

$^{81}\text{Br}$  and  $^{35}\text{Cl}$  NQR of 4-chloro-2,6-dibromoaniline

(NQR/Zeeman effect/4-chloro-2,6-dibromoaniline)

Mitsuo MISHIMA\*

The title compound gives a single  $^{35}\text{Cl}$  and two  $^{81}\text{Br}$  NQR lines. The Zeeman effect on  $^{35}\text{Cl}$  and  $^{81}\text{Br}$  lines in a single crystal has been observed at room temperature. The locations of the principal  $z$  axes of the field gradient have been determined with an uncertainty of  $0.05^\circ$ . The angles between the C - X and C - Y bonds (X, Y=Cl or Br) are deduced on the basis of the orientations of the  $z$  axes. The angle between the C - Br bonds is  $123.8^\circ$  and the angles between the C - Cl and C - Br bonds are  $116.5^\circ$  and  $119.6^\circ$ .

NQR spectra of many halogenated anilines have been recorded and the resonance frequencies arising from  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ , and  $^{81}\text{Br}$  were reported.<sup>1-9)</sup> Some of these aniline derivatives were studied by Zeeman analysis.<sup>3-9)</sup> However, the mixed halogen derivatives of aniline have not been studied by NQR. It is of interest to know how the replacement of the atoms bonded to the ring of aniline by other atomic species affects bond angles and bond character.

In this paper, the resonance frequencies of 4-chloro-2,6-dibromoaniline (CDBA) and 4-bromo-2,6-dichloroaniline (BCDA) are reported. The Zeeman splitting of the  $^{35}\text{Cl}$  and  $^{81}\text{Br}$  NQR spectra of CDBA was observed to obtain information about molecular structure and bond character of the C - X bonds (X=Cl or Br). The results were interpreted on the basis of the single model in which the electric field gradient (efg) arises solely from the  $\sigma$  and  $\pi$  character of the C - X bond.

## Experimental

Commercial products of CDBA and BCDA (Tokyo Chemical Industry) were purified by recrystallization in ethanol. A single crystal of CDBA was grown from the melt using the Bridgeman technique. The spectrometers used for detecting the  $^{35}\text{Cl}$  and  $^{81}\text{Br}$  NQR lines were described elsewhere.<sup>10)</sup> The frequencies were determined by a frequency counter. Attempt was made to detect  $^{14}\text{N}$  NQR lines in CDBA using a sample of 20g by means of a home-made regenerative spectrometer.<sup>11)</sup> No resonances could be observed, though the  $\sigma$  and  $\pi$  lines in *p*-chloroaniline were easily detected using a sample of 2.5g.

The Zeeman effect was studied by means of the zero-splitting cones method. The Zeeman field supplied by a Helmholtz coil is about 20 mT. The orientation of the magnetic field was determined in polar coordinates ( $\theta$ ,  $\phi$ ) fixed to the crystal, where  $\theta$  and  $\phi$  are polar and azimuthal angles, respectively. Temperatures were determined with a Yokogawa 5763 thermometer by use of a copper-constantan thermocouple.

## Results and Discussion

CDBA shows a single  $^{35}\text{Cl}$  and double  $^{81}\text{Br}$  NQR lines, whereas BCDA shows double  $^{35}\text{Cl}$  and single  $^{81}\text{Br}$  lines. The  $^{81}\text{Br}$  lines were assigned on the basis of the known quadrupole moment ratio,  $Q(^{79}\text{Br})/Q(^{81}\text{Br})=1.1970$ . The resonance frequencies of CDBA are plotted against temperature in Fig. 1. The  $^{35}\text{Cl}$ , lower-frequency  $^{81}\text{Br}$ , and

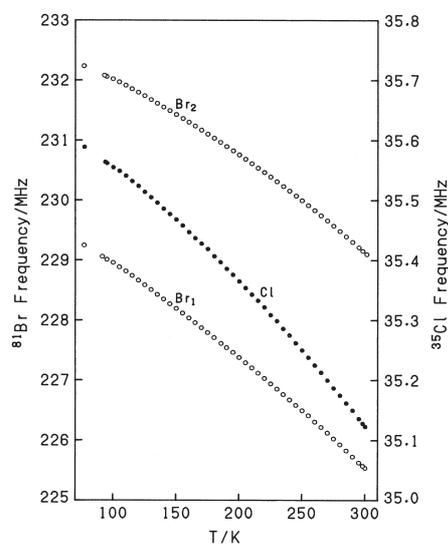


Fig. 1. Temperature dependence of  $^{35}\text{Cl}$  resonance frequencies of 4-chloro-2,6-dibromoaniline.

