^{79}Br and ^{127}I Nuclear Quadrupole Resonance Investigations of Ortho-Substituted Anilinium Halides, 2-$RC_6H_4NH_3^{\oplus}$ $X^{\ominus}$ with X = Br, I and R = Cl, CN, C_2H_5, NH_2, and $NH_3^{\oplus}$ $X^{\ominus}$

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The ^{79}Br and ^{127}I nuclear quadrupole resonance, NQR, spectra of ortho-substituted anilinium bromides and iodides 2-$RC_6H_4NH_3^{\oplus}$ $X^{\ominus}$ with X = Br, I and R = Cl, CN, C_2H_5, NH_2, and $NH_3^{\oplus}$ $X^{\ominus}$ have been investigated in the temperature range $77 \leq T/K \leq 420$. Phase transitions occur in 2-$(C_2H_5)C_6H_4NH_3^{\oplus}$ $Br^{\ominus} \cdot \frac{1}{2} H_2O$ at $T_c = 164$ K, in 2-$(C_2H_5)C_6H_4NH_3^{\oplus}$ $I^{\ominus}$ at $T_c = 214$ K, in $[1,2\text{-}C_6H_4(N(H,D)_3)_2]^{2\oplus}[Br^{\ominus}]_2$ at $T_c = 209$ K, and in $[1,2\text{-}C_6H_4(NH_3)_2]^{2\oplus}[I^{\ominus}]_2$ at $T_c = 173$ K. The NQR data are discussed and compared with NQR spectra of para-substituted anilinium halides.

Introduction

In anilinium halides $RC_6H_4NH_3^{\oplus}$ $X^{\ominus}$ (X = Br, I) hydrogen bonds N – H … X distort strongly the spherical charge distribution of the halogen ion $X^{\ominus}$. This leads to an electric field gradient (EFG) at the site of the halogen nucleus which can be determined by nuclear quadrupole resonance (NQR) spectroscopy. It is of interest to study the influence of substituents R on the EFG. Substitution at the phenyl ring should influence the N – H … X hydrogen bonds as well as the packing of the molecules in the crystal lattice. An important aspect in the investigation of anilinium halides is also the occurrence of phase transitions in these compounds which are often connected with the motions of the NH_3-group around the C – N axis. The phase transitions in anilinium bromide, $C_6H_5NH_3^{\oplus}$ $Br^{\ominus}$, and anilinium iodide, $C_6H_5NH_3^{\oplus}$ $I^{\ominus}$, were studied with NQR spectroscopy [1–3], X-ray and neutron diffraction [4–6] as well as dilatometry [3].

NQR investigations on substituted anilinium halides were mostly done for 4-substituted compounds [2, 7–11]. In addition ^{79}Br and ^{127}I NQR data are available for some disubstituted anilinium halides [11, 12] and for a few meta- and ortho-substituted substances [10, 12].

For the present NQR study we have chosen some 2-substituted anilinium bromides and iodides. In case of 2-substituted compounds one would expect effects on the EFG due to the volume and the ability of the substituent, in ortho-position to the NH_3-group, to form intramolecular hydrogen bonds as well as additional intermolecular ones with the anion.

Experimental

Preparation

2-Chloro- and 2-ethylaniline were purified by vacuum destillation, 2-cyanoaniline was recrystallized from ethanol and 1,2-phenylenediamine was used without further purification. The anilines were dissolved in ethanol/water mixtures and equimolar amounts of concentrated aqueous solutions of HBr and HI, respectively, were added. Cooling of the solutions or evaporating the solvent lead to the crystallization of the anilinium bromides and iodides. The salts were recrystallized from ethanol or water and dried on air or in a dessicator. All investigated compounds were analyzed for C, H, N, and halogen. The content of crystal water in 2-ethylanilinium bromide hemihydrate, 2-$(C_2H_5)C_6H_4NH_3^{\oplus}$ $Br^{\ominus} \cdot \frac{1}{2}H_2O$, was determined from the weight loss by drying a small amount of the compound at ≈420 K. In Table 1 a characterization (habitus, melting point, chemical analysis) of the compounds studied is given.

Nuclear Quadrupole Resonance

The ^{79,81}Br and ^{127}I NQR spectra of the halide ions of the title compounds were recorded with a su-

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Table 1. Characterization of the compounds investigated. The chemical analysis is given in weight %.

Compound	Habitus	Mp/K	C		H		N		Halogen (Br, I)	
			exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
$2\text{-ClC}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{Br}^{\ominus}$	white crystals	508 [a]	34.04	34.57	3.32	3.38	6.66	6.72	37.93	38.33 [b]
$2\text{-(CN)C}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{Br}^{\ominus}$	white needles	373 [a]	42.77	42.24	3.45	3.54	14.39	14.07	40.29	40.14
$2\text{-(CN)C}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{I}^{\ominus}$	white needles	423 [a]	33.66	34.17	2.76	2.87	11.28	11.39	51.63	51.58
$2\text{-(C}_2\text{H}_5\text{)C}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{Br}^{\ominus} \cdot \frac{1}{2}\text{H}_2\text{O}$	white plates	463	45.49	45.52	5.80	6.21	6.62	6.64	37.82	37.85
$2\text{-(C}_2\text{H}_5\text{)C}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{I}^{\ominus}$	white needles	423 [a]	38.71	38.58	4.86	4.86	5.60	5.62	51.20	50.95
$2\text{-(NH}_2\text{)C}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{Br}^{\ominus}$	white-pink col. needles	417 [a]	37.83	38.12	4.83	4.80	14.69	14.82	42.41	42.27
$2\text{-(NH}_2\text{)C}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{I}^{\ominus}$	pink lathes	443 [a]	30.34	30.58	3.79	3.84	11.91	11.87	53.72	53.76
$[1,2\text{-C}_6\text{H}_4(\text{NH}_3)_2]^{2\oplus}\ [\text{Br}^{\ominus}]_2$	pink square plates	450 [a]	26.51	26.69	3.70	3.73	10.37	10.38	59.16	59.20
$[1,2\text{-C}_6\text{H}_4(\text{NH}_3)_2]^{2\oplus}\ [\text{I}^{\ominus}]_2$	white rectan. crystals	487 [a]	20.08	19.80	2.80	2.77	7.81	7.70	69.41	69.73

[a] Decomposition, [b] Br (Cl not determined).

