Phase Transition in $4\text{-}(CH_3)C_6H_4NH_3^{\oplus}X^{\ominus}$ (X = Br, I)

V. Seshu Bai * and Alarich Weiss
Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt

Z. Naturforsch. **39 a**, 366 – 370 (1984); received December 21, 1983

By ^{79,81}Br and ^{127}I NQR spectroscopy $4\text{-}(CH_3)C_6H_4NH_3^{\oplus}X^{\ominus}$, X = Br and I, and $4\text{-}(CH_3)C_6H_4ND_3^{\oplus}I^{\ominus}$ were studied in the temperature range $77 \leqq T/\text{K} \lessapprox 340$. The three compounds experience phase transitions, most likely of higher order. Two reversible transitions are observed for the para-toluidinium iodide, $T_{\text{I} \rightleftharpoons \text{II}}$ being in the temperature range $247 \lessapprox T/\text{K} \lessapprox 258$, $T_{\text{II} \rightleftharpoons \text{III}}$ in the range $174 \lessapprox T/\text{K} \lessapprox 179$. The deuterated compound shows slight shift of the transition temperatures compared to the protonated one, whereas the ^{127}I-NQR resonance frequencies are considerably lowered as is the nuclear quadrupole coupling constant. The asymmetry parameter η, however, increases through deuteration of the NH_3 group. The room temperature phase of the iodide crystallizes with an orthorhombic space group (Pmmn or Pmn2_1, $Z = 2$). Temperature dependence of the ^{79}Br NQR spectrum of p-toluidinium bromide indicates a phase transition near $T = 281$ K.

Introduction

The ammonium ion, $NH_4^{\oplus}$, plays an important role in solid state phase transitions. It behaves like an alkali ion by its electronegativity and its radius, but due to its nonspherical symmetry and the ability to form hydrogen bonds, various packings and coordinations are possible which promote phase transitions. Replacement of one hydrogen atom of the ion by a group R lowers the symmetry of the ion but the possibility of hydrogen bonding to the anions in the crystal lattice and the ease of rotation of the group $-NH_3^{\oplus}$ around the bond $R-NH_3^{\oplus}$ offers a variety of phases in the solid state which differ only little in lattice energy.

In recent years we have studied several crystalline halides $RNH_3^{\oplus}X^{\ominus}$ (X = Br, Cl) where R is the benzene ring or a substituted benzene ring. In case of $R = C_6H_5$ a ferroelastic phase transition occurs for both the anilinium bromide and the anilinium iodide and this transition was followed up by ^{79,81}Br and ^{127}I nuclear quadrupole resonance (NQR) [1]. The crystal structures of both the high and low temperature phases of $C_6H_5NH_3^{\oplus}X^{\ominus}$ (X = Br, I) were studied by X-ray and neutron diffraction [2–4]. Substitution of the benzene ring hydrogens by chlorine at different positions was investigated by NQR [5]. In detail we have studied the influence of a substituent at the para position of the anilinium ion. Phase transitions have been observed in $4\text{-}ClC_6H_4NH_3^{\oplus}I^{\ominus}$ [6], and in $4\text{-}FC_6H_4NH_3^{\oplus}X^{\ominus}$, $4\text{-}(C_2H_5)C_6H_4NH_3^{\oplus}X^{\ominus}$ (X = Br, I) [7]. Recently a phase transition was observed in $4\text{-}(CN)C_6H_4NH_3^{\oplus}X^{\ominus}$ (X = Br, I) [8]. In the following we report NQR experiments on the para toluidinium halides $4\text{-}(CH_3)C_6H_4NH_3^{\oplus}X^{\ominus}$ (X = Br, I), and on the phase transitions which occur in these crystalline compounds.

