

Hydrogen Bonding Spectra of Pyridinium Hydrochlorides in Dimethyl Sulfoxide Solution and as Mulls

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Abstract: Infrared spectra stretching frequencies in the 2000–3500-cm⁻¹ region are reported for the hydrochlorides of 24 pyridines and several other amines, both as mulls in hexachlorobutadiene and as 0.1 M solutions in dimethyl sulfoxide. The results are compared with each other and with other criteria of hydrogen bonding. The 2,6-di-*tert*-butylpyridinium salt is a bichloride (DTBPH⁺ ClHCl⁻). It gives no evidence of hydrogen bonding in the mull but shows clear evidence of hydrogen bonding in Me₂SO solution.

Introduction

Substituted pyridines provide a nearly incomparable series of bases for studying steric, electronic, and solvation effects. We are engaged in examining the response of pyridines and pyridinium ions to a variety of interactions which develop positive charge on the pyridine nucleus. Of particular interest is the interplay between internal charge delocalization to substituent groups and dispersion of charge to the medium.¹⁻³ We proposed recently³ that the difference between pyridine protonation equilibria in water and in the gas phase is determined largely by hydrogen bonding from the pyridinium ions to water and from water to the neutral pyridines. Although it is possible to study hydrogen bonding of water to pyridines directly,^{4,5} we can see no way to examine the Py-H⁺...OH₂ hydrogen bonding without complications due to proton transfer to water from the ion, or without interference by hydrogen bonding from water to the counteranion An⁻...HOH, or from water itself.

Dimethyl sulfoxide (Me₂SO) is an excellent hydrogen bond acceptor⁶ but should be too weak as a donor to interact with chloride ions from pyridinium chlorides. It is also too weak a Brønsted base⁶ to make proton transfer a problem during a study of pyridinium salts in this medium. The present report describes our investigation of a series of pyridinium chlorides by infrared spectroscopy both as 0.1 M solutions in Me₂SO and as mulls in hexachlorobutadiene (HCB). Comparison will be made with other spectral and hydrogen-bonding studies of these systems.

Experimental Section

Pyridinium chlorides were prepared by passing anhydrous HCl gas through an ethereal solution of the pyridine. The resulting precipitates were recrystallized from acetone-methanol mixtures varying as needed over a range from 99:1 to 90:10. Elemental microanalyses of pyridinium chlorides by Galbraith Laboratories, Inc., were generally consistent (within the usual ±0.4 error range) with the formation of 1:1 salts. However, analysis of the 2,6-di-*tert*-butylpyridine hydrochloride indicated formation of a 1:2 salt (PyH⁺Cl⁻HCl) consistent with the observation of Brown and Kanner.⁷ This was also demonstrated by titrating a solution of the salt in 50:50 water-methanol with NaOH solution. Two equivalents of NaOH was used to neutralize 1 equiv of the salt.

Repeated attempts to make a hydrochloride from pentachloropyridine all failed.

Infrared spectra for the salts were recorded on Perkin-Elmer 247 and 21 spectrometers with sodium chloride cells. Mulls were prepared in hexachlorobutadiene, a medium which is transparent across the range of hydrogen bonding frequencies. Spectra for all the salts were also recorded as 0.1 M solutions in Me₂SO. Since most of the salts are hygroscopic, the mulls and solutions were prepared in an argon-filled drybox (Kewaunee Scientific Equipment).

Dimethyl sulfoxide (Aldrich) was stirred for 12 h under vacuum with 20 mL/L of a 1.6 M *n*-butyllithium solution (in hexane), an increment of 10 mL/L of *n*-butyllithium solution was then added, and the Me₂SO was doubly distilled at 1 mm pressure. The distilled Me₂SO was then stored under argon in a taped solvent bottle fitted with an automatically zeroing buret. A positive pressure of argon was constantly maintained in the system. Water content was measured by means of a Karl-Fischer automatic titrator and was maintained at less than 50 ppm of water.

Results

Most of the pyridinium chlorides reported here have not been described previously. Accordingly, we have listed melting points along with spectral data in Table I. Microanalytical data were unsatisfactory for the following substituted pyridinium chlorides: 2-fluoro (Anal. Calcd for C₅H₅NCIF: C, 44.97; H, 3.78; N, 10.49. Found: C, 44.27; H, 4.76; N, 10.12). 3-aldehyde (Anal. Calcd for C₆H₆ONCl: C, 50.20; H, 4.21; N, 9.76. Found: C, 47.25; H, 4.56; N, 9.25). 3-sulfonic acid (Anal. Calcd for C₅H₆NCISO₃: C, 30.70; H, 3.09; N, 7.16. Found: C, 37.69; H, 3.14; N, 8.60).

