

# The Correlation of $^{81}\text{Br}$ NQR Frequency with $\text{p}K_{\text{b}}$ Value and with the N-H $\cdots$ Br Hydrogen Bond in Some Ammonium Bromide Salts

Takeharu IWAKIRI, Emiko YAMAKAWA, Masashi NODA,  
Michio NAKASHIMA, Hideta ISHIHARA

## Summary

$^{81}\text{Br}$  NQR of guanidinium bromide  $\text{C}(\text{NH}_2)_3\text{Br}$  (I), hydrazinium bromide  $\text{N}_2\text{H}_5\text{Br}$  (II), phenylenediammonium bromide  $\text{H}_3\text{NC}_6\text{H}_5\text{NH}_3\text{Br}_2$  (III), and diphenylammonium bromide  $(\text{C}_6\text{H}_5)_2\text{NH}_2\text{Br}$  (IV) are observed and these frequencies are well correlated with  $\text{p}K_{\text{b}}$  values of original amines. This tendency could be explained by the strength of N-H $\cdots$ Br hydrogen bonds. The crystal structure of (I) is orthorhombic ( $Pnma$ ,  $Z=4$ ,  $a=866.2(1)$ ,  $b=680.9(1)$ , and  $c=833.3(1)$  pm). The crystal structure of (III) is triclinic ( $P\bar{1}$  with  $Z=1$ ,  $a=610.5(2)$ ,  $b=872.4(2)$ ,  $c=448.6(2)$  pm,  $\alpha=104.77(2)$ ,  $\beta=100.98(3)$ ,  $\gamma=70.23(2)^\circ$ ). The observed distances of N-H $\cdots$ Br hydrogen bonds in (I) and (III) are also correlated with  $^{81}\text{Br}$  NQR frequencies. The results of EFG calculation of Br atoms in the giant molecules of (I) and (III) cut off from each crystal structure could reproduce the difference of NQR frequency between (I) and (III). The temperature dependence of  $^{81}\text{Br}$  NQR frequencies of (II)-(IV) showed normal feature which could be explained by lattice vibration (Bayer theory), but no unique feature caused by hydrogen bond.

*Key words* : Crystal Structure, Hydrogen Bond, Br NQR, Dissociation Constant

## Introduction

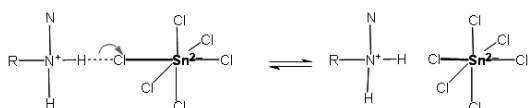
In solution, the ability of the proton transfer of acid is discussed often on the basis of the dissociation constant  $\text{p}K_{\text{a}}$ . In the case of amine, this constant refers to the conjugate acid, or the ammonium cation. The  $\text{p}K_{\text{a}}$  dissociation constant corresponds to the acidity of the ammonium cation (conjugate acid), and conversely to the basicity of the amine molecule (original base);  $\text{p}K_{\text{a}} + \text{p}K_{\text{b}} = \text{p}K_{\text{w}}$ , where  $K_{\text{w}}$  is the ionization constant of water.

Sugimoto *et al.* showed that the strength of the hydrogen bonding increased as the  $\text{p}K_{\text{b}}$  value of anions decreased in the series of triprotonated tris (2-pyridylmethyl) amine,  $\text{H}_3\text{TPA}^{3+}$  [1]. They used X-ray, IR,  $^1\text{H}$ -NMR, and cyclic voltammogram (CV) to estimate the strength of the hydrogen bonds.

The nuclear quadrupole resonance (NQR) spectroscopy is an experimental technique which is very useful to elucidate the electronic distributions around the relevant nucleus in the

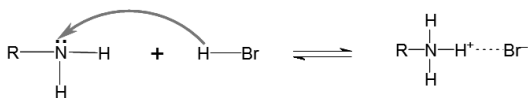
crystalline solids and has thus been intensively used in studying of chemical bonding, crystal structures, and phase transitions, *etc.* Therefore, NQR can also give a good measure to estimate the strength of hydrogen bonds.

Borchers and Weiss suggested that the strength of the hydrogen bond  $N-H\cdots Cl$  in  $A_2$  [ $SnCl_6$ ] and  $A'$  [ $SnCl_6$ ] series increases with increasing  $pK_b$  of organic base [2], according to the results of  $^{35}Cl$  NQR measurements.



We have applied the halogen NQR to investigate the hydrogen transfer of intermolecular H-bonds in solids by measuring temperature dependencies of the  $^{35}Cl$  NQR relaxation in a series of the complex compounds of diazines [3–5], revealing that the intermolecular H-transfer can be observed by the NQR technique.

