Effects of Solvent, Protonation, and N-Alkylation on the ^{15}N Chemical Shifts of Pyridine and Related Compounds[1]

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Abstract: The ^{15}N chemical shift of pyridine has been measured in the gas phase and in a variety of solvents. The solvent-induced resonances are all upfield of the gas phase and correlate qualitatively with hydrogen-bonding capacity. The finding of a reasonable linear correlation with the Kosower Z values indicates that the solvent shifts are dominated by the contribution of the n→π* transition to the secondary paramagnetic shift term. No correlation was found with either the solvent dielectric constant, ϵ, or the function $(\epsilon - 1)/(2\epsilon + 2.5)$. Large solvent effects were found for the ^{15}N resonances of pyridine hydrochlorides, and these require that interpretation of protonation shifts be made with care. In contrast to protonation shifts, methylation shifts are essentially solvent and counterion independent. The changes in ^{15}N chemical shifts of 4-substituted pyridines, on changing the solvent from benzene to methanol, correlate with the basicity of the solute, which also indicates the importance of hydrogen bonding in determining the solvent dependences of pyridine-nitrogen shifts.

The characteristics of the nuclear magnetic resonance spectra of azine-type nitrogens have been studied by a number of techniques in different laboratories.[2] The chemical shifts of substituted pyridines have been correlated with π-charge densities,[2b] and SCF-MO calculations for pyridine[2d] suggest a large paramagnetic deshielding effect arising from mixing in of a low-lying electronic state corresponding to an n→π* transition of the nitrogen unshared pair.[3] As a consequence, bond formation involving the unshared pair of an azine nitrogen by protonation or alkylation is expected (and found) to have a large shielding effect, ~100 ppm, on the nitrogen resonance position.[2a,d] The approximately 10-ppm shielding effect produced by adding 0.5 equiv of methanol to neat pyridine has been attributed to hydrogen bonding with methanol, which can be dissected into covalent, ionic, and charge-transfer contributions.[2c] In a more recent study,[2e] the ^{15}N chemical shifts of ^{15}N-enriched pyridine have been reported for the liquid and solid phases, and the mechanism of the longitudinal relaxation has been scrutinized. From the 20.6-ppm shift difference between the average shifts of solid and liquid pyridine, it was concluded that liquid pyridine is not very anisotropic. Chemical-shift anisotropy and intermolecular dipole–dipole interactions are the dominant relaxation mechanisms at low temperature with spin rotation becoming more important at elevated temperatures.[2e]

In the present research, solvent, protonation, and alkylation effects on the nitrogen resonance of pyridine and related compounds were determined by ^{15}N nuclear magnetic resonance, which yields quantitatively more reliable results than ^{14}N NMR. It was found possible to measure the ^{15}N chemical shift of gaseous pyridine samples with the aid of a Bruker WH-180 spectrometer using a 25-mm sample tube. The purpose of the work was to find out whether the solvent shifts on the pyridine-nitrogen resonances correlate with solvent effects on the n→π* transition energies, as they should, if second-order paramagnetic effects are important. Other possible contributions to the solvent effects could arise from polarization of the pyridine π-electron system by polar solvents[4] or by the positive charge on nitrogen resulting from hydrogen bonding or bond formation to the unshared pair.[3c]

Experimental Section

The ^{15}N NMR spectra were taken with a Bruker WH-180 spectrometer operating at 18.25 MHz. Nitric acid at 1 M concentration, enriched to 96% ^{15}N, in D_2O contained in a 5-mm NMR tube held in the center of the 25-mm diameter sample tube by a Teflon plug served as an external standard for the shift measurements and also provided an internal deuterium lock signal. The chemical shift of this reference is 6.2 ppm upfield of external neat nitromethane, 298.7 ppm downfield from urea (2 M in H_2O), 332.8 ppm downfield from tetramethylammonium chloride (2 M in H_2O), and 355.0 ppm downfield from the ammonium resonance of ammonium nitrate (2 M in H_2O). For bulk susceptibility corrections, the relation $\delta^{cor} = \delta^{exp} - 4\pi/3(K^{ref} - K^{sample}) \times 10^{-6}$ was used, which applies for the case of the magnetic field parallel to the axis of a cylindrical sample and chemical shifts with the same sign as the screening constant.[5] The bulk susceptibilities of the reference (1 M HNO_3), $-0.715 \pm 0.005 \times 10^{-6}$, Me_2SO, $-0.618 \pm 0.005 \times 10^{-6}$, and trifluoroethanol, $-0.626 \pm 0.005 \times 10^{-6}$, have been determined by ^1H NMR, using coaxial sample cells with acetone as standard in the outer annular cell.[6] The susceptibilities of the sample mixtures were calculated from the susceptibilities and the volume fractions of the pure compounds, using the relation[5] $K_{a,b} = \nu_a K_a + \nu_b K_b$.

