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NUCLEAR QUADRUPOLE RESONANCE STUDY OF ANILINIUM BROMIDES AND IODIDES

Br^{79} (and Br^{81}) and I^{127} nuclear quadrupole resonance frequencies (ν) were detected for the anilinium salts $YC_6H_4NH_3^+X^-$ ($Y = o-, m-, p-, CH_3$; $o-, m-, p-NO_2$; $p-CF_3$. $X = Br$ and/or I). The asymmetry parameter η (for $X = I$) and the fraction of ionic character of the halide bond were estimated for these compounds and the results demonstrate a polarisation of the halide electron cloud which was interpreted by considering the conceivable formation of $NH \cdots X^-$ hydrogen bonds with predominant electrostatic character.

Linear dependences of ν upon Hammett's σ constants for the para and the meta Y substituent were observed and are object of discussion.

I — INTRODUCTION

Hydrogen-bonding plays an important role in various chemical and biological systems but, although it has been widely studied, the examples selected usually involve the most commonly accepted hydrogen bond former atoms and groups. The halogens have received comparatively less attention, to the exception of their hydric acids, notably HF, perhaps for lack of suitable experimental techniques. Indeed, a wide variety of methods has been applied to the detection of this type of bonding, namely based on the measurement of vapour pressure, density, molecular weight, molar volume, dielectric constant, thermal and electric conductivity, refractive index, etc., but they are all indirect and hydrogen bonding is postulated on the basis of some deviation from expected «normal» physical properties. More direct evidence for formation of this type of bonds has been achieved by X-ray analysis and spectroscopic techniques (infrared, Raman and nuclear magnetic resonance) [1]. In the last decade, nuclear quadrupole resonance (N.Q.R.) spectroscopy (which has a more specific character than those spectroscopic methods and provides a quantitative interpretation of the results) has also been applied to the detection of this type of bonding, but only a few examples have been reported, e.g., on studies of ammonia and ammonium hydrate [2], guanidinium ion [3], hexamethylenetetramine and its complexes [4], hexamethylenetetramine triphenol [5], 2,5-dichlorophenol [6], trichloroacetic acid [7], carboxylic acids and alcohols [8], systems involving carbonyl groups [9], HCl_2^- salts [10], adducts of chloroacetic acids with pyridine [11], adducts of 2,6-dichloro-4-nitrophenol with amine [12] and systems with nonlinear hydrogen (deuterium) bonds [13].

Fraústo da Silva and Vilas-Boas have also reported [14] the results obtained with a variety of alkylammonium bromides and iodides, $R_3NH^+X^-$ ($R_3 = Me_3, Me_2H, MeH_2, Et_3, Et_2H, EtH_2$

or PrH_2 ; $X=\text{Br}$ or I) which were interpreted [14] on the basis of formation of hydrogen bonding of the type $\text{N}^+\text{H} \dots \text{X}^-$, with predominant electrostatic character; the effects of temperature and deuteration on the hydrogen bonds of some of these alkylammonium halides were also studied by N.Q.R. by other authors [15].

The present work extends the N.Q.R. study to the related anilinium bromides and iodides of the type $\text{YC}_6\text{H}_4\text{NH}_3^+\text{X}^-$ ($\text{Y} = \text{o-,m-p-Me}$; o-,m-,p-NO_2 ; p-CF_3 ; p-Cl) and $\text{C}_6\text{H}_5\text{NMeH}_2^+\text{X}^-$ which afford further information on these less studied hydrogen bond formers. The corresponding chloride salts were not studied since their N.Q.R. frequencies are lower than the measuring range of the spectrometer used. The investigation by N.Q.R. of the hydrogen bonding, the ^1H - ^2D isotope effect and the order-disorder phase transition in the anilinium bromides $\text{C}_6\text{H}_5\text{NH}_3^+\text{Br}^-$, $\text{C}_6\text{H}_5\text{ND}_3^+\text{Br}^-$ and $\text{C}_6\text{D}_5\text{NH}_3^+\text{Br}^-$ has been reported by other authors [16].

II—THEORETICAL BASIS OF THE METHOD

Nuclei with spin equal or greater than one present a non-spherical charge distribution which can be interpreted in terms of a nuclear quadrupole moment given by eQ where e is the elementary charge and Q is the electric quadrupole which measures the deviation from the spherical symmetry.