In solid ammonium bromide salts, proton transfer from HBr to base is influenced by strength of base, or  $pK_b$ . The complete proton transfer to base leads to form a symmetrical  $Br^-$  ion and the electric field gradient at Br site becomes zero and then Br NQR is not observed. Therefore the NQR frequency of Br gives a measure to estimate the strength of the hydrogen bonds.



## Results and discussion

The  $^{81}Br$  NQR frequencies of guanidinium bromide  $C(NH_2)_3Br$  (I), hydrazinium bromide  $N_2H_5Br$  (II), phenylenediammonium bromide  $H_3$

$NC_6H_5NH_3Br_2$  (III), and diphenylammonium bromide  $(C_6H_5)_2NH_2Br$  (IV) are listed in Table 1 with the result of 4-Cl- $C_6H_4NH_3Br$  [6].

The temperature dependencies of  $^{81}Br$  or  $^{79}Br$  NQR frequencies of (II)–(IV) are shown in Fig. 1 and 2 and unique features, which was supposed to be due to the effect of hydrogen bond, did not appear.

Figure 3 shows the correlation between the  $^{81}Br$  NQR frequency of (II)–(IV) at 77 K except for (I) at 298 K and  $pK_b$  values of original amines with reported frequencies [R1–R10]. In the case of diacidic base, the smaller value of  $pK_b$  is used to plot the figure. This figure suggests the strong correlation between NQR frequencies and  $pK_b$  values as suggested above.

The crystal structure determination was carried out to confirm the existence of hydrogen bond. Experimental conditions for the crystal structure determination and crystallographic data of  $C(NH_2)_3Br$  (I) and  $H_3NC_6H_5NH_3Br_2$  (III) are listed in Table 2. The atomic coordinates are listed in Table 3. Bond lengths, bond angles and short contacts are listed in Table 4. The crystal structures of (I) and (III) are shown in Fig. 4 and 5. In comparison of the  $Br\cdots N$  and  $Br\cdots H$  distances of (I) with (III), the distances of (I) are longer than (III) and it is obvious that the strength of N–H bond in (I) is larger than (III) which can be guessed according to the  $pK_b$  value as seen in Table 1. The data of crystal structure of 4-Cl- $C_6H_4NH_3Br$  [7] and  $NH_2NH_3Br$  [8] are listed together for comparison.

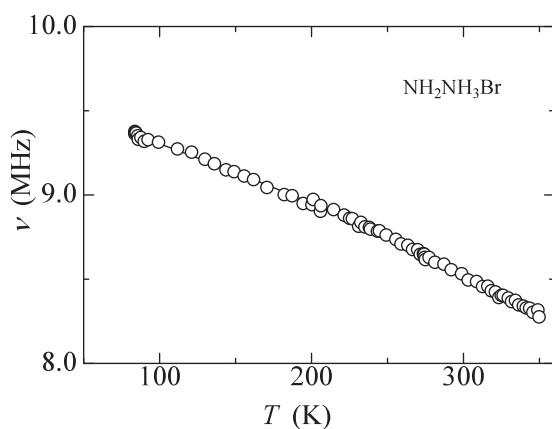
Figure 6 shows the result of IR measurement of (III) with IR spectra of original diamine. The N–H deformation vibration at  $1625\text{ cm}^{-1}$  and C–N stretching vibration at  $1270\text{ cm}^{-1}$  of original amine are moved to  $1570\text{ cm}^{-1}$  and  $1490\text{ cm}^{-1}$ , and to  $1320\text{ cm}^{-1}$  of (III), respectively. This observation shows the formation of  $NH_3^+$  group from  $NH_2$

Table 1.  $^{81}\text{Br}$  NQR frequencies at 77 K and  $\text{p}K_{\text{b}}$  values

Compounds	( I )	( II )	( III )	( IV )	4-Cl-C <sub>6</sub> H <sub>4</sub> NH <sub>3</sub> Br
$\nu_{\text{obs}}(^{81}\text{Br})$ (MHz)	8.00 <sup>a)</sup>	9.369	15.985	25.772 25.438	16.676[6]
Av. of $\nu$	8.00	9.369	15.985	25.624	16.676
$\text{p}K_{\text{b}}$	0.3	6.07 15.05	7.69 11.09	13.21	10.02
$\text{NH}\cdots\text{Br}$ (pm)	262	—	244 <sup>b)</sup>	—	252[7]
$\text{N}\cdots\text{Br}$ (pm)	349 <sup>b)</sup>	334 <sup>b)</sup> [8]	336 <sup>b)</sup>	—	338 <sup>b)</sup>
$\nu_{\text{cal}}(^{81}\text{Br})$ (MHz)	5.76	—	14.92	—	14.49
$\eta_{\text{cal}}$	0.578	—	0.875	—	0.792