Table 2. ^{79}Br NQR frequencies, ^{127}I NQR frequencies, signal-to-noise ratios (S/N), nuclear quadrupole coupling constants $e\Phi_{zz}Qh^{-1}(^{127}\text{I})$ and asymmetry parameters $\eta(^{127}\text{I})$ for the 2-substituted anilinium halides studied at selected temperatures; X = Br, I.

Compound	$\frac{T}{\text{K}}$	$\frac{\nu(^{79}\text{Br})}{\text{MHz}}$	$\frac{S}{N}$	$\frac{\nu(^{127}\text{I})}{\text{MHz}}$	$\frac{S}{N}$	$\eta(^{127}\text{I})$	$\frac{e\Phi_{zz}Qh^{-1}(^{127}\text{I})}{\text{MHz}}$
$2\text{-ClC}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{Br}^{\ominus}$ [a]	77	24.824	76				
	273.6	23.307	20				
	303.4	23.043	32				
$2\text{-(CN)C}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{X}^{\ominus}$	77	22.242	4	21.674	24	0.7908	79.175
				18.161	71		
	274.1	20.964	30	21.284	27	0.6938	76.480
				16.364	30		
	302.5	20.756	14	21.177	23	0.6784	75.899
				16.060	21		
$2\text{-(C}_2\text{H}_5\text{)C}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{X}^{\ominus}$ [b]	77	–	–	–	–	–	–
				21.825	15		
	273.0	22.883 (ν^{II})	37	35.513	11	0.4186	122.223
		21.363 (ν^{I})	53	21.542	22		
	304.0	22.842	15	34.879	10	0.4163	120.002
		21.340	23	21.118	27		
$2\text{-(NH}_2\text{)C}_6\text{H}_4\text{NH}_3^{\oplus}\ \text{X}^{\ominus}$	77	26.927	78	21.336	25	0.3222	72.539
				12.048	39		
	273.4	24.598	76	18.249	63	0.4903	63.458
				11.739	33		
	302.8	24.246	39	17.411	39	0.5471	61.077
				11.759	16		
$[1,2\text{-C}_6\text{H}_4(\text{NH}_3)_2]^{2\oplus}\ [\text{X}^{\ominus}]_2$ [c]	77	21.883	61	27.464 (ν_2^{II})	87	0.5071	95.739
				17.913 (ν_1^{II})	38		
				11.180 (ν_2^{I})	13	(1.0849)	42.796
				11.958 (ν_1^{I})	16	0.9151	
	273.3	21.993	34	28.614	68	0.2485	96.538
				15.425	18		
				12.622	12	0.8513	46.574
				11.144	12		
	302.9	21.917	24	28.455	56	0.2735	96.236
				15.568	15		
				12.846	14	0.8367	47.285
				11.200	10		

[a] $\nu(^{35}\text{Cl}) = 35.975$ MHz (77 K); $\nu(^{35}\text{Cl}) = 35.522$ MHz (~ 298 K); see also [22]. [b] For X = Br: hemihydrate. [c] For X = Br, deuterated compound: 77 K: $\nu(^{79}\text{Br}) = 21.377$ MHz; 273.3 K: $\nu(^{79}\text{Br}) = 21.497$ MHz; 302.9 K: $\nu(^{79}\text{Br}) = 21.428$ MHz.

perregenerative spectrometer; working conditions: Zeeman modulation, lock-in technique, and time constant 10 s. Sideband suppression was used to determine the centre of unsymmetrical signals. The error of the measured frequencies is about ±5 kHz which is due to the line width of the resonances. For the hydrobromides the ^{81}Br NQR frequencies were also observed at some temperatures to assure the assignment of the ^{79}Br NQR signals. The NQR frequencies were recorded as a function of temperature in the range $77 \leq T/\mathrm{K} \leq 420$. At 77 K the sample holder was immersed into liquid nitrogen. In the range $110 \leq T/\mathrm{K} \leq 200$ a temperature and flow regulated gas stream of nitrogen, produced by evaporation of liquid N_2, was used to cool the sample. A methanol thermostat and an oil thermostat cover the temperature ranges $200 \leq T/\mathrm{K} \leq 300$ and $300 \leq T/\mathrm{K} \leq 420$, respectively. The temperature in the sample holders was measured with a copper-constantan thermocouple to ±0.5 K.

Results

2-Chloroanilinium Bromide, 2-$ClC_6H_4NH_3^{\oplus}\ Br^{\ominus}$, 2-Cyanoanilinium Bromide, 2-$(CN)C_6H_4NH_3^{\oplus}\ Br^{\ominus}$, and 1,2-Phenylenediamine Monohydrobromide, 2-$(NH_2)C_6H_4NH_3^{\oplus}\ Br^{\ominus}$

For 2-chloroanilinium bromide four NQR signals were detected in the frequency range $11 \leq \nu/\mathrm{MHz} \leq 36$. The two resonances at lower frequencies belong to the ^{81}Br and ^{79}Br isotopes and the two signals at higher frequencies to the nuclei ^{37}Cl and ^{35}Cl. Therefrom we conclude that there is one formula unit in the asymmetric unit of the unit cell. The temperature dependence of the ^{79}Br resonance was measured in the temperature range $77 \leq T/\mathrm{K} \leq 417$.

