molecules; the charge transfer occurs from one end molecule to the molecule on the other end. For example, in linear $(\text{HF})_6$, the total charges in the HF moieties in $\text{F–H} \cdots (\text{F–H})_4 \cdots \text{F–H}$ are 10.039, 10.005, 10.001, 9.999, 9.996, and 9.962.[31] While there are some differences in the charge distribution in the middle monomeric units compared to the free monomer, these differences are small compared to the charge redistribution in the end units. From the results in other linear polymers, we can expect that in $\text{HCN} \cdots (\text{HCN})_n \cdots \text{HCN}$ the middle HCN units will also have very nearly equal total charges. Using this as a basis, we will assume that from the point of view of nuclear shielding, there will be four general types of nuclear sites in liquid HCN: two end sites (A and B), a free monomer site, and a site for middle monomeric units in linear polymers of various lengths. The next question we have to answer is, to what extent do the shielding at the A and B sites depend on the length of the chain? Again, we have no real basis for an answer, ex-

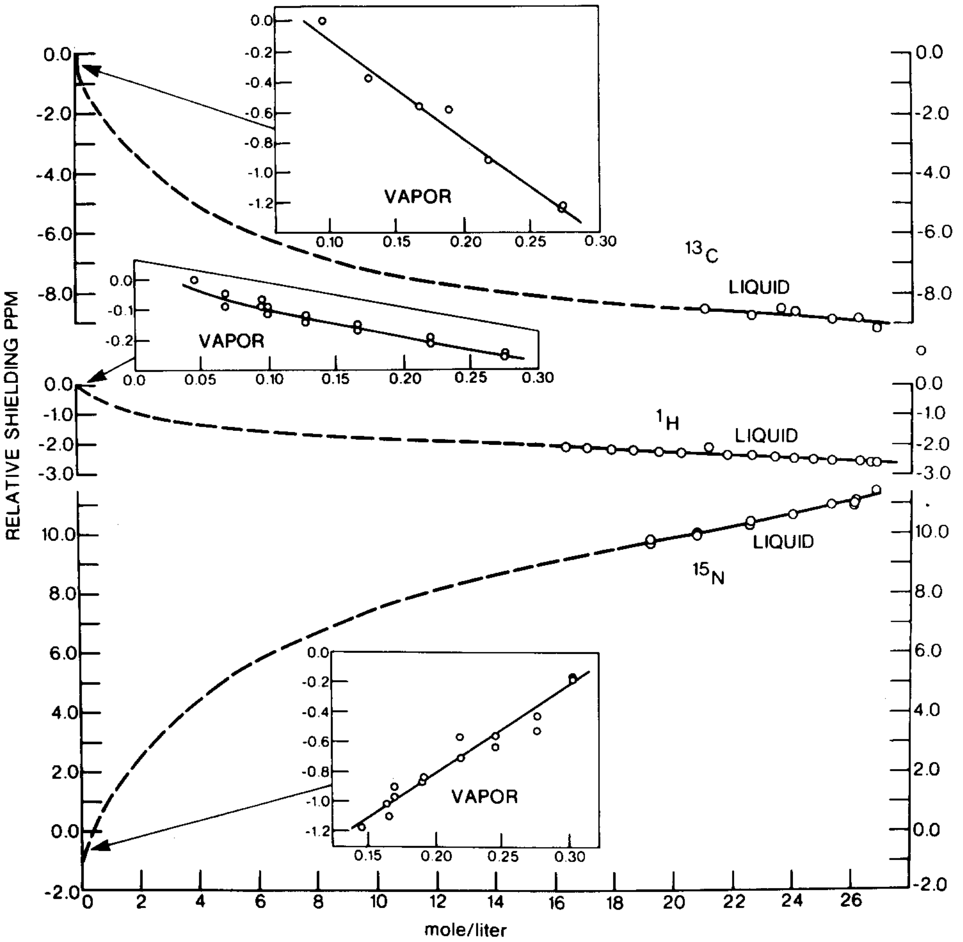


FIG. 6. Variation of ^{1}H, ^{13}C, and ^{15}N nuclear shielding in HCN with concentration.