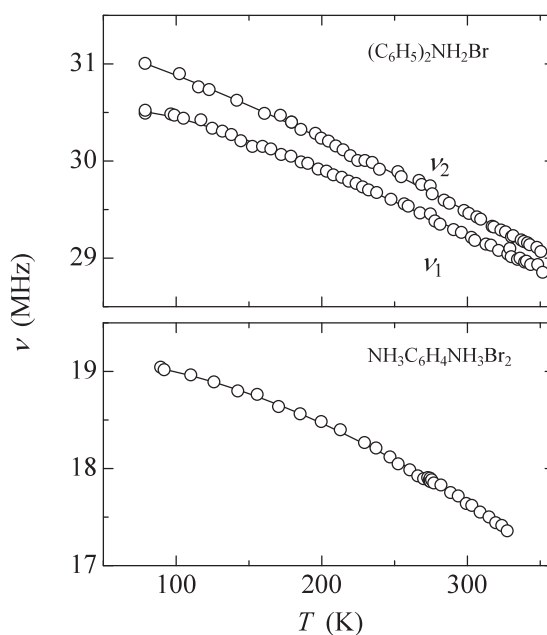
a) Frequency at 298 K

b) The averaged value

Fig. 1. Temperature dependence of  $^{81}\text{Br}$  NQR frequency of ( II ). The solid line shows the fitting curve by least-squares method (Appendix I).

group.

Molecular orbital calculation of the  $^{81}\text{Br}$  NQR frequency was carried out and the results are listed in Table 1. The calculated frequency estimated from the occupation number of the  $4p$  valence shell of the Br atom could not reproduce the observed frequency, but we could obtain the listed values in consideration of the crystal field

Fig. 2. Temperature dependence of  $^{79}\text{Br}$  NQR frequency of ( IV ) (upper part) and ( III ) (lower part). The solid line shows the fitting curve by least-squares method (Appendix I).

effect which leads to about 7 %. The electron density on the concerned  $\text{Br}^-$  ion: ( I ) 7.940, ( III ) 7.925, and 4-Cl-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>Br 7.931. The electron density of ( I ) is the greatest and this indicates the lowest  $^{81}\text{Br}$  NQR frequency. In the case of 4-Cl-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>Br, the calculated  $^{81}\text{Br}$  NQR frequency is less affected by the crystal field than ( III ): 14.49 in MHz from 13.80 MHz without the

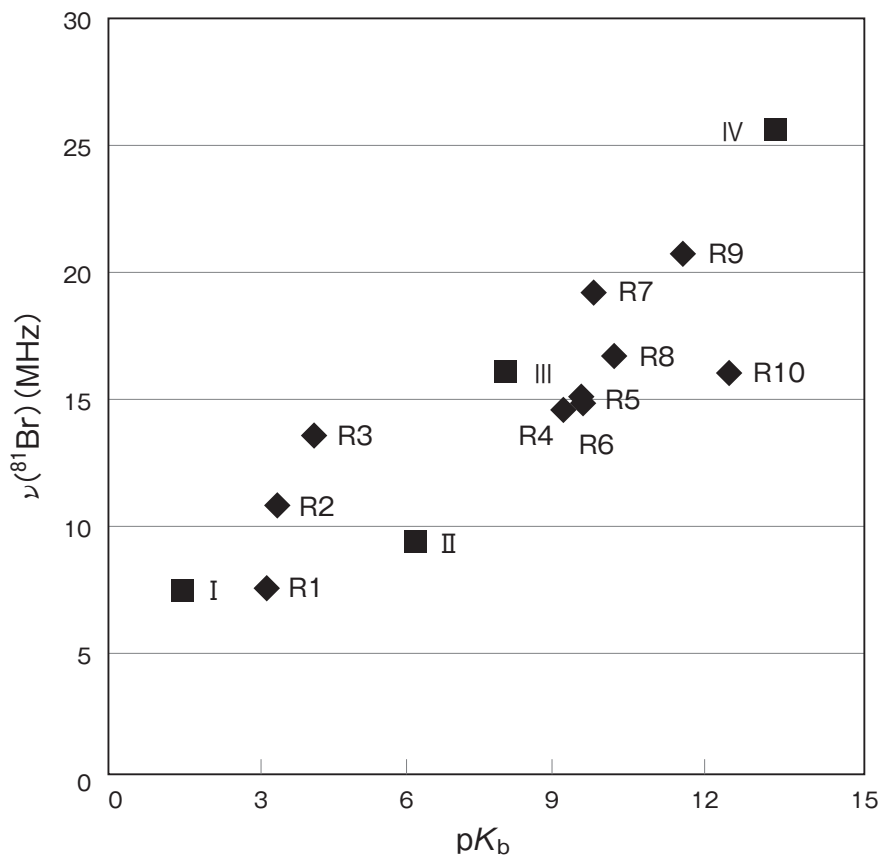


Fig. 3. The relation between  $^{81}\text{Br}$  NQR frequency and  $\text{p}K_{\text{b}}$ .

