of chloride or acetylene was observed. The work-up and analysis procedures were as described above and it was shown that, when the acetates are dissolved in acetic acid and submitted to the work-up procedure, no conversion to ketone results.

The ratio of **3** to **4** did not vary throughout the reaction, indicating that the chlorides are not interconverted under the reaction conditions. This was also demonstrated by showing that an approximately equal molar mixture of **3** and **4** did not significantly change in composition after 10 hr in a 1.00 *M* hydrogen chloride solution at 50°. Using known mixtures, it was shown that the vpc procedure was valid (peak area ratios equal mole ratios) and that no product fractionation occurs in the work-up procedure.

Acknowledgment. We wish to thank the National Science Foundation for a grant (GP-2137) aiding the purchase of the nmr spectrometer used in these studies.

The N-Decoupled Proton Magnetic Resonance Spectra of Aqueous Pyridine and Pyridinium Ion

J. B. Merry and J. H. Goldstein

Contribution from the Departments of Chemistry and Physics, Emory University, Atlanta, Georgia 30322. *Received August 8, 1966*

Abstract: The proton magnetic resonance (pmr) spectra of neat pyridine and of its aqueous solutions over a range of pH values have been observed under conditions of nitrogen decoupling. With the additional spectral details so obtained, theoretical analyses were carried out leading to complete sets of pmr parameters for neat pyridine, aqueous pyridine, and aqueous pyridinium ion. The effect of protonation on these parameters has been determined, including, in particular, the proton–proton couplings. These results are discussed in terms of electronic and other factors which are likely to be involved.

The earliest reported complete analysis of the proton magnetic resonance spectrum of neat pyridine was carried out in 1957 by Schneider, Bernstein, and Pople,[1] and their results have subsequently provided the initial basis for analyzing the spectra of many pyridine derivatives.[2] The five-spin pyridine system gives rise to a complex spectral pattern which is further complicated by the fact that broadening of the α-proton resonances by the quadrupolar N atom results in a loss of detailed features necessary for a complete analysis. Recently, Diehl, Jones, and Bernstein have analyzed the β and γ portions of the pyridine spectrum alone by the method of subspectral analysis.[3] Their partial set of parameters differs somewhat from those of Schneider, *et al.*, especially in the case of J_{23} (in this paper the numbering of ring positions begins with the N atom). Baldeschwieler and Randall demonstrated that the effects of quadrupolar broadening in pyridine could be eliminated by double irradiation but did not report an analysis of the decoupled spectrum.[4]

The pyridinium ion has been examined in trifluoroacetic acid by Smith and Schneider.[5] Their spectrum is broad and poorly resolved, and no complete analysis was attempted. Kotowycz, Schaefer, and Bock have reported chemical shifts for pyridinium salts (Cl, Br, and I) in several nonaqueous media.[6] Neither pyridine nor the pyridinium ion appear to have been studied in detail in aqueous solution, in spite of the widespread interest in the properties of these structures in water. Interpretations and correlations of results for both pyridine and the ion have been concerned solely with the chemical shifts.[5–8]

This communication describes the results of a detailed study of the pmr spectra of pyridine, both as the neat liquid and in aqueous solution, and of the pyridinium ion in aqueous solution over a wide pH range. Double irradiation at the resonance frequency of the N atom was used when required, and this provided sharp and well-resolved spectra for purposes of refined theoretical analysis, yielding complete sets of spectral parameters for all cases studied. Of particular interest are the values of the H–H coupling parameters for aqueous pyridine and pyridinium ion which are now available for the first time, and which reflect the influence of the positive charge on the electronic (and possibly geometrical) structure of the ring.

Experimental Section

Matheson Spectrograde, or Reagent Grade, pyridine were used throughout this study without further purification. The aqueous solutions were acidified with concentrated HCl and the volume adjusted to a final concentration of 7 mole % of pyridine. The pH measurements were carried out with a Radiometer TTT-1 pH meter at room temperature (~24°).