Experimental

Preparation

p-toluidinium bromide, $4\text{-}(CH_3)C_6H_4NH_3^{\oplus}Br^{\ominus}$, and p-toluidinium iodide, $4\text{-}(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$, were prepared by slow addition of hydrobromic acid and hydroiodic acid, respectively, in stoichiometric quantity to p-toluidine, $4\text{-}(CH_3)C_6H_4NH_2$, dissolved in ethanol-water mixture. The solution was concentrated and left for crystallization at $T = 277$ K. Polycrystalline solids with light pink ($4\text{-}(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$) or light yellow ($4\text{-}(CH_3)C_6H_4NH_3^{\oplus}Br^{\ominus}$) tinge precipitated from the solution. The substances were filtered, washed with ethanol-water mixture, and dried in a dessicator over $CaCl_2 + KOH$. The chemical analysis (C, N, H) of the iodide showed $(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$, without any water of crystallization.

In order to study the isotope effect, $4\text{-}(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$ was dissolved in D_2O and the solution was concentrated over P_2O_5 in a dessicator.

---

* Present address: School of Physics, University of Hyderabad, Hyderabad-500 134, India.

Reprint requests to Prof. Dr. Al. Weiss, Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt, Petersenstraße 20, D-6100 Darmstadt, West Germany.

0340-4811 / 84 / 0400-0366 $ 01.3 0/0. – Please order a reprint rather than making your own copy.

The process was repeated thrice for assurance of complete deuteration resulting in crystalline 4-$(CH_3)C_6H_4ND_3^{\oplus}I^{\ominus}$.

NQR experiments

The ^{79,81}Br- and ^{127}I-NQR spectra were studied with a Decca-Radar spectrometer using Zeeman modulation and side band suppression. Usually a time constant of 10 s was employed. Samples of about 5 g (polycrystalline material) were used. Frequencies were measured accurate to ±5 kHz [1]. For variation of the temperature of the sample it was thermostated by circulating water (range $310 \leqq T/K \leqq 350$), methanol ($195 \leqq T/K \leqq 310$), and cool nitrogen gas obtained from boiling liquid N_2 ($125 \leqq T/K \leqq 195$). The temperature at the site of the sample was determined with the help of an iron-constantan thermocouple to ±0.2 K in the range $270 \leqq T/K \leqq 310$ and to ±0.3 K outside this range.

X-ray diffraction

Small single crystals for X-ray diffraction studies were grown from the solution of the iodide by slow evaporation of the solvent at 295 K. Needle like crystals of 4-$(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$ are formed within a few days. Single crystal X-ray studies were done by Weissenberg and precession photographs.