\*Department of Chemistry

higher-frequency  $^{81}\text{Br}$  lines are designated as  $\text{Cl}$ ,  $\text{Br}_1$ , and  $\text{Br}_2$ , respectively. The frequencies of these lines decrease monotonously with an increase in temperature. The line-widths of the  $\text{Br}_1$  and  $\text{Br}_2$  lines are about 25 kHz and 65 kHz at 77 K, respectively. The  $\text{Br}_2$  line became gradually narrow with an increase in temperature, whereas the temperature dependence of the width of the  $\text{Br}_1$  line was not so remarkable. No appreciable difference in width between these lines was found at room temperature. The NQR frequencies of CDBA and BDCA are given at 77 K and at room temperature in Table 2 along with those of the related compounds; 2,4,6-tribromoaniline (TBA),<sup>3)</sup> 2,4,6-trichloroaniline (TCA),<sup>10)</sup> 2,6-dibromoaniline (DBA),<sup>3)</sup> 4-bromoaniline (BA),<sup>8)</sup> and 4-chloroaniline (CA).<sup>4,5,9)</sup>

The dependence of the NQR frequency  $\nu(T)$  on temperature can approximately be expressed by the polynomial.

$$\nu(T) = \nu_0(1 + a_{-1}T + a_1T + a_2T^2) \quad (1)$$

The coefficients for CDBA are given in Table 2. The value of  $a_{-1}$  for the  $\text{Br}_2$  line is about one-fifth of that for the  $\text{Br}_1$  line. The value of  $a_{-1}$  varies inversely as the moment of inertia of a torsional motion of a molecule.<sup>13)</sup> The moment of inertia for the  $\text{Br}_2$  line is required to be seemingly much larger than those for the other lines, suggesting that the torsional motions of the  $\text{Br}_2$  atom are hindered to some degree by some cause. The  $\text{Br}_2$  atom may participate in intermolecular or intramolecular interaction like hydrogen bonding, though details cannot be discussed at this stage because of lack of knowledge of the crystal structure of CDBA.

Table 2. Expansion coefficients of  $\nu_0(T)$  and standard deviation  $\sigma$ .

Coefficient	Cl	$\text{Br}_1$	$\text{Br}_2$
$\nu_0/\text{MHz}$	35.7369	230.450	232.925
$a_{-1} \cdot 10^2/\text{K}$	-6.60256	-4.66429	-0.98013
$a_1 \cdot 10^5/\text{K}^{-1}$	-3.79938	-5.53190	-3.00880
$a_2 \cdot 10^8/\text{K}^{-2}$	-6.18183	-5.05625	-8.03588
$\sigma/\text{MHz}$	0.0008	0.0060	0.0049

The zero-splitting patterns of CDBA obtained from the Zeeman effect of the  $^{35}\text{Cl}$  and  $^{81}\text{Br}$  lines are shown in Fig. 2. A pair of loci were obtained for each line, suggesting that there are at least two crystallographically equivalent sites in the crystal. They are arbitrarily termed the sites A and B. The asymmetry parameter  $\eta$  and the directions of

the efg axes can be determined by transforming the zero-splitting locus in the coordinate system  $(x, y, z)$  into the principal axis system  $(x_i, y_i, z_i)$ , in which the locus is expressed for  $I=3/2$  as follows:<sup>14)</sup>

$$\sin^2 \theta (3 - \cos 2\theta) = 2, \quad (1)$$

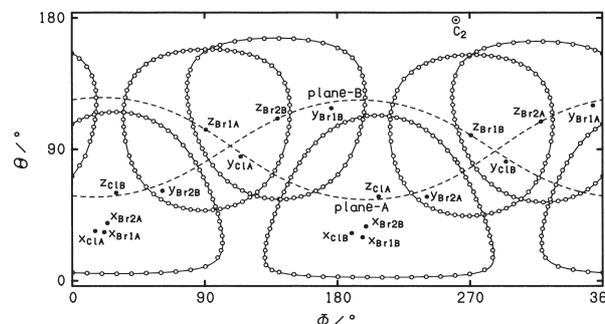


Fig. 2. Zero-splitting patterns of  $^{35}\text{Cl}$  NQR lines in 4-chloro-2,6-dibromoaniline.  $x_i$ ,  $y_i$ , and  $z_i$  indicate the directions of the principal efg axes at the halogen nucleus giving a  $\nu_i$  line. The dashed lines represent the planes made up of the  $Z_{\text{Br}1}$  and  $Z_{\text{Br}2}$  axes at the site A or B.