All spectra were obtained with a Varian Associates Model A-60 spectrometer. The modifications required to provide this instrument with a double-resonance capability are rather extensive and will be reported in detail later. Calibrations were performed by the usual side-band technique using a Krohn–Hite 440-B audio oscillator continuously monitored by a Hewlett–Packard 5245L frequency counter. The peak fequencies are generally the average of two forward and two reverse 50-cps scans taken at 500 cps/sec, with an average deviation of ~0.1 cps. The spectra were calibrated relative to external cyclohexane contained in the outer annulus of a precision coaxial sample tube. For the two cases of aqueous pyridine at 0 and 99% protonation the bulk susceptibilities of the

---

[1] W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Can. J. Chem.*, **35**, 1487 (1957).

[2] See, for example, W. Brugel, *Z. Elektrochem.*, **66**, 159 (1962).

[3] P. Diehl, R. G. Jones, and H. J. Bernstein, *Can. J. Chem.*, **43**, 81 (1965).

[4] J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 303 (1961).

[5] I. C. Smith and W. G. Schneider, *Can. J. Chem.*, **39**, 1158 (1961).

[6] G. Kotowycz, T. Schaefer, and E. Bock, *ibid.*, **42**, 2541 (1964).

[7] V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, **60**, 248 (1964).

[8] A. H. Gawer and B. P. Dailey, *J. Chem. Phys.*, **42**, 2658 (1965).

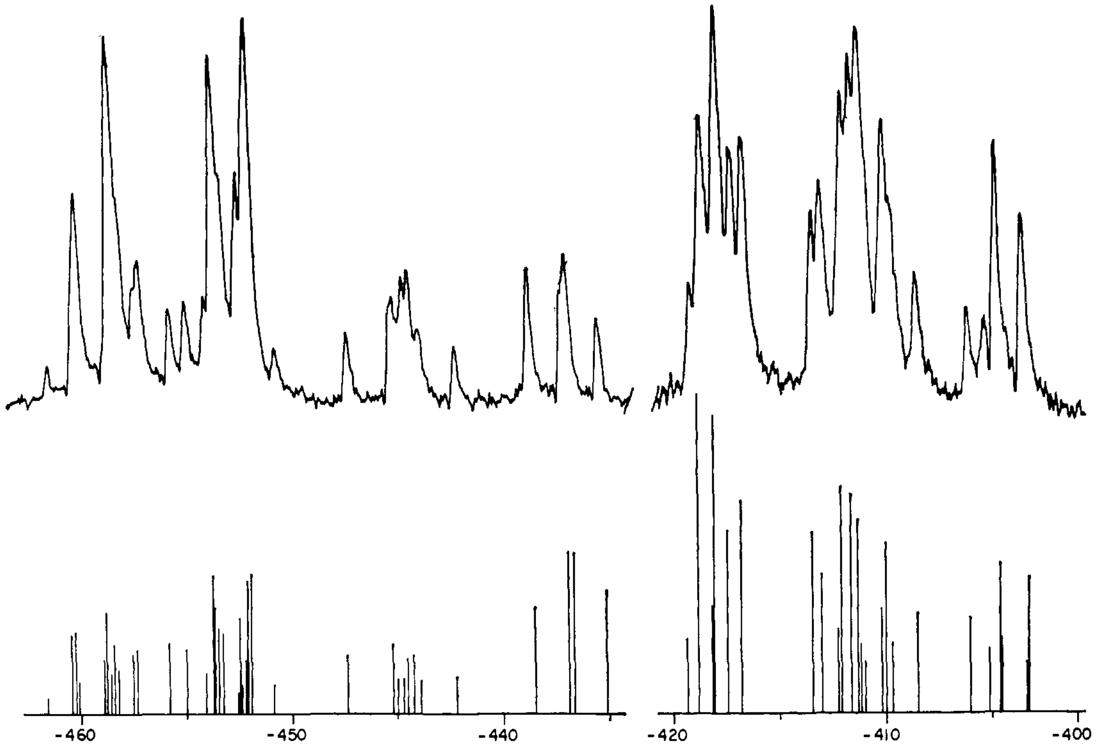


Figure 1. Observed and calculated spectra of aqueous pyridine at a pH of 3.1 (99% protonated).