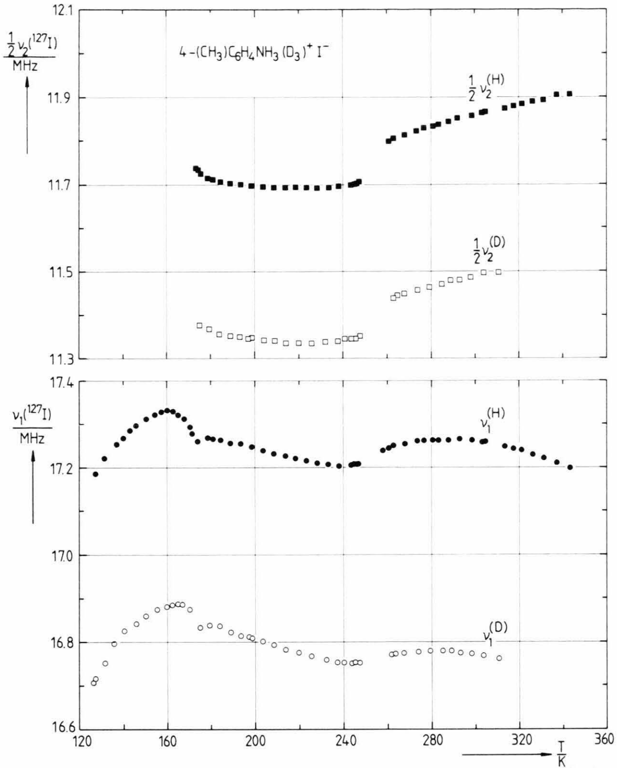

Fig. 1. ^{127}I NQR frequencies of 4-$(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$ [●: $\nu_1(m=\pm\frac{1}{2} \rightleftharpoons m=\pm\frac{3}{2})$; ■: $\frac{1}{2}\nu_2(m=\pm\frac{3}{2} \rightleftharpoons m=\pm\frac{5}{2})$] and 4-$(CH_3)C_6H_4ND_3^{\oplus}I^{\ominus}$ [○: $\nu_1(m=\pm\frac{1}{2} \rightleftharpoons m=\pm\frac{3}{2}$; □: $\frac{1}{2}\nu_2(m=\pm\frac{3}{2} \rightleftharpoons m=\pm\frac{5}{2})$] as a function of temperature.

Results

4-$(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$

The ^{127}I NQR spectrum of para-toluidinium iodide at $T = 292.8$ K consists of two lines. These resonances are associated with the transitions $\nu_1(m=\pm\frac{1}{2} \rightleftharpoons m=\pm\frac{3}{2})$ and $\nu_2(m=\pm\frac{3}{2} \rightleftharpoons m=\pm\frac{5}{2})$, respectively and therefrom it is concluded that there is only one iodine ion in the asymmetric unit of the crystallographic unit cell. In Fig. 1 the two ^{127}I NQR frequencies are plotted as a function of temperature for the range $125 \leqq T/K \leqq 343$. From these data and the equations given by Creel et al. [9] the nuclear quadrupole coupling constant $e^2\Phi_{zz}Qh^{-1}(^{127}I)$ and the asymmetry parameter $\eta(^{127}I)$ have been evaluated. In Fig. 2 $\eta(^{127}I) = f(T)$ and $e^2\Phi_{zz}Qh^{-1}(^{127}I) = f(T)$ of 4-$(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$ are shown.

As seen from Figs. 1 and 2 no ^{127}I NQR signals have been observed in the temperature range $247 \leqq T/K \leqq 258$. Within this temperature interval the signal to noise ratio, S/N, of the NQR signals was too low to observe the transition, whereas at $T > 258$ as well as at $T < 247$ S/N was 25 for ν_1 and 10 for ν_2. This behaviour is associated with the occurrence of a phase transition from phase I, stable in the range from 258 K up to at least 340 K to phase II which appears below $T \approx 247$ K.

A second phase transition is observed at $T \approx 174$ K. The upper transition ν_2 was not any more observable below this temperature and ν_1 changes strongly around this temperature. There is again a "transition region" $174 \lesssim T/K \lesssim 179$ observed and we conclude that there is a second phase transition in the range $174 \leqq T_{III \rightleftharpoons II} \leqq 179$. Below 174 K phase III is the stable one. In Table 1 ^{127}I NQR frequencies, η, and $e^2\Phi_{zz}Qh^{-1}$ are listed for some selected temperatures.

From the X-ray single crystal studies on 4-$(CH_3)C_6H_4NH_3I$ at $T = 295$ K we find that the unit cell of phase I is either D_{2h}^{13}-Pmmn or C_{2v}^{7}-Pmn2_1. The lattice constants are approximately $a = 670.8$ pm, $b = 678.5$ pm, and $c = 941.1$ pm.

4-$(CH_3)C_6H_4ND_3^{\oplus}I^{\ominus}$

There is a pronounced effect on the halogen NQR frequencies through replacement of the three hydrogen atoms bonded to the nitrogen in anilinium halides by deuterium atoms [1, 4, 7]. In the compound discussed here, the frequency shift is about 450 kHz for ν_1 and 750 kHz for ν_2 and the frequencies are lowered by the H → D exchange. In Fig. 1 $\nu_1^{(D)} = f(T)$ and $\nu_2^{(D)} = f(T)$ are shown and in Fig. 2 the temperature dependence of $e^2\Phi_{zz}Qh^{-1}(^{127}I)$ and $\eta(^{127}I)$ are plotted for 4-$(NH_3)C_6H_4ND_3^{\oplus}I^{\ominus}$.