2-Cyanoanilinium bromide shows in the frequency range $15 \leq \nu/\mathrm{MHz} \leq 24$ two NQR lines with the frequency ratio $\nu(^{79}\mathrm{Br})/\nu(^{81}\mathrm{Br}) = 1.197$. The NQR signal of the ^{79}Br isotope was followed up in the temperature range $77 \leq T/\mathrm{K} \leq 417$. According to the NQR spectrum, also in 2-cyanoanilinium bromide there is one formula unit in the asymmetric unit of the unit cell.

In the NQR spectrum of 1,2-phenylenediamine monohydrobromide two NQR frequencies were found in the range $12 \leq \nu/\mathrm{MHz} \leq 27.5$. The ^{79}Br resonance was measured in the temperature range $77 \leq T/\mathrm{K} \leq 352$. Again we propose one formula unit in the asymmetric unit of the unit cell.

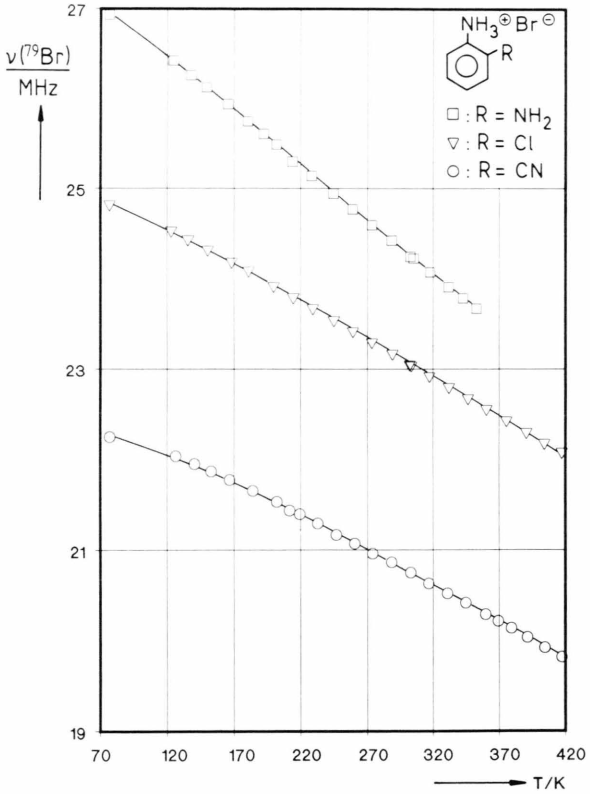

Fig. 1. ^{79}Br NQR frequencies of 2-chloroanilinium bromide, 2-$ClC_6H_4NH_3^{\oplus}\ Br^{\ominus}$, 2-cyanoanilinium bromide, 2-$(CN)C_6H_4NH_3^{\oplus}\ Br^{\ominus}$, and 1,2-phenylenediamine monohydrobromide, 2-$(NH_2)C_6H_4NH_3^{\oplus}\ Br^{\ominus}$, as functions of temperature.

In Fig. 1 the ^{79}Br NQR frequencies are plotted as functions of temperature for 2-chloroanilinium bromide, 2-cyanoanilinium bromide, and 1,2-phenylenediamine monohydrobromide. The temperature dependence of the resonances behaves similar for all three compounds; the ^{79}Br NQR frequencies decrease with increasing temperature. No phase transitions have shown up in the Br NQR spectrum. In Table 2 ^{79}Br frequencies are listed at a few selected temperatures.

2-Cyanoanilinium Iodide, 2-$(CN)C_6H_4NH_3^{\oplus}\ I^{\ominus}$, and 1,2-Phenylenediamine Monohydroiodide, 2-$(NH_2)C_6H_4NH_3^{\oplus}\ I^{\ominus}$

2-Cyanoanilinium iodide shows two NQR signals in the frequency range $13 \leq \nu/\mathrm{MHz} \leq 39.8$ corresponding to the two ^{127}I NQR transitions with $m = \pm 5/2 \rightleftharpoons m = \pm 3/2$ and $m = \pm 3/2 \rightleftharpoons m = \pm 1/2$. The tempera-

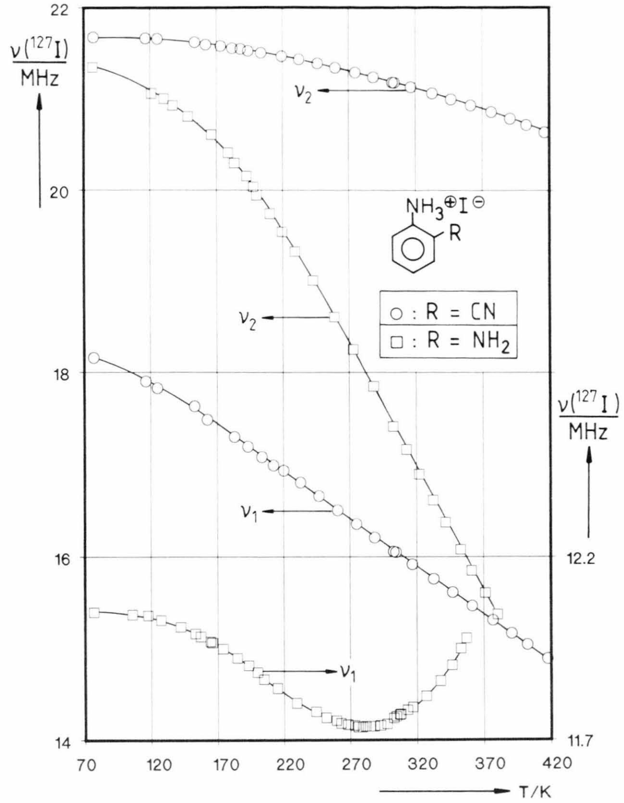

Fig. 2. ^{127}I NQR frequencies in 2-cyanoanilinium iodide, 2-(CN)$C_6H_4NH_3^{\oplus}$ $I^{\ominus}$, and 1,2-phenylenediamine monohydroiodide, 2-(NH$_2$)$C_6H_4NH_3^{\oplus}$ $I^{\ominus}$, as functions of temperature; ν_1: $m = \pm 1/2 \rightleftarrows m = \pm 3/2$, ν_2: $m \pm 3/2 \rightleftarrows m = \pm 5/2$.