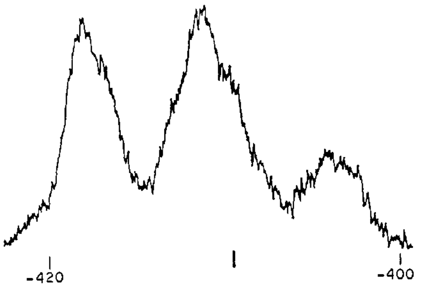


Figure 2. β pattern of the pyridinium ion (99% protonated) before decoupling.

samples were determined using the nonrotating coaxial tube method and appropriate susceptibility corrections were applied.[9,10]

At 20° the pK_a of pyridine and its temperature coefficient are 5.23 and -0.015 deg^{-1}, respectively.[11] These values were used in the calculations to be described later. The difference between the probe temperature, ~32°, and the temperature at which the pH measurements were carried out is equivalent to only ~0.1 unit in pH or pK_a. The corresponding effect on the final results is inconsequential.

Results

In addition to neat pyridine, aqueous solutions were observed at pH values of 9.0, 5.5, 5.2, 4.65, and 3.1. The corresponding percentages of pyridine present as the pyridinium ion are 0, 26, 41, 72, and 99%, respectively, as determined from the relationship

$$f = [1 + \text{antilog}\,(\text{pH} - \text{p}K_a)]^{-1} \qquad (1)$$

where f is the fraction of base protonated and pK_a = 5.05 at 32°.

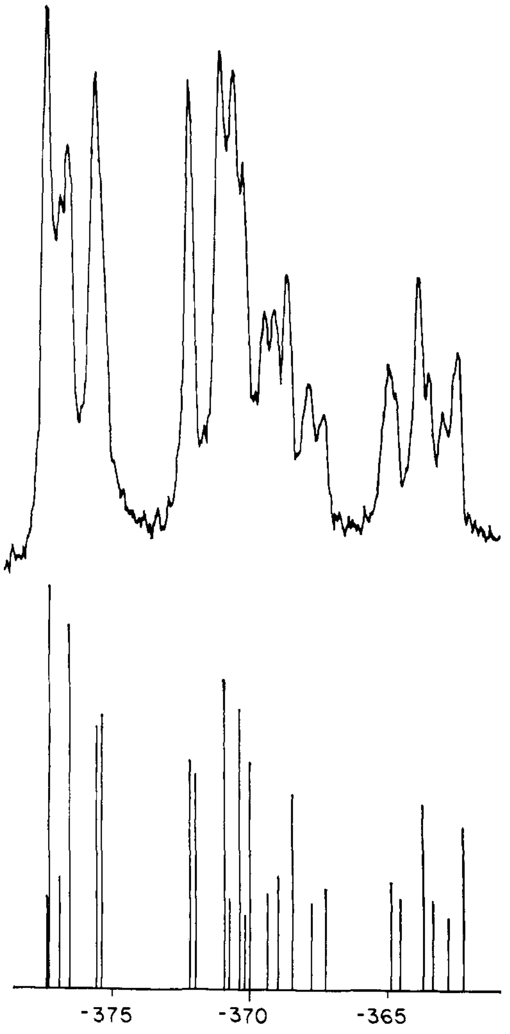


Figure 3. Observed and calculated spectrum of aqueous pyridine, 41% protonated, after decoupling.

---

(9) C. A. Reilly, H. M. McConnell, and R. C. Meisenheimer, *Phys. Rev.*, 97, 264A (1955).

(10) N. C. Li, L. Johnson, and J. N. Shoolery, *J. Phys. Chem.*, 65, 1902 (1961).

(11) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 14, 145.