Our observations on the infrared spectra of the few salts recorded previously by other workers agreed reasonably well with theirs; see Table I. However, the breadth and lack of definition of the hydrogen bonded peaks for most of the compounds puts a serious limit on how precisely the points of maximum absorbance may be stated. Since the choice of a single value along the manifold for ν_{N⁺-H...Cl⁻} absorption was often subjective and arbitrary we doubt if the listed values should be considered as significant within less than ±50 cm⁻¹ even though they are reproducible to ±5 cm⁻¹.

Again the behavior of 2,6-di-*tert*-butylpyridinium salt was exceptional since it displayed a band lying at a much higher frequency than the others. This was very sharply defined with no evidence of hydrogen bonding in the mull. However, in Me₂SO a broad hydrogen bonded peak was observed. If we recall that this salt is a bichloride (DTBPH⁺ ClHCl⁻) instead of the normal hydrochloride (PyH⁺Cl⁻) used for the other salts, the behavior may be rationalized. In the mull only the biochloride ion is available as a hydrogen bond acceptor from the sterically hindered di-*tert*-butylpyridinium cation. One would expect the ClHCl⁻ ion to be a much weaker acceptor than Cl⁻ since in the former case the chloride ion can be considered as already strongly hydrogen bonded from HCl. In Me₂SO the solvent serves as a very good hydrogen bond acceptor, whereas in HCB neither the solvent nor the counterion provides this role.

Partial confirmation of this interpretation is provided by the fact that the salts of DTBPH⁺ with weak acceptor anions, FHF⁻ and I⁻, show no hydrogen bonding in HCB mulls while

Table I. N-H Stretching Frequencies and Melting Points for Amine Hydrochlorides

	Salts	Mp, °C	$\nu_{\text{N-H...Cl}}$, cm^{-1}	
			Hexachloro-1,3-butadiene (mull)	Me ₂ SO (soln) concn 0.1 M
Substituted Pyridines				
1.	2,6-(C(CH ₃) ₃) ₂ (bichloride)	141-145 (145-146) ^a	3360	3280, 2215, 1950
2.	2,4,6-(CH ₃) ₃	Subl ~210-272	2452	2300, 1950
3.	2,6-(CH ₃) ₂	Subl and dec ~195-240	2439 (2450) ^b	2300, 1955
4.	3,5-(CH ₃) ₂	Subl ~190-231	2439	2300, 2050, 1960
5.	4-CH ₃	161.0-165	2430	2285, 1960
6.	4-C(CH ₃) ₃	151.7-154.8	2439	2275, 1965
7.	4-OCH ₃	152.7-154.8 (subl)	2445	2300, 1955
8.	H	143.5-146.0 (140-142, ^c 144, ^d 145 ^e)	2443 (2450, ^f 2439 ^c 2450, ^g 2400 ^h)	2275, 1950
9.	4-Cl	Subl and dec >181	2353	2250, 1945
10.	4-Br	Dec >~199	2337	2250, 1955
11.	4-CN	Subl 199.5-206.8	2299, 2000	2210, 1950
12.	3,5-Cl ₂	122.8-139.3 (subl)	2208, 2046, 1916	2250, 1945
13.	3-SO ₃ H	Dec >300	2782	2250, 1955
14.	3-OH	107.8-110.4	2745 (2725) ⁱ	2550, 2300, 1960
15.	3-CHO	Subl and dec 143.4-176.5	2465	2250, 1950
16.	3-CH ₃	88.7-93.9	2429	2280, 1955
17.	3-Cl	136.2-143.4 (subl)	2330	2200, 1940
18.	3-Br	~140-165 (subl)	2310	2215, 1945
19.	3-CN	~160-176 (subl)	2295, 1950	2210, 1945
20.	2-CH ₃	77.0-88.7	2425	2290, 1960
21.	2-Cl	~99.0-109.5 (subl and dec)	2300, 1900	
22.	2-Br	(198-200) ^j	(2273) ^j	
23.	2-F	132.0-143.4	2315	
24.	2-CN	114.4-132.0 (subl and dec)	2193, 1935	2210, 1945
Other Amines				
25.	8-Hydroxy-quinolinol	217-227 (subl and dec)	2740	2565, 2310, 1960
26.	Quinoline	88.5-124.0	2545, 2310	2255, 1950
27.	Trimethyl-amine	>275 (subl)	2625, 2450 (2600, ^k 2670 ^l)	2550, 2300
28.	Triethyl-amine	232.5-257.7 (subl)	2595, 2475 (2600, ^k 2610, ^l 2620 ^h)	2550, 2300
29.	Quinuclidine	>300 (subl)	2555	2500, 2420, 2310
30.	2,2-Bipyridine	~179-207	2328	2250, 1945
31.	1,8-Bis-(dimethyl-amino)-naphthalene			2200, 2060, 1960