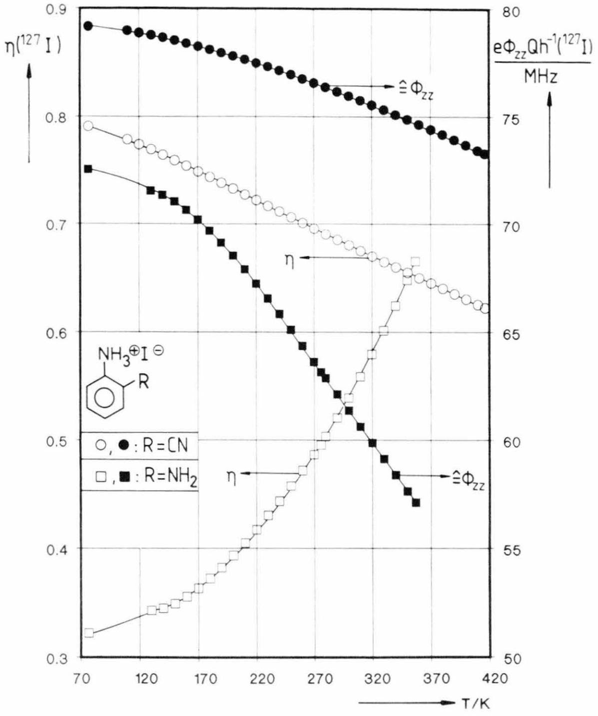

Fig. 3. Asymmetry parameters $\eta(^{127}I)$ and nuclear quadrupole coupling constants $e\Phi_{zz}Qh^{-1}(^{127}I)$ in 2-cyanoanilinium iodide, 2-(CN)$C_6H_4NH_3^{\oplus}$ $I^{\ominus}$, and 1,2-phenylenediamine monohydroiodide, 2-(NH$_2$)$C_6H_4NH_3^{\oplus}$ $I^{\ominus}$, as functions of temperature.

ture dependences of both frequencies are measured in the range $77 \leq T/K \leq 416$. There is no indication of a phase transition between 77 K and 416 K. For 1,2-phenylenediamine monohydroiodide two ^{127}I frequencies could be found in the range $7.2 \leq \nu/MHz \leq 41.1$. The resonances were followed up within $77 \leq T/K \leq 380$. $\nu_1 = f(T)$ shows a minimum at $T_{min} \approx 278$ K. In Fig. 2 the ^{127}I NQR frequencies of 2-cyanoanilinium iodide and 1,2-phenylenediamine monohydroidide are plotted in their temperature dependence.

For the ^{127}I nucleus with spin $I = 5/2$ one can calculate the asymmetry parameter $\eta = |\Phi_{xx} - \Phi_{yy}|/|\Phi_{zz}|$ and the quadrupole coupling constant $e\Phi_{zz}Qh^{-1}$ directly from the NQR frequencies [13]. In Fig. 3 $\eta(^{127}I) = f(T)$ and $e\Phi_{zz}Qh^{-1}(^{127}I) = f(T)$ are plotted for both compounds. $\eta(^{127}I)$ and $e\Phi_{zz}Qh^{-1}(^{127}I)$ of 2-cyanoanilinium iodide decrease with increasing temperature. In 1,2-phenylenediamine monohydroiodide $e\Phi_{zz}Qh^{-1}(^{127}I)$ decreases with increasing temperature, too, whereas the asymmetry parameter of the EFG-tensor at the iodine site in 2-(NH$_2$)$C_6H_4NH_3^{\oplus}$ $I^{\ominus}$ increases with increasing temperature.

For both compounds $\nu(^{127}I)$, $\eta(^{127}I)$, and $e\Phi_{zz}Qh^{-1}$ (^{127}I), at selected temperatures, are listed in Table 2.

2-Ethylanilinium Bromide Hemihydrate, 2-(C_2H_5)$C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$ · ½H_2O

Studying 2-ethylanilinium bromide hemihydrate, four ^{79,81}Br NQR signals were detected in the frequency range $10 \leq \nu/MHz \leq 23$. Therefore, there must be two formula units in the asymmetric unit of the unit cell. In the hemihydrates of 4-chloroanilinium bromide and of 4-bromoanilinium bromide there are two crystallographically inequivalent sites for the bromine

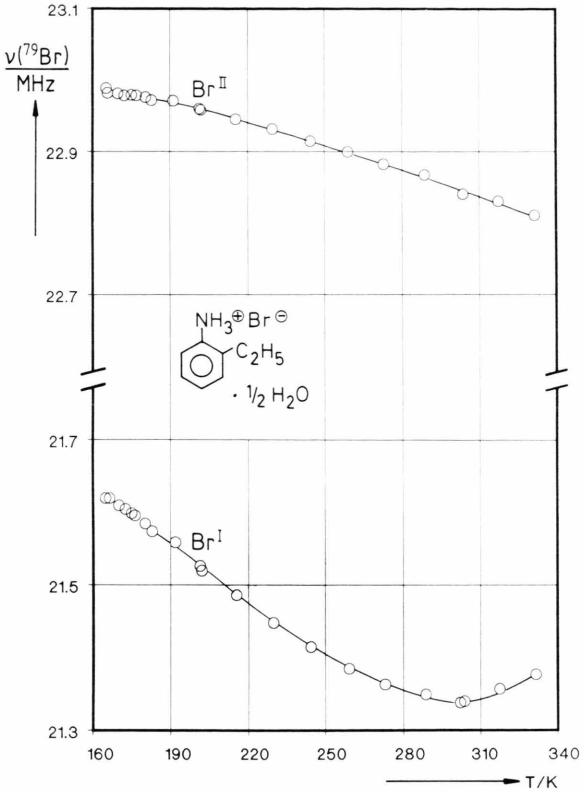

Fig. 4. Temperature dependence of the two ^{79}Br NQR frequencies in 2-ethylanilinium bromide hemihydrate, 2-(C_2H_5)-$C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$ · ½H_2O.