For reasonable signal-to-noise ratios for the pyridine bases, which generally have rather long relaxation times, 100–400 pulses (70°/55 μs) were accumulated using a repetition rate of 100 s. The proton noise decoupler was switched on only during the acquisition time, 0.8–2.0 s, to avoid the small unfavorable NOE. Continuous proton noise decoupling and faster pulsing were used for the measurements of the hydrochlorides. For these substances, cooling with a stream of 0 °C nitrogen was necessary to keep the samples at ambient temperature. For the gas-phase shift measurement of pyridine, the sample tube shown in Figure 1 was used. This tube was made with a relatively large gas volume outside the transmitter coil to help shorten the overall relaxation time of the gaseous sample by diffusion and to improve the sensitivity. The upper part of the tube was filled with water which, when the tube was heated, facilitates transfer to the otherwise cool upper part of the gas volume. For the measurements, 27 mg of pyridine-^{15}N (96.9 atom %, Prochem) was placed in the tube, which was then cooled to liquid-nitrogen temperature and sealed at a pressure of 0.08 Torr. Assuming ideal gas behavior, a partial pressure of 163 Torr of a substance enriched to 96.9% in ^{15}N corresponds to a 2 M solution of a material with ^{15}N at the natural-abundance level. The temperature corresponding to such a vapor pressure of pyridine is about 70 °C.[7] Because of the construction of the probe and sample tube, it was very difficult to maintain uniform temperatures, and when the gas passing through the probe was at 80 °C, the water contained in the sample tube only reached about 50 °C. Because this was the coolest part of the tube, the pyridine refluxed in this region. The gas-phase molarity of pyridine vapor corresponding to 50 °C is about 3.6×10^{-3}, which, in ^{15}N context, is comparable to a 1 M solution at the natural-abundance level. The 5-mm reference tube in the center of the sample tube contained a solution of 25 mg of pyridine-^{15}N in 836 mg of $(CD_3)_2SO$. This reference was found to be 1.4 ppm downfield of an external solution of pyridine in benzene which was 55.8 ppm upfield from external 1 M HNO_3 (all at 80 °C). The pyridine-$(CD_3)_2SO$ reference was itself found to be 57.2 ppm upfield of external

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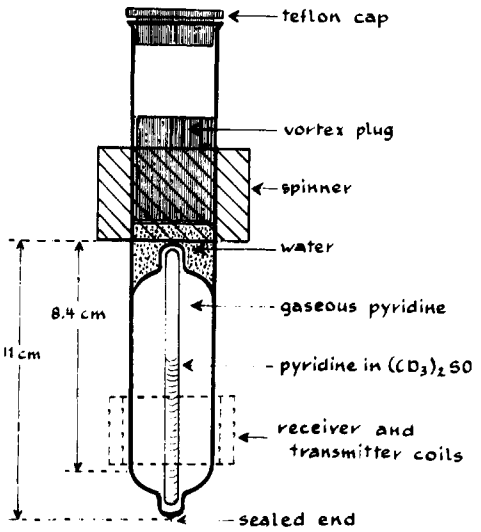

Figure 1. Sample tube for gas-phase measurements.