If such a nucleus lies within a non-homogeneous (non-spherical) electric field (due to the electrons which are in its vicinity and which belong to the same atom or which are involved in the bonding to this atom), an interaction occurs between its nuclear quadrupole moment and the electric field gradient and the energy of this nuclear quadrupole coupling is given by

$$E_Q = eQq_{zz} \frac{3m_I^2 - I(I+1)}{4I(2I-1)} \quad (1)$$

In this expression eQ is the quadrupole moment, eQq_{zz} is the nuclear quadrupole cou-

pling constant, I is the nuclear spin, m_I is the magnetic nuclear quantum number and q_{zz} is the maximum electric field gradient given by

$$q_{zz} = \frac{\partial^2 V}{\partial z^2} \quad (2)$$

where V is the electrostatic potential due to the charges in the vicinity of the nucleus and z is the direction of the maximum gradient. Equation [1] is valid only when the electric field gradient has axial symmetry, *i.e.*, when q_{xx} equals q_{yy} and the following relationship is obeyed:

$$q_{xx} = \frac{\partial^2 V}{\partial x^2} = q_{yy} = \frac{\partial^2 V}{\partial y^2} \quad (3)$$

In other cases, an asymmetry parameter, η , may be defined as

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} \quad (4)$$

and it has to be considered in the expression which allows to estimate E_Q , which is then more complex than equation (1) [17].

Equation (1) shows that the nuclear energy levels are doubly degenerate (E_Q depends on m_I^2 and, hence, on $|m_I|$) and, according to the selection rule $\Delta m_I = \pm 1$, the frequency of the allowed transitions is given by

$$\nu_r = E'_Q - E''_Q = \frac{3eQ q_{zz}}{4hI(2I-1)} (2M_I - 1) \quad (5)$$

where M_I is the highest value of m_I corresponding to each energy level (m_I may have a total of $2I+1$ possible values: $-I, -I+1, \dots, I-1, I$).

Since Br^{79} (and Br^{81}) and I^{127} nuclei have $I = 3/2$ and $5/2$, respectively, only one transition ($\pm 3/2 \leftarrow \pm 1/2$) and two transitions ($\pm 5/2 \leftarrow \pm 3/2$ and $\pm 3/2 \leftarrow \pm 1/2$), respectively, are expected to be observed and

their frequencies are given by the following equations:

For $I = 3/2$ (Br^{79} or Br^{81}):

$$\nu_r = \frac{eQ q_{zz}}{2h} (1 + \eta^2/3)^{1/2} \quad (6)$$

For $I = 5/2$ (I^{127}):

$$\nu_1 = \frac{3eQ q_{zz}}{20h} (1 + 1.092 \eta^2 - 0.634 \eta^4) \quad (7)$$

$$\nu_2 = \frac{3eQ q_{zz}}{10h} (1 - 0.203 \eta^2 + 0.162 \eta^4) \quad (8)$$

In the latter case ($I = 5/2$), since two resonance frequencies are observed, it is possible to estimate both the nuclear quadrupole coupling constant ($eQ q_{zz}$) and the η parameter of the electric field gradient.

Moreover, from the knowledge of the quadrupole coupling constant, it is possible [18] to estimate roughly the fraction of ionic character of the bond according to the following simplified expression:

$$i = 1 - \frac{|eQ q_{\text{mol}}|}{|eQ q_{\text{at}}|} \quad (9)$$

where $eQ q_{\text{mol}}$ is the quadrupole coupling constant of the halogen atom in the molecule under study and $eQ q_{\text{at}}$ is the quadrupole coupling constant of the free halogen atom [$eQ q_{\text{at}}$ (Br^{79}) = -769.756 and $eQ q_{\text{at}}$ (I^{127}) = $+2292.712$].

It should also be pointed out that the above mentioned transitions will only occur if the halogen nucleus is surrounded by a non-spherical electronic distribution ($q_{zz} \neq 0$), as it will happen if the electronic cloud is directionally polarized by some kind of interaction, e.g., hydrogen bonding.