^a C. McGary, Jr., Ph.D. Thesis, Purdue University, 1955. ^b Reference 16. ^c Reference 9. ^d C. H. Mathew and F. R. Gilson, *Can. J. Chem.*, **48**, 2625 (1970). ^e See ref 9. ^f Reference 8. ^g Reference 10. ^h Reference 11. ⁱ Reference 12. ^j Reference 16. ^k Reference 13. ^l Reference 14.

the monobromide salt shows a modest development of the broadened, diffuse hydrogen bond manifold.

Discussion

Several authors⁸⁻¹⁷ have discussed the vibrational spectra of pyridinium salts; of these the most recent is Odinokov et al.,¹⁵ who cite much of the earlier literature. Cook's thorough discussion⁹ provides a detailed analysis of the important bands in the spectra of salts obtained from pyridine and ten protonic acids and also the corresponding deuterated salts. All prior investigators accept, as do we, the assignment of the broad manifold in the 3000-2000-cm⁻¹ region to the ⁺N-H...X⁻ hydrogen bond from the pyridinium ion to the counteranion.

Our study, in contrast to the others, employs a series of substituted pyridinium cations with a single anion and is focused entirely on the hydrogen bonding region. Our discussion of results will therefore be restricted to matters which are relevant to this question.

It is obvious from Table I that only a small and nearly constant decrease in the hydrogen bonding frequency results from transfer of the salt from the mull to the crystalline state to solution in Me₂SO. Previous studies of the pyridinium salts were mostly performed with mulls (usually Nujol or Fluorolube), the results being quite similar to ours. Chenon and Sandorfy¹¹ observed similar small effects for the low-frequency hydrogen bonds of some amine hydrochlorides on going from mulls to water. We

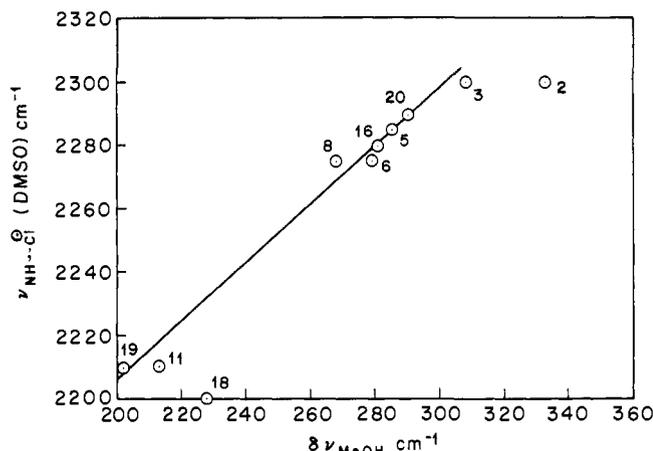


Figure 1. Correlation of $N^+-H\cdots Cl^-$ frequencies for pyridinium ions as hydrogen bond donors in Me_2SO vs. $N\cdots HOCH_3$ for corresponding pyridines as hydrogen bond acceptors.

know of no previous study of this kind in a dipolar aprotic solvent and call attention to the fact that in Me_2SO two peaks were found both of which are more clearly defined than the broad envelopes seen in the mulls. The high-frequency band in solution is close to that in the mull and responds in a similar way to substitution on the pyridinium nucleus. We assign it to the $^+N-H\cdots Cl^-$ stretching vibration.