- [R1]  $(\text{CH}_3)_3\text{CNH}_3\text{Br}$ : M. Shabazi, S. Dou, and Al. Weiss, *Z. Naturforsch.* **47a**, 171–176 (1992).  
 [R2]  $\text{CH}_3\text{NH}_3\text{Br}$ : J. J. R. Frausto Da Silva, L. F. V. Boas, *Rev. Port. Quim.* **14**(2), 115–116 (1972).  
 [R3]  $\text{NH}_3(\text{CH}_2)_2\text{NH}_3\text{Br}_2$ : J. Hartmann, S. Dou, and Al. Weiss, *Z. Naturforsch.* **44a**, 41–55 (1989).  
 [R4]  $4\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_3\text{Br}$ : V. S. Bai and Al. Weiss, *Z. Naturforsch.* **39a**, 366–370 (1984).  
 [R5]  $4\text{-FC}_6\text{H}_4\text{NH}_3\text{Br}$ : V. G. Krishnan and Al. Weiss, *Ber. Bunsenge. Phys. Chem.* **87**, 254–263 (1983).  
 [R6]  $\text{C}_6\text{H}_5\text{NH}_3\text{Br}$ : W. Pies and Al. Weiss, *Bull. Chem. Soc. Jpn.* **51**, 1051–1061 (1978).  
 [R7]  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{H}_2\text{Br}$ : V. G. Krishnan and Al. Weiss, *Ber. Bunsenge. Phys. Chem.* **87**, 254–263 (1983).  
 [R8]  $4\text{-ClC}_6\text{H}_4\text{NH}_3\text{Br}$ : J. Hartmann, S. Dou, and Al. Weiss, *Ber. Bunsenges. Phys. Chem.* **94**, 1110–1121 (1990).  
 [R9]  $2\text{-ClC}_6\text{H}_4\text{NH}_3\text{Br}$ : J. Hartmann and Al. Weiss, *Z. Naturforsch.* **46a**, 367–375 (1991).  
 [R10]  $4\text{-CNC}_6\text{H}_4\text{NH}_3\text{Br}$ : V. G. Krishnan and Al. Weiss, *J. Mol. Struct.* **111**, 379–396 (1983).

crystal field in  $4\text{-Cl-C}_6\text{H}_4\text{NH}_3\text{Br}$ , but 14.92 MHz from 10.39 MHz in (III). This means the strength of  $\text{H}\cdots\text{Br}$  bond of  $4\text{-Cl-C}_6\text{H}_4\text{NH}_3\text{Br}$  is larger than (II), *i. e.*, the electric field gradient due to  $\text{H}\cdots\text{Br}$  bond is decisive in  $4\text{-Cl-C}_6\text{H}_4\text{NH}_3\text{Br}$ .

## Conclusion

The  $^{81}\text{Br}$  NQR frequencies are correlated with  $\text{p}K_{\text{b}}$  values and this fact can be explained by the

difference of the strength of  $\text{N-H}\cdots\text{Br}$  hydrogen bond. This explanation is supported by the X-ray structure analysis and MO calculation.

## Experimental Section

### Sample preparation

Guanidinium bromide  $\text{C}(\text{NH}_2)_3\text{Br}$  (I),  
 hydrazinium bromide  $\text{N}_2\text{H}_5\text{Br}$  (II),  
 phenylenediammonium bromide  $\text{H}_3\text{NC}_6\text{H}_5\text{NH}_3\text{Br}_2$

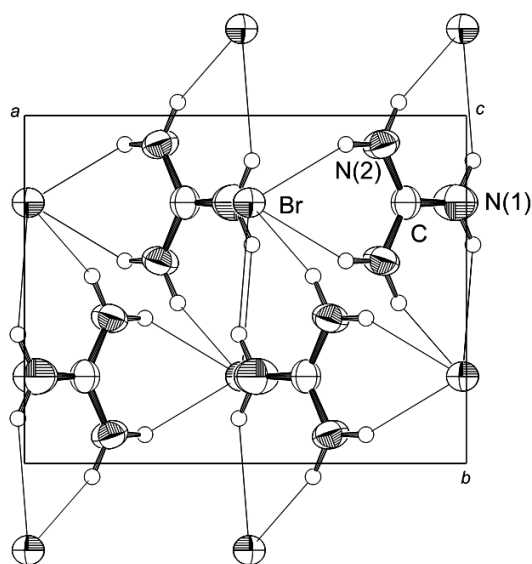


Fig. 4. The projection of the crystal structure of (I) along  $c$ -axis. The thin lines show hydrogen bonds. Thermal ellipsoid (50%) was made by ORTEP-3[9].