III — RESULTS AND DISCUSSION

General aspects

In the compounds studied in the present work a single nuclear quadrupole resonance

for Br^{79} (or Br^{81}) and two resonances for I^{127} were observed, in the bromide and iodide salts, respectively, at the frequencies given by Table I, which also shows the estimated fraction of ionic character of the postulated $^+\text{NH} \dots \text{X}^-$ bond and the asymmetry parameter of the field gradient in the case of the iodides. This parameter, η_I , was estimated from equations (7) and (8) whereas the corresponding fraction of ionic character of the $^+\text{NH} \dots \text{I}^-$ bond, i_I , was estimated from equation (9) where $|eQ q_{\text{mol}}|$ was $|eQ q_{zz}|$ calculated from expressions (7) and (8).

Since the evaluation of η_{Br} was not possible in this study, $|eQ q_{\text{mol}}|$ [to be used in expression (9)] was estimated from equation (6) by considering $(1 + \eta^2/3)^{1/2} \approx 1$; this simplification leads to an error for i_{Br} which is not greater than ca. 0.2 %, assuming that η_{Br} is not higher than η_I for the analogous iodide salts (the highest and, hence, the least favourable value is $0.47 \approx 0.5$ observed for N-methylanilinium iodide).

Apart from the compounds listed in Table I, other anilinium salts were prepared and tested but no nuclear quadrupole resonance frequencies could be observed even after repeated crystallisations and thermal treatments possibly due to lattice defects that were not removed by these treatments. Among these are the following: $p\text{-CH}_3\text{OC}_6\text{H}_4\text{NH}_3^+.\text{Br}^-$, $p\text{-CH}_3\text{COC}_6\text{H}_4\text{NH}_3^+.\text{Br}^-$, $o\text{-HOC}_6\text{H}_4\text{NH}_3^+.\text{Br}^-$ and $p\text{-ClC}_6\text{H}_4\text{NH}_3^+.\text{Br}^-$. However, a frequency, assigned to the chlorine atom, was observed at 34.4 MHz (at ca. 300 K) for $p\text{-ClC}_6\text{H}_4\text{NH}_3\text{Br}$. This value is higher than that known [19] for $p\text{-chloroaniline}$ (at the same temperature, the frequency is lower than 33.974 MHz which is the value observed [19] at 196 K) possibly on account of the electron withdrawing inductive ability of the $-\text{NH}_3^+$ group which leads to an increase of the electric field gradient (q_{zz}) at the Cl atom; a similar effect results from the elimination of the possibility of the $-\text{NH}_2$ group (with a + R resonance effect) to con-

Table I

Nuclear quadrupole resonance frequencies (ν)^a of anilinium bromide and iodide salts, fraction of ionic character of the halide bond (i) and asymmetry parameter (η) of the iodide electric field

Anilinium salt	X = Br ^{b)}			X = I			
	ν (Br ⁷⁹)	ν (Br ⁸¹)	i (Br ⁷⁹)	ν (I ¹²⁷)		i (I ¹²⁷)	η (I ¹²⁷)
				$\nu_1(3/2 \leftarrow 1/2)$	$\nu_2(5/2 \leftarrow 3/2)$		
C ₆ H ₅ NH ₃ ⁺ X ⁻	16.9 ^{c)}	14.2	0.956	15.0	24.9	0.963	0.42
<i>p</i> -CH ₃ C ₆ H ₄ NH ₃ ⁺ X ⁻	16.3	13.9	0.958	17.3	23.8 ^{d)}	0.963	0.68
<i>m</i> -CH ₃ C ₆ H ₄ NH ₃ ⁺ X ⁻ ^{e)}	16.25	13.8	0.958				
<i>o</i> -CH ₃ C ₆ H ₄ NH ₃ ⁺ X ⁻	25.9	21.9	0.933	15.8	28.6	0.958	0.29
<i>p</i> -NO ₂ C ₆ H ₄ NH ₃ ⁺ X ⁻ ^{e)}	17.9	15.2	0.954				
<i>m</i> -NO ₂ C ₆ H ₄ NH ₃ ⁺ X ⁻ ^{e)}	22.9	19.4	0.941				
<i>o</i> -NO ₂ C ₆ H ₄ NH ₃ ⁺ X ⁻ ^{e)}	20.4	17.2	0.947				
<i>p</i> -CF ₃ C ₆ H ₄ NH ₃ ⁺ X ⁻ ^{f)}				24.5	33.2	0.948	0.70
C ₆ H ₅ N(CH ₃)H ₂ ⁺ X ⁻	18.5	15.5	0.952	21.9	35.0	0.948	0.47

a) Values (with an estimated error below ca. 0.1 %) in MHz measured at ca. 298 K.

b) ν (Br⁷⁹)/ ν (Br⁸¹) \approx Q (Br⁷⁹)/Q (Br⁸¹) = 1.197.

c) A more precise value, ν (Br⁷⁹) = 16.664 MHz at T = 289.8 K, is reported in reference [15].

d) Weak resonance.

e) N.Q.R. frequency not observed for X = I.

f) N.Q.R. frequency not observed for X = Br.

jugate with the aromatic ring as a result of its protonation to give -NH₃⁺.

