Halogen NQR and Crystal Structure of Ammonium Halides $(R-NH_3)^+ X^-$ and $(X^-) (^+H_3NR'NH_3^+) (X^-)$. $R=(HOCH_2)_3C$, $R'=CH_2C(CH_3)_2CH_2$; $X=I, Br$ *

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The ^{127}I-NQR of $(HOCH_2)_3CNH_3^+ I^-$ was determined in the range $77 \leq T/K \leq 310$. At $T=310$ K the NQR signal fades out ($T_m=463$ K). The ^{127}I spectrum ($T=77$ K): $\nu_1=29.195$ MHz, $\nu_2=14.597$ MHz, $\eta(^{127}I)=0$, $eQ\Phi_{zz}h^{-1}(^{127}I)=97.315$ MHz, is in agreement with the crystal structure.

The ^{127}I NQR spectrum of 1,3-diammonium-2,2-dimethylpropane diiodide, $(H_3NCH_2C(CH_3)_2CH_2NH_3)^{2+} \cdot 2I^-$, is a quartet within the whole temperature range investigated, and the lines correspond to two crystallographically independent iodines: Space group $P2_1/c$, $Z=4$, $a=731.2(3)$ pm, $b=689.0(3)$ pm, $c=2255.1(8)$ pm, $\beta=104.90(1)°$. At $T=77$ K the ^{127}I NQR quartet is (MHz): $\nu_1=34.145$, $\nu_2=32.805$, $\nu_3=22.113$, $\nu_4=16.787$; at 295 K (same order, MHz): 30.559, 29.729, 19.810, 15.651. There are two combinations of the NQR frequencies. Considering the coordination of I^-, the hydrogen bonds $N-H \cdots I$, $eQ\Phi_{zz}Qh^{-1}$, and η, we choose for $I^{(1)}$ ν_1 and ν_3, for $I^{(2)}$ ν_2 and ν_4. At 77 K $eQ\Phi_{zz}h^{-1}(I^{(1)})=118.86$ MHz, $\eta(^{127}I^{(1)})=0.498$, $eQ\Phi_{zz}h^{-1}(I^{(2)})=109.75$ MHz, $\eta(^{127}I^{(2)})=0.135$ follow for the two iodine atoms. Both, $eQ\Phi_{zz}h^{-1}(I^{(1)})$ and $e\Phi_{zz}Qh^{-1}(I^{(2)})$ decrease smoothly with increasing T: $\eta(I^{(2)})$ increases with increasing T whereas $\eta(^{127}I^{(1)})$ is almost constant within $77 \leq T/K \leq 406$.

The $^{79.81}$Br NQR spectrum of 1,3-diamino-2,2-dimethylpropane dihydrobromide is also a quartet, showing two crystallographic inequivalent Br atoms in the unit cell. The frequencies are ($T=273$ K, MHz): $\nu_1(^{79}Br)=14.303$, $\nu_2(^{79}Br)=12.884$, $\nu_1(^{81}Br)=11.951$, $\nu_2(^{81}Br)=10.781$; space group $C2/c$, $Z=8$, $a=2136.4(6)$ pm, $b=854.6(3)$ pm, $c=1125.8(3)$ pm, $\beta=93.23(1)°$.

Crystal structures and NQR results are discussed.

Introduction

Recently we became interested in the structure and dynamics of orientationally disordered solids. Since we have studied by halogen NQR a rather large variety of ammonium salts $RNH_3^+ X^-$, $X=Br,I$ [1–6], we found it favorable to investigate by ^{127}I NQR tris-(hydroxymethyl)methylamine hydroiodide (2-hydroxymethyl-2-amino-1,3-propandiol hydroiodide), $((HOCH_2)_3C(NH_3))^+ I^-$ **1**, for which compound the crystal structure is known [7]. Neither for the hydrobromide of tris-(hydroxymethyl) methylamine nor for the hydroiodide by DSC [7] a phase transition that suggests the onset of orientational disorder and a plastic phase, was observed. Since NQR is quite sensitive to deviations of a crystallized compound from perfect ordering, we have studied the ^{127}I NQR on **1** and report and discuss the results of this study. The propane derivative tris-(hydroxymethyl)aminomethane (=3-amino-2,2-dihydroxymethyl-propanol-1) may form hydrogen bonds which involve the three OH-groups and the NH_2 hydrogen atoms (the NH_3 hydrogen atoms in the hydrohalides, respectively). A search for ^{79,81}Br NQR in $(HOCH_2)_3CNH_3^+ Br^-$ **2** was not successful.

It was also of interest to compare **1** with propane derivatives having similar molecular shape, but fewer possibilities for forming hydrogen bonds, namely the dihydroiodide **3** and dihydrobromide **4** of 1,3-diamino-2,2-dimethylpropane. The crystal structures of the two salts are reported here, as is the ^{127}I and ^{79,81}Br NQR. We compare the hydrogen bond with that of 1,3-diaminopropane dihydroiodide [1, 2].

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Experimental

The compounds have been prepared from aqueous solutions of the respective amines which are commercially available (Aldrich) and hydroiodic acid (hydrobromic acid). The solutions (pH about 3) were concentrated at room temperature by evaporating the solvent slowly, and crystallized.

Small crystals of **3** and **4** were selected and the crystal structures were determined from four circle X-ray diffractometer data. For experimental details see Table 1. The intensities were corrected for absorption and Lorentz-polarisation factor. The structure was determined by direct methods [8]. Hydrogen positions were located from difference Fourier syntheses and all atomic coordinates were refined by least procedure [9].

The ^{127}I NQR spectra have been recorded with a superregenerative spectrometer as function of temperature T. The signal to noise ratio was ≥ 20, using the lock-in technique and a time constant of 10 s. The required temperature at the sample site was created by a temperature- and flow-regulated nitrogen gas stream and by immersion of the sample in liquid nitrogen, respectively. T was measured via a copper-constantan thermocouple to $\pm 0.5°$. The frequencies were measured with a frequency-counter. Their accuracy is determined by the line width to ± 5 kHz. The ^{79,81}Br NQR spectrum showed low signal to noise ratio, $S/N \leq 3$ and the temperature dependence of the spectrum was followed up over a restricted range only.

Results

*The crystal structures of $(H_3NCH_2C(CH_3)_2CH_2NH_3)^{2+}\ 2I^-$ **3** and $(H_3NCH_2C(CH_3)_2CH_2NH_3)^{2+}\ 2Br^-$ **4***

3 crystallizes monoclinic, space group $C^5_{2h}-P2_1/c$, with $Z=4$ formula units in the unit cell. The lattice constants are $a=731.2(3)$ pm, $b=689.0(3)$ pm, $c=2255.1(8)$ pm, $\beta=104.90(1)°$. For further crystallographic data see Table 1. The positional and thermal parameters of the atoms are given in Table 2 and in Table 3 intra- and intermolecular (ionic) distances and angles are listed. For the structure amplitudes, see [10]. In Fig. 1 we show a projection of the unit cell along b (short axis) onto the ac plane.

4 crystallizes monoclinic, space group C^6_{2h}–$C2/c$, $Z=8$, $a=2136.4(6)$, $b=854.6(3)$, $c=1125.8(3)$, $\beta=93.23(1)$. The positional and thermal parameters are given in Table 4, the intra- and intermolecular (ionic) distances and angles in Table 5. For the structure amplitudes, see [10]. In Fig. 2 the unit cell of the compound is projected along the twofold axis [010] onto the ac plane.