cept to compare charge redistributions for various chain lengths. In HF, the linear hexamer charge redistribution is more pronounced than in the dimer.[31] For linear chains of various lengths the average charge shifts for H (or for F) has been found to increase with chain length, and to approach the value for a middle unit. The shielding difference between the two end sites (A and B) can be expected to become progressively larger as the length of the chain increases. However, the average shielding will not change very much in going from n mer to $n+1$ mer since most of the HCN units will be middle units. The average shielding in the liquid can be expected to approach the value characteristic of the middle site as the latter become predominant.

In summary, our model for liquid HCN is as follows. The composition of the liquid is straight chain n mers of varying lengths which undergo chain forming and breaking such as to maintain the integrity of the monomeric unit. The change in nuclear shielding with liquid density will be monotonic, and the shielding will approach an asymptotic value (the average nuclear shielding in a middle HCN unit in an n mer). We see that the curves in Fig. 6, in which the average nuclear shielding is plotted as a function of the total concentration of HCN, are consistent with this description.

DISCUSSION

In Fig. 7, we compare the behavior of ^{1}H and ^{15}N in NH_3 and in HCN as archetypes of hydrogen bonding systems with nitrogen sites of class I and II. We note that the ^{1}H behavior with density (and temperature) is very similar for the two compounds. Furthermore, both are very similar, qualitatively, to ^{1}H behavior in systems not involving hydrogen bonding, e.g., ^{1}H in ethane.[32] On the other hand, intermolecular interactions may lead to decreased ^{15}N shielding, as in NH_3 and other class I nitrogens or to increased shielding, as in HCN and other class II nitrogens.

As discussed earlier, the qualitative behavior of N shielding in class I sites appears to be "normal," e.g., no different from ^{129}Xe interacting with any molecule. On the other hand, the behavior of N shielding in class II sites appears to be the opposite of the usual norm and thus needs some explanation. We desire a self-consistent explanation for the unusual behavior of only the ^{15}N in class II sites which at the same time (a) predicts "normal" behavior (that is, a decrease in shielding due to intermolecular interactions) for the other nuclei in the same molecule, (b) does not require specific interactions such as hydrogen-bonding, (c) but does become more pronounced with hydrogen bonding or similar interactions, (d) does not apply to ^{15}N in class I sites, with or without hydrogen-bonding, and (e) does not apply in general to ^{1}H, ^{19}F, or other nuclei in almost any molecule interacting with other molecules. We think there may be a clue in the blue shifts observed in $n \rightarrow \pi^*$ electronic spectra of molecules with class II nitrogen sites.