The data quoted in Table I deserves a few general comments:

- a) The observation of nuclear quadrupole resonance frequencies evidences a non-spherical electronic distribution ($q_{zz} \neq 0$) around the bromide or iodide nucleus which rules out an unperturbed s²p⁶ spherical electronic distribution in the halide ion. Since they are unlikely to arise from second order lattice effects in a 100 % ionic compound, these results

may be interpreted, as proposed [14] in the N.Q.R. study of alkylammonium bromide and iodide salts, in terms of the involvement of the halide ion in hydrogen bonding, i.e., polarization of the electron clouds of the bromide and iodide ions caused by the hydrogens of the ammonium groups. The high value of ν (⁷⁹Br) observed in anilinium bromide (and its deuterated analogues), the large ¹H-²D isotopic shift of this frequency (ca. 400KHz at 77K) by deuteration of the ammonium group, the lack of free rotation of the -NH₃⁺ group and the fact that the dis-

tance $N \dots Br^-$ is shorter than that corresponding to the van der Waal's radius of $-NH_4^+$ plus the ionic radius of Br^- have also been considered by other authors [16,20c] as evidence for $N^+H \dots Br^-$ hydrogen bonding. Short $N \dots I^-$ distances have also been taken as evidence for $N^+H \dots I^-$ bonds in trimethylammonium iodide [25b].

b) The estimated fraction of ionic character of the halide bond is high ($i_{Br}, i_I > 0.94$); hence the corresponding hydrogen bonds have predominant electrostatic nature, $N^+H \dots X^-$. In other terms, the deformation of the electron cloud of the bromide and iodide ions is small.

c) The η asymmetry parameter (estimated for the iodide ion) presents values which are well above zero (mainly for the *para* substituted anilinium salts, $p-CF_3C_6H_4NH_3^+I^-$ and $p-CH_3C_6H_4NH_3^+I^-$), thus showing a non-axial electric field around the iodide nucleus and suggesting an interaction of this ion with neighbouring hydrogen atoms which is more complex than that resulting from a single hydrogen-bonding per halide ion (an axial symmetry, $\eta = 0$, would then be expected).

A similar observation was reported [14] for the ethyl- and diethyl-ammonium iodide salts where the formation of three hydrogen bonds per iodide is suspected [20].

d) The N.Q.R. frequency of the halide ion and the asymmetry parameter appear to be strongly dependent on the organic group(s) bound to the nitrogen atom of the ammonium salt, but no general trends can be recognized.

Hence, although the comparison among $C_6H_5NH_3^+X^-$, $CH_3NH_3^+X^-$ [14] and $C_3H_7NH_3^+X^-$ [14], and between $C_6H_5N(CH_3)_2H_2^+X^-$ and $(CH_3)_2NH_2^+X^-$ [14], may suggest that the replacement of an alkyl

by a phenyl group at the nitrogen in a primary or secondary amine appears to lead to an increase of the N.Q.R. frequency and of the asymmetry parameter and to a decrease of the ionic character of the $N^+H \dots X^-$ bond, these trends are not followed by the ethylammonium salts which present a very high N.Q.R. frequency and asymmetry parameter (even higher than those observed for the anilinium salts).

Moreover, in the anilinium series, the secondary ammonium salt $C_6H_5N(CH_3)_2H_2^+X^-$ presents N.Q.R. halide frequencies which are higher than those exhibited by the primary anilinium salt $C_6H_5NH_3^+X^-$. Hence, the replacement of a hydrogen atom by a methyl group leads to an increase of the halide frequency.