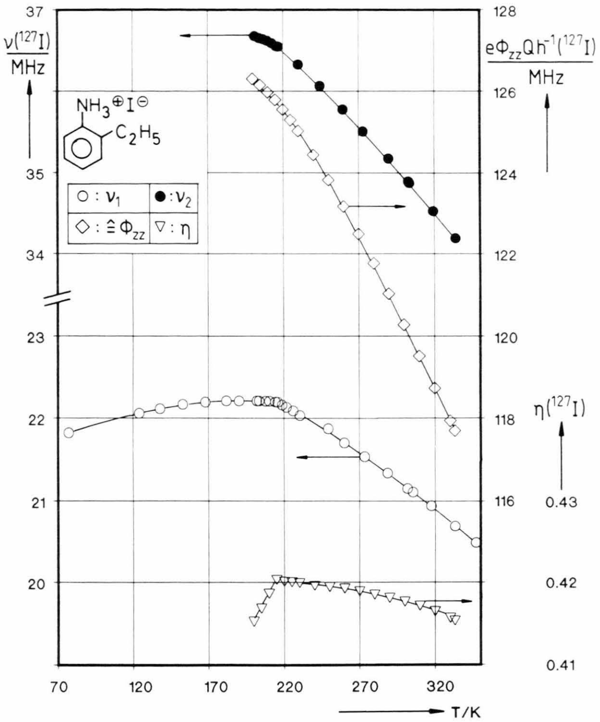

Fig. 5. ^{127}I NQR frequencies, asymmetry parameter $\eta(^{127}I)$, and quadrupole coupling constant $e\Phi_{zz}Qh^{-1}(^{127}I)$ in 2-ethylanilinium iodide, 2-$(C_2H_5)C_6H_4NH_3^{\oplus}$ $I^{\ominus}$, as functions of temperature.

anions, too [10]. In these compounds the inequivality is due to different hydrogen bonding systems in which the $Br^{\ominus}$ anions are involved. In 2-$(C_2H_5)C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$ · ½H_2O the difference of the ^{79}Br frequencies of the two crystallographically inequivalent bromine ions $\Delta\nu = \nu(^{79}Br^{II}) - \nu(^{79}Br^{I}) \approx 1.5$ MHz at room temperature. Both ^{79}Br resonances could be followed up from 164 K to 331 K. In the range $164 \leq T/K \leq 170$ the intensities of both signals decrease. For samples which are cooled below 164 K no NQR signals could be observed after warming up at room temperature. Waiting a few weeks, it was possible to detect again one of the two ^{79}Br resonances. It seems that at $T = 164 \pm 1$ K a phase transition occurs.

In Fig. 4 both ^{79}Br NQR frequencies are plotted as functions of temperature. The frequency of the bromine ion Br^{I} shows a minimum at $T_{min} \approx 300$ K. For numerical Br NQR frequencies, see Table 2.

2-Ethylanilinium Iodide, 2-$(C_2H_5)C_6H_4NH_3^{\oplus}$ $I^{\ominus}$

2-Ethylanilinium iodide crystallizes without crystal water. In a NQR spectrum, searched for in the frequency range $11.5 \leq \nu/MHz \leq 42.6$, two NQR signals were observed. In contrast to the bromide (a hemihydrate) there is only one molecule in the asymmetric unit of the iodide. The first NQR transition, ν_1 can be observed in the temperature range $77 \leq T/K \leq 346$. In contrast, the frequency $\nu_2(^{127}I)$ could only be detected in the range $201 \leq T/K \leq 333$. Below 214 K the signal intensity of this resonance decreases and its line width increases strongly.

Figure 5 shows $\nu(^{127}I)$, $\eta(^{127}I)$, and $e\Phi_{zz}Qh^{-1}$ (^{127}I) of 2-$(C_2H_5)C_6H_4NH_3^{\oplus}$ $I^{\ominus}$ as functions of temperature. At $T \approx 214$ K the temperature coefficient $\Delta\nu_1/\Delta T$ changes from ≈ -12.6 kHz/K ($T = 273$ K) to $\approx +3.3$ kHz/K ($T = 145$ K). This change of the temperature coefficient is strongly reflected in $\eta(^{127}\text{I}) = f(T)$.

In Table 2 we have listed $\nu(^{127}\text{I})$, $\eta(^{127}\text{I})$, and $e\Phi_{zz}Qh^{-1}$ (^{127}I) at some selected temperatures.

1,2-Phenylenediammonium Dibromide, $[1,2\text{-}C_6H_4(NH_3)_2]^{2\oplus}\ [Br^{\ominus}]_2$

For 1,2-phenylenediammonium dibromide, two NQR signals with the frequency ratio $\nu(^{79}\text{Br})/\nu(^{81}\text{Br}) = 1.197$ are found in the frequency range $7 \leq \nu/\text{MHz} \leq 47.3$. The crystal structure (space group Pmmn, $Z = 2$) [14] indicates that there must be two crystallographically inequivalent sites for the bromine ions in the unit cell. Therefore we assume that the NQR frequency of the second Br ion lies outside the range of the used spectrometer. The found ^{79}Br frequency was followed up in the temperature range $77 \leq T/\text{K} \leq 405$.