Table I. Observed and Calculated Spectrum of Aqueous Pyridine (pH 9.0)[a]

Frequencies		Intensities	
Calcd[b]	Obsd	Calcd[b]	Obsd
−417.91		0.43	
−417.83		0.41	
	−417.41		3.72
−417.42		1.75	
−417.31		1.76	
−415.55		1.39	
−415.53		1.89	
	−415.47		6.61
−415.48		1.90	
−415.43		1.41	
−414.49		0.97	
−414.45		0.96	
	−414.47		4.39
−414.44		0.99	
−414.43		0.99	
−413.34		1.47	
	−413.30		2.89
−413.19		1.50	
−411.45		2.08	
	−411.41		4.59
−411.41		2.08	
−410.98		0.52	
−410.79		0.50	
−410.59		1.11	
	−410.54		5.22
−410.55		1.12	
−410.55		1.09	
−410.53		1.08	
−409.59		2.26	
	−409.54		4.52
−409.48		2.28	
−380.19	−380.20	0.54	0.55
−378.36		0.53	
	−378.35		1.13
−378.30		0.52	
−376.47	−376.44	0.51	0.55
−373.90	−373.89	+0.80	0.81
−371.39	−371.30	1.08	
		0.70	1.91
−371.14	−371.06	0.71	
−371.10			
−370.43		0.92	
	−370.44		2.17
−370.40		0.92	
−369.98	−370.00	0.72	1.00
−367.80	−367.79	0.92	1.03
−365.10	−365.10	1.92	1.89
−363.25		1.72	
	−363.21		3.17
−363.16		1.70	
−361.31	−361.36	1.52	1.48
−351.29		3.00	
−351.18	−351.24	0.66	3.52
−351.02		0.69	
−350.53	−350.57	2.70	2.64
−349.41	−349.35	2.15	3.95
−349.37		2.11	
−346.54	−346.54	1.81	3.32
−346.45		1.78	
−345.26	−345.21	2.44	2.52
−344.79		0.58	
−344.77	−344.70	0.56	3.60
−344.69		2.25	
−344.24	−344.23	1.64	1.94
−343.22		0.79	
	−343.23		1.81
−343.16		0.78	
−342.50	−342.49	1.36	1.49
−341.52		0.66	
	−341.45		1.31
−341.43		0.66	
−339.33		0.74	
	−339.26		1.61
−339.26		0.74	
−338.20	−338.20	1.41	1.51
−337.63		0.62	
	−337.61		1.26
−337.53		0.62	
−336.59	−336.58	1.21	1.21

[a] At 60 Mc/sec relative to external cyclohexane. [b] Insufficiently resolved sets of peaks have been grouped together with regard to both frequency and intensity.

The spectrum of neat pyridine exhibits broadening in the α-proton region, which is easily decoupled to yield a sharp, analyzable pattern. These spectra are similar to those described by Baldeschwieler and Randall[4] and will not be given here. On the other hand, the spectra of aqueous solutions of pyridine (pH = 9.0) show only slight signs of broadening and can be analyzed without decoupling. As the pH is decreased the broadening increases progressively. This effect is noticeable first in the α region and extends successively to the β and γ regions. Except for the case of pH 9.0, all the spectra were calibrated in the decoupled condition.

The upper part of Figure 1 shows the decoupled spectrum of pyridinium ion (99% protonated). Figure 2 shows the β pattern of this sample before decoupling. The decoupled β region of the partially protonated (41%) sample is given in the upper part of Figure 3. The observed frequencies and intensities of neutral aqueous pyridine (pH 9.0) and pyridinium ion (pH 3.1) are given under the appropriate headings of Tables I and II.

Analysis

All spectra were analyzed as AA'BB'C systems in the notation of Pople, *et al.*[12] Initially the decoupled spectrum of neat pyridine was calculated using the parameters reported by Schneider, *et al.*[1] Since this procedure did not adequately account for the observed spectrum, the parameters were varied until a reasonable fit was obtained. The final calculation was carried out by a least-squares procedure adapted from Bothner-by, *et al.*[13] The analyses of the aqueous spectra were carried out in the order of increasing protonation. This minimized both the changes in the spectra and those required in the parameters.

The calculated spectra for aqueous pyridine and pyridinium ion are shown in Tables I and II. There is considerable overlapping of lines in these two spectra, but for the well-resolved peaks the agreement obtained is of the order of 0.05 cps. Comparable results were obtained for all cases studied. The final values for the parameters are listed in Table III. The estimated certainties in these values, as indicated by the least-squares procedure, are ~0.03 cps for the shifts and ~0.03–0.05 cps for the couplings, respectively. The

(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonnace," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 98.