Although the main reason for such a behaviour cannot be ascertained, a few tentative explanations may be put forward: in the secondary ammonium salt the positive charge is localized in a smaller number of hydrogen atoms and a stronger polarizing distortion of the electronic charge distribution in the neighboring halide may result with an increase of q_{zz} and, hence, of the N.Q.R. frequency; an effect of the same kind may also result from the polarizing effect (of the induced positive charge) of the methyl group (as a result of its resonance and inductive electron donor character) on the halide electronic cloud.

Within the group of aryl ammonium salts, the N.Q.R. frequency depends also on the phenyl substituent but this behaviour is discussed separately.

N.Q.R. halide frequency and Hammett's σ constant of the phenyl substituent.

The electron donor/acceptor ability of a substituent at a phenyl ring may be expressed by the known Hammett's σ constant and since the postulated hydrogen bond to the halide ions in the compounds studied in the present work would be expected to be

dependent on such an ability, the possibility of a correlation between the Hammett's σ constant and the N.Q.R. halide frequency (ν) may be anticipated (which is also, if verified, a confirmation of the soundness of the hypothesis of occurrence of hydrogen bonding in the system studied).

Figure 1 shows a plot of ν (Br^{79} or I^{127}) for the anilinium ion and its derivative salts,

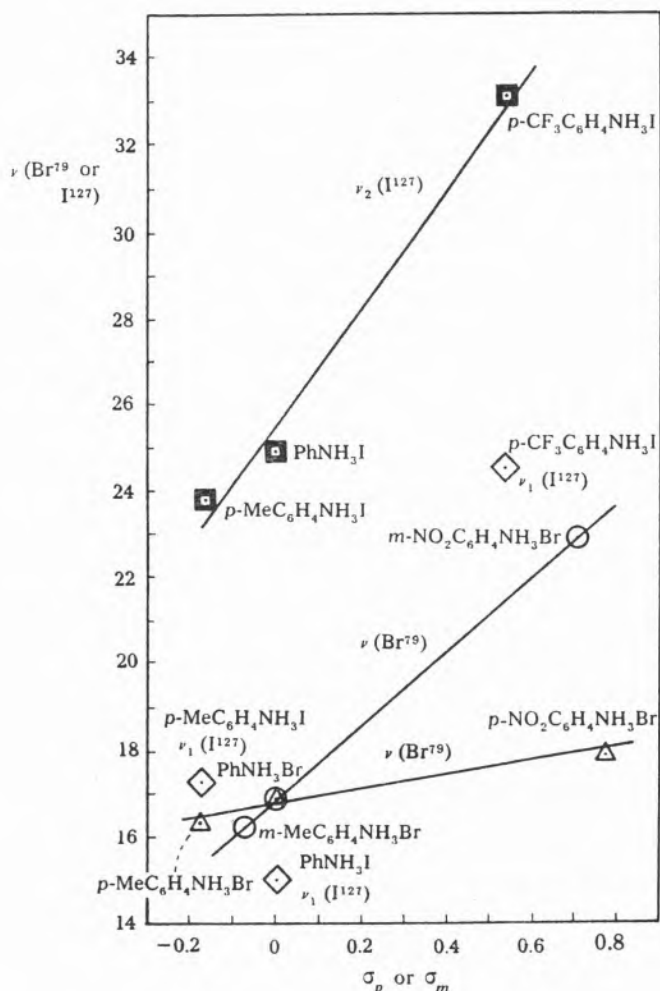


Fig. 1

Plot of ν (Br^{79} or I^{127}) versus the Hammett's σ constant of the substituent (Y) in compounds $\text{YC}_6\text{H}_4\text{NH}_3\text{X}$ (X = Br or I)

- \triangle — ν (Br^{79}) in compounds with para-Y.
- \circ — ν (Br^{79}) in compounds with meta-Y.
- \diamond — ν_1 (I^{127}) in compounds with para-Y.
- \blacksquare — ν_2 (I^{127}) in compounds with para-Y.

$\text{YC}_6\text{H}_4\text{NH}_3^+\text{X}^-$, versus the Hammett's σ constant [21] for the Y substituent (in *para* or *meta* position); as can be seen, the halide N.Q.R. frequency appears to increase linearly with σ , except in the case of ν_1 (I^{127}). Hence, an increase of the electron withdrawing ability of the substituent leads to a distortion of the electronic charge distribution in the halide (X^-) ion (increase of q_{zz} and, hence, of ν) with an increase in the covalent component of the $\text{NH}^+ \dots \text{X}^-$ bond, as commented on later.

