Preparation of 3′,6′-Dimethoxybenzonorbornylene (III). 3′,6′-Dimethoxybenzonorbornadiene[20] was hydrogenated using 5% Pd–C (Parr apparatus, 40 psi H_2, 2 hr). After removing the catalyst and the ethanol, the crude 3′,6′-dimethoxybenzonorbornylene was purified by sublimation under reduced pressure; mp 38–40°; nmr (CCl_4): δ 1.48 (4 H, $H_{5,6}$) AB multiplet, 1.52 (2 H, H_7) AB multiplet, 3.51 (2 H, $H_{1,4}$) singlet, 3.68 (6 H, $-OCH_3$) singlet, 6.46 (2 H, $H_{4',5'}$) singlet.

Spectroscopic Data. Absorption spectra were recorded with a Bausch and Lomb Spectronic 505 and with a Carey Model 14 spectrophotometer. Emission spectra were recorded at 80°K using a recording instrument which has been described in detail elsewhere.[5] The slit width on the emission monochromator was 2 nm giving 32-Å resolution. Samples were contained in sealed 1.5 mm o.d. quartz tubes. The standard for quantum yield determinations was a sample of *p*-terphenyl in hexane for which a fluorescence yield of 0.9 (room temperature) was assumed.[5]

Acknowledgments. We thank Mrs. B. Feuer for her capable technical assistance and Dr. J. Eisinger for the use of his emission spectrophotometer and for helpful discussions.

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Intramolecular Hydrogen Bonding in 2-Hydroxyalkylpyridines and 2-Hydroxyalkylpiperidines

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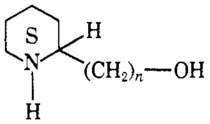
Abstract: Strong intramolecular hydrogen bonds were found to be present in 3-hydroxypropylpyridine, 2-hydroxyethylpyridine, and the corresponding piperidines. The hydrogen bond in hydroxymethylpyridine is much stronger than anticipated. This is attributed to the fact that the hydrogen-donor group is on an sp^3 carbon and the acceptor group is on an sp^2 carbon, allowing the dihedral angle to be close to zero degrees and consequently producing a very short hydrogen bond. Hydroxymethylpiperidine has a normal $\Delta\nu$ but only a very small equilibrium constant for hydrogen bond formation. This hydrogen bond requires that the lone pair of electrons on nitrogen be equatorial. The small equilibrium constant can be rationalized by assuming that the lone pair of electrons on nitrogen prefers to be axial and the amino hydrogen to be equatorial.

Although there have been numerous studies[3] of hydrogen bonding in amino alcohols, compounds having the structures **1** and **2** have not been previously examined in this regard. We present here the results of a study of the infrared spectra of **1** and **2**, where *n* is 1, 2, and 3, and compare these with the available data on acyclic amino alcohols as listed in Table I.



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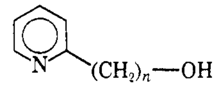

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Results and Discussion

The frequency shift of the O–H band, $\Delta\nu$, is an accepted measure of the strength of the hydrogen bond. Generally the strength of the hydrogen bond can be correlated with a polar factor and a steric factor. An estimate of the polar factor can be obtained from the $\Delta\nu$ of intermolecular hydrogen bonds in compounds without bulky groups which could give rise to steric hindrance. We see in Table I that the hydrogen bond CH_3OH–pyridine ($\Delta\nu$ = 275 cm^{-1}) is weaker than the hydrogen bond CH_3OH–diethylamine ($\Delta\nu$ = 430 cm^{-1}). Clearly pyridine is a weaker base and a poorer hydrogen acceptor than diethylamine. The diethylamino group forms a hydrogen bond which is 1.6 times stronger than the hydrogen bond having a pyridine moiety as the hydrogen acceptor.