(13) A. A. Bothner-by, C. Naar-Colin, and H. Gunther, *J. Am. Chem. Soc.*, 84, 2748 (1962).

Table II. Observed and Calculated Spectrum of Aqueous Pyridinium (pH 3.1)[a]

Frequencies		Intensities		Frequencies		Intensities	
Calcd[b]	Obsd	Calcd[b]	Obsd	Calcd[b]	Obsd	Calcd[b]	Obsd
−461.68	−461.69	0.36	0.58	−444.53		1.07	
−460.45		1.46		−444.24	−444.28	1.12	2.01
	−460.37		3.28	−443.84	−443.84	0.62	0.91
−460.15		0.60		−442.07	−442.05	0.74	0.81
−458.91		1.02		−438.45	−438.50	2.05	1.92
−458.76		1.93		−436.91		1.57	
−458.69		1.90			−436.77		2.20
	−458.65		5.74	−436.65		1.50	
−458.59		0.69		−435.12	−435.14	1.17	1.10
−458.44		1.27		−419.33	−419.34	0.70	1.09
−458.25		0.80		−418.87	−418.84	3.02	2.78
−457.54		1.12		−418.17		1.04	
	−457.48		2.20		−418.16		3.36
−457.31		1.24		−418.10		2.78	
−455.82	−455.83	1.31	1.46	−417.41	−417.40	1.74	2.12
−454.99	−455.03	1.14	1.52	−416.81	−416.81	2.07	2.07
−454.10	−454.10	0.75	1.50	−413.47	−413.49	1.69	1.63
−453.76		1.98		−413.01	−413.05	1.36	1.78
−453.75	−453.70	0.66	5.65	−412.26		0.80	
−453.71		2.02			−412.08		2.65
−453.47		1.61		−412.08		2.13	
	−453.40		3.44	−411.65	−411.65	2.03	2.81
−453.25		1.50		−411.31		1.80	
−452.58		0.44		−411.15	−411.24	0.66	2.88
−452.54		0.60		−410.95		0.48	
	−452.51		3.67	−410.16		0.99	
−452.53		1.13			−410.08		2.22
−452.41		0.55		−410.00		1.60	
−452.18		1.01		−409.65	−409.69	0.67	1.43
−452.17	−452.05	2.57	5.74	−408.49	−408.45	0.95	0.98
−451.96		2.65		−406.03	−406.01	0.92	0.79
−450.84	−450.83	0.48	0.78	−405.15	−405.21	0.60	0.76
−447.32	−447.29	1.09	1.07	−404.64		1.39	
−445.18		1.31			−404.62		1.97
	−445.16		1.69	−404.64		0.76	
−444.97		0.64		−403.37		0.47	
−444.68		0.64			−403.36		1.52
	−444.60		1.91	−403.36		1.26	

[a] At 60 Mc/sec relative to external cyclohexane. [b] Insufficiently resolved sets of peaks have been grouped together with regard to both frequency and intensity.

Table III. Pmr Parameters for Pyridine[a]

		pH				
	Neat	9.0	5.5	5.2	4.65	3.1
		% protonated				
	...	0	26	41	72	99
J_{23}	4.84	5.04	5.27	5.45	5.65	5.96
J_{24}	1.79	1.79	1.70	1.62	1.57	1.54
J_{25}	1.00	1.00	0.97	0.90	0.93	0.81
J_{26}	−0.02	−0.02	0.28	0.38	0.68	0.99
J_{34}	7.62	7.73	7.75	7.80	7.83	7.95
J_{35}	1.45	1.38	1.34	1.36	1.29	1.38
ω_2	403.61	413.34	423.88	427.77	444.53	455.96
ω_3	314.02	344.84	363.65	370.67	396.03	411.95
ω_4	336.06	369.62	390.38	398.15	426.32	443.75
ω_2'	405.6	404.0				439.7
ω_3'	316.0	335.6				395.6
ω_4'	338.1	360.3				427.5

[a] All values are in cps at 60 Mc/sec relative to external cyclohexane. The numbering of the ring positions begins at the N atom.

chemical shifts designated as ω_i' contain the adjustments for bulk susceptibility effects, and are subject to an additional uncertainty estimated to be within 2 cps.