In Fig. 6 the temperature dependence of the ^{79}Br resonance is shown. At $T = 209$ K a change in the slope of $\nu(^{79}\text{Br}) = f(T)$ occurs. Obviously a phase transition takes place. To get some information about this phase transition an exchange $^1\text{H} \rightarrow {}^2\text{D}$ of the NH_3 protones was carried out. In the compound $[1,2\text{-}C_6H_4(ND_3)_2]^{2\oplus}[Br^{\ominus}]_2$ the ^{79}Br NQR frequency is shifted to lower frequencies. Such a deuteration shift is often observed in organic ammonium halides (see e.g. [1, 7, 15, 16]). The difference of the ^{79}Br frequencies of the protonated and the deuterated compound is $\Delta\nu = \nu(^{79}\text{Br})^{(\text{H})} - \nu(^{79}\text{Br})^{(\text{D})} \approx 420$ kHz at room temperature and ≈ 500 kHz at 77 K. The temperature dependence of the ^{79}Br resonance of the deuterated substance was observed in the range $77 \leq T/\text{K} \leq 419$; the experimental points are plotted in Fig. 6. As in the protonated compound, the slope of $\nu(^{79}\text{Br})^{(\text{D})} = f(T)$ changes at $T_c = 209 \pm 1$ K. There is no shift in the phase transition temperature, in contrast to observations with other anilinium halides [3]. ^{79}Br NQR frequencies at selected temperatures can be found in Table 2.

1,2-Phenylenediammonium Diiodide, $[1,2\text{-}C_6H_4(NH_3)_2]^{2\oplus}\ [I^{\ominus}]_2$

Four ^{127}I NQR signals could be detected in the frequency range $7 \leq \nu/\text{MHz} \leq 47$ for 1,2-phenylenediammonium diiodide. The two resonances at lower frequencies belong to the NQR transitions of one iodine, and the two signals at higher frequencies belong to the other iodine ion. (This is a rather nice example for a unic assignment of the frequencies by using the boundary condition: $\nu_2 \leq 2\,\nu_1$). The two iodine atoms in the molecule are crystallographic inequivalent, and this is confirmed by the crystal structure [17]. 1,2-Phenylenediammonium diiodide and the analogous dibromide are isomorphous at room temperature [14].

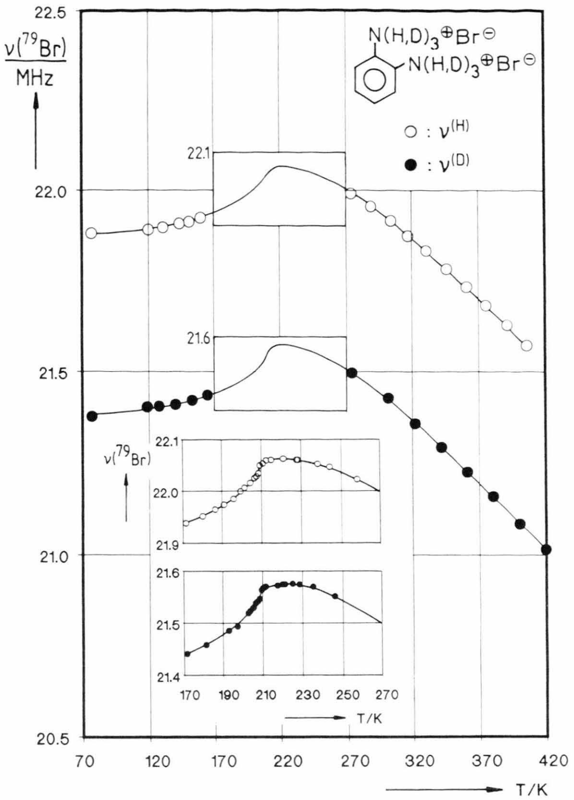

Fig. 6. Temperature dependence of the ^{79}Br NQR frequencies in protonated and deuterated 1,2-phenylenediammonium dibromide, $[1,2\text{-}C_6H_4(N(H,D)_3)_2]^{2\oplus}\ [Br^{\ominus}]_2$.

The four ^{127}I NQR frequencies were measured in the temperature range $77 \leq T/\text{K} \leq 418$ and the results are plotted in Figure 7. At $T_c = 173 \pm 1$ K a phase transition takes place. Near T_c the temperature dependence of ν_1^{II} becomes very strong ($\Delta\nu_1^{\text{II}}/\Delta T \approx 150$ kHz). The NQR frequencies of the iodine atom I cross at $T \approx 153$ K. At this temperature the asymmetry parameter $\eta(^{127}\text{I})$ becomes 1. For temperatures $T < 153$ K the axes of the EFG tensor have to be changed. Quite a similar behaviour was observed in 3-chloroanilinium iodide [12].

The asymmetry parameters and nuclear quadrupole coupling constants are plotted as functions of

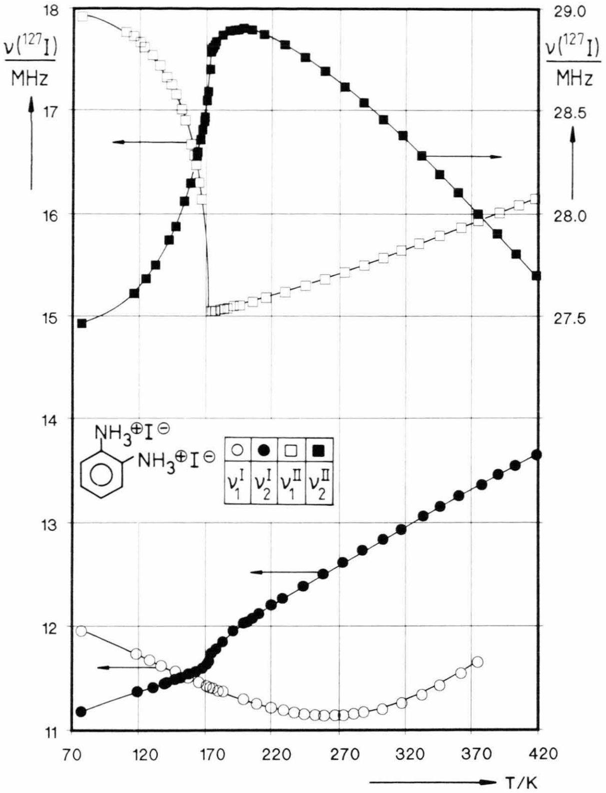

Fig. 7. ^{127}I NQR frequencies of the two crystallographic inequivalent iodine atoms in 1,2-phenylenediammonium diiodide, $[1,2\text{-}C_6H_4(NH_3)_2]^{2⊕}\ [I^⊖]_2$, as functions of temperature.