Insofar as the polar effect is concerned, the $\Delta\nu$ of an intramolecular hydrogen bond should be the same as the $\Delta\nu$ of an intermolecular hydrogen bond involving the identical hydrogen donor and acceptor groups. However, intramolecular hydrogen-bonded systems show wide variations in $\Delta\nu$ which can be correlated with steric and geometric effects. In diols, 1,2 and 1,3 isomers exhibit weaker cyclic hydrogen bonding (smaller $\Delta\nu$) than the intermolecular hydrogen bonding between two alcohol molecules. On the other hand, 1,4 diols show an inverse characteristic; the intramolecular bond is stronger (larger $\Delta\nu$) than the intermolecular.[4] The data in Table I demonstrate that hydrogen bonding in cyclic and acyclic amino alcohols is closely parallel to what is observed for diols. Again, the 1,2 and 1,3 amino alcohols experience cyclic hydrogen bonding which is weaker than the intermolecular, but intramolecular hydrogen bonding in 1,4 amino alcohols is considerably stronger than that which occurs between two molecules possessing the same donor and acceptor functions. In attributing these differences in $\Delta\nu$ to geometric and steric effects we mean to consider both the length of the hydrogen bond and the O–H- - -N bond angle. It is unfortunate that these two parameters cannot be varied separately for we cannot tell which plays the larger role

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(3) (a) P. J. Kreuger and H. D. Mettee, *Can. J. Chem.*, **43**, 2970 (1965); (b) G. Hitte, E. Smissman, and R. West, *J. Am. Chem. Soc.*, **82**, 1207 (1960); (c) H. H. Friedman, *ibid.*, **83**, 2900 (1961).

(4) L. P. Kuhn, *ibid.*, **74**, 2492 (1952).

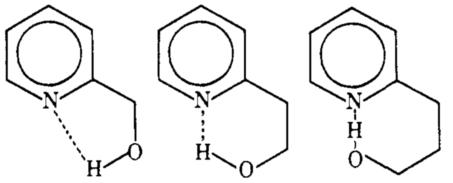
Table I. Frequency Shift of the OH Bands in Amino Alcohols

Amino alcohol	Compound	ν(OH)		$\Delta\nu$, cm^{-1}	Ref
		Free	Bonded		
1,4	4-Diethylaminobutanol-1			485	*a*
3,4	3-(2-Piperidyl)propanol-1	3642	3194	450	This work
1,4	3-(2-Pyridyl)propanol-1	3642	3285 3400	357	This work
1,3	3-Aminopropanol-1	3630	3395	235	3
1,3	3-Diethylaminopropanol-1			360	*a*
1,3	2-(2-Piperidyl)ethanol-1	3641	3334	307	This work
1,3	2-(2-Pyridyl)ethanol-1	3638	3435	203	This work
1,2	Aminoethanol	3640	3526	114	3
1,2	Diethylaminoethanol			170	*a*
1,2	Methylaminoethanol	3641	3515	126	3
1,2	3-Hydroxypiperidine		3539	100	*b*
1,2	2-Piperidylmethanol	3650	3520	130	This work
1,2	2-Pyridylmethanol	3642	3450	192	This work
Intermolecular	Methanol–pyridine			275	This work
Intermolecular	Methanol–diethylamine			430	This work

[a] N. Mori, E. Nakamura, and U. Tsuzuki, *Bull. Chem. Soc. Japan*, **40**, 2191 (1967). [b] R. Lyle, D. H. McMahon, W. E. Krueger, and C. K. Spicer, *J. Org. Chem.*, **31**, 4164 (1966).

in determining $\Delta\nu$. Although there is reason to believe that 180° is the preferred O–H- - -N angle in hydrogen-bonded molecules, there are many examples in the literature[5] of both inter- and intramolecular hydrogen bonds in which this angle is considerably less than 180°. We have calculated the O–H- - -N angle and the O- - -N distance for the three hydroxyalkylpyridines with the help of Dreiding models. The results are shown in Chart I.

Chart I



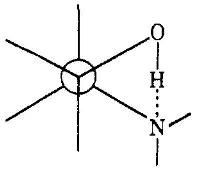
$\nu\sqrt{\ }$, cm^{-1}	192	203	357
O–H- - -N angle, deg	125	145	180
O- - -N distance, Å	2.6	2.2	1.6

Although there is a substantial difference in the O–H- - -N angle in the hydroxymethyl and the hydroxyethyl pyridines, the difference in $\Delta\nu$ is very small indicating in this case that the bond angle is probably not very important.