The effect of variations of the parameters on the calculated spectra was studied in some detail. It was found that all parameters except J_{26} and J_{35} affected the spectra in the manner generally expected from first-order considerations. The effect of J_{26} is particularly interesting since it controls the splittings of numerous doublets in the calculated spectra, a fact which is very useful in analyzing the pyridinium pattern. For the six of these doublets which appear in the β region (see Figure 3), the calculated splittings increase with the magnitude of J_{26} and the observed splittings increase with extent of protonation. Detailed calculations for six doublets in the cases of 41 and 99% protonated pyridine demonstrated that J_{26} must be of the same sign as the major couplings and it is therefore given a positive value in Table III. (Only the sign of J_{26} was in question originally.) These assignments rest on the assumption that an acceptable fit cannot be achieved unless the other couplings are appreciably altered. The value of $J_{26} = -0.02$ cps in Table III is simply the result of the least-squares fitting procedure and is to be regarded as indistinguishable from zero.

Discussion

The relative positions of the chemical shifts obtained here for neat pyridine are essentially the same as those reported by Schneider, *et al.*,[1] and Diehl, *et al.*[3] The present values of the couplings are reasonably close to the corresponding partial set of the latter but differ significantly with respect to the values of J_{23} and J_{26} given by the former (5.50 and 0.42 cps, respectively).

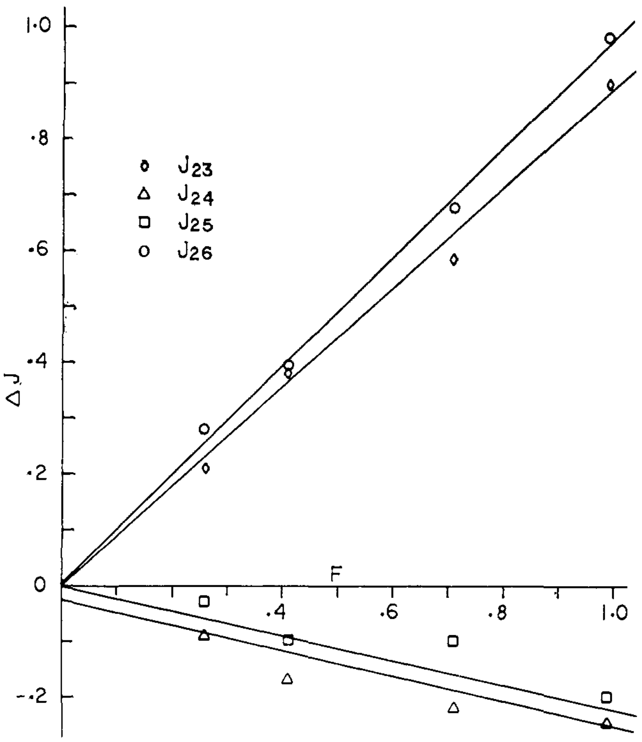
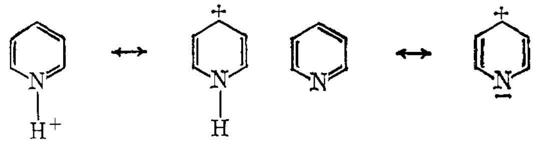


Figure 4. Effect of protonation on coupling parameters of aqueous pyridine.

Other things being equal, it is reasonable to prefer the values obtained from decoupled spectra, and further discussion of the coupling parameters will involve only the values obtained in this study.

The coupling values in neat pyridine and aqueous pyridine at pH 9.0 are quite similar, the largest difference being 0.20 cps for J_{23}. On the other hand, increasing protonation in water produces progressive, and apparently quite real, changes in five of the six couplings. Figure 4 shows how the four couplings involving the α proton vary with the extent of protonation, which brings about both positive and negative changes. The most significant variations, ~1 cps with complete protonation, occur in the case of J_{23} and J_{26}. The latter variation is by far the largest on a relative basis and is especially interesting since it involves a long-range parameter.