The ^{127}I and ^{79,81}Br NQR results

In Fig. 3 the NQR transitions, respectively the frequencies $\frac{1}{2}\nu_1$ and ν_2 of **1** in their dependence on T are plotted and in Fig. 4 $e\Phi_{zz}Qh^{-1}(^{127}\text{I})=f(T)$ is shown. The asymmetry parameter $\eta(^{127}\text{I})=f(T)$ is constant and equal to zero as the NQR experiment shows, in agreement with the crystal structure deter-

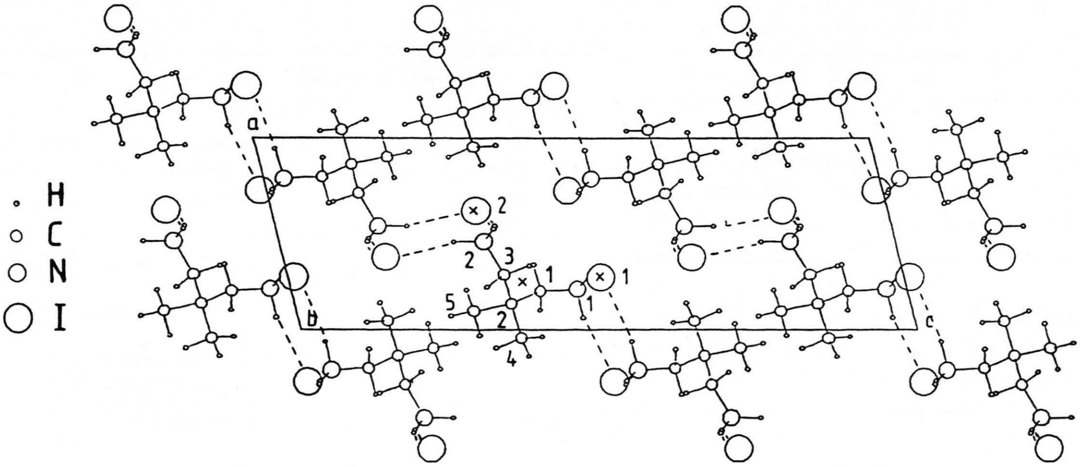

Fig. 1. Projection of the unit cell of $(H_3NCH_2C(CH_3)_2CH_2NH_3)^{2+}2I^-$ (**3**) along the twofold axis [010] onto the *ac* plane. The hydrogen bonds are marked by dashed lines. The atoms for which the coordinates are given in Table 2 are numbered and marked by asterisk.

Table 1. Experimental conditions for the crystal structure determination and crystallographic data for $[H_3NCH_2(CH_3)_2)CH_2NH_3]^{2+}$ $(2I^-)$ (**3**) and $[H_3NCH_2(CH_3)_2CH_2NH_3]^{2+}$ $(2Br^-)$ (**4**). Diffractometer: Stoe-Stadi 4; wavelength: 71.069 pm (MoKα); Monochromator: Graphite (002); scan: $2\vartheta/\omega$; $M = 358.00$ **3**, 264.00 **4**.

Formula	$C_5H_{16}I_2N_2$ (**3**)	$C_5H_{16}Br_2N_2$ (**4**)
Crystal size/mm³	$0.2 \times 0.4 \times 0.8$	$0.25 \times 0.35 \times 0.41$
Colour	colourless	colourless
Temperature/K	295	301
Absorption coefficient (μ/m^{-1})	5610	7770
$(\sin\vartheta/\lambda)_{max}$	0.0065	0.0065
Number of reflexions measured	3759	3395
Symmetry independent	2510	2357
Considered ($F \le 2\sigma(F)$)	2432	2130
F (000)	664	107
R (F)	0.062	0.053
R_w (F)	0.059	0.045
R_m (F)	0.062	0.046
Lattice constants:		
a/pm	731.2(3)	2136.4(6)
b/pm	689.0(3)	854.6(3)
c/pm	2255.1(8)	1125.8(3)
β/°	104.90(1)	93.23(1)
$V_{\text{unit cell}} \cdot 10^{-6}/(\text{pm})^3$	1097.9(11)	2052.2(18)
Space group	$C^5_{2h}-P2_1/c$	$C^6_{2h}-C2/c$
Formula units/ Ecell Z	4	8
$\varrho_{calc}/(\text{Mg} \cdot \text{m}^{-3})$	2.165(2)	1.709(2)
Point positions	All atoms in 4e: $(x, y, z; \bar{x}, \bar{y}, \bar{z};$ $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z;$ $x, \frac{1}{2}-y, \frac{1}{2}+z)$	All atoms in 8f: $(000, 1/2, 1/2, 1/2)^+$ $x, y, z; \bar{x}, \bar{y}, \bar{z};$ $\bar{x}, y, \frac{1}{2}-z$ $x, \bar{y}, \frac{1}{2}+z$

mination [7]. (There is probably a printing error in [7]; we calculate from the published coordinates and the space group (cubic body centered) a distance N–H · · I which is far below the sum of the ionic radii of NH_4^+ and I^-).

In agreement with the results of the crystal structure, the ^{127}I NQR spectrum of **3** is a quartet of which two lines correspond to the transition $m = \pm 1/2 \leftrightarrow m = 3/2$, and two to the transition $m = \pm 3/2 \leftrightarrow m = 5/2$ ($I(^{127}I) = 5/2$). In Fig. 5 the ^{127}I NQR frequencies are plotted as function of T. Assigning ν_1 and ν_3 to one of the two crystallographically independent iodines, ν_2 and ν_4 to the other one, the

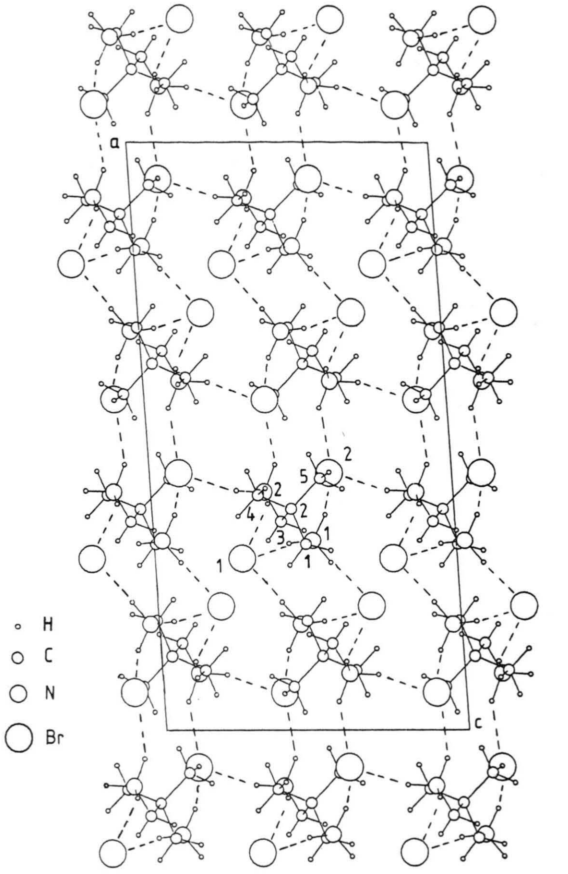

Fig. 2. Projection of the unit cell of $(H_3NC_2C(CH_3)_2CH_2NH_3)^{2+}$ $2Br^-$ (**4**) along the twofold axis [010] onto the *ac* plane. The hydrogen bonds are marked by dashed lines. The atoms for which the coordinates are given in Table 4 are numbered and marked by asterisk.