The lower frequency band is nearly constant and we are unable to assign it unequivocally. Since it appears as a result of transfer of the salt to Me_2SO we have several suggestions for its origin. First is the possibility that we are observing the $NH^+\cdots Me_2SO$ hydrogen bond. In view of the high concentration of salt (0.1 M) and the high degree of association of hydrogen bonded ion pairs this would seem unlikely were it not for the great ability of Me_2SO to accept hydrogen bonds. Chenon and Sandorfy¹¹ studied the IR spectra of amine hydrochlorides as mulls and as aqueous solutions and they concluded that water was the hydrogen bond acceptor in the latter case, although they could observe only the lower frequency bands. The work of Kolthoff's group in fact shows that Me_2SO may be superior to water for dissociating some ammonium salts.¹⁸ It would thus seem possible to observe $N^+-H\cdots Me_2SO$ bonds in these solutions.

It is also possible that the bands in the 2500-cm^{-1} region are due to hydrogen bonding from the methyl groups of Me_2SO to the chloride ion. Finally, it is possible that they are the result of an unassignable medium effect on some of the many C-H vibrations in the system, or on the $N^+-H\cdots Cl^-$ bond.¹⁹

An interesting comparison can be made between the ability of the pyridinium ions to donate a hydrogen bond to a common acceptor and that of the corresponding pyridine bases to accept a hydrogen bond from a common donor. Joris and Schleyer²⁰ compared the effect of a variety of pyridines on the OH stretching frequency of methanol. Figure 1 shows a generally good correlation between $\nu_{N^+-H\cdots Cl^-}$ in Me_2SO and $\nu_{MeOH-Py}$ for ten pyridines and their ions. Although the systems are not directly comparable, we note the much greater effect of substituents on the donor ability of the charged pyridinium ions compared to their effect on the neutral acceptors. The almost fivefold difference in sensitivity corresponds to our previous proposal.³

Finally, we note the good correlation between $\nu_{N^+-H\cdots Cl^-}$ and the $pK_{a,s}$ of the corresponding pyridines in aqueous solution (see Figure 2). Since most other acid-base properties of the pyridines are linear functions of their $pK_{a,s}$ this is not surprising.

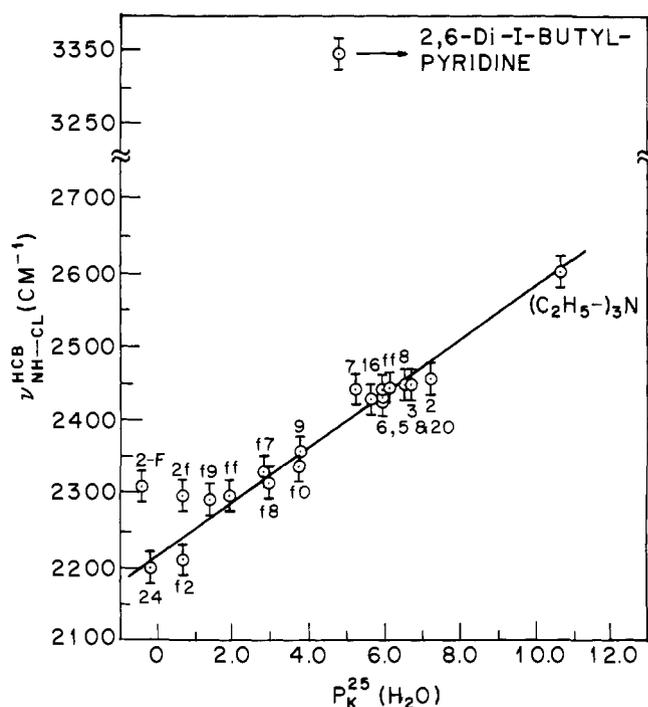


Figure 2. Correlation of $NH^+\cdots Cl^-$ frequencies of pyridinium chlorides as mulls in hexachlorobutadiene vs. $pK_{a,s}$ of corresponding pyridinium ions in water at $25^\circ C$ (from tabulation in E. M. Arnett and G. Scorrano, *Adv. Phys. Org. Chem.*, **13**, 83 (1976), and ref 7).

Deviations from the correlation lines are seen for 2,6-di-*tert*-butylpyridine in Figure 2 and for 2,4,6-trimethylpyridine in Figure 1. Steric hindrance is readily proposed to explain both cases. We shall consider this matter in some detail in a later article.

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