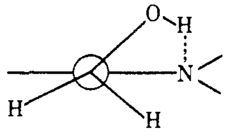
In the 1,4-amino alcohols, the 3-(2-piperidyl)propanol-1 has a larger $\Delta\nu$ than the corresponding pyridylpropanol because of the greater basicity of the piperidyl nitrogen as compared with the pyridyl nitrogen. The pyridylpropanol has two bonded OH bands, the stronger one being at 3285 cm^{-1} and the weaker one appearing as a shoulder at 3400 cm^{-1}. These probably correspond to two different conformations. The larger value, ($\Delta\nu$ = 485 cm^{-1}), of the acyclic diethylamino butanol as compared with the piperidylpropanol ($\Delta\nu$ = 450 cm^{-1}), can be attributed to the fact that the tertiary amino group is more basic than the secondary amino group.

In the 1,3-amino alcohols we note that the tertiary amino group in diethylaminopropanol-1 ($\Delta\nu$ = 360 cm^{-1}) is more basic than the primary amino group in aminopropanol-1 ($\Delta\nu$ = 245 cm^{-1}). The $\Delta\nu$ of the secondary amino alcohol 2-(2-piperidyl)ethanol-1 ($\Delta\nu$ = 310 cm^{-1}) is intermediate between the two. Correspondingly, the piperidylethanol is more basic than the pyridylethanol by a factor of 1.6, the same factor that is observed in the comparison of intermolecular hydrogen bond strengths.

The order of increasing $\Delta\nu$ in the series of 1,2-amino alcohols, aminoethanol (114 cm^{-1}), methylaminoethanol (125 cm^{-1}), and diethylaminoethanol (170 cm^{-1}) again correlates directly with the increase of basicity of amines in going from primary to tertiary amines. The $\Delta\nu$ values of the cyclic 3-hydroxypiperidine and 2-piperidylmethanol are comparable with those of the acyclic amino alcohols. An interesting and unexpected feature of the data presented in Table I is the fact that the $\Delta\nu$ of 2-pyridylmethanol (190 cm^{-1}) is larger than the $\Delta\nu$ of all of the other 1,2-amino alcohols, both cyclic and acyclic, despite the fact that the pyridyl moiety is a weaker base than either the piperidyl moiety or the acyclic amino groups. We attribute this large $\Delta\nu$ of the pyridylcarbinol directly to the fact that the O–H---N distance is shortest in this compound. This distance is largely determined by the dihedral angle formed by the C–O and C–N bonds. In the pyridyl carbinol this angle is formed by an sp^3 carbon and an sp^2 carbon. In all of the other 2,1-amino alcohols shown in Table I the dihedral angle is formed between two sp^3 carbon termini. In saturated acyclic compounds and in cyclohexane derivatives the dihedral angle is close to 60° and the barrier to rotation is several kilocalories per mole. The H---N distance when the dihedral angle is 60° is approximately 2.5 Å. On the other hand, the barrier to rotation of a bond formed by an sp^2 and an sp^3 carbon is extremely small and can be considered negligible for our purposes.[6] The attractive force of the hydrogen



2-piperidylcarbinol



2-pyridylcarbinol

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(5) See for full discussion of this point G. C. Pimentel and A. C. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(6) H. Rudolf and H. Seiler, *Z. Naturforsch.*, **20A**, 1682 (1965).

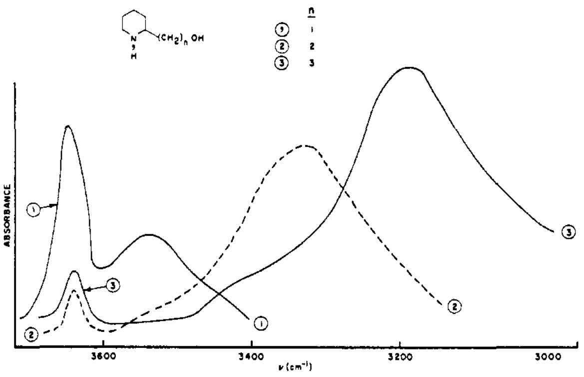


Figure 1.