(III), and diphenylammonium bromide ( $\text{C}_6\text{H}_5$ ) $_2\text{NH}_2\text{Br}$  (IV) were prepared by mixing amine and hydrobromic acid in the stoichiometric ratio. The water solution was kept in a desiccator charged with  $\text{P}_2\text{O}_5$  to crystallize.

#### Crystal structure determination

The crystal structures were determined using a four circle X-ray diffractometer Rigaku AFC5S ( $\text{MoK}\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ , graphite monochromator, attenuator Zr foil,  $\omega/2\theta$  scans). The positions of hydrogen atoms were calculated with standard bond lengths and angles. All

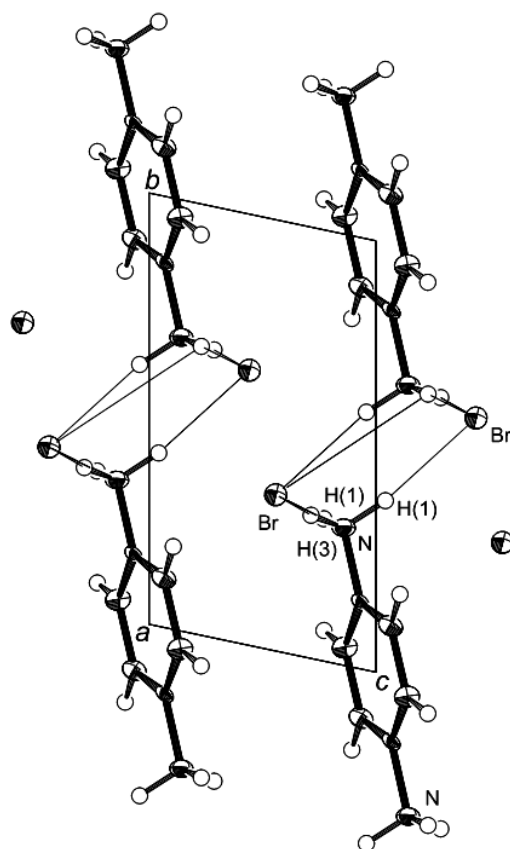


Fig. 5. The projection of the crystal structure of (III) along  $a$ -axis. The thin lines shown hydrogen bonds. Thermal ellipsoid (50%) was made by ORTEP-3[9].

calculations were performed using CRYSTALSTRUCTURE 3.8 Crystal Structure Analysis Package [10].

#### NQR measurement

Nuclear quadrupole resonance (NQR) spectra were measured between 8–35 MHz using a homemade Dean-type external-quenching super-regenerative oscillator made of 6C4 tubes with Zeeman magnetic modulation and recorded through a lock-in amplifier. The  $^{81}\text{Br}$  NQR lines observed were identified by observing the corresponding  $^{79}\text{Br}$  lines of the known frequency