The substitution H → D at the $NH_3^{\oplus}$ group does not change the polymorphism of 4-$(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$ in principle but may change the transition temperature [1, 7]. For 4-$(CH_3)C_6H_4ND_3^{\oplus}I^{\ominus}$ we found $248 \leqq T_{II \rightleftharpoons I}/K \leqq 262$ and $171 \leqq T_{III \rightleftharpoons II}/K\,179$ (see Figs. 1 and 2).

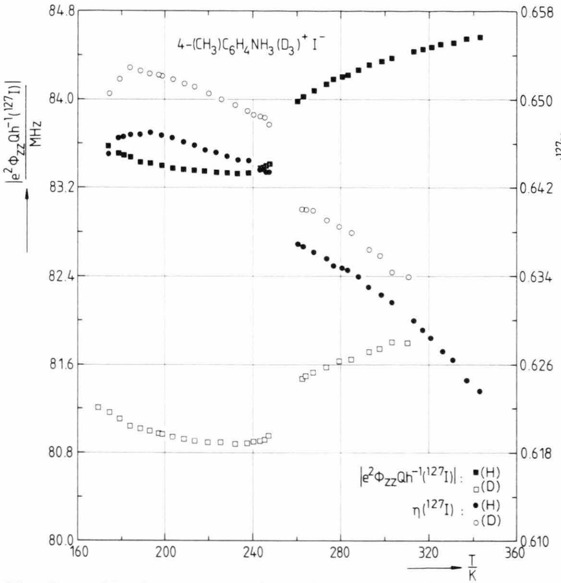

Fig. 2. Nuclear quadrupole coupling constant ($e^2\Phi_{zz}Qh^{-1}(^{127}I)$) and asymmetry parameter $\eta(^{127}I)$ of 4-$(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$ [●: $e^2\Phi_{zz}Qh^{-1}(^{127}I)$; ■: $\eta(^{127}I)$] and 4-$(CH_3)C_6H_4ND_3^{\oplus}I^{\ominus}$ [○: $e^2\Phi_{zz}Qh^{-1}(^{127}I)$; □: $\eta(^{127}I)$] as a function of temperature.

4-$(CH_3)C_6H_4NH_3^{\oplus}Br^{\ominus}$

A single line spectrum is observed for 4-(CH_3)-$C_6H_4NH_3Br$, with a signal $\nu(^{79}Br) = 16.386$ MHz at $T = 295$ K. The corresponding ^{81}Br NQR frequency is observed too. In Fig. 3 $\nu(^{79}Br) = f(T)$ is shown for the range of investigation, $282.5 \leqq T/K \leqq 333$. We have not observed a $^{79,81}Br$ NQR signal in the range $203 \leqq T/K \leqq 280$, while at 77 K the signal reappeared at $\nu = 17.506$ MHz.

The temperature coefficient of $\nu(^{79}Br)$ is about 2 kHz/K in the range $286 \leqq T/K \leqq 333$. It increases drastically to 13 kHz/K at 283 K. From this and the disappearance of the resonance line below 282 K we conclude that there is at least one solid state phase transition of 4-$(CH_3)C_6H_4NH_3^{\oplus}Br^{\ominus}$ in the range $77 \leqq T/K \leqq 282$.

Discussion

The exchange H → D at the amino group, 4-$(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$ → 4-$(CH_3)C_6H_4ND_3^{\oplus}I^{\ominus}$ lowers $e^2\Phi_{zz}Qh^{-1}(^{127}I)$ and raises $\eta(^{127}I)$ considerably.

Table 1. NQR frequencies ν, nuclear quadrupole coupling constants ($e^2\Phi_{zz}Qh^{-1}$) and asymmetry parameters η for para-toluidinium halides at selected temperatures.