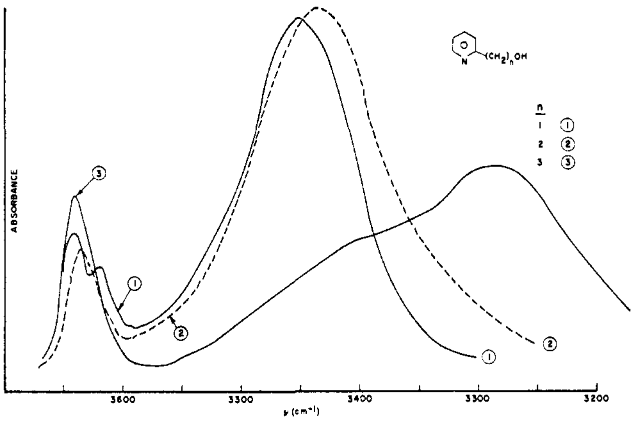
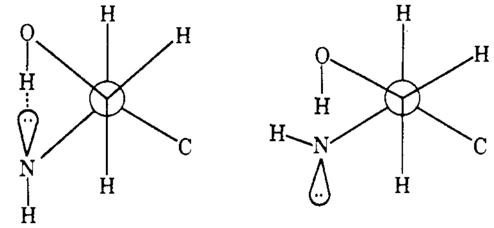


Figure 2.

bond causes this dihedral angle to be 0°, which results in an H---N distance of about 2 Å.

The O–H bands of dilute solutions of the hydroxyalkyl piperidines in carbon tetrachloride are given in Figure 1 and the O–H bands of the hydroxyalkyl pyridines are presented in Figure 2. It has been shown[7,8] that in both O–H---O and O–H---N intramolecularly bonded systems of acyclic compounds, the equilibrium constant for hydrogen bond formation decreases as the number of carbon atoms between donor and acceptor groups increases from two to four. The curves in Figure 2 indicate that the hydroxyalkyl pyridines follow the same pattern of behavior. It is also apparent that the bonded OH bands (lower frequency) are much stronger than the free OH bands, indicating that the equilibrium constants for the formation of the hydrogen-bonded conformations are much greater than one. In the hydroxyalkyl piperidine series exhibited in Figure 1, the 1,3- and 1,4-amino alcohols exist largely in hydrogen-bonded conformations but the 1,2-amino alcohol is anomalous in that it has a much stronger free OH band and a much weaker bonded OH band than all the others. The reluctance of 2-hydroxymethylpiperidine to form an intramolecular hydrogen bond can be rationalized as follows. We make the justifiable assumption that the 2-hydroxymethyl group takes an equatorial rather than an axial position. There are two possible conformations around the nitrogen atom. Either the hydrogen is axial and the unshared electron pair is equatorial, in which case there would be a substantial hydrogen bond formed because the O–H is well situated for bonding with an equatorial unshared electron pair. The second possibility is that the hydrogen is equatorial and the unshared electron pair is axial, in which case linkage between the two centers would be established only with difficulty. These two possibilities are illustrated in Chart II. Since this compound has a strong, free OH and a weak, bonded OH, the conformer population having the lone pair electrons at nitrogen in an axial position, unfavorable for hydrogen bond formation, must be the more abundant. There has been considerable controversy over the question of the conformation of piperidine and substituted piperidines. Thus, Lambert, *et al.*,[9] on the basis of nmr and infrared studies found that the lone pair is predominantly equatorial. Booth,[10] using nmr measurements only, came to the conclusion that there were approximately equal amounts of the two conformers. From data obtained through microwave spectroscopy Buckley, *et al.*,[11] deduced that the conformer with lone pair equatorial constituted 40% of the mixture. Finally, on the basis of semiempirical calculations, Allinger, *et al.*,[12] suggested that the equatorial lone pair is favored by 0.6 kcal/mol.

Chart II



hydrogen, axial
electron pair, equatorial
favorable for H bond

hydrogen, equatorial
electron pair, axial
unfavorable for H bond

Because of the small concentration of free OH groups, their bands as they appear in Figures 1 and 2 are often too weak for careful examination. We have therefore obtained the free OH bands in more concentrated solutions and these are shown in Figures 3 and 4. The free OH band of hydroxymethylpiperidine has a shoulder at the low-frequency side corresponding to a second band at about 3625 cm^{-1}. A similar shoulder at about 3625 cm^{-1} has been observed[1] in the OH band of ethanolamine and of propanolamine. It has been suggested that this band is due to an O–H group whose oxygen is acting as a hydrogen acceptor for an amino group, N–H---O–H. A much stronger shoulder is also found at the low-frequency side of the free OH band in the hydroxyalkylpyridines. Since pyridine has no N–H group, this absorption band at 3620 cm^{-1} must be due to another interaction. An attractive explanation relates this band to an intramolecular interaction between the O–H group and the π electrons of the pyridine ring. This is quite analogous to the shoulder at 3618 cm^{-1} observed in the O–H band of benzyl alcohol which has been attributed to the interaction of the O–H with the π electrons of the benzene ring.[13]

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(7) L. Kuhn and R. Wires, *J. Am. Chem. Soc.*, **81**, 2167 (1964).