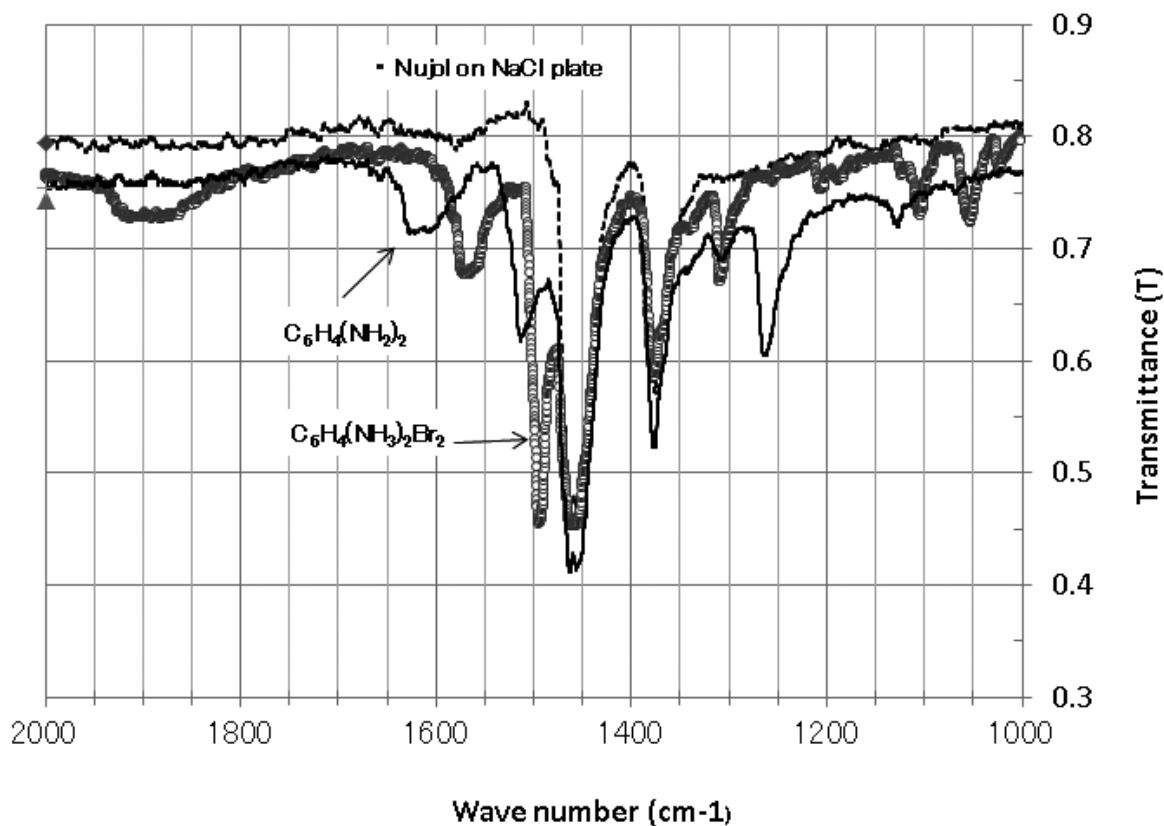


Fig. 6. IR spectra of (III) and 4-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>.

ratio.

#### MO calculation

MO calculation on PM3 basis was carried out by Win GAMESS, a general *ab initio* quantum chemistry package [11]. The Mulliken population analysis of the 4*p* orbitals of two bromine atoms, which symmetrically located at the center of the assumed molecules of (I) [(C(NH<sub>2</sub>)<sub>3</sub>)<sub>10</sub>Br<sub>6</sub>]<sup>4+</sup>, [(4-ClC<sub>6</sub>H<sub>5</sub>NH<sub>3</sub>)<sub>6</sub>Br<sub>14</sub>]<sup>8+</sup>, and (III) [(H<sub>3</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>8</sub>Br<sub>22</sub>]<sup>6+</sup> cut off from the each crystal structure, was performed in order to obtain the number of unbalanced *p*-electron (*U<sub>p</sub>*) and then the components of the electric field gradient (EFG) tensor, *eq<sub>ij</sub>* (*i, j* = *x, y, z*). The crystal field effect was considered by calculating electric field

due to point charge estimated from MO calculation. The principal values of the EFG tensor and the asymmetric parameters were obtained by diagonalization of *eq<sub>ij</sub>* including 7.5 % of crystal field effect in each case. For support of MO calculation, WINMOSTAR and MERCURY were used [12].

#### IR (Infrared spectroscopy) measurements

HITACHI 260-10 Infrared spectrometer was used to observe IR spectra. Sample is mixed with nujol in a mortar to make a mull and is placed between sodium chloride plates.

Table 2. Experimental conditions for the crystal structure determinations and crystallographic data of C(NH<sub>2</sub>)<sub>3</sub>Br (I) and H<sub>3</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>Br<sub>2</sub> (III), Rigaku AFC5S;  $\omega$ - $2\theta$  Scan, wavelength 71.069 pm (MoK $\alpha$ ), monochromator: graphite, Attenuator Zr foil. (I)  $M = 138.98$ , (III)  $M = 269.97$ .