If we consider the Taft σ_1 constant [21] (which only takes into consideration the inductive contribution of the substituent) instead of the Hammett's constant, a better linear correlation is observed for ν_2 (I^{127}) and the points corresponding to ν_1 (I^{127}) become closer to obeying a linear correlation. However, if the Taft σ_R^0 constant [21] (which measures the polar resonance effect of the substituent) is considered instead of the Hammett's σ constant, a general deviation from the linearity is observed for all sets of frequencies.

These observations suggest that the N.Q.R. halide frequency follows the phenyl substituent inductive effect closer than its resonance effect.

Moreover, ν (Br^{79}) is more sensitive to a change of electronic properties of the phenyl substituent (measured by Hammett's σ constant) when this is in the *meta* rather than in the *para* position, in accordance with the higher importance of the inductive effects and the weaker resonance effects associated to the former position relative to the latter. From the slopes of the plots of figure 1, it may also be observed that ν (I^{127}) is more sensitive than ν (Br^{79}) to a variation in the electronic properties of the substituent (Hammett's σ constant), in agreement with the higher polarizability of the iodide relative to the bromide ion.

In the above mentioned discussion, only the *para* and the *meta* substituent positions were considered, since ν (X) for compounds with

an *ortho* substituent presents a more complex dependence on the substituent and on the halide [e.g., the bromide salt $o\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_3^+\text{Br}^-$ has the highest $\nu(\text{Br}^{79})$ value observed in this study, whereas the analogous iodide salt has a very low $\nu(\text{I}^{127})$ and $o\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_3^+\text{Br}^-$ exhibits $\nu(\text{Br}^{79})$ at an intermediate value between the corresponding *meta* and *para* compounds].

Anomalies of behaviour associated to *ortho* substituents are well known and have also been reported in N.Q.R. studies by other authors [22]. Among the reasons for the anomalies, stereochemical effects, which, e.g., may cause steric hindrance or decrease the planarity of the molecule (hence, the N-phenyl ring resonance with resulting decrease of ν) may be cited as prominent factors; different crystalline structures; polarizing effect of the charge of the *ortho* substituent (as a result of resonance and inductive effects) upon the electronic shell of the halide are other possible reasons.

Linear correlations of halogen N.Q.R. coupling frequencies with the Hammett's σ constant have also been referred to by other authors [19, 23, 24] in different compounds (e.g., chlorobenzene derivatives), and, in some cases, it was observed [24] that the changes in the N.Q.R. frequency were mainly determined by the inductive rather than the resonance effect which, in some instances, only leads to small differences which are of the same order of magnitude as those due to crystalline field effects.

N.Q.R. halide frequency and the fraction of ionic character of the halide bond

From equations (6) to (9) and for a constant asymmetry parameter (η), an inverse linear relationship is expected between the halide N.Q.R. frequency (ν) and the fraction of ionic character (i) of the halide-hydrogen bond, i.e., the greater the deviation from the spherical symmetry of the electronic cloud around the nucleus (increase of q_{zz} and of ν) the lower the ionic character of the $\text{NH}^+\dots\text{X}^-$ bond. However, if the asymmetry para-

meter η varies along a series of compounds, the above mentioned general correlation is no longer valid.

The plots of the N.Q.R. frequency for Br^{79} and I^{127} of the salts $\text{YC}_6\text{H}_4\text{NH}_3^+\text{X}^-$ versus the fraction of ionic character, $i(\text{Br}^{79})$ and $i(\text{I}^{127})$, are depicted in figures 2 and 3, respectively, where, for comparison, is also included the data previously reported [14] for the related alkylammonium salts.

The expected linear variation is observed (figure 2) for the bromide salts since, as mentioned above, the fraction of ionic character of the bromide bond was estimated by neglecting the effect of η . The highest ionic character of the bromide bond (with the corresponding lowest N.Q.R. frequency) is found in some alkylammonium bromides whereas some substituted anilinium bromides display the lowest ionic character of the bromide-hydrogen bond.