Compound	T / K	$\nu_1(^{127}I)$ / MHz	$\nu_2(^{127}I)$ / MHz	$e^2\Phi_{zz}Qh^{-1}(^{127}I)$ / MHz	$\eta(^{127}I)$	(^{79}Br) / MHz
4-$(CH_3)C_6H_4NH_3^{\oplus}I^{\ominus}$	292.8	17.266	23.704	84.32	0.6330	
	273.5	17.260	23.644	84.14	0.6352	
	218.5	17.220	23.384	83.35	0.6454	
4-$(CH_3)C_6H_4ND_3^{\oplus}I^{\ominus}$	293.0	16.775	22.960	81.72	0.6364	
	273.5	16.780	22.910	81.58	0.6390	
	219.5	16.775	22.670	80.09	0.6505	
4-$(CH_3)C_6H_4NH_3^{\oplus}Br^{\ominus}$	333					16.288
	318					16.316
	298					16.352
	77					17.506

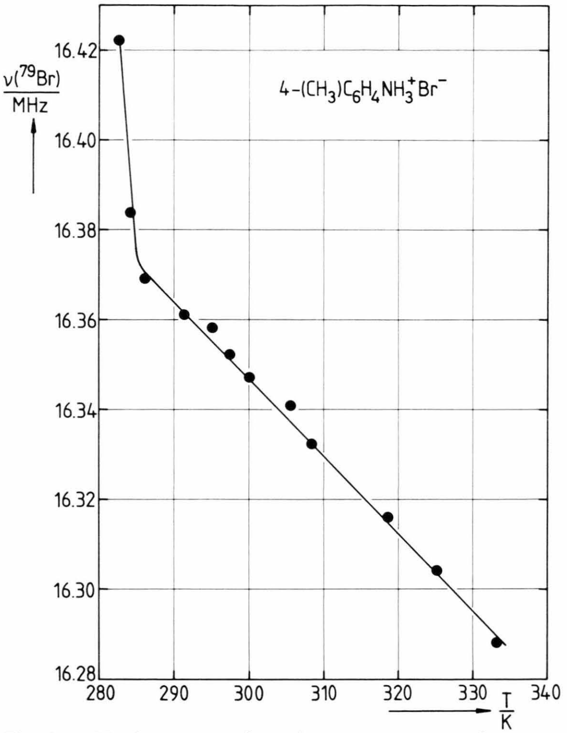

Fig. 3. Nuclear quadrupole resonance frequency $\nu(^{79}Br) = f(T)$ for 4-$(CH_3)C_6H_4NH_3Br$.

This shows that the hydrogen bonds have a strong influence on these two parameters of the nuclear quadrupole coupling tensor. In Table 2 $e^2\Phi_{zz}Qh^{-1}(^{127}I)$ and $\eta(^{127}I)$ of several substituted anilinium iodides ($R-NH_3^{\oplus}I^{\ominus}$ and $R-ND_3^{\oplus}I^{\ominus}$) are given. It is seen that the p-toluidinium iodide fits well into this group of compounds.

An interesting point is the magnitude of $|e^2\Phi_{zz}Qh^{-1}(^{127}I)|$ and $\eta(^{127}I)$ for the para substituted anilinium iodides. In Table 2 the room temperature data are collected for the basic compound, 4-$HC_6H_4NH_3^{\oplus}I^{\ominus}$, and the substitutes, F, Cl, CN, NH_3, and C_2H_5 in para position. The room temperature data belong in all cases to the high temperature phase I of the compounds. From the crystal structure determination of $C_6H_5NH_3^{\oplus}I^{\ominus}$ (phase I and phase II) [2–4] and from the crystal structures of 4-$FC_6H_4NH_3^{\oplus}I^{\ominus}$ (phase I and phase II) [10] we find, that in phase I of these compounds the group $-NH_3^{\oplus}$ performs a hindered rotation, occupying thereby two distinct positions in the lattice. From the ^{127}I NQR study of all other compounds we conclude that a similar mechanism is valid for them in phase I too. Table 2 shows that there is no straight forward relation between $|e^2\Phi_{zz}Qh^{-1}(^{127}I)|$ and the electronegativity of the para substituent. Furthermore the asymmetry parameter $\eta(^{127}I)$ reveals the influence of the lattice symmetry, changing from zero for X = Cl and CN to 0.8 for $X = C_2H_5$.