	(I)	(III)
Crystal size/(mm <sup>3</sup> )	0.50 × 0.50 × 0.20	0.40 × 0.40 × 0.40
Temperature/K	296	298
Absorption coeff./(cm <sup>-1</sup> )	82.23	93.42
$\theta$ -range for data collected	3.0 ≤ $\theta$ /° ≤ 27.5	2.8 ≤ $\theta$ /° ≤ 27.5
Index ranges	0 ≤ $h$ ≤ 11, 0 ≤ $k$ ≤ 8, 0 ≤ $l$ ≤ 10	0 ≤ $h$ ≤ 7, -10 ≤ $k$ ≤ 11, -5 ≤ $l$ ≤ 5
Space group	<i>Pnma</i>	$P\bar{1}$
Lattice parameter		
$a$ /pm	866.2(1)	610.5(2)
$b$ /pm	680.9(1)	872.4(2)
$c$ /pm	833.3(1)	448.6(2)
$\alpha$ /°	90.00	104.77(2)
$\beta$ /°	90.00	100.98(3)
$\gamma$ /°	90.00	70.23(2)
$V \times 10^{-6}$ /(pm <sup>3</sup> )	491.5(1)	216.0(1)
Formula units $Z$	4	1
$\rho_{\text{cal}}$ /(Mg m <sup>-3</sup> )	1.892	2.076
$F(000)$	272.0	130.0
Independent reflections	610	984
Data ( $I > 2\sigma(I)$ )	372	925
Restraints/parameters	0/33	0/52
Goodness of fit $S(\text{obs.})$	0.879	1.212
Final $R$ ( $I > 2\sigma(I)$ )	$R = 0.043$ , $Rw = 0.093$	$R = 0.048$ , $Rw = 0.119$
Largest diff. (peak, hole)/(10 <sup>-6</sup> e(pm <sup>3</sup> ))	0.80 and -0.63	1.16 and -1.15
Max. and min. trans.	0.193 and 0.036	0.024 and 0.010
Point positions.	Br, N(1), C atoms in 4c and N(2) and H atoms in 8d.	All atoms in 2i.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters  $B_{\text{eq}}$  for (I) and (III).  $B_{\text{eq}}$  is defined as the following equation by the anisotropic displacement parameters  $U_{ij}$ . The anisotropic displacement parameters  $U_{ij}$ , and atomic coordinates for hydrogen atoms are given elsewhere [13].

$$B_{\text{eq}} = 8/3\pi^2[(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\pi + 2U_{13}(aa^*cc^*)\cos\pi + 2U_{23}(bb^*cc^*)\cos\pi]$$

C(NH <sub>2</sub> ) <sub>3</sub> Br (I)				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/(10^{-1}\text{pm}^2)$
Br	0.5087(1)	-0.2500	0.6739(1)	4.24(3)
N(1)	0.5249(11)	0.2500	0.7695(13)	7.0(3)
N(2)	0.6927(7)	0.0823(8)	0.9325(6)	4.71(16)
C	0.6367(11)	0.2500	0.8785(10)	3.9(2)
H(1)	0.4845	0.1292	0.7312	8.5
H(2)	0.7729	0.0833	1.0103	5.7
H(3)	0.6528	-0.0391	0.8945	5.7
H <sub>3</sub> NC <sub>6</sub> H <sub>4</sub> NH <sub>3</sub> Br <sub>2</sub> (III)				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/(10^{-1}\text{pm}^2)$
Br	0.8068(1)	0.3621(1)	0.5584(2)	2.50(2)
N	0.3636(10)	0.3184(6)	0.8565(14)	2.29(14)
C(1)	0.4360(11)	0.1525(7)	0.9280(14)	1.72(14)
C(2)	0.2828(11)	0.1124(8)	1.0614(16)	2.25(16)
C(3)	0.3489(11)	-0.0435(8)	1.1364(16)	2.16(16)
H(1)	0.3328	0.4014	1.0404	2.7
H(2)	0.4856	0.3294	0.7678	2.7
H(3)	0.2259	0.3317	0.7125	2.7
H(4)	0.1343	0.1906	1.1027	2.6
H(5)	0.2443	-0.0725	1.2280	2.7



Table 4. Bond lengths (pm), bond angles ( $^\circ$ ), and short contact. The hydrogen atoms have been determined in the least-squares refinements of the structures by fixing the bond lengths (95 pm) of N-H and C-H and bond angles with the atoms involved.

C(NH <sub>2</sub> ) <sub>3</sub> Br ( I )			
Connection	<i>d</i> /pm	Connection	Angle/ $^\circ$
N(1)-C	132.8(13)	N(1)-C-N(2)	120.1(4)
N(2)-C	132.0(7)	N(2)-C-N(2) <sup>#1</sup>	119.9(7)
Short contact in ( I )			
Connection	<i>d</i> (N $\cdots$ Br)/pm	<i>d</i> (H $\cdots$ Br)/pm	$\angle$ (N-H $\cdots$ Br)/ $^\circ$
N(1)-H(1) $\cdots$ Br	349.9	263.2	152.0
N(2)-H(2) $\cdots$ Br <sup>#2</sup>	347.0	259.6	153.1
N(2)-H(3) $\cdots$ Br	350.7	264.1	151.8
#1: <i>x</i> , 0.5- <i>y</i> , <i>z</i> ; #2: 1.5- <i>x</i> , 0.5+ <i>y</i> , 0.5+ <i>z</i> .			
H <sub>3</sub> NC <sub>6</sub> H <sub>4</sub> NH <sub>3</sub> Br <sub>2</sub> ( III )			
Connection	<i>d</i> /pm	Connection	Angle/ $^\circ$
N-C(1)	146.4(9)	N-C(1)-C(2)	118.0(5)
C(1)-C(2)	137.8(12)	C(1)-C(2)-C(3)	119.1(5)
C(2)-C(3)	139.2(10)	C(3)-C(1)-C(2) <sup>#1</sup>	122.2(6)
#1: 1- <i>x</i> , - <i>y</i> , 2- <i>z</i>			
Short contact in ( III )			
Connection	<i>d</i> (N $\cdots$ Br)/pm	<i>d</i> (H $\cdots$ Br)/pm	$\angle$ (N-H $\cdots$ Br)/ $^\circ$
N-H(1) $\cdots$ Br <sup>#2</sup>	333.0	239.2	169.0
N-H(2) $\cdots$ Br	340.5	245.5	177.8
N-H(3) $\cdots$ Br <sup>#3</sup>	333.8	246.1	153.4
#2: 1- <i>z</i> , 1- <i>y</i> , 2- <i>z</i> , #3: -1+ <i>x</i> , <i>y</i> , <i>z</i>			