It is not a simple matter to account for the variations noted here since we are dealing with a molecule of the aromatic type containing a heteroatom and probably significantly perturbed, electronically and geometrically, by protonation. For the simpler aromatic cases of benzene and naphthalene, the theoretical calculations of McConnell indicate that σ contributions are dominant for *ortho* and *meta* couplings while the π contribution dominates the *para* coupling.[14,15] It has been pointed out, however, that *meta* couplings are too large to be explained on this basis.[16] Moreover, and on a more empirical level, a linear correlation between *ortho* couplings and the associated π-bond orders has been reported for several fused aromatic compounds.[17] It may be noted, in this connection, that the following structures show that pyridinium ion can more easily support certain fixed double-bonded structures more readily than neutral pyridine since the latter requires charge separation.



However, such arguments could not be convincingly extended to account for all the observed changes. It is significant, though not surprising, that the greatest absolute changes produced by protonation involve the α proton, with appreciably smaller effects in the C_3–C_4–C_5 segment of the ring. This could indicate that the effect proceeds largely through perturbation of the σ framework of the ring, to which the proton is attached. Consideration should also be given to the effect of changes in molecular geometry produced by protonation, but neither the magnitude nor the relative influence of such changes are known for aqueous pyridine. It would appear, then, that until the various factors implicated can be more reliably separated and evaluated, interpretations of the variations noted here should be offered with some restraint.

Palmer and Semple have reported variations of H–H coupling parameters with protonation in some quinolines, isoquinolines, pyridines, and cinnalines.[18] However, they describe these variations as being quite specific, affecting principally J_{23} by 1.0 cps, whereas the other variations did not exceed 0.3 cps. No variations of cross-ring couplings such as have been observed here for J_{25} were reported. These workers have used their results to identify the site of protonation in various nitrogen heterocyclic structures. In a previous study of the effect of protonation of purine we have also observed a specific effect on the J_{26} coupling, which is somewhat analogous to the J_{25} coupling in pyridine.[19]

The α-proton shift in neat pyridine appears to be anomalously low when compared to the values for the other protons. Moreover, protonation in aqueous media (Table III) or in trifluoroacetic acid[5] affects the α shift much less than the others. These observations have been accounted for in terms of the magnetic anisotropy of the N atom and the intramolecular electric field effects produced by the lone-pair electrons.[4,7] Both of these contributions are affected by protonation, since this involves bonding to the lone-pair electrons.

Although the shifts in neat pyridine and aqueous pyridine and pyridinium ion can be compared using the values adjusted for bulk susceptibility (see ω_i' in Table III), the number of factors capable of influencing the shieldings in these systems is too great to allow a unique interpretation. These include, in addition to the two mentioned above, solute–solute association,[20] reaction field effects,[21] the effects of H bonding and protona-

---

(14) H. M. McConnell, *J. Mol. Spectry.*, 1, 11 (1957).

(15) H. M. McConnell, *J. Chem. Phys.*, 30, 126 (1959).

(16) S. Sternhell, *Rev. Pure Appl. Chem.*, 14, 15 (1964).

(17) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1966, p 772.

(18) M. H. Palmer and B. Semple, *Chem. Ind.* (London), 1766 (1965).

(19) J. M. Read, Jr., and J. H. Goldstein, *J. Am. Chem. Soc.*, 87, 3440 (1965).

(20) J. N. Murrell and V. M. S. Gil, *Trans. Faraday Soc.*, 61, 402 (1965).

(21) A. D. Buckingham, *Can. J. Chem.*, 38, 300 (1960).

tion on the charge distribution in pyridine,[22] and possible changes in the ring-current anisotropy. Examination of the values of ω_i' (Table III) shows that the effect of dissolving pyridine in water is quite small at the α position. Since some degree of solvation *via* H bonding is to be expected, and since the β and γ positions are now ~20 cps lower than in the neat liquid, the behavior of the α proton probably involves extensive cancellation of two or more factors. In the case of aqueous pyridinium ion, all shifts are appreciably displaced to lower field, but the γ shift is now only ~12 cps above the α value and, in fact, the spread of values is reduced to about half of that observed in neat pyridine.