However, for the iodide salts (figure 3), families of plots of $\nu(\text{I}^{127})$ versus $i(\text{I}^{127})$ have to be considered according to the estimated values of the asymmetry parameter. An increase of this parameter results in an increase of $\nu_1(\text{I}^{127})$ but in a decrease of $\nu_2(\text{I}^{127})$. Each line was drawn for each group of compounds with similar η values, and it corresponds roughly to the plot of the equation, which relates $\nu(\text{I}^{127})$ with $i(\text{I}^{127})$, obtained from expressions (7) [or (8)] and (9) for η equal to the average of the η values of those compounds.

The lowest value of the asymmetry parameter η is observed for some of the alkylammonium iodide salts (methyl-, trimethyl- and propyl-ammonium iodides), whereas the *para*-substituted anilinium salts display the highest η values conceivably as a result of a more complex multi-hydrogen bonding between the halide ion and various hydrogen atoms belonging to different molecules as it was pointed out earlier [14] and is supported by some X-ray studies, e.g., of anilinium- [16, 20b, 20c] and monoethylammonium- [15, 20a] -halide (bromide or iodide) salts (high η values are displayed by the

iodide compounds); moreover, a higher axial symmetry of the hydrogen-bonds around the halide ion is shown also by X-ray data, e.g., on methylammonium salts [15,25] and accordingly, low η (iodide) values are observed. In conclusion, it can be said that alkylammonium and arylammonium halides exhibit $N^+H \dots X^-$ interactions whose single/multiple character depend on the halide considered and are highly sensitive to the organic group bound to nitrogen in the ammonium salt.

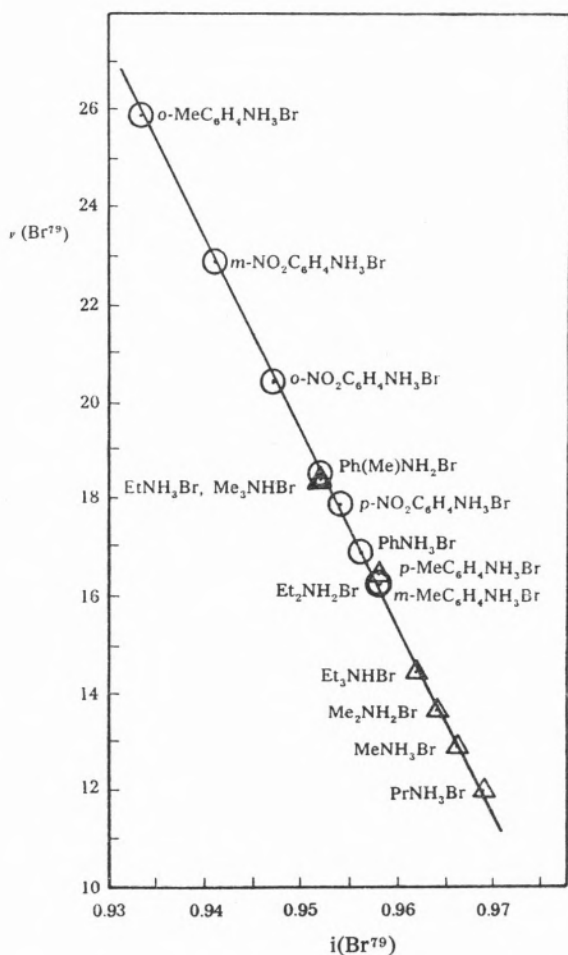


Fig. 2

Plot of $\nu(\text{Br}^{79})$ versus the fraction of ionic character of the bromide bond, $i(\text{Br}^{79})$

- — Arylammonium bromide salts
 △ — Alkylammonium bromide salts [14]