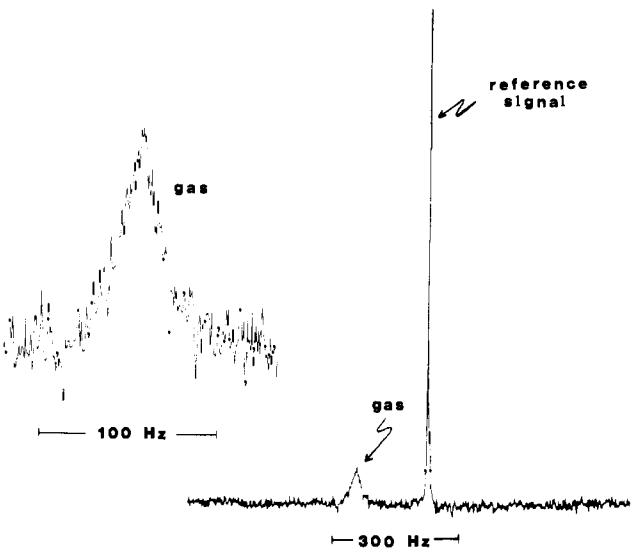

Figure 2. The ^{15}N NMR signals observed for pyridine in the gas phase and pyridine dissolved in deuteriodimethyl sulfoxide.

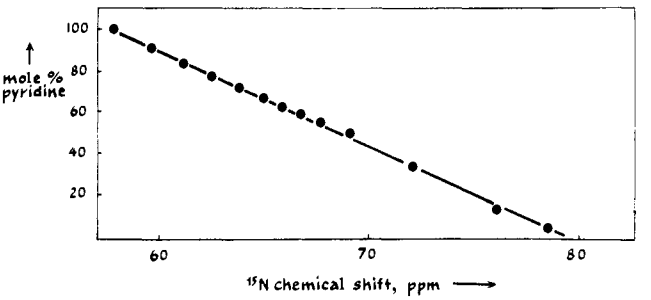

Figure 3. Concentration dependence of the ^{15}N chemical shift of pyridine in water solutions with reference to external ^{15}N nitric acid.

1 M HNO_3 (our usual standard) at 80 °C, and this becomes 57.7 ppm from nitric acid at ambient temperature when corrected by the previously determined temperature dependence of the nitric acid reference.[8] The shift of pyridine vapor from the pyridine-$(CD_3)_2SO$ reference, 9.3 ppm downfield, is thus 48.4 ppm upfield from external 1 M nitric acid at ambient temperature. For the bulk-susceptibility corrections, the susceptibility of the pyridine vapor was neglected.

^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer, proton spectra on a Varian A-60A instrument.

4-Methoxypyridine was prepared by reduction of commercially available 4-methoxypyridine *N*-oxide with phosphorus trichloride in chloroform.[9]

$\Delta^{1,9}$-Octahydroquinoline was obtained following the procedure reported by Parcell and Hanck.[10]

The hydrochlorides were prepared by passing gaseous hydrogen chloride into solutions of the corresponding bases in either anhydrous ether or cyclohexane. The precipitated salts were collected by filtration, washed with ether, and dried under reduced pressure (high vacuum). The extremely hygroscopic pyridine hydrochloride was sublimed at about 100 °C and 0.05 Torr prior to making up the solutions.

The *N*-methylpyridium iodides were obtained by treating the pyridine bases with excess methyl iodide in methanol at ambient temperature and in the dark. The salts were purified by recrystallization from either chloroform–acetone, acetone–methanol, or ether–methanol. The orange color of *N*-methyl-4-acetylpyridinium iodide most probably arises from charge-transfer complex formation.[11]

The *N*-methylpyridinium chlorides were obtained from the iodides either by adding 1 equiv of lead chloride dissolved in hot water to an aqueous solution of the iodide, or by heating a mixture of 2 equiv of lead chloride and an aqueous solution of the iodide overnight. The precipitated salts were removed by filtration and the excess lead chloride was separated by evaporation of the water and dissolution of the pyridinium salts in methanol. The very sensitive *N*-methyl-4-acetylpyridinium chloride partially decomposed during this procedure.

All of the other compounds were commercially available products. Pyridine, 4-methoxypyridine, and *N*-methylimidazole were distilled from calcium hydride, and 4-acetylpyridine from molecular sieves prior to making up the solutions for the spectra measurements.