asymmetry parameter $\eta(^{127}I)$, $\eta = |\Phi_{XX} - \Phi_{YY}|/|\Phi_{zz}|$ and the nuclear quadrupole coupling constant (NQCC), $eQ\Phi_{zz}h^{-1}(^{127}I)$, e = unit charge, Q = nuclear electric quadrupole moment, Φ_{zz} = main principal axis of the electric field gradient tensor, EFGT, can be calculated. In Fig. 6 the results for **3** are shown in their dependence from T. It is common practice to describe the temperature dependence of NQR frequencies by a power series $\nu = \sum_{i=-1}^{2} (a_i T^i)$. The coefficients a_i are given in Table 6 for **1** and **3**. Frequencies at selected temperatures are included. Table 7 gives $\eta(^{127}I)$, $eQ\Phi_{zz}h^{-1}(^{127}I)$ for selected temperatures, for **1** and **3** and the coefficients of the power series $\eta(^{127}I) = \sum_{i=-1}^{2} (a_i T^i)$ and $e\Phi_{zz}Qh^{-1}(^{127}I) = \sum_{i=-1}^{2} (a_i T^i)$.

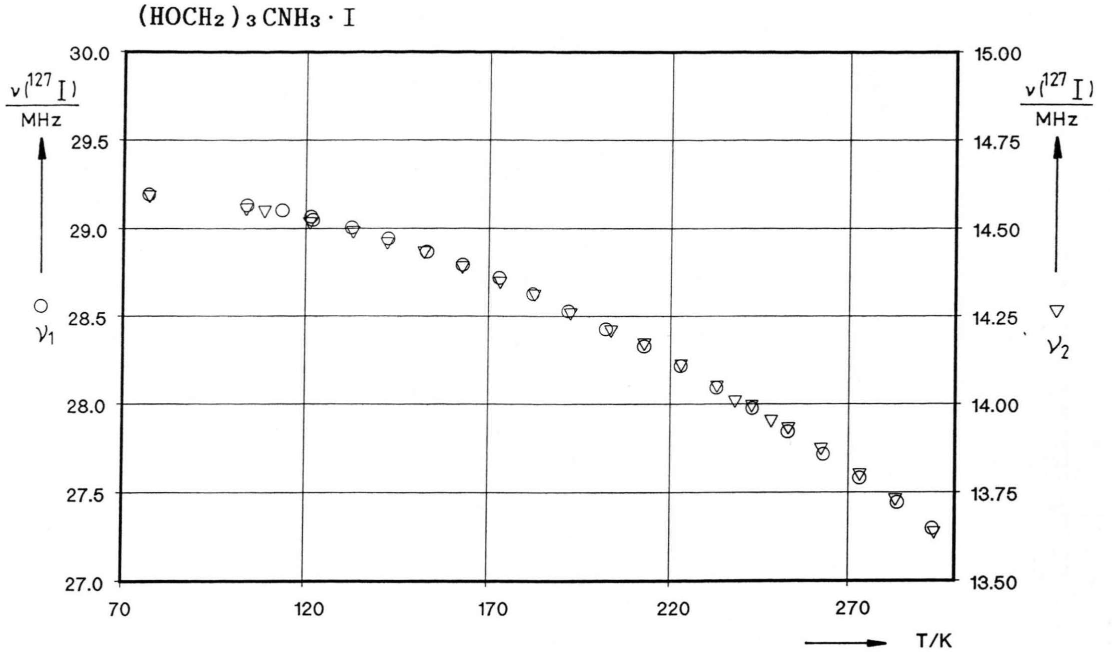

Fig. 3. $\frac{1}{2}\nu_2(^{127}I)$ and $\nu_1(^{127}I)$ of $(HOCH_2)_3CNH_3^+ I^-$ (**1**) as a function of temperature. Only one curve results because of $\eta(^{127}I)$ is zero by the point symmetry of the iodine atom (threefold axis).

Table 2. Positional and thermal parameters of **3**. The temperature factor is of the form: $T=\exp\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+U_{12}hka^*b^*+U_{13}hla^*c^*+U_{23}klb^*c^*)\}$. The U_{ij} are given in (pm^2); U is the isotropic mean squares thermal amplitude.

Atom	x/a	y/b	z/c	U_{11}, U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$I^{(1)}$	0.2737(1)	0.7182(1)	0.5100(1)	335(4)	334(5)	278(3)	13(3)	65(3)	15(3)
$I^{(2)}$	0.6220(1)	0.8608(1)	0.3333(1)	487(5)	329(5)	558(5)	−16(4)	241(4)	−42(4)
$N^{(1)}$	0.2112(11)	0.2135(13)	0.4668(3)	313(42)	396(54)	236(38)	9(41)	50(33)	18(37)
$N^{(2)}$	0.4604(10)	0.3722(13)	0.3331(4)	208(38)	399(56)	429(46)	10(40)	109(35)	106(42)
$C^{(1)}$	0.2013(13)	0.1347(14)	0.4053(4)	479(55)	475(65)	438(50)	−40(42)	113(44)	46(42)
$C^{(2)}$	0.1358(14)	0.2847(15)	0.3520(4)	423(54)	410(62)	563(58)	−43(50)	−61(46)	2(50)
$C^{(3)}$	0.2882(12)	0.4428(14)	0.3516(4)	379(48)	530(66)	489(51)	−38(61)	172(41)	33(50)
$C^{(4)}$	−0.0450(13)	0.3868(16)	0.3549(5)	426(56)	786(90)	593(62)	164(61)	206(50)	88(61)
$C^{(5)}$	0.0969(17)	0.1615(17)	0.2905(4)	845(82)	781(89)	391(52)	−246(74)	202(56)	−214(58)
$H^{(N1,1)}$	0.2693(11)	0.0841(13)	0.4916(3)	600					
$H^{(N1,2)}$	0.0664(11)	0.2319(13)	0.4689(3)	600					
$H^{(N1,3)}$	0.2935(11)	0.3380(13)	0.4872(3)	600					
$H^{(N2,1)}$	0.5302(10)	0.5055(13)	0.3514(4)	600					
$H^{(N2,2)}$	0.4559(10)	0.3611(13)	0.2850(4)	600					
$H^{(N2,3)}$	0.5375(10)	0.2502(13)	0.3575(4)	600					
$H^{(C1,1)}$	0.3402(13)	0.0828(14)	0.4048(4)	600					
$H^{(C1,2)}$	0.1026(13)	0.0150(14)	0.3970(4)	600					
$H^{(C3,1)}$	0.3342(12)	0.5026(14)	0.3973(4)	600					
$H^{(C3,2)}$	0.2227(12)	0.5555(14)	0.3200(4)	600					
$H^{(C4,1)}$	−0.1510(13)	0.2833(16)	0.3599(5)	600					
$H^{(C4,2)}$	−0.0890(13)	0.4547(16)	0.3103(5)	600					
$H^{(C4,3)}$	−0.0281(13)	0.4962(16)	0.3902(5)	600					
$H^{(C5,1)}$	0.0717(17)	0.2533(17)	0.2504(4)	600					
$H^{(C5,2)}$	−0.0319(17)	0.0869(17)	0.2913(4)	600					
$H^{(C5,3)}$	0.2059(17)	0.0572(17)	0.2891(4)	600					