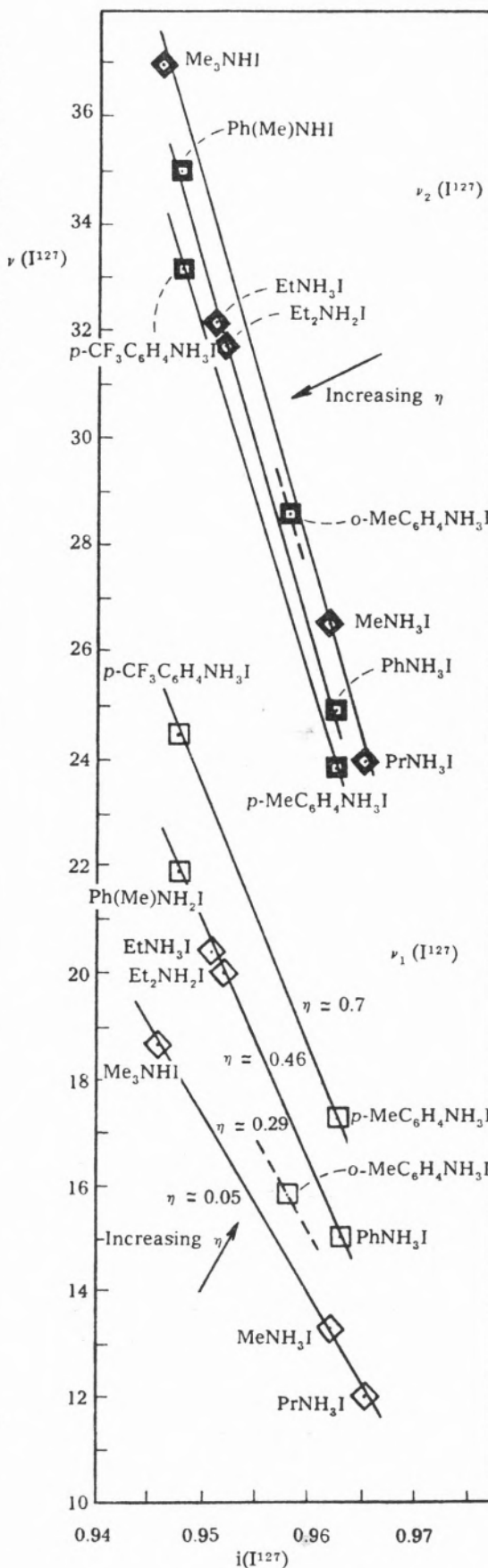


Fig. 3
 Plot of $\nu_1(\text{I}^{127})$ and $\nu_2(\text{I}^{127})$ versus the fraction of ionic character of the iodide bond, $i(\text{I}^{127})$
 □ — Arylammonium iodide salts (ν_1)
 ◇ — Alkylammonium iodide salts (ν_2) [14]

The correlations observed and the changes found on going from primary to secondary amines are consistent with a directional character of these interactions of the type normally referred to as hydrogen bonding. Although this type of bonds is not usually invoked in systems with the less electronegative halides Br^- and I^- , there is no theoretical objection to their inclusion even if the corresponding interactions are naturally weaker than those with F^- , Cl^- , nitrogen or oxygen.

IV — EXPERIMENTAL

The anilinium salts were prepared by reaction of the corresponding base with an excess of the appropriate acid (HBr or HI); ethanol or dichloromethane were used as solvents in a few cases (for the preparation of $p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_3\text{X}$ and $o\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_3\text{X}$ or $p\text{-ClC}_6\text{H}_4\text{NH}_3\text{X}$, respectively). The isolated products were purified by repeated recrystallization from ethanol or ethanol/dichloromethane.

The N.Q.R. studies were performed on crystalline samples (ca. 2-3g) contained in a 12mm thin-walled tube, at a temperature of 298K, by using a WILKS N.Q.R.-1A spectrophotometer equipped with a General Radio Co. frequency meter.

The accuracy of the measurements is of the order of 0.1% due to the instrument error and uncertainty in locating the fundamental bands.

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RESUMO

Estudo de ressonância de quadripolo nuclear de brometos e iodetos de anilínio.

As frequências de ressonância de quadripolo nuclear (ν) de Br^{79} (e Br^{81}) e I^{127} foram detectadas nos sais de anilínio $\text{YC}_6\text{H}_4\text{NH}_3^+\text{X}^-$ ($\text{Y} = \text{o-,m-,p-CH}_3$; o-,m-,p-NO_2 ; p-CF_3 , $\text{X} = \text{Br}$ e/ou I). O parâmetro de assimetria η (para $\text{X} = \text{I}$) e a fracção de carácter iónico da ligação do halogeneto foram estimados para estes compostos e os resultados obtidos demonstraram a ocorrência de polarização da nuvem electrónica do halogeneto, o que foi interpretado considerando a possível formação de ligações de hidrogénio $\text{N}^+\text{H} \dots \text{X}^-$ com carácter electrostático predominante.

Observaram-se ainda dependências lineares, que são objecto de discussão, entre ν e as constantes σ de Hammett para os substituintes em posição para e meta.