Results and Discussion

Table I summarizes the ^{15}N shifts of pyridine and related compounds in different media as well as the shifts of their corresponding conjugate acids. The shifts of the three pyridines, and their hydrochlorides as well, show the π-electron charge-density dependence reported previously for ^{14}N chemical shifts.[2b] The 4-methoxy substituent has a shielding effect (+22.8 ppm) while the 4-acetyl group has a deshielding effect (−11.7 ppm). Two ^{15}N signals were observed for solutions of 4-acetylpyridine hydrochloride in methanol. The one at lower field corresponds to the expected shift value. The ^{13}C NMR spectrum of the solution suggests that the other ^{15}N peak at higher field, close to the resonance of pyridine hydrochloride itself, arises from hemiketal and/or ketal formation with the solvent catalyzed by the rather acidic ammonium salt.

The spectrum of pyridine in the gas phase shown in Figure 2 is the result of accumulation of 23 500 pulses (70°/55 μs) at a repetition rate of 5 s. The rather short repetition rate for compounds of this type was possible because of the importance of spin rotation as a gas-phase relaxation mechanism of the pyridine nitrogens.[2e] The width of the broad signal is 25 Hz at half height and about 75 Hz at the base. The reported shift corresponds to the maximum of the somewhat unsymmetrical peak (Figure 2). The broadness and lack of symmetry of the signal may be due to poor H_0 field homogeneity, or possibly to local fields induced by the rapid motions of the gaseous molecules. The corrected shift of pyridine vapor is 6.3 ppm downfield from the shift of neat liquid pyridine. This difference may account for part of the reported discrepancies of calculated and experimental shift values.[2d]

Litchman and co-workers[12] found linear relations between ^{15}N shifts measured in solution and concentrations in mole percent and could therefore extrapolate solvent effects to infinite dilution. We have found the same for susceptibility-corrected shifts of pyridine–water mixtures, as shown in Figure 3 (correlation coefficient of 0.9993). The ^{15}N chemical shifts of pyridine in various solvents at infinite dilution, listed in Table II, were obtained by simple linear extrapolation from the

Table I. Solvent Effects on the Nitrogen Chemical Shifts of Some Compounds with Azine Nitrogens and Their Conjugate Acids

compd	solvent	concn[a]	$\delta^{15}N$ obsd[b]	$\delta^{15}N$ cor[c]	hydrochlorides concn[a]	hydrochlorides $\delta^{15}N$[b]
pyridine	gas phase[d]		48.4	51.4 ± 1.8		
	neat	100	57.3	57.7		
	C_6H_{12}	14.3	53.2	53.6		
	C_6H_6	14.3	56.1	56.5		
	C_2Cl_4[d]	0.003	54.7	54.3		
	CCl_4	14.3	55.9	56.0		
	CH_2Cl_2	14.3	60.1	60.1		
	$CHCl_3$	14.3	63.0	63.0	16.0	161.6
	Me_2SO	14.3	57.8	58.2	15.6	159.4
	CH_3OH	14.3	72.9	73.6	4.0	170.4
	H_2O	14.3	75.9	76.1	4.3	173.4
	CF_3CH_2OH	14.3	86.1	86.5		
4-methoxypyridine	neat	100	80.4			
	C_6H_6	14.3	78.9			
	CH_3OH	14.3	97.1		4.0	191.3
	H_2O				4.1	193.7
4-acetylpyridine	neat	100	45.6			
	C_6H_6	14.3	44.4			
	CH_3OH	14.3	58.1		4.0	163.4
	H_2O				3.2	165.2
	Me_2SO				10.5	139.5
4-acetylpyridine hemimethoxy ketal or methoxy ketal	CH_3OH				4.0	172.0
N-methylimidazole	C_6H_{12}	27.4	111.4	pyridine N		
			215.7	pyrrole N		
	CH_3OH	11.9	127.8	pyridine N	8.6	200.7
			212.5	pyrrole N		202.5
benzalaniline	C_6H_{12}	24.4	44.1			
	$CHCl_3$	23.7	47.9			
	CH_3OH	10.8	53.5			
	C_6H_6	16.7	45.1			
$\Delta^{1,9}$-octahydroquinoline	C_6H_{12}	14.6	66.0			
	$CHCl_3$	13.5	77.7		10.3	173.0
	C_2H_5OH	10.0	86.0			
azobenzene	C_6H_{12}	9.7	−134.7			
	$CHCl_3$	7.4	−134.0			
	2-propanol	6.3	−134.0			
	H_2SO_4/H_2O[e]				3.3	16.4
	C_2H_5OH					