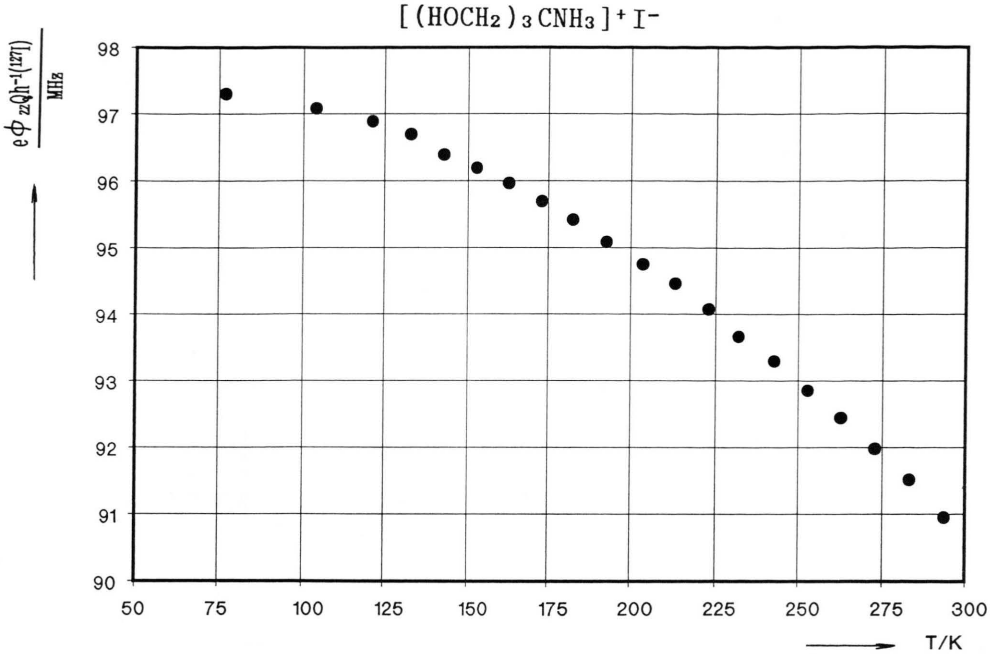

Fig. 4. Nuclear quadrupole coupling constant $e\Phi_{zz}Qh^{-1}(^{127}\mathrm{I})$ of **1** as function of temperature. $\eta(^{127}\mathrm{I})$ is, by symmetry, zero.

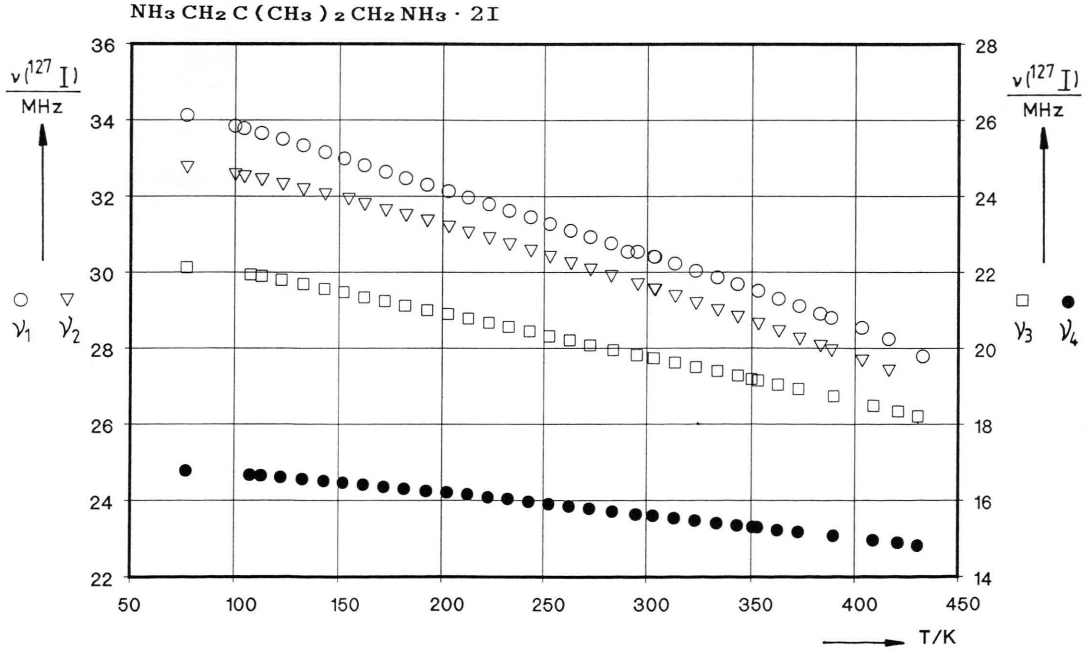

Fig. 5. The temperature dependence of the four $^{127}\mathrm{I}$ NQR frequencies $\nu_{1..4}$ of **3**.

Table 3. Intra- and intermolecular (ionic) distances and angles in the crystal structure of **3.** The distances *d* are given in pm, the angles in degree.

Connection	*d*/pm	Connection	Angle/°
$N^{(1)}-C^{(1)}$	147.4(10)	$C^{(1)}-C^{(2)}-C^{(3)}$	112.8(8)
$C^{(1)}-C^{(2)}$	156.4(12)	$C^{(1)}-C^{(2)}-C^{(4)}$	111.8(9)
$C^{(2)}-C^{(3)}$	156.0(13)	$C^{(1)}-C^{(2)}-C^{(5)}$	105.6(8)
$C^{(2)}-C^{(4)}$	151.4(13)	$C^{(3)}-C^{(2)}-C^{(4)}$	108.0(8)
$C^{(2)}-C^{(5)}$	158.7(13)	$C^{(3)}-C^{(2)}-C^{(5)}$	109.7(8)
$N^{(2)}-C^{(3)}$	150.6(11)	$C^{(4)}-C^{(2)}-C^{(5)}$	108.9(8)
$N^{(1)}\cdot\cdot I^{(1)}$	360.8(9)	$N^{(1)}-C^{(1)}-C^{(2)}$	114.3(8)
$N^{(1)}\cdot\cdot I^{(1)\prime}$	354.7(9)	$N^{(2)}-C^{(3)}-C^{(2)}$	115.1(8)
$N^{(1)}\cdot\cdot I^{(1)\prime\prime}$	374.4(9)		
$N^{(2)}\cdot\cdot I^{(2)}$	365.8(8)		
$N^{(2)}\cdot\cdot I^{(2)\prime}$	371.6(8)		
$N^{(2)}\cdot\cdot I^{(2)\prime\prime}$	364.5(8)		
$I^{(1)}\cdot\cdot I^{(1)\prime\prime\prime}$	457.8(1)		
$I^{(1)}\cdot\cdot I^{(2)\prime\prime\prime}$	448.3(1)		
$I^{(2)}\cdot\cdot I^{(2)\prime\prime\prime\prime}$	507.1(1)		

Hydrogen bond scheme

Connection	$d(N\cdots I)$	$d(H\cdots I)$	$\sphericalangle(N-H\cdots I)$
$N^{(1)}-H^{(1,1)}\cdot\cdot I^{(1)\prime}$	354.7	255	155
$H^{(1,2)}\cdot\cdot I^{(1)\prime\prime}$	374.4	267	166
$H^{(1,3)}\cdot\cdot I^{(1)}$	360.8	268	145
$N^{(2)}-H^{(2,1)}\cdot\cdot I^{(2)}$	356.8	260	146
$N^{(2)}-H^{(2,2)}\cdot\cdot I^{(2)\prime\prime}$	364.5	258	167
$N^{(2)}-H^{(2,3)}\cdot\cdot I^{(2)\prime}$	371.6	284	139

$I^{(1)\prime}: x, y-1, z$; $I^{(1)\prime\prime}: -x, 1-y, 1-z$; $I^{(1)\prime\prime\prime}: 1-x, 1-y, 1-z$; $I^{(2)\prime}: x, y-1, z$; $I^{(2)\prime\prime}: 1-x, y-\frac{1}{2}, \frac{1}{2}-z$; $I^{(2)\prime\prime\prime}: 1-x, 2-y, 1-z$; $I^{(2)\prime\prime\prime\prime}: 1-x, y+\frac{1}{2}, \frac{1}{2}-z$.