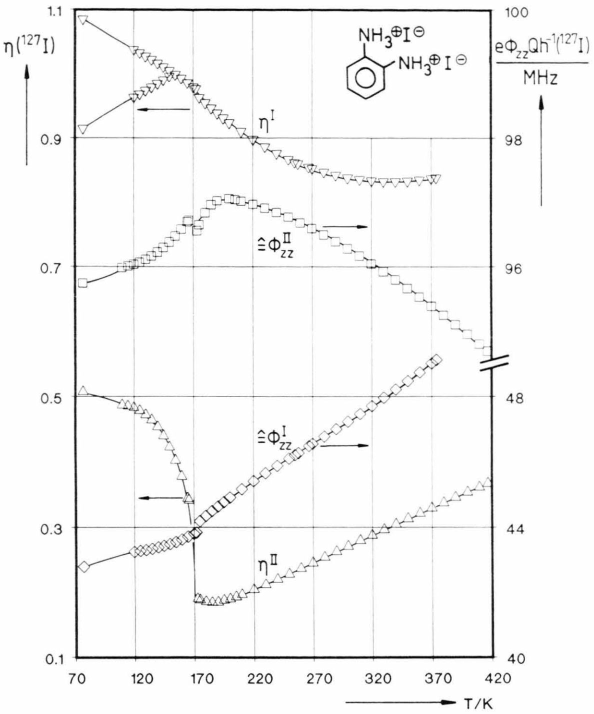

Fig. 8. Asymmetry parameters $\eta(^{127}I)$ and quadrupole coupling constants $e\,\Phi_{zz}\,Q\,h^{-1}\,(^{127}I)$ of the iodine atoms in 1,2-phenylenediammonium diiodide, $[1,2\text{-}C_6H_4(NH_3)_2]^{2⊕}\ [I^⊖]_2$, as functions of temperature.

temperature for both iodine atoms in Figure 8. The phase transition at $T_c = 173 \pm 1$ K shows up clearly. ^{127}I NQR frequencies, asymmetry parameters, and quadrupole coupling constants at selected temperatures are listed in Table 2. The experimental results $\nu(^{79}Br, ^{127}I)$ are rationalized by the expansion

$$\nu_i = \sum_i a_i\, T^i, \qquad i = -1, \dots, 2. \tag{1}$$

The parameters a_i are given in Table 3 for the investigated compounds. In case of phase transitions or of maxima and minima in $\nu = f(T)$, the temperature range is broken up in appropriate sections.

Discussion

Phase Transitions

The phase transitions in 2-ethylanilinium bromide hemihydrate and 2-ethylanilinium iodide are connected with the disappearance of NQR resonance lines or broadening of the signals. These effects on the NQR spectra may be due to freezing of motions of the ethyl group. In case of the hydrobromide the kinetics of the phase transition is an interesting aspect. The transition from the high temperature phase I to the low temperature phase II is fast, but the transition from the phase II to the phase I takes long time.

For 1,2-phenylenediammonium diiodide a total freezing in of the NH$_3$-group rotation (as in anilinium bromide and iodide) can be excluded. Measurements of the second moment of the protons above and below the phase transition temperature T_c show that the rotation of the ammonium groups does not stop even at 77 K [18]. It is possible that only small shifts of the molecules in the crystal packing take place or, more likely, the flipping mechanism of the NH$_3$ groups is changing at T_c, but their frequency is still fast compared to the ^{1}H NMR line width. Such a behaviour

Table 3. Power series expansion of the NQR frequencies $\nu = f(T)$ for the investigated 2-substituted anilinium halides: $f(T) = \sum a_i T^i$; ΔT = temperature range, z = number of experimental points, σ = standard deviation.

