

HYDROGEN-BONDED SPECIES OF SUBSTITUTED PYRIDINIUM SALTS IN NONAQUEOUS MEDIA

**A Thesis Submitted
In Fulfilment of the Requirement for the Degree of
DOCTOR OF PHILOSOPHY**

**By
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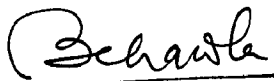
**to the
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C_E_R_T_I_F_I_C_A_T_E

This is to certify that the thesis entitled
" HYDROGEN-BONDED SPECIES OF SUBSTITUTED PYRIDINIUM SALTS IN
NONAQUEOUS MEDIA" being submitted by Mr. Sharad Kumar Mehta
to the Indian Institute of Technology, Delhi, for the award
of DOCTOR OF PHILOSOPHY in Chemistry, is a record of bonafide
research work carried out by him.

Mr. Mehta has worked under my guidance and
supervision and has fulfilled the requirements for the
submission of his thesis which to my knowledge has reached
the requisite standard.

The results contained in this dissertation have
not been submitted, in part or in full, to any other university
or institute for the award of any degree or diploma.



(B. Chawla)

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November, 1982

A C K N O W L E D G E M E N T

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A _ B _ S _ T _ R _ A _ C _ T

The thesis entitled "Hydrogen-Bonded Species of Substituted Pyridinium Salts in Nonaqueous Media" deals with the systematic spectroscopic, thermodynamic and other related studies which are sensitive to the structural interactions. These studies have been used to deduce the effects of the salt concentration and the nature of organic solvent employed on the behaviour of H-bonded species of these salts. The work described in the thesis also attempts to correlate the H-bond donating ability of pyridinium cations with their aqueous acidities (pK_a 's).

Chapter I gives a brief account of present status of the knowledge about the various equilibria existing between the various species of salts of acids and bases of varying strength in a number of organic solvents.

Chapter II describes the conductance measurements of H-bonded salts of substituted pyridines and halogenoacetic acids in various nonaqueous solvents over a wide range of concentration at a constant temperature. Following observations from the conductance measurements have been made:

- i. the equivalent conductances of the salts
show ring substitution and anion dependence,
- ii. the concentration at which the formation of

higher ionic aggregates (triple ions) starts is characteristic of the nature of ring substitution,

- iii. all salts show similar conductance behaviour, and
- iv. different ionic species of H-bonded salts are present in solution depending upon nonaqueous media.

Chapter III deals with the thermometric titrations of a series of substituted pyridines with a number of halogenoacetic acids in various nonaqueous solvents at 25°C. In order to understand the concentration effect on heats of reaction of these systems, the measurements on systems of three pyridines with trifluoroacetic acid in chloroform are carried out over entire possible concentration range. The results have been used to discuss the energetics of formation of various species in solutions. It has been observed that the formation of H-bonded ion-pairs is energetically favoured if the H-donating ability of pyridinium cations is decreased. The observed decreasing order in ΔH for the reaction, $B + HA \rightarrow B^+H-\bar{A}$, of substituted pyridines is as follows:

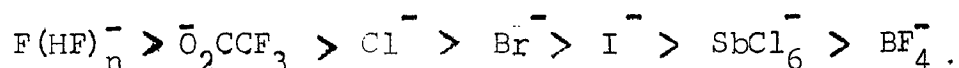
2,4,6-trimethylpyridine > 2,6-dimethylpyridine >
4-methylpyridine > pyridine > 4-cyanopyridine etc.

The most interesting observation made from calorimetric results is that the association of H-bonded ion-pairs to higher aggregates is an entropy driven process.

Chapter IV deals with the infrared spectroscopic study on the hydrogen-bonded salts of substituted pyridines and halogenoacetic acids, both in solid (as hexachloro-butadiene mull) and in solution (chloroform). The infrared spectra were recorded on Unicam SP 1200 Infrared Grating spectrometer. Since $\nu_{\text{N}^+\text{H} \cdots \bar{\text{A}}}$ absorption is sensitive to the extent of H-bonding present, the shift of $\nu_{\text{N}^+\text{H} \cdots \bar{\text{A}}}$ band has been used to examine the response of 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 of substituent groups and dispersion of charge to the counter ion or to the medium. The peak positions of ionized and un-ionized carboxylic group have also been measured and discussed in terms of presence of various H-bonded species in solutions of these salts.

Chapter V deals with the proton and carbon-13 magnetic resonance data on H-bonded ion-pairs of salts of substituted pyridines and various protonic acids in nonaqueous media. The measurements of N-H proton shift for pyridinium trifluoroacetate have been made over a wide range of salt concentration in D-chloroform. The increasing trend of N-H shift with salt concentration has been explained in terms of

association of H-bonded ion-pairs to higher aggregates. Similar observation has also been made from the results of para carbon shifts of pyridinium cation at higher salt concentration in chloroform. In order to explore the possibility of using C-13 magnetic resonance spectroscopy for understanding the behaviour of H-bonded ion-pairs in solution, the para carbon shifts of salts of pyridine with various acids have been recorded in chloroform, acetonitrile and trifluoroacetic acid. The C-13 data suggests that the strength of H-bonding of pyridinium cation with various anions decreases in the following order:



An attempt has also been made to compare the of H-bonding strength of pyridinium cation with 2,6-di-tert-butylpyridinium cation to halide anions in solution. The data described in this Chapter clearly suggest that C-13 magnetic resonance technique can be very useful in understanding, qualitatively as well as quantitatively, the behaviour of H-bonded ion-pairs in solution.

Care has been taken to give proper credit for investigations done by other workers. The author would like to apologize for any omission which might have occurred by oversight or error in judgement.

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