Table 5. Intra(inter)molecular(ionic) distances (in pm) and angles (in degree) for **4**.

Connection	*d*/pm	Connection	Angle/°
$N^{(1)}-C^{(1)}$	150.2(7)	$C^{(1)}-C^{(2)}-C^{(3)}$	102.6(5)
$C^{(1)}-C^{(2)}$	153.0(8)	$C^{(1)}-C^{(2)}-C^{(4)}$	111.4(5)
$C^{(2)}-C^{(3)}$	154.8(8)	$C^{(1)}-C^{(2)}-C^{(5)}$	110.7(5)
$C^{(2)}-C^{(4)}$	152.3(8)	$C^{(3)}-C^{(2)}-C^{(4)}$	110.3(5)
$C^{(2)}-C^{(5)}$	154.5(8)	$C^{(3)}-C^{(2)}-C^{(5)}$	110.7(5)
$N^{(2)}-C^{(3)}$	149.5(7)	$C^{(4)}-C^{(2)}-C^{(5)}$	110.9(5)
$N^{(1)}\cdots Br^{(1)\prime}$	329.8(3)	$N^{(1)}-C^{(1)}-C^{(2)}$	113.0(5)
$N^{(1)}\cdots Br^{(1)\prime\prime}$	332.0(3)	$N^{(2)}-C^{(3)}-C^{(2)}$	114.0(5)
$N^{(1)}\cdots Br^{(2)\prime}$	326.5(3)		
$N^{(2)}\cdots Br^{(2)\prime\prime}$	343.1(3)		
$N^{(2)}\cdots Br^{(2)\prime\prime\prime}$	331.1(3)		
$N^{(2)}\cdots Br^{(2)\prime\prime\prime}$	343.1(3)		

Hydrogen bond scheme

Connection	$d(N\cdots Br)$	$d(H\cdots Br)$	$\sphericalangle(N-H\cdots Br)$
$N^{(1)}-H^{(1,3)}\cdots Br^{(1)\prime}$	329.8	222	178
$N^{(1)}-H^{(1,1)}\cdots Br^{(1)\prime\prime}$	332.0	225	172
$N^{(1)}-H^{(1,2)}\cdots Br^{(2)\prime}$	326.5	238	138
$N^{(2)}-H^{(2,1)}\cdots Br^{(2)\prime\prime}$	343.1	247	147
$N^{(2)}-H^{(2,2)}\cdots Br^{(2)\prime\prime\prime}$	331.1	226	165
$N^{(2)}-H^{(2,3)}\cdots Br^{(1)\prime\prime\prime}$	343.1	257	136

$Br^{(1)\prime}: 1-x, 1-y, 1-z$; $Br^{(1)\prime\prime}: \frac{1}{2}+x, \frac{1}{2}+y, z$; $Br^{(1)\prime\prime\prime}: \frac{1}{2}+x, y-\frac{1}{2}, z$; $Br^{(2)\prime}: 1-x, 1-y, 1-z$; $Br^{(2)\prime\prime}: 1+x, y, z$; $Br^{(2)\prime\prime\prime}: 1-x, -y, 1-z$.

Table 4. Positional and thermal parameters of **4**. For the definition of $U_{i,k}$, see Table 2.

Atom	x/a	y/b	z/c	U_{11}, U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Br^{(1)}$	0.2908(1)	0.351(1)	0.2907(1)	449(4)	399(4)	380(4)	10(30)	17(3)	−49(3)
$Br^{(2)}$	0.0633(1)	0.1571(1)	0.4015(1)	451(4)	447(4)	370(4)	−32(3)	21(3)	51(3)
$N^{(1)}$	0.8218(2)	0.6023(5)	0.5284(5)	428(31)	318(27)	367(34)	64(24)	65(27)	20(26)
$N^{(2)}$	0.9047(2)	0.0905(5)	0.3784(5)	511(33)	259(26)	259(26)	1(23)	40(28)	8(25)
$C^{(1)}$	0.8158(3)	0.4295(7)	0.5058(7)	347(36)	317(33)	317(33)	26(28)	45(34)	4(33)
$C^{(2)}$	0.8760(3)	0.3559(6)	0.4639(5)	325(32)	256(30)	256(30)	−8(25)	64(28)	4(28)
$C^{(3)}$	0.8545(3)	0.1886(8)	0.4282(7)	396(37)	290(33)	290(33)	−19(29)	41(33)	1(33)
$C^{(4)}$	0.8994(3)	0.4421(7)	0.3566(6)	564(43)	298(33)	298(33)	−5(30)	176(38)	0(33)
$C^{(5)}$	0.9272(3)	0.3507(8)	0.5664(6)	472(40)	497(42)	497(42)	39(33)	−78(35)	−105(37)
$H^{(N1,1)}$	0.8166(2)	0.6745(5)	0.4497(5)	500					
$H^{(N1,2)}$	0.8660(2)	0.6280(5)	0.5755(5)	500					
$H^{(N1,3)}$	0.7839(2)	0.6261(5)	0.5854(5)	500					
$H^{(N2,1)}$	0.9514(2)	0.0923(5)	0.4204(5)	500					
$H^{(N2,2)}$	0.9068(2)	0.1194(5)	0.2853(5)	500					
$H^{(N2,3)}$	0.8848(2)	−0.0249(5)	0.3870(5)	500					
$H^{(C1,1)}$	0.7792(26)	0.4196(68)	0.4475(56)	500					
$H^{(C1,2)}$	0.8048(26)	0.3929(68)	0.5877(55)	500					
$H^{(C3,1)}$	0.8219(26)	0.1885(72)	0.3807(57)	500					
$H^{(C3,2)}$	0.8395(26)	0.1269(65)	0.5031(57)	500					
$H^{(C4,1)}$	0.9403(3)	0.3839(7)	0.3260(6)	500					
$H^{(C4,2)}$	0.9117(3)	0.5595(7)	0.3848(6)	500					
$H^{(C4,3)}$	0.8635(3)	0.4471(7)	0.2851(6)	500					
$H^{(C5,1)}$	0.9690(3)	0.2966(8)	0.5354(6)	500					
$H^{(C5,2)}$	0.9096(3)	0.2816(8)	0.6375(6)	500					
$H^{(C5,3)}$	0.9383(3)	0.4671(8)	0.5985(6)	500					

Table 6. ^{127}I NQR frequencies at selected temperatures and coefficients of the power series for **1** and **3**. The power series to describe $= f(T)$ is $\nu = \sum_{i=-1}^{2} (a_i T^i)$. The frequencies are given in MHz. z is the number of measurements, σ is the mean squares deviation. For **1** the power series is valid for the range $77 \leq T/\mathrm{K} \leq 294$. For **3** the range is $77 \leq T/\mathrm{K} \leq 431$.