[a] Mole percent solute. [b] Shift in parts per million from external 1 M $H^{15}NO_3$; positive values correspond to upfield shifts. [c] Corrected for bulk susceptibility effects. [d] Pyridine-^{15}N (96 atom %). [e] 34 mol % H_2SO_4, 43 mol % H_2O, and 23 mol % ethanol, H_2SO_4/azobenzene = 10:1.

Table II. Solvent Shifts of Pyridine

solvent	$\delta^{15}N$[a]	$\Delta\delta$ solvent[b]	$(\epsilon - 1)/(2\epsilon + 2.5)$[c]	Z[d]
cyclohexane	52.9	1.5	0.156	60.1
tetrachloroethene	54.3	2.9		
carbon tetrachloride	55.7	4.3	0.177	
benzene	56.3	4.9	0.180	
pyridine (neat)	57.7	6.3	0.417	64.0
dimethyl sulfoxide	58.3	6.9	0.477	70.4
dichloromethane	60.5	9.1	0.391	64.2
chloroform	63.9	12.5	0.314	63.2[e]
methanol	76.3	24.9	0.467	83.6
water	79.5	28.1	0.485	94.6
trifluoroethanol	91.3	39.9		96.3[f]

[a] Shifts of 14.3 mol % solutions, corrected for susceptibility effects and extrapolated to infinite dilution. [b] δ(solvent) − δ(gas). [c] Function of dielectric constant ε expected to be linear with reaction-field effects; see ref 4. [d] Kosower Z values; see ref 14. [e] $CHCl_3$ (0.13 M in C_2H_5OH). [f] Value for 2,2,3,3-tetrafluoropropanol, ref 14.

susceptibility-corrected values measured for 14.3 mol % solutions. The pyridine solvent shifts of Table II are all upfield, and these contrast with the downfield shifts usually found for saturated tertiary amines.[12b,13] However, the shift of pyridine in cyclohexane (52.9 ppm) falls between the extremes of the broad gas-phase resonance, 49.6–53.2 ppm, and is only 1.5 ppm upfield from its maximum at 51.4 ppm. Especially large upfield shifts reaching 40 ppm for trifluoroethanol are found for solvents capable of hydrogen bonding to the nitrogen unshared pair of pyridine. That the dielectric constant of the solvent does not correlate well with the magnitude of these solvent shifts is clearly shown by the relatively small shift in the very polar dimethyl sulfoxide, and also by the fact that the shift in dichloromethane is downfield from the shift in chloroform, which has a lower dielectric constant. Figure 4 shows the variation of the solvent shifts of the pyridine ^{15}N resonance with a function of the dielectric constant, $(\epsilon - 1)/(2\epsilon + 2.5)$, which is expected to correlate linearly with reaction-field effects.[4] The correlation coefficient is only 0.67.

It is especially interesting to compare the solvent shift of the pyridine resonance with the solvent dependence of the n→π* excitation energy, which is postulated to contribute substantially to the ^{15}N chemical shift of pyridine through domination of the $1/\Delta E$ term of the paramagnetic screening contribution. The blue shift observed for the n→π* transitions of azines[3] is

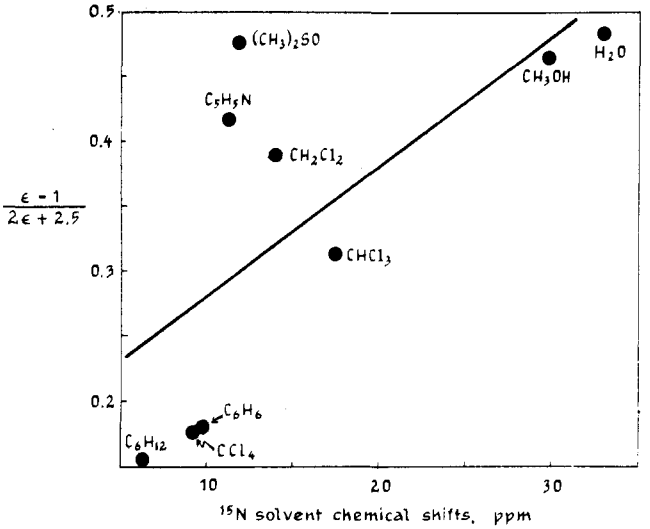

Figure 4. Correlation of ^{15}N NMR shifts of pyridine in various solvents and solvent mixtures as a function of dielectric constant with reference to the gas-phase shift. The line corresponds to the linear least-squares fit.

