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## N. Q. R. STUDIES ON HYDROGEN BONDING IN AMINE HYDROHALIDES

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Nuclear quadrupole resonance spectroscopy has been used previously to detect the existence of hydrogen bonds in several compounds by measuring the resonance frequency of the nucleus of certain atoms involved in predominantly covalent bonding, such as  $^{14}\text{N}$  in ammonia (1) and ammonia hemihydrate (2),  $^{35}\text{Cl}$  in chloroacetic acid-pyridine complexes (3) and salts of the bichloride ion  $\text{HCl}_2^-$  (4).

In the present work it is shown that formation of such bonds originates the appearance of nuclear quadrupole resonance frequencies in the range 10-40 MHz for bromide and iodide ions involved in predominantly ionic interactions with alkylammonium groups. This is the range where absorption frequencies for  $^{79}\text{Br}$  and  $^{127}\text{I}$  in  $\text{CdBr}_2$  and  $\text{CdI}_2$  are found (5) indicating a similarly polarised electron cloud of the halogen ions in this and the above mentioned compounds.

The amine hydrohalides used were prepared from the corresponding amines and hydrobromide or hydroiodide acids in slight excess. The products were recrystallized once or more times — when necessary — from water-ethanol mixtures.

The resonance frequencies (Table 1) were firstly detected on a WILKS N.Q.R. 1A spectrometer and measured at 33°C in a DECCA-RADAR Spectrometer using 2-3 g samples in thin walled glass tubes. The precision of the measurements is of the order of 0.1 %.

The values of the resonance frequencies suggest that the spherical symmetry of the electron cloud of the halide ions is distorted to some extent since the effect is so pronounced that it cannot be originated only by second order lattice effects in a 100 % ionic structure. These findings thus support the formation of hydrogen bonds in amine hydrohalides which was postulated in several X-ray and IR structural studies (6). The very large values of the asymmetry parameter  $\eta$  for ethylammonium and diethylammonium iodides also agree with the postulated existence of multiple hydrogen bonding in these compounds (7), whereas the negligible  $\eta$  values for the methyl, trimethyl and propylammonium iodides are clearly coherent with axial symmetry in the  $\text{N-H} \cdots \text{X}$  bond (8).

The percent of ionic character of the  $\text{H} \cdots \text{X}$  bond calculated using a simplified version of TOWNES and DAILEY's theory (9) is higher for

Table I

*N. Q. R. frequencies of  $^{79}\text{Br}$  and  $^{127}\text{I}$  in alkylammonium bromides and iodides at 33°C (MHz)*

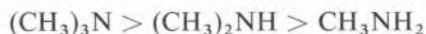
Amine	$^{79}\text{Br}$	$^{127}\text{I}$	Asymmetry parameter ( $^{127}\text{I}$ )
Methylamine	12.88 (S)	13.30 (S); 26.58 (S)	0.04
Dimethylamine	13.71 (S)	no signals detected	
Trimethylamine	18.40(M)	18.67 (M); 37.08 (M)	0.05
Ethylamine	18.43 (S)	20.41 (M); 32.12 (M)	0.48
Diethylamine	16.48(M)	20.03 (M); 31.80 (M)	0.47
Triethylamine	14.43(W)	no signals detected	
Propylamine	12.01(M)	12.00 (W); 23.96 (W)	0.06

Data obtained on a Decca-Radar Spectrometer with 2/3 g samples and reliable to 0.01 MHz.

S (strong); M (medium); W (weak).

the bromides than for the corresponding iodide compounds, in agreement with the higher polarizability of the  $\text{I}^-$  ion compared with that of the  $\text{Br}^-$  ion. In both cases, the fraction of ionic character of the  $\text{H} \cdots \text{X}$  bond is higher than 95 %.

A rather curious result is that of opposite trends observed in the resonance frequencies of methyl and ethyl substituted amines (see Table); if one accepts the current idea of positive inductive effect of methyl groups, in agreement with the order of decreasing gas phase basicities of the substituted amines (10)



one would expect an increase on the percent of the electrostatic component of the hydrogen bond  $-\text{N}^+-\text{H} \cdots \text{X}^-$  with the number of substituent methyl groups. The inverse is found for the series methylammonium, dimethylammonium and trimethylammonium bromides and iodides and this implies either that the electronic inductive effect of the methyl groups is not positive as usually assumed or that steric effects are predominant in the solids.

The last hypothesis seems unlikely in view of the opposite trend observed for the ethyl substituted amines and of a probable trend for propyl substituted amines similar to that of the corresponding methylamines.

Although it is not possible to offer definite conclusions it is likely that an explanation based on recent views on the inductive effect of methyl groups, — which seems to be negative rather than positive (11) — and on the alternation of induced charges in hydrocarbon chains (12), may rationalize the apparently conflicting results obtained in the present work.

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