	77 K	295 K	z	σ / kHz	a_0 / MHz	a_{-1} / MHz · K	$a_1 \cdot 10^3$ / MHz · K^{-1}	$a_2 \cdot 10^6$ / MHz · K^{-2}
$(HOCH_2)_3CNH_3^+\ I^-$ (**1**)								
ν_1	29.196	27.297[a]	22	5.9	29.849	−30.92	−1.524	−23.244
ν_2	14.596	13.640[b]						
$(H_3NCH_2C(CH_3)_2CH_2NH_3)^{2+}\ 2I^-$ (**3**)								
ν_1	34.145	30.559	34	16.8	35.615	−14.707	−15.862	−3.785
ν_2	32.805	29.729	34	6.0	34.367	−42.068	−12.385	−9.549
ν_3	22.119	19.811	34	14.9	23.779	−47.328	−13.392	1.780
ν_4	16.788	15.651	34	8.8	17.636	−28.355	−6.363	0.011

[a] 293.6 K; [b] 294.0 K

Table 7. Nuclear quadrupole coupling constants $e\Phi_{zz}Qh^{-1}$ (^{127}I) and asymmetry parameters η(^{127}I) for **1** and **3**. z is the number of measurements, σ is the mean squares deviation. For **1** η(^{127}I) is zero over the whole temperature range covered. The range for which the polynomials are valid is $77 \leq T/\mathrm{K} \leq 294$ for **1**, $77 \leq T/\mathrm{K} \leq 431$ for **3**.

T / K	$e\Phi_{zz}Qh^{-1}$ / MHz; (η)	z	σ / kHz	a_0 / MHz	a^{-1} / MHz · K	$a_1 \cdot 10^4$ / MHz · K^{-1}	$a_2 \cdot 10^7$ / MHz · K^{-2}
$(HOCH_2)_3CNH_3^+\ I^-$ (**1**)							
77	97.314	20	20	98.756	−67.2621	−3.32629	−858.344
273.0	91.850						
293.8	90.962						
$(H_3NCH_2C(CH_3)_2CH_2NH_3^+\ 2I^-$ (**3**)							
a) $I^{(1)}, \nu_1, \nu_3; e\Phi_{zz}Qh^{-1}(^{127}I^{(1)})$							
77	118.900	31	5.7	125.634	−132.323	−638.289	2.82163
272.8	107.760						
373.0	101.500						
b) $I^{(2)}, \nu_2, \nu_4; e\Phi_{zz}Qh^{-1}(^{127}I^{(2)})$							
77	109.755	31	3.2	115.390	−165.137	−435.584	−233.018
272.8	101.157						
373.0	95.390						
a) $\eta^{(1)}, \nu_1, \nu_3; \eta(^{127}I^{(1)})$							
77	0.4990	31	0.0011	0.53611	−1.80437	−1.37775	−1.74666
272.8	0.5000						
373.0	05010						
b) $\eta^{(2)}, \nu_2, \nu_4; \nu(^{127}I^{(2)})$							
77	0.1350	31	0.0016	0.10709	0.06377	2.43085	2.83684
272.8	0.1970						
373.0	0.2420						

Table 8. $(H_3NCH_2C(CH_3)_2CH_2NH_3)^{2+}\ 2Br^-$ (**4**): ^{79,81}Br NQR frequencies at selected temperatures and coefficients of the power series development $\nu(T) = \sum_{i=-1}^{2} (a_i T^i)$. The development is valid in the range $228 \leq T/\mathrm{K} \leq 354$. z, the number of measurements, is 10 for each $\nu_1(^j\mathrm{Br})$, σ is the mean squares deviation, given in kHz.

ν_i	228 K	300 K	σ	a_0 / MHz	a_{-1} / MHz · K	$a_1 \cdot 10^3$ / MHz · K^{-1}	$a_2 \cdot 10^6$ / MHz · K^{-2}
ν_1 (^{79}Br)	14.520	14.148	12.3	7.316	685.645	28.664	−44.910
ν_2 (^{79}Br)	13.651	12.461	21.7	20.163	−106.096	−32.885	28.124
ν_1 (^{81}Br)	12.121	11.832	11.2	9.056	293.784	13.583	−25.298
ν_2 (^{81}Br)	11.403	10.488	19.1	16.919	−130.713	−26.578	20.578

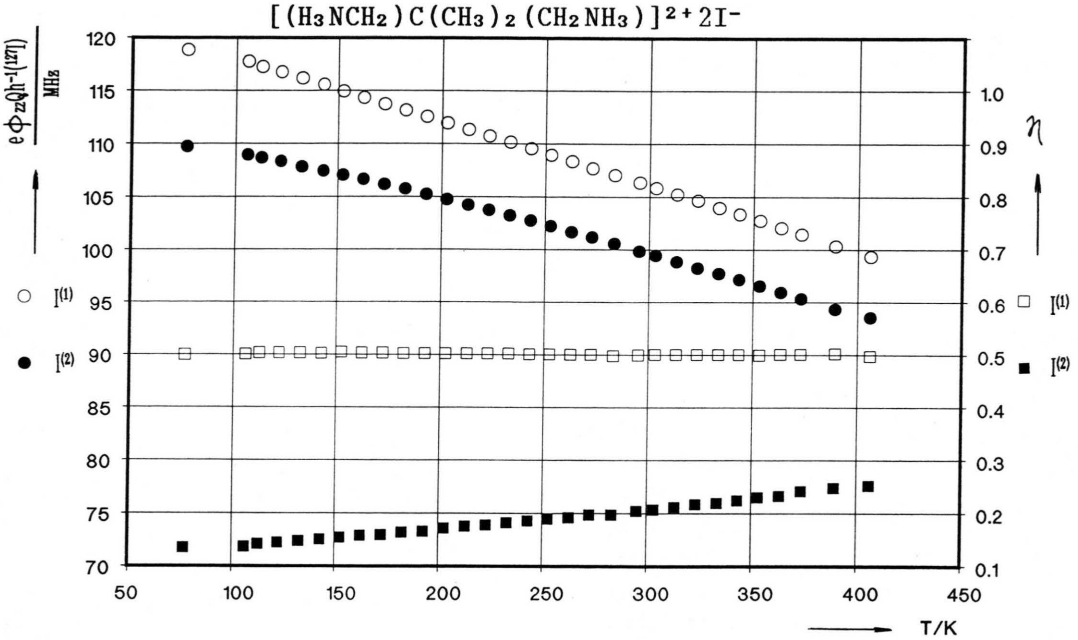

Fig. 6. The temperature dependence of $e\Phi_{zz}Qh^{-1}$ (^{127}I) and η(^{127}I) of **3**. From the possible combinations of frequencies in calculating the curves ν_1 and ν_3 have been assigned to the one ($I^{(1)}$) of the two crystallographical independent iodines, ν_2 and ν_4 to $I^{(2)}$.