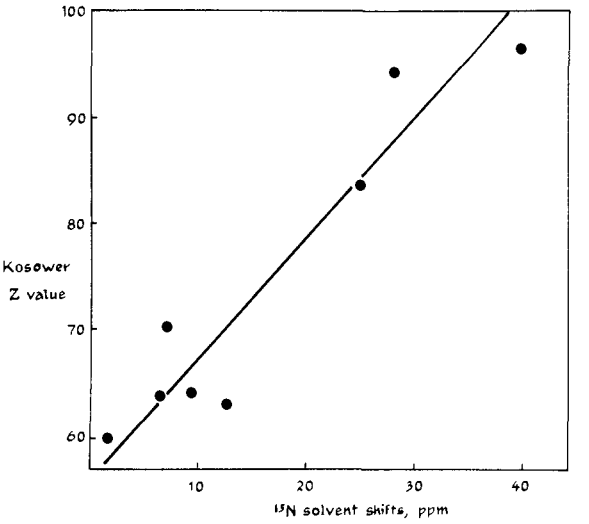

Figure 5. Correlation of ^{15}N NMR solvent shifts of pyridine with the Kosower Z values of the solvents with reference to the gas-phase shift of pyridine.

Table III. Solvent Effects on the Nitrogen-15 Protonation Shifts of the Conjugate Acids of Compounds with Azine Nitrogens

compd	solvent	Δδ of protonation[a]	Δδ of solvent[b]
pyridine	$CHCl_3$	98.6	16.8
	Me_2SO	101.6	
	CH_3OH	97.5	
	H_2O	97.6	
4-methoxypyridine	CH_3OH	94.2	18.2
4-acetylpyridine	CH_3OH	105.3	13.7
N-methylimidazole	CH_3OH	72.9	16.4 pyridine N
		−10.0	−3.2 pyrrole N
$\Delta^{1,9}$-octahydroquinoline	$CHCl_3$	95.3	20.0[c]
azobenzene	$CHCl_3$	150.4[d]	−0.7

[a] δ(hydrochloride) − δ(free base). [b] δ(methanol) − δ(benzene). [c] δ(ethanol) − δ(cyclohexane). [d] Protonated in a mixture of 34 mol % H_2SO_4 (10 equiv), 43 mol % H_2O, and 23 mol % ethanol.

caused by preferential hydrogen bonding to the nitrogen unshared pair in the ground state. Increases in ΔE would decrease the paramagnetic screening and therefore cause upfield shifts for hydrogen-bonding solvents. Quantitative ultraviolet data bearing on this point are difficult to obtain for pyridine because the weak n→π* band is only visible as a shoulder on the more intense π→π* absorption, except in quite nonpolar solvents.[3a] Attempts have been made to correlate solvent effects on the pyridine ^{15}N chemical shift with other solvent characteristics which would be expected to be related to the solvent effects of n→π* transitions. The hydrogen-bonding energy, which was shown by Del Bene[3c] to correlate with the ultraviolet shift of pyridine but not piperazine in water, is not a reliable measure for the shift of the ultraviolet maximum, even taking account of solvent interactions with the excited state, because vertical excitation (Franck-Condon principle) does not necessarily correspond to a 0-0 transition.[15] Kosower and co-workers[14] were able to show that the strongly solvent-dependent energy of the charge-transfer excitation of *N*-ethyl-4-carbomethoxypyridinium iodide gives an excellent linear correlation with the solvent dependence of the n→π* transition of cyclohexanone and other solvent-affected ultraviolet absorptions. Figure 5 shows the degree of correlation of Kosower's Z values (Table II) which correspond to the energy of this charge-transfer excitation in a given solvent with the solvent shifts of the pyridine nitrogen resonance. The trend of the solvent effects on the ^{15}N chemical shift is reasonably well represented by the Z values in having a linear correlation coefficient of 0.944. The relation between the solvent effects on the ^{15}N chemical shift of pyridine and n→π* excitation energies thus seems to have experimental as well as theoretical[2d] validity.