Further support for the freezing in of the $-NH_3^{\oplus}$ group rotation during the transition $I \rightleftharpoons II$ as the common property of all para substituted anilinium iodides is given by the similarity of the effect the exchange H → D has on ^{127}I frequency shift and coupling constant.

The phase transitions in 4-$(CH_3)C_6H_4NH_3I$ are more complicated than the transitions observed for the other compounds listed in Table 2. The loss of the ^{127}I NQR signals in a fairly wide range around the transition temperature $T_{I \rightleftharpoons II}$ in this compound suggests that the transition proceeds via several steps. It is likely that the structures of phase I and phase II are incommensurable. Also the transition $II \rightleftharpoons III$ is most probably not following a simple mechanism. It seems to be very likely that the transition $II \rightleftharpoons III$ is connected with a freezing in of the $-CH_3$ group rotation. It has to be mentioned that both phase transitions are reversible. A small single crystal of the compound, cooled slowly from room temperature down to 77 K and warmed up

Table 2. Nuclear quadrupole coupling constants $e^2\Phi_{zz}Qh^{-1}(^{127}I)$ and asymmetry parameters $\eta(^{127}I)$ of para substituted anilinium iodides (4-$XC_6H_4NH_3^{\oplus}I^{\ominus}$).

4-$XC_6H_4NH_3^{\oplus}I^{\ominus}$	T / K	$e^2\Phi_{zz}Qh^{-1}(^{127}I)$ / MHz	$\eta(^{127}I)$	Ref.
X = H	293.5	84.95	0.4033	[1, 4]
$X = CH_3$	292.8	84.32	0.6330	this paper
$X = C_2H_5$	291.5	115.13	0.8197	[7]
X = F	292.8	105.73	0.4694	[7]
X = Cl	295	143.70	0	[6]
X = CN	301.5	145.02	0	[8]

thereafter is still a single crystal as optical inspection as well as Weissenberg photographs show.

The phase transition of 4-$(CH_3)C_6H_4NH_3^{\oplus}Br^{\ominus}$, $T_{I \rightleftharpoons I} \sim 281$ K, is probably of the same origin as the transition I ⇌ II in the anilinium iodides discussed.

Acknowledgement

We are grateful to the "Deutsche Forschungsgemeinschaft" for support of this work.

[1] W. Pies and Al. Weiss, Bull. Chem. Soc. Japan, **51,** 1051 (1978).
[2] G. Fecher, Al. Weiss, W. Joswig, and H. Fuess, Z. Naturforsch. **36a,** 956 (1981).
[3] G. Fecher, Al. Weiss, and G. Heger, Z. Naturforsch. **36a,** 967 (1981).
[4] G. Fecher and Al. Weiss, unpublished results.
[5] W. Pies and Al. Weiss, J. Magn. Res. **30,** 469 (1978).
[6] W. Pies, M. Shahbazi, and Al. Weiss, Ber. Bunsenges. Phys. Chem. **82,** 594 (1978).
[7] V. G. Krishnan and Al. Weiss, Ber. Bunsenges. Phys. Chem. **87,** 254 (1983).
[8] V. G. Krishnan and Al. Weiss, J. Molec. Struct. **111,** 379 (1983).
[9] R. B. Creel, H. R. Brooker, and R. G. Barnes, J. Magn. Res. **41,** 146 (1980).
[10] G. Klebe, V. G. Krishnan, H. Fuess, and Al. Weiss, unpublished results.