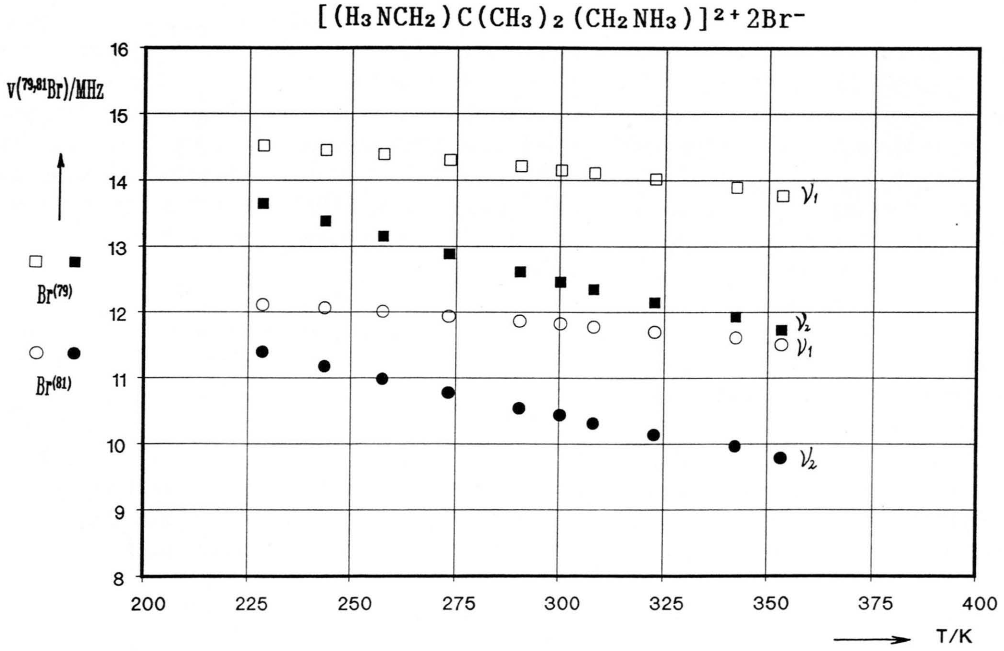

Fig. 7. Temperature dependence of the ^{79,81}Br NQR spectrum of **4** within the restricted range $228 \leq T/\mathrm{K} \leq 353$.

For the Br NQR of **4** frequencies at selected T and the coefficients of $v_i = \sum_{i-1}^{2} (a_i\, T^i)$ are given in Table 8; the functions $v_i = f\,(T)$ are shown graphically in Figure 7. For numerical values of frequencies as function of T see [10].

Discussion

^{127}I NQR of $(HOCH_2)_3CNH_3^+ I^-$ **1**

The low bleach out temperature of the ^{127}I NQR signal in **1** points the onset of orientational disorder of the cation $[(HOCH_2)_3CNH_3]^+$. There is no true phase transition from the ordered phase II to a possible orientational disordered phase (plastic phase) I as the investigations of Reuben et al. [7] have shown. However the excitation of reorientational motions of the NH_3 group and of OH groups may well lead to rather broad ^{127}I NQR lines and make the NQR resonance unobservable by the method we have used. ^{2}H NMR as a function of T on the deuterated cation $[DOCH_2)_3ND_3]^+$ should clear up this point.

Structure and ^{127}I NQR of $[H_3NCH_2C(CH_3)_2CH_2NH_3]^{2+}\ 2I^-$ **3**

The crystal structure of **3** is a quite regular packing of cations and anions in the unit cell. The carbon atoms $C^{(2)}$, $C^{(1)}$, $C^{(3)}$, $C^{(4)}$, and $C^{(5)}$ form a tetrahedron with $C^{(2)}$ in the center and distances $d(C^{(2)}-C^{(i)})$ between 159 and 151 pm, $\langle d \rangle = 155.6$ pm, a value within the range expected for aliphatic C–C bonds. There is a weak distortion due to the shortening of the bond $C^{(2)}-C^{(4)}H_3$ and a lengthening of $d(C^{(2)}-C^{(5)}H_3)$ compared to the mean value, due to the overcrowded geometry around $C^{(2)}$. Also the deviations of the angles which include $C^{(2)}$ from 109° are induced by the dense packing around $C^{(2)}$. The mean is 108° but the extreme values are 113° and 106°, see Table 3. Since angles are rather weak bond parameters, the angular distortion of the C_5 tetrahedron is not surprising.

If we take the ionic radii of NH_4^+ and I^- from literature [11], 160 pm and 200 pm, respectively, ($\Sigma = 360$ pm), we see that the distances N ·· I we observe, 355 pm to 374 pm (Table 3), correspond to ionic crystals. For comparison: In 1,3-diaminopropane dihydroiodide d(N ·· I) is between 360 pm and 370 p for $I^{(1)}$ ·· N and 352 pm and 360 pm for $I^{(2)}$ ·· N [1]. In the NaCl-type phase of NH_4I the distance N ·· I is 362 pm [12], for the CsCl-type phase it is 378 pm [13].

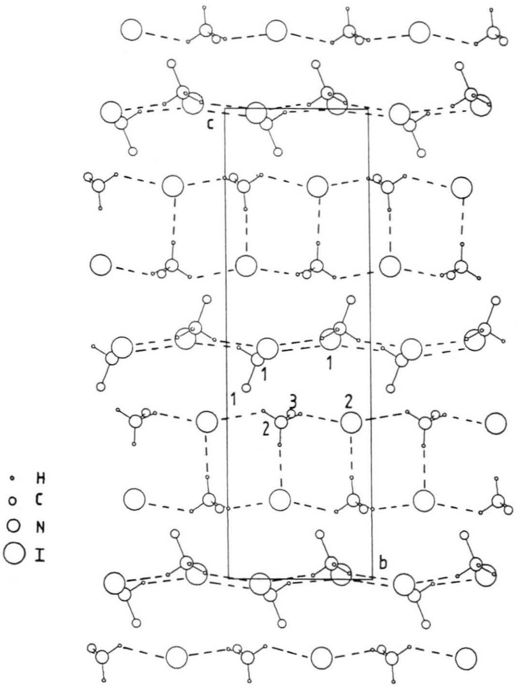

Fig. 8. Projection of the unit cell of **3** along [100] onto the *bc* plane. The hydrogen bonds N–H ·· I are marked by dashed lines.

The hydrogen bonds N–H ·· I in the title compound are such, that three such bonds connect the group $N^{(1)}H_3$ with $I^{(1)}$, respectively $N^{(2)}H_3$ with $N^{(2)}$. There is not much difference in the bond N ··· I distances between $N^{(1)}$ ·· $I^{(1)}$ and $N^{(2)}$ ·· $I^{(2)}$. In Fig. 8 we show a projection of the unit cell of **3** along [100] onto the *bc* plane. Comparing Fig. 8 with Fig. 1 one can see that there is a hydrogen bond network which connects anions and cations. However within this network there are planes which are connected by van der Waals forces only.