If we use a very simple model for the paramagnetic

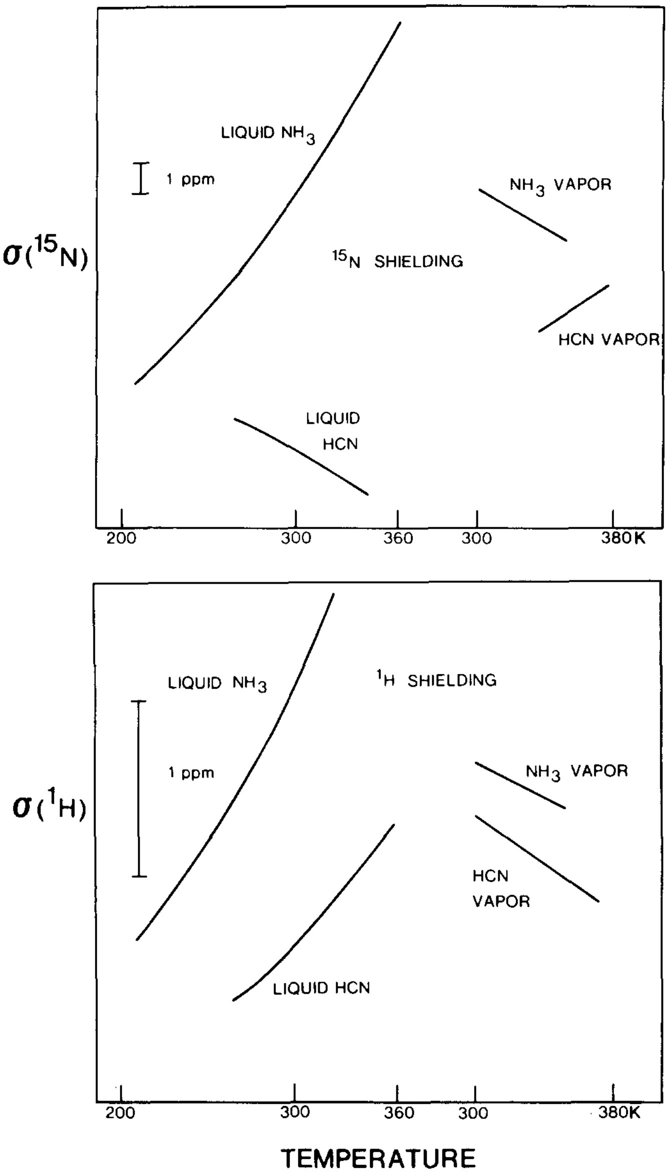


FIG. 7. Comparison of the temperature dependence of ^{1}H and ^{15}N NMR frequencies in hydrogen bonded systems of two types. Note that this figure is drawn solely for comparison of the temperature dependence of shielding in each phase. The relative chemical shifts between these phases are not shown. The ^{15}N shifts at 300 K have been reported previously on an absolute ^{15}N shielding scale: 263.5 ppm for ^{15}N in NH_3 (vapor), 244.6 ppm in NH_3 (liquid), −8.3 ppm in HCN (liquid), and −20.4 ppm in HCN (vapor). The ^{1}H nuclear shielding at 300 K for these phases [based on the ^{1}H absolute shielding for NH_3 reported by S. G. Kukolich, J. Am. Chem. Soc. **97**, 5704 (1975)] are: 30.7 ppm for ^{1}H in NH_3 (vapor), 29.0 ppm in NH_3 (liquid), 28.0 ppm in HCN (vapor), and 25.6 ppm in HCN (liquid).

term in nuclear shielding, involving the average energy approximation[33]

$$\sigma = \sigma^d + \sigma^p \ ,$$

we may write for the paramagnetic term

$$\sigma^p \simeq -(2e^2\hbar^2/3m^2c^2\Delta E)(\langle 1/r^3\rangle_p P_u + \langle 1/r^3\rangle_p D_u) \ .$$

Here, P_u and D_u can be expressed in terms of orbital populations, and $\langle 1/r^3\rangle$ is some average atomic value for nitrogen. If all other terms remain the same, an increase in ΔE would mean a smaller σ^p term and thus an increase in nuclear shielding. It is generally found that N containing π systems such as azines undergo a large blue shift in their $n \rightarrow \pi^*$ electronic spectra in going from the free molecule (gas phase) to the solution in any proton donor solvent.[34] This is understood in terms of the ground state energy being considerably lowered by specific interactions (of the hydrogen-bonding sort) with the lone pair electrons, whereas the excited state which no longer has a lone pair is hardly affected. These blue shifts can be of the order of 3000 cm^{-1}. On the other hand, electronic spectra of most molecules usually undergo small blue or red shifts in going from the gas phase to the liquid or solution.[35] Since a change in the local electronic distribution at the nitrogen is involved in going from the ground state to the excited state in an $n \rightarrow \pi^*$ transition, these excited states are probably of major importance in the sum over states which appears in the second order perturbation term σ^p for nuclear shielding. Intermolecular interactions involving the lone pair electrons of a nitrogen affect the electronic energy levels of the molecule in such a way as to cause the observed blue shift in the $n \rightarrow \pi^*$ transitions. Since the shielding of the nitrogen nucleus is influenced to a large extent by the local electronic distribution around it, any effects involving the participation of the lone pair may be expected to be important for nitrogen, and may be less important for the other nuclei in the molecule. The above explanation satisfies conditions (a) through (e).