The protonation shifts of pyridine and related compounds (Table III) might be expected to provide a measure of the magnitude of the contribution to the chemical shift corresponding to the n→π* transition energies. However, the shifts of the hydrochlorides listed in Table I can be seen to be so solvent dependent as to make it difficult to draw very reliable conclusions. The solvent shifts of ^{15}N resonances of hydrochlorides probably result from changes in the solvation of tight ion pairs with solvent structural changes. This leads us to conclude that for theoretical analysis, it seems simpler to compare shift differences between salts measured in a very polar solvent and free bases measured in a poorly solvating

Table IV. ^{15}N NMR Chemical Shifts and Shift Changes of Pyridines with Solvent, Protonation, and N-Methylation (ppm)

		$\delta^{15}N(N\text{-}CH_3^+)X$				Δδ	Δδ	Δδ on
		concn[a]	$X^- = I^-$	concn[a]	$X^- = Cl^-$	on	on	solvent[d,e]
compd	solvent					protonation[b]	N-methylation[c]	change
pyridine	H_2O	4.4	174.5	3.7	174.0	117.3	117.9	16.8 (14.3%)
4-methoxypyridine	H_2O	4.4	195.6	4.1	195.3	114.8	116.4	18.2 (15.6%)
	$CHCl_3$	10.0	196.3					
4-acetylpyridine	H_2O	4.4	168.4	2.6	167.8	120.8	123.4	13.7 (11.1%)

[a] Mole percent of solute. [b] δ(hydrochloride in CH_3OH) − δ(free base in benzene). [c] δ(pyridinium chloride in H_2O) − δ(free base in benzene). [d] δ(methanol) − δ(benzene) of free bases. [e] Parenthetical values are percent that the solvent-change shift is of the N-methylation shift.

medium, preferably the gas phase, rather than the protonation shift in the same solvent. Table IV lists protonation shifts defined as shift differences between the ^{15}N resonances of hydrochlorides measured in methanol and free bases measured in benzene for pyridine, 4-methoxy-, and 4-acetylpyridine. Also included are the changes in shifts associated with N-methylation.

The ^{15}N chemical shifts of the *N*-methylpyridinium salts are essentially unaffected by change of the counterion and, in contrast to the hydrochlorides, also show only minor solvent effects. They are therefore more reliable than protonation shifts to assess the effects of bond formation to the nitrogen unshared pair of a pyridine. It is interesting that alkylation and protonation shifts listed in Table IV show little variation for the three different pyridines studied. The slightly smaller effects for the *p*-methoxy derivative may be the result of an increase of the $n\rightarrow\pi^*$ transition energy associated with introduction of an electron-donating group, as is generally observed.[3] Conjugation with the acetyl group may be responsible for the opposite, and larger, shift effect found for 4-acetylpyridine. The solvent shifts of the free bases (benzene to methanol) do not correlate well with the protonation shifts (Table IV). The reason is that the solvent shifts are dominated by formation of hydrogen bonds to the nitrogen unshared pairs in methanol and the extent of this hydrogen bonding is affected to a much greater degree by the basicity of the pyridine than are the overall shift changes resulting from protonation with a strong acid or by N-methylation. Thus, the solvent shifts were 13.7 ppm (11% of the N-methylation shift) for 4-acetylpyridine, for which the electron-withdrawing substituent decreases the basicity, and 18.2 ppm (16% of the N-methylation shift) for the electron-donating *p*-methoxy group. The extreme of this kind of behavior is found for azobenzene, the ^{15}N chemical shift of which is seen to be almost solvent independent (Table I), but which undergoes a very large change on protonation of +150.4 ppm (Table III).[16] The reason is that the nitrogens of azobenzene are relatively weakly basic and do not therefore undergo significant hydrogen bonding in a solvent such as methanol. Protonation requires rather strong acid, and when it occurs, there is a large change in the second-order paramagnetic contribution to the nitrogen shifts. Also interesting is *N*-methylimidazole, whose pyridine-like nitrogen shows characteristically large upfield solvent and protonation shifts, while its pyrrole-like nitrogen behaves in a manner analogous to saturated tertiary amines with deshielding hydrogen bonding and protonation effects.[13]