## References

- [1] H. Sugimoto, H. Miyake and H. Tsukube, *J. Chem. Soc., Dalton Trans.*, **2002**, 4535–4540.
- [2] D. Borchers and Al. Weiss, *Ber. Bunsenges. Phys. Chem.*, **93**, 559–568 (1989).
- [3] T. Nihei, S. Ishimaru, H. Ishida, H. Ishihara, and R. Ikeda, *Chem. Phys. Letters*, **329**, 7–14 (2000).
- [4] T. Nihei, S. Ishimaru, H. Ishida, H. Ishihara, and R. Ikeda, *Chem. Letters*, **2000**, 1346–1347.
- [5] R. Ikeda, S. Tkahashi, the late T. Nihei, H. Ishihara, and H. Ishida, *Bull. Chem. Soc. Japan*, **78**, 1241–1245 (2005).
- [6] J. Hartmann and Al. Weiss, *Ber. Bunsenges. Phys. Chem.*, **94**, 110–1121 (1990).
- [7] M. Zaho, *Acta Crystallogr. Sect E, Struct. Rep. Online* **68**, o2022 (2012).
- [8] K. Sakurai and Y. Tomiie, *Acta Crystallogr.* **5**, 289 (1952).
- [9] ORTEP-3 for Windows, L. J. Farrugia, *J. Appl. Cryst.* **45**, 849–854 (2012).
- [10] CRYSTALSTRUCTURE 3.8 Crystal Structure Analysis Package, Rigaku and Rigaku Americans (2000–2007).
- [11] GAMESS Ver.11, M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **14**, 1347–1363 (1993).
- [12] WINMOSTAR (ED) V4.100, X-ability Co.Ltd. MERCURY 3.3 Windows, the Cambridge Crystallographic Data Centre (CCDC).
- [13] CCDC 1004899 for (I) and CCDC 1004900 for (III) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Appendix

I. Fitting parameters of  $\nu = a + b/T + c \times T + d \times T^2$  and standard deviation by the least squares method.

$\text{NH}_2\text{NH}_3\text{Br}$ (II)	$a$ (MHz)	$b$ (MHz·K)	$c$ (MHz/K)	$d$ (MHz/K <sup>2</sup> )	Standard Deviation (MHz)
$\nu_1$ (73) <sup>a)</sup>	9.4870	5.4865	$-1.9390 \times 10^{-3}$	$-4.4263 \times 10^{-6}$	$1.398 \times 10^{-3}$

a) The number of data in parenthesis.

$\text{H}_3\text{NC}_6\text{H}_4\text{NH}_3\text{Br}_2$ (III)	$a$ (MHz)	$b$ (MHz·K)	$c$ (MHz/K)	$d$ (MHz/K <sup>2</sup> )	Standard Deviation (MHz)
$\nu_1$ (33) <sup>a)</sup>	19.3642	-7.5981	$-1.5707 \times 10^{-3}$	$-1.3647 \times 10^{-5}$	$2.440 \times 10^{-3}$

a) The number of data in parenthesis.

$(\text{C}_6\text{H}_5)_2\text{NH}_2\text{Br}$ (IV)	$a$ (MHz)	$b$ (MHz·K)	$c$ (MHz/K)	$d$ (MHz/K <sup>2</sup> )	Standard Deviation (MHz)
$\nu_1$ (51) <sup>a)</sup>	31.4569	-32.4415	$-6.7630 \times 10^{-3}$	$-8.8938 \times 10^{-7}$	$2.605 \times 10^{-3}$
$\nu_2$ (44) <sup>a)</sup>	31.5214	-4.5302	$-5.5068 \times 10^{-3}$	$-4.1611 \times 10^{-6}$	$3.432 \times 10^{-3}$

a) The number of date in parenthesis.