The observation of a linear hydrogen-bonded HCN dimer by infrared spectroscopy[36] confirms that hydrogen bonding may be the reason for the large apparent σ_1 values for ^{13}C and ^{15}N. At 300 K, HCN vapor consists of approximately 10% dimer and 3% trimer.[30] The HCN dimer $H{-}C{\equiv}N \cdots H{-}C{\equiv}N$ has been studied by infrared spectroscopy of the isolated dimeric species in an argon matrix at a low temperature.[36] The vibrational frequencies of the monomer are 3305 (CH stretch), ~2110 (CN stretch), and 721 cm^{-1} (angle deformation).[37] The CN bond not involved in the hydrogen bonding is assigned to 2112, while the hydrogen bonded CN stretch is at 2093 cm^{-1}. The CH bond stretch is virtually identical in the monomer and the non-hydrogen-bonding CH of the dimer; but the hydrogen-bonded CH stretching frequency is at 3213 cm^{-1}, shifted by about 100 cm^{-1}.[36] Solvents are known to further shift the CH stretch in HCN about 33 to 115 cm^{-1} relative to the vapor, and the bending frequency 13 to 44 cm^{-1} relative to the vapor.[38] To explain the vibrational frequency shifts, interactions of the type $R{-}X \cdots H{-}C{\equiv}N$ as well as $H{-}C{\equiv}N \cdots H{-}R$ have been proposed.

There are two sites for each nucleus in the dimer $(HCN)_2$. For example, the nitrogen nuclear sites may be denoted A and B

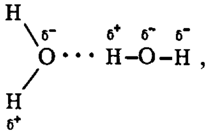
$$H{-}C{\equiv}N_A \cdots H{-}C{\equiv}N_B \ .$$

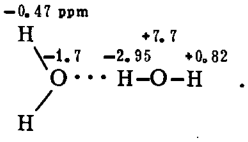
If we neglect the trimer, in the gas phase we observe the nitrogen shielding averaged over the two sites and the monomer. For HCN, it appears that one or both of the nitrogen shielding changes $(\sigma_A - \sigma_m)$ and $(\sigma_B - \sigma_m)$ are positive, with the average nitrogen shielding in the dimer being greater than that in the monomer. On the other hand, the average ^1H and ^{13}C shielding in the dimer is less than that in the monomer. The individual nuclear sites (monomer, site A in dimer, site B in dimer) are not observed, the exchange is sufficiently rapid for that. However, the HCN moiety must remain intact in these exchanges because the $^1H-^{13}C$ and the $^1H-^{15}N$ couplings are clearly observed. HCN is unlike HF, in which there are rapid monomer-breaking exchange processes in the vapor and liquid phase.[39] The coupling constants we report here are likewise averages between the couplings in the monomer, in the $H-C\equiv N_A$, and in the $H-C\equiv N_B$ parts of the dimer.

Population analysis of complexes and the isolated monomers are usually performed in theoretical studies of energies and geometries of hydrogen-bonded systems. The following generalizations have emerged.[40] Upon hydrogen bond formation, (1) the hydrogen in the H bond loses electrons. (2) The electronegative atoms gain electrons; more electrons are gained by the electronegative atom on the proton donor molecule. (3) All hydrogens attached to the electronegative atom of the proton donor molecule (away from the hydrogen bond) gain electrons. (4) The hydrogen (or carbon) attached to the electronegative atom of the proton acceptor molecule loses electrons. (5) The charge changes on the atoms immediately attached to the three-center H bond are of the same magnitude as those in the bond. Applying these to $(HCN)_2$, the charge redistribution would be

$$\begin{array}{l} H-C\equiv N_A \cdots H-C\equiv N_B \\ \delta^+ \ \delta^+ \ \delta^- \quad\ \ \delta^+ \ \delta^- \ \delta^- \ . \end{array}$$