(8) See footnote *a*, Table I.

(9) J. Lambert, R. Keske, R. Carhart, and A. Jovanovich, *J. Am. Chem. Soc.*, **89**, 3761 (1967).

(10) H. Booth, *Chem. Commun.*, 802 (1968).

(11) P. Buckley, C. Costain, and J. Parkin, *ibid.*, 668 (1968).

(12) N. Allinger, J. Hirsch, and M. Miller, *Tetrahedron Letters*, 3729 (1967).

(13) (a) M. Oki and I. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 950 (1959); (b) P. Schleyer, D. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

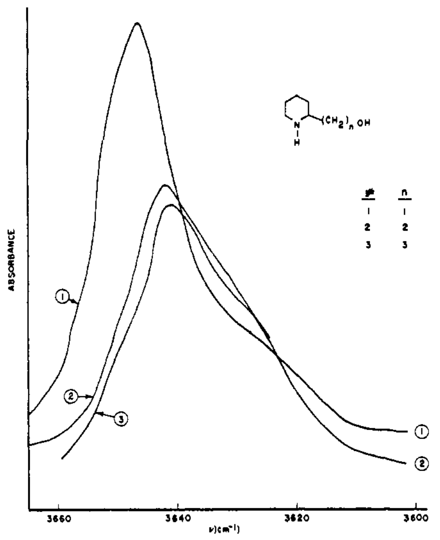

Figure 3.

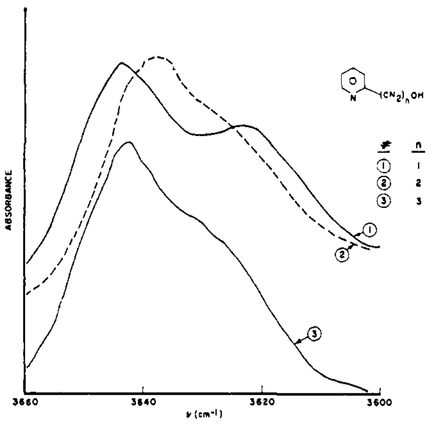

Figure 4.

Experimental Section

Preparation of Materials. The hydroxyalkylpyridines were obtained from the Aldrich Chemical Company. They were first purified by distillation and reduced by a procedure analogous to that described in the literature.[14] A solution of 370 g (3.0 mol) of the appropriate pyridine in distilled water (300–400 ml) was hydrogenated over 60 g of 5% palladium on charcoal at 3000 psi and 130–135°. Hydrogen uptake attained theoretical in all three cases within 6 hr. After removal of the catalyst the solution was saturated with potassium carbonate. The organic layer which separated was distilled under vacuum to afford about 300 g (*ca.* 70–80%) of the corresponding hydroxyalkylpiperidine. The boiling points of all the saturated products corresponded closely with those reported in the literature.[14]

The hydroxyalkylpyridines were freshly distilled before use. They had the following boiling points: hydroxymethylpyridine, 109° (14 torr); 2-hydroxyethylpyridine, 120° (11 torr); 3-hydroxypropyl pyridine, 140° (11 torr).

The hydroxymethylpyridine and the hydroxymethylpiperidine react with carbon tetrachloride and so it is necessary to use fresh solutions to get a meaningful OH band. The carbon tetrachloride was stored over molecular sieves before use.

Spectroscopic Measurements. The spectra were obtained with a Beckman IR-12 grating spectrophotometer continuously purged with dry air. The operating conditions were period −2, slit 0.5 mm at 3600 cm^{-1}, speed 0.5 cm^{-1}/sec. The spectra were taken with 1- and 2-cm infrared transparent quartz cells.

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(14) E. R. Davagnmo, R. R. Chauvette, W. N. Cannon, and E. C. Kornfeld, *J. Am. Chem. Soc.*, **82**, 2604 (1960).