Compound	Nucl.	Assign	ΔT/K	z	σ/kHz	$\frac{a_1}{\text{MHz}\cdot\text{K}}$	$\frac{a_0}{\text{MHz}}$	$\frac{10^3 \cdot a_1}{\text{MHz}\cdot\text{K}^{-1}}$	$\frac{10^6 \cdot a_2}{\text{MHz}\cdot\text{K}^{-2}}$
2-$ClC_6H_4NH_3^{\oplus}$ $Br^{\ominus}$	^{79}Br		77–417	23	5.3	−30.326	25.938	−9.453	0.84
2-$(CN)C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$	^{79}Br		77–417	24	7.3	−37.369	23.353	−8.099	−0.35
2-$(CN)C_6H_4NH_3^{\oplus}$ $I^{\ominus}$	^{127}I	ν_2	77–416	26	3.8	−8.346	21.828	−0.065	−6.57
		ν_1	77–416	25	12.5	−48.069	19.692	−11.955	1.70
2-$(C_2H_5)C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$	$^{79}Br^{II}$		165–332	20	2.3	−42.187	23.604	−2.403	1.21
· ½H_2O	$^{79}Br^{I}$		165–332	21	3.8	−279.284	26.264	−23.489	34.00
2-$(C_2H_5)C_6H_4NH_3^{\oplus}$ $I^{\ominus}$	^{127}I	ν_2	201–303	16	17.4	−1229.441	52.001	−50.767	25.33
		ν_1	77–210	11	2.7	18.210	20.708	14.157	−35.44
			214–346	15	12.8	−544.559	29.157	−20.804	0.97
2-$(NH_2)C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$	^{79}Br		77–353	20	9.1	−38.013	28.600	−15.789	6.04
2-$(NH_2)C_6H_4NH_3^{\oplus}$ $I^{\ominus}$	^{127}I	ν_2	121–380	25	24.7	−534.900	29.905	−38.082	9.11
		ν_1	77–276	23	8.8	−43.398	13.020	−5.892	6.41
			279–357	17	4.4	175.956	13.234	−17.314	34.72
$[1{,}2\text{-}C_6H_4(NH_3)_2]^{2\oplus}[Br^{\ominus}]_2$	^{79}Br		77–208	17	3.6	−35.483	22.864	−8.857	27.18
			209–405	20	2.4	−418.922	26.168	−11.493	6.71
$[1{,}2\text{-}C_6H_4(ND_3)_2]^{2\oplus}[Br^{\ominus}]_2$	^{79}Br		77–208	17	4.1	−59.039	22.921	−12.931	36.80
			209–225	8	5.5	−509.133	34.651	−88.850	181.43
			228–419	11	2.3	−365.057	25.221	−10.184	5.33
$[1{,}2\text{-}C_6H_4(NH_3)_2]^{2\oplus}[I^{\ominus}]_2$	^{127}I	ν_2^{II}	77–171	16	18.0	−495.249	41.872	−138.509	453.14
			172–198	11	28.9	3438.262	−43.944	480.059	−1009.84
			205–418	16	3.6	−180.051	31.128	−6.028	−2.74
		ν_1^{II}	77–166	17	37.0	1003.980	−11.718	−287.912	−939.44
			173–417	25	2.4	167.794	12.626	9.025	−3.75
		ν_2^{I}	77–172	12	8.1	−147.694	14.877	−30.644	97.94
			174–418	23	9.5	−280.433	13.153	0.038	6.64
		ν_1^{I}	77–258	20	4.2	−53.627	13.781	−16.854	28.70
			266–374	10	3.3	172.347	12.400	−16.803	36.25

Table 4. Comparison of ^{79}Br NQR frequencies in 2- and 4-substituted anilinium bromides at $T \approx 273$ K.

Compound	2-substituted $\nu(^{79}Br)$/MHz	Ref.	4-substituted $\nu(^{79}Br)$/MHz	Ref.
$ClC_6H_4NH_3^{\oplus}$ $Br^{\ominus}$ [a]	24.824	[b]	19.962	[10]
$(CN)C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$	20.964	[b]	17.815	[8]
$(CH_3)C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$	25.860	[11]	16.352 [c]	[9]
$(C_2H_5)C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$	22.883 [d] 21.363	[b]	15.906	[7]
$[C_6H_4(NH_3)_2]^{2\oplus}$ $[Br^{\ominus}]_2$	21.993	[b]	17.813	[11]

[a] $T = 77$ K. [b] This work. [c] $T = 298$ K. [d] Hemihydrate of 2-$(C_2H_5)C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$.

is reported in [19]. A similar mechanismus as for 1,2-phenylendiammonium diiodide can be assumed for 1,2-phenylenediammonium dibromide.

Comparison of 2-Substituted Anilinium Halides with 4-Substituted Anilinium Halides

In Table 4 we have listed the ^{79}Br NQR frequencies in 2- and 4-substituted anilinium bromides with the same substituent R. The frequencies in the 2-substituted compounds are higher than in the analogous 4-substituted substances. We conclude that the influence of a substituent in ortho-position on the EFG is much stronger than that of a comparable para-position. The ^{79}Br NQR frequency in 2-$(NH_2)C_6H_4NH_3^{\oplus}$ $Br^{\ominus}$ is very high (≈ 27 MHz at 77 K, see Table 2). It is possible that in this compound very weak hydrogen bonds between the NH_2-group and the halogen

Table 5. Comparison of ^{127}I quadrupole coupling constants $e\Phi_{zz}Qh^{-1}$ and asymmetry parameters η in 2- and 4-substituted anilinium iodides at $T \approx 273$ K.

Compound	2-substituted		Ref.	4-substituted		Ref.
	η	$e\Phi_{zz}Qh^{-1}$/MHz		η	$e\Phi_{zz}Qh^{-1}$/MHz	
$ClC_6H_4NH_3^{\oplus}\ I^{\ominus}$	–	–[a]	[10]	0	143.70[b]	[2]
$(CN)C_6H_4NH_3^{\oplus}\ I^{\ominus}$	0.6938	76.480	c	0	146.073	[8]
$(CH_3)C_6H_4NH_3^{\oplus}\ I^{\ominus}$	0.2884	97.840	[11]	0.6352	84.14	[9]
$(C_2H_5)C_6H_4NH_3^{\oplus}\ I^{\ominus}$	0.4186	122.223	c	0.7971	116.65	[7]
$[C_6H_4(NH_3)_2]^{2\oplus}\ [I^{\ominus}]_2$	0.2485 0.8513	96.538 46.574	c	0	143.036	[11]

[a] No ^{127}I NQR, only ^{35}Cl NQR. [b] $T = 295$ K. [c] This work.

anion exist. This was found in the chloride 2-$(NH_2)C_6H_4NH_3^{\oplus}\ Cl^{\ominus}$ [20]. Monohydrobromide and monohydrochloride of 1,2-phenylenediamine are isomorphous [21].

In contrast, the nuclear quadrupole constants, $e\Phi_{zz}Qh^{-1}(^{127}I)$, of the 2-substituted anilinium iodides are higher as well as lower than $e\Phi_{zz}Qh^{-1}(^{127}I)$ in the 4-substituted compounds (see Table 5). The same is true for the asymmetry parameters $\eta(^{127}I)$. The influence of the substituent in the 2-position of the anilinium iodides seems to be not as strong as for the bromides. Additionally the crystal structure plays an important role for the magnitude of the EFG at the site of the halogen nucleus. Unfortunately it is not possible to separate the different influences of the substituent and of the crystal structure.

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