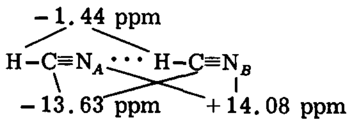
Indeed, the population analysis by Johansson *et al.*[41] gives the values +0.0095, +0.0208, −0.0146, +0.0271, −0.0202, and −0.0226, respectively, for the atoms in the above structure from left to right. A simple-minded translation of these charge shifts to shielding changes would lead to deshielding for both H nuclei, increased shielding for both N nuclei, deshielding for one carbon nucleus, and increased shielding for the other carbon, with an average deshielding effect for the two. Loss of electronic charge does not always lead to deshielding, however. For comparison, we look at the charge shifts for $(H_2O)_2$[42] and the shielding changes calculated by Ditchfield[43]





For HCN, we have, in the δ values shown in Table II, the average shielding changes in going from HCN to the hydrogen bonded dimer $(HCN)_2$ if we neglect nonspecific medium effects (σ_1)

$$\begin{array}{l} H-C\equiv N_A \cdots H-C\equiv N_B \\ \delta^+ \ \delta^+ \ \delta^- \quad\ \ \delta^+ \ \delta^- \ \delta^- \ , \end{array}$$



Since only the average shielding is observed, we have no empirical way of obtaining shielding changes for each of the two types of ^{15}N (or ^{13}C or ^1H).

HCN is the simplest polyatomic molecule capable of forming hydrogen bonds. Moreover, the geometry of the hydrogen-bonded dimer is known.[36] A theoretical calculation of ^1H, ^{13}C, and ^{15}N shielding in $H-C\equiv N \cdots H-C\equiv N$ compared with the isolated HCN would be helpful in understanding the disparate effects of hydrogen bonding on the nuclear shielding of the three nuclei.

ACKNOWLEDGMENTS

This research was supported in part by National Science Foundation grants to the University of Illinois at Chicago Circle (CHE77-09133) and Loyola University (CHE77-09197).

[1] F. H. A. Rummens, in *NMR Basic Principles and Progress*, edited by P. Diehl, E. Fluck, and R. Kosfeld (Springer, New York, 1975), Vol. 10, pp. 1–118.
[2] C. J. Jameson, Bull. Magn. Reson. **3**, 3 (1980).
[3] W. T. Raynes, A. D. Buckingham, and H. J. Bernstein, J. Chem. Phys. **36**, 3481 (1961).
[4] J. Homer, Appl. Spectrosc. Rev. **9**, 1 (1975).
[5] W. C. Dickinson, Phys. Rev. **81**, 717 (1951).
[6] A. D. Buckingham, T. Schaefer, and W. G. Schneider, J. Chem. Phys. **32**, 1227 (1960).
[7] F. J. Adrian, Phys. Rev. A **136**, 980 (1964).
[8] J. P. Riley, I. H. Hillier, and W. T. Raynes, Mol. Phys. **38**, 353 (1979).
[9] A. J. Sadlej, M. Zaucer, and A. Azman, Mol. Phys. **35**, 1397 (1978).
[10] K. Jackowski, W. T. Raynes, and A. J. Sadlej, Chem. Phys. Lett. **54**, 128 (1978).
[11] M. Alei, W. M. Litchman, and J. F. O'Brien, J. Phys. Chem. **75**, 932 (1971).
[12] P. Laszlo, in *Progress in NMR Spectroscopy* edited by J. W. Emsley, J. Feeny, and L. H. Sutcliffe (Pergamon, Oxford, 1967), Vol. 3, Chap. 6.
[13] M. Witanowski, L. Stefaniak, and H. Januszewski, in *Nitrogen NMR*, edited by M. Witanowski and G. A. Webb (Plenum, London, 1973), p. 163.
[14] G. C. Levy and R. L. Lichter, *Nitrogen–*15 *Nuclear Magnetic Resonance Spectroscopy* (Wiley, New York, 1979).
[15] M. Alei, A. E. Florin, and W. M. Litchman, J. Am. Chem. Soc. **92**, 4828 (1970).
[16] M. Witanowski and H. Januszewski, Can. J. Chem. **47**, 1321 (1969).
[17] A. Loewenstein and Y. Margalit, J. Phys. Chem. **69**, 4152 (1965).
[18] H. Saito, Y. Tanaka, and S. Nagata, J. Am. Chem. Soc. **95**, 324 (1973).
[19] R. O. Duthaler and J. D. Roberts, J. Am. Chem. Soc. **100**, 4969 (1978).
[20] G. A. Olah and T. E. Kiovsky, J. Am. Chem. Soc. **90**, 4666 (1968).
[21] R. O. Duthaler and J. D. Roberts, J. Magn. Reson. **34**, 129 (1979).
[22] C. J. Jameson, A. K. Jameson, S. M. Cohen, H. Parker, D. Oppusunggu, P. M. Burrell, and S. Wille, J. Chem. Phys. **74**, 1608 (1981).
[23] T. Volker, Angew. Chem. **72**, 379 (1960).
[24] K. Ziegler, in *Organic Syntheses*, edited by H. Gilman and A. H. Blatt (Wiley, New York, 1941), Vol. 1, pp. 314–316.
[25] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. **59**, 4540 (1973).
[26] G. Binsch and J. D. Roberts, J. Phys. Chem. **72**, 4310 (1968).
[27] K. J. Friesen and R. E. Wasylishen, J. Magn. Reson. **41**,