The solvent and protonation shifts of aromatic and saturated imines (Tables I and III) are very similar to the effects observed for other azine nitrogens. The observation of relatively low-energy $n\rightarrow\pi^*$ transitions[17] implies operation of the second-order paramagnetic effect in much the same way as for pyridines.

It seems safe to conclude that the shielding solvent effects observed for the ^{15}N resonances of pyridines, and indeed more generally of sp^2-hybridized nitrogens, are associated with hydrogen bonding to the nitrogen unshared pairs. Such hydrogen bonding changes the $n\rightarrow\pi^*$ transition energies and, hence, the paramagnetic screening which appears to be the dominant influence on the chemical shifts of these compounds. The possibility of other less important solvent effects may be indicated by the less-than-perfect correlation of the solvent effects with the Kosower *Z* values. One such possibility is polarization of the π-electron system as the result of reaction-field effects in polar media.

References and Notes

(1) Supported by the Public Health Service, Research Grant GM-11072 from the Division of General Medical Sciences, and by the National Science Foundation.
(2) (a) M. Witanowski and G. A. Webb, "Nitrogen NMR", Plenum Press, New York, N.Y., 1973, pp 218–229; (b) M. Witanowski, L. Stefaniak, H. Januszewski, and G. A. Webb, *Tetrahedron*, **27**, 3129 (1971); (c) H. Saito and K. Nukada, *Tetrahedron Lett.*, 111 (1965); (d) H. Kato, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, **43**, 1921 (1970); (e) D. Schweizer and H. W. Spiess, *J. Magn. Reson.*, **15**, 529 (1974).
(3) (a) F. Holverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951); (b) J. W. Sideman, *Chem. Rev.*, **58**, 689 (1958); (c) J. E. Del Bene, *J. Am. Chem. Soc.*, **97**, 5330 (1975).
(4) (a) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936); (b) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).
(5) J. Homer, *Appl. Spectrosc. Rev.*, **9**, 1 (1975).
(6) J. L. Deutsch, A. C. Lawson, and S. M. Poling, *Anal. Chem.*, **40**, 839 (1968).
(7) Landolt and Börnstein, "Zahlenwerte und Funktionen", Vol. II, Part 2, 6th ed, Springer-Verlag, West Berlin, 1960, p 134.
(8) G. R. Sullivan and J. D. Roberts, unpublished results.
(9) Houben-Weyl, "Methoden der Organischen Chemie", Vol. XI/1, Georg Thieme Verlag, Stuttgart, 1957, p 518.
(10) R. F. Parcell and F. P. Hanck, Jr., *J. Org. Chem.*, **28**, 3468 (1963).
(11) E. M. Kosower and P. E. Klinedienst, Jr., *J. Am. Chem. Soc.*, **78**, 3493 (1956).
(12) (a) W. M. Litchman, M. Alei, Jr., and A. E. Florin, *J. Am. Chem. Soc.*, **91**, 6574 (1969); (b) M. Alei, Jr., A. E. Florin, and W. M. Litchman, *ibid.*, **92**, 4828 (1970).
(13) R. O. Duthaler, K. L. Williamson, D. D. Giannini, W. H. Bearden, and J. D. Roberts, *J. Am. Chem. Soc.*, **99**, 8406 (1977).
(14) (a) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958); (b) E. M. Kosower and G.-S. Wa, *ibid.*, **83**, 3142 (1961).
(15) G. C. Pimentel, *J. Am. Chem. Soc.*, **79**, 3323 (1957).
(16) J. B. Lambert, G. Binsch, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **51**, 735 (1964).
(17) H. H. Jaffé, S.-J. Yah, and R. W. Gardner, *J. Mol. Spectrosc.*, **2**, 120 (1958).