Our assignment, v_1 and v_3 belonging to $I^{(1)}$, v_2 and v_4 to $I^{(2)}$ is based on several arguments. At first, the combination v_1, v_4, and v_2, v_3 is excluded because v_1/v_4 is >2. Secondly the combination v_1, v_2 and v_3, v_4 leads to an asymmetry parameter $\eta(^{127}I)$ almost 1 for v_1, v_2 which is quite unlikely, as we know from other investigations of the EFGT (^{127}I) in iodides with bonds N–H ·· I, particularly also with respect to the pseudotrigonal axis I ·· H_3N. One could assure the chosen combination by investigating v_i (^{127}I) in the partially deuterated compound $(D_3NCH_2C(CH_3)_2CH_2ND_3)^{2+}\ 2I^-$. The deuteration shift should be slightly different for the two iodines and therefore for

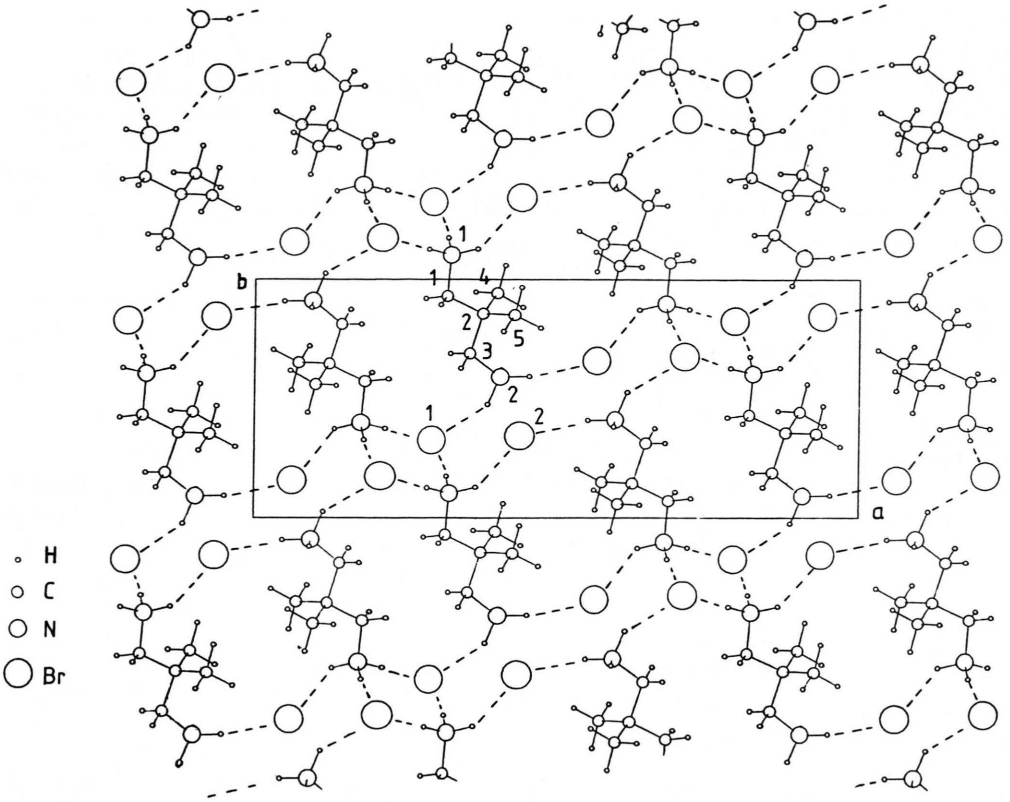

Fig. 9. Projection of half of the unit cell, $0.25 \leq z \leq 0.75$, of **4** along [001] onto the *ab* plane. Hydrogen bonds are marked by dashed lines.

the corresponding frequency pair. The third argument for the frequency combination chosen is the dependence of frequencies, NQCC and asymmetry parameter from *T*. For $I^{(1)}$ $\eta(^{127}I)$ is constant = 0.500(5) over the whole range $77 \leq T/K \leq 406$ and $e\Phi_{zz}Qh^{-1}$ ($^{127}I^{(1)}$) decreases smoothly with *T*, see Figure 6. $\eta(^{127}I^{(2)})$ decreases continuously with *T* as does the NQCC. We have no really strong argument for the assignment of the two NQCC and the two η to $I^{(1)}$ and $I^{(2)}$ as we did. The coordinates of the NH_3 hydrogen atoms are not accurate enough to use hydrogen bond arguments for the assignment. The way out of the problem would be either a single crystal Zeeman NQR or a spin echo double resonance (SEDOR) experiment I ↔ ^2H with deuterated compound.

Structure and $^{79,81}Br$ *NQR of* $[H_3NCH_2C(CH_3)_2CH_2NH_3]^{2+}\ 2\,Br^-$ **4**

As the structure of **3**, the crystal structure of the corresponding dihydrobromide **4** is a quite regular packing of cations and anions, too. The characteristics of the symmetry in the dihydroiodide **3**, the chemical bond of two crystallographic inequivalent CH_3 groups and two inequivalent CH_2NH_3 groups to the tertiary carbon $C^{(2)}$ is repeated in the dihydrobromide. Also here, the cation is "crystallographic" unsymmetric besides the higher symmetry of the space group. The carbon-carbon distances in the cation of **4** are found between 152 pm and 155 pm, mean value 153.7 pm (see Table 5), within the range one expects for d(C–C) in aliphatic bonds, somewhat shorter as d(C–C) in **3**. This is not a point to be discussed because of the limits of error.

In Fig. 9 the unit cell of **4** is projected along [001] from $z = 0.25$ to $z = 0.75$ onto the *ab* plane. In contrast to **3**, we find (compare Fig. 2 and Fig. 9) that in **4** there is a three-dimensional network of hydrogen bonded anions and cations. The size difference between Br^- and I^- may cause this difference in the structure. There is another interesting difference in the hydrogen bond scheme between **3** and **4**. In **3** we have hydrogen bonds $N^{(1)}H_3 \cdots I^{(1)}$ and $N^{(2)}H_3 \cdots I^{(2)}$ (see Table 3) whereas in (**4**) there is a "mixed" bond. $N^{(1)}H_3$ forms two bonds with $Br^{(1)}$, one bond with $Br^{(2)}$ and $N^{(2)}H_3$ is connected twice to $Br^{(2)}$ and once to $Br^{(1)}$.

No problem arises in sorting the Br NQR lines into two groups because of the wellknown ratio of the nuclear quadrupole moments $Q(^{79}Br)/Q(^{81}Br) = 1.197$. However there is no chance to prove our assignment of ν_1 (^{79}Br) to $Br^{(1)}$ which determines the assignment of the other Br resonances, too. The allocation of ν_1 (^{79,81}Br) to $Br^{(1)}$ cannot be proved as it was not unique in case of **3**. Comparing the Br NQR of **4** with the NQCC(^{127}I) of **3**, for isomorphous salts we should find very similar coupling constant ratios NQCC($Br^{(1)}$/NQCC($Br^{(2)}$) and NQCC($^{127}I^{(1)}$)/NQCC ($^{127}I^{(2)}$) [14]. Using the relation $\nu = \frac{1}{2} e\Phi_{zz} Q h^{-1} (1+\eta^2/3)^{1/2}$, and $\eta = 0.50$, respectively $\nu_1(^{79,81}Br)$ for $Br^{(1)}$, $\eta = 0.21$, respectively $\nu_2(^{79,81}Br)$ for $Br^{(2)}$, we find $e\Phi_{zz} Q h^{-1} (^{79,81}Br^{(1)})/e\Phi_{zz} h^{-1} (^{79,81}Br^{(2)}) = 1.10$. The corresponding quotient for $I^{(1)}$, $I^{(2)}$ is 1.06. Although the compounds are not isomorphous, they have similar hydrogen bond schemes $NH_3 \cdot\cdot I$ and $NH_3 \cdot\cdot Br$ and we can assume that the EFG at the halogen atoms is small (pseudotrigonal axis $I(Br) \cdots H_3$) and the assignment

$$\nu_1\,(^{79,81}Br) \leftrightarrow Br^{(1)}, \; \nu_2(^{79,81}Br) \leftrightarrow Br^{(2)}$$

is correct. However the final answer of assignment cannot be given on the basis of the present experiments.

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