189 (1980).
[28]A. K. Jameson, J. W. Moyer, and C. J. Jameson, J. Chem. Phys. **68**, 2873 (1978).
[29]*Landolt-Bornstein, Zahlenwerte und Funktionen* (Springer, Berlin, 1967) Vol. IV. p. 302.
[30]W. F. Giauque and R. A. Ruehrwein, J. Am. Chem. Soc. **61**, 2626 (1939).
[31]D. Hankins, J. Moskowitz and F. Stillinger, Chem. Phys. Lett. **4**, 581 (1970).
[32]F. H. A. Rummens, Mol. Phys. **21**, 535 (1971).
[33]C. J. Jameson and H. S. Gutowsky, J. Chem. Phys. **40**, 1714 (1964).
[34]F. Halverson and R. C. Hirt, J. Chem. Phys. **19**, 711 (1951).
[35]R. S. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence* (Wiley, New York, 1969) pp. 34–41.
[36]J. Pacansky, J. Phys. Chem. **81**, 2240 (1977).
[37]J. Pacansky and G. V. Calder, J. Mol. Struct. **14**, 363 (1972).
[38]G. L. Caldow and H. W. Thompson, Proc. R. Soc. London Ser. A **254**, 1 (1960).
[39]D. K. Hindermann and C. D. Cornwell, J. Chem. Phys. **48**, 2017 (1968).
[40]P. A. Kollman and L. C. Allen, Chem. Rev. **72**, 283 (1972).
[41]A. Johansson, P. Kollman, and S. Rothenberg, Theor. Chim. Acta **26**, 97 (1972).
[42]D. Hankins, J. Moskowitz, and F. Stillinger, J. Chem. Phys. **53**, 4544 (1970).
[43]R. Ditchfield, J. Chem. Phys. **65**, 3123 (1976).
[44]W. M. Litchman, M. Alei, and A. E. Florin, J. Chem. Phys. **50**, 1031 (1969).
[45]W. M. Litchman, M. Alei, and A. E. Florin, J. Am. Chem. Soc. **91**, 6574 (1969).
[46]C. J. Jameson, A. K. Jameson, D. Oppusunggu, S. Wille, P. M. Burrell, and J. Mason, J. Chem. Phys. **74**, 81 (1981).