The variation of spectral broadening of aqueous pyridine with N-decoupling and with protonation leads to some interesting conclusions. Since this broadening can be completely removed by irradiation of nitrogen, it can be inferred that the broadening is caused by a N-ring proton interaction and not chemical exchange of the N-H proton. The progressive increase of ring proton broadening with protonation, therefore, can be attributed to a decreased electric field gradient about the nitrogen.[23] This decreased gradient is provided by the addition of a proton to the nitrogen, thus making its environment more electrically symmetric.

Acknowledgments. We wish to thank the National Institutes of Health for a grant in partial support of this work.

---

[22] S. Mataga and N. Mataga, *Z. Physik. Chem.* (Frankfurt), **19**, 231 (1959); *Bull. Chem. Soc. Japan*, **32**, 521 (1959).

[23] J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

The Nuclear Magnetic Resonance Spectrum of 2-Butanol

L. M. Jackman[1] and N. S. Bowman[2]

Contribution from the Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37916. *Received August 10, 1966*

Abstract: The nmr spectra of *erythro-* and *threo-*2-butanol-3-*d* as well as 2-butanol itself have been observed both undiluted and in carbon tetrachloride solution, and these spectra have been explicitly analyzed. It has been found that the methylene protons are magnetically nonequivalent and that the extent of nonequivalence decreases with dilution. From a knowledge of the coupling constants and chemical shifts, this behavior has been interpreted in terms of an alteration of conformer populations as a consequence of hydrogen-bonding rupture on dilution.

It was recognized early in the development of proton nmr that the position of a resonance line as determined by its relationship to a reference such as TMS or another line in the same spectrum is often dependent on concentration or the nature of the solvent. In certain cases these solvent shifts are quite large, amounting to as much as several ppm. This type of solvent dependence is illustrated by the behavior of the hydroxyl proton in alcohols and phenols, the position of aromatic proton resonances when diluted with nonaromatic solvents, and the shift in line positions of nonaromatic compounds when diluted with aromatic solvents. Because the change in spectral appearance on dilution in these cases is quite dramatic, they were the subject of early investigations and theoretical treatment; consequently, it is felt that their origin is reasonably well understood.[3]

When the proton nmr spectra of compounds of types other than those just discussed are examined, it is often found that many of the resonance lines are likewise displaced from a reference by changes in solvent or concentration. For the majority of such compounds and typical nmr-solvent systems, these displacements are rather small and may be, characteristically, in the range of 0.01-0.1 ppm. The origin and interpretation of solvent shifts in such compounds have not been the subject of extensive investigation since their study presents serious difficulties. First, as has already been noted, the magnitudes of these dilution shifts are often quite small, and thus careful calibration and analyses of errors are required; furthermore, not all lines in a given spectrum will be affected equally or even necessarily in the same direction. In addition, the concentration dependence associated with a given solute-solvent system may be effectively eliminated in most cases by using moderately dilute solutions; under these conditions the observed resonances do not usually differ significantly from those obtained by extrapolation to infinite dilution, and thus the existence of a small solvent dependence does not interfere with the interpretation or other information which may be sought from the spectrum.

A special case of the latter type of dilution effect involves the chemical shift difference between two magnetically nonequivalent geminal protons. Several investigators have observed that the degree of nonequivalence, as evidenced by the difference in chemical shifts between these protons, may vary with the nature of the solvent. Thus Finegold[4] was able to increase the separation between the nonequivalent methylene

---

[1] National Science Foundation Senior Foreign Scientist Fellow, The University of Tennessee, 1965; from the University of Melbourne, Parkville, Victoria, Australia.

[2] To whom all inquiries should be directed.

[3] For a discussion of early studies and theoretical interpretations of solvent dependence of this type, see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapters 15 and 16.

[4] H. S. Finegold, *Proc. Chem. Soc.*, 283 (1960).