where  $\theta$  and  $\phi$  are polar and azimuthal angles, respectively. The loci were analyzed by the method of the least squares. The two-fold axis corresponding to the two-fold or screw axis of the crystal was determined from the distributions of the  $z$  axes. The  $x$  axes, which are almost parallel to the  $\text{C}-\text{Br}$  bond directions, are divided into two distinct groups, as can be seen in Fig. 2. The  $z$  axes were assigned to either of the two sites on the basis of the orientations of the  $x$  axes. The angles between the  $z$  axes are listed in Table 3. The angles between the  $\text{C}-\text{Cl}$  and  $\text{C}-\text{Br}_1$  bonds, between the  $\text{C}-\text{Cl}$  and  $\text{C}-\text{Br}_2$  bonds, between the  $\text{C}-\text{Br}_1$  and  $\text{C}-\text{Br}_2$  bonds are estimated to be  $119.63^\circ \pm 0.02^\circ$ ,  $116.52^\circ \pm 0.02^\circ$ , and  $123.82^\circ \pm 0.01^\circ$  on average, respectively, assuming that the  $z$  axis is parallel to the  $\text{C}-\text{Br}$  bond direction. The angle between the two  $\text{C}-\text{Br}$

Table 3. Angles (degrees) between the efg  $z$  axes in 4-chloro-2,6-dibromoaniline

Line	$\text{Cl}_B$	$\text{Br}_{1A}$	$\text{Br}_{1B}$	$\text{Br}_{2A}$	$\text{Br}_{2B}$	$\text{C}_2^{a)}$
$\text{Cl}_A$	116.68	119.61	72.78	116.54	84.38	58.34
$\text{Cl}_B$		72.75	119.65	84.41	116.50	58.35
$\text{Br}_{1A}$			168.24	123.82	46.99	79.13
$\text{Br}_{1B}$				46.99	123.83	79.11
$\text{Br}_{2A}$					141.18	70.58
$\text{Br}_{2B}$						70.60

a)  $\text{C}_2$  represents the two-fold or screw axis of the crystal.

bonds is fairly larger than 120°, as expected from the large van der Waals radius of the Br atom and the presence of the amino group lying between the Br atoms. This angle, however, is not so strikingly large, since the angles between the C - Cl bonds are 125.2° in 2,6-dichlorobenzyl chloride,<sup>15)</sup> 125.1° in 2,6-dichlorobenzyl bromide,<sup>16)</sup> and 129.0° in 2,6-dichlorobenzaldehyde.<sup>17)</sup> The increment angle between the C - Br bonds is shifted to the angle between the C - Cl and C - Br<sub>2</sub> bonds.

The three C - X bonds appear to be coplanar, because the sum of these angles is 359.97°. The dashed lines in Fig. 2 represent the planes made up of the two C - Br bonds within a molecule. The C - Cl bonds are slightly out-of-plane. The angle between the plane and the C - Cl bond is estimated to be 1.79° ± 0.01°. Considering this angle, the sum of the angles between the C - X bonds is calculated to be exactly 359.97°. The molecular shape of

CDBA, therefore, is considerably distorted and slightly puckered. It is of interest to compare the molecular shape of CDBA with TBA. Unfortunately, no information about the orientation of the efg axes can be obtained for TBA.

The quadrupole coupling constants ( $e^2Qqh^{-1}$ ) were calculated from the asymmetry parameter and the NQR frequency ( ) according to the following relation;

$$2 = e^2Qqh^{-1}(1 + \eta^2/3)^{1/2}. \quad (3)$$

The details are listed in Table 1. All the asymmetry parameters for the halogen atoms are comparably small, and there is no appreciable difference in asymmetry parameter between CDBA and the other halogenated anilines, as seen in Table 1. The coupling constant and the asymmetry parameter are related to the ionic character ( $\delta$ ) and the character ( ) of the C - X bond by the following equations:<sup>18)</sup>

Table 1. <sup>35</sup>Cl and <sup>81</sup>Br NQR parameters for halogenated anilines.

Line or Atom	Frequency/MHz		/ % <sup>a)</sup>	$e^2Qqh^{-1a)}$ MHz	Ref.
	77K	298K			
4-chloro-2,6-dibromoaniline (CDBA)					
Cl(p)	35.589	35.128	5.0 ± 0.1	70.23	This work
Br <sub>1</sub> (o)	229.251	225.575	6.4 ± 0.1	450.84	
Br <sub>2</sub> (o)	232.237	229.158	6.5 ± 0.1	458.00	
4-bromo-2,6-dichloroaniline (BDCA)					
Cl(o)	35.088	34.598			This work
	35.103	34.473			
Br(p)	235.675	232.093			
2,4,6-tribromoaniline (TBA)					
Br(o)	230.095	227.569 <sup>b)</sup>	7.4		3
	230.572	227.875 <sup>b)</sup>			
Br(p)	233.563	230.658 <sup>b)</sup>	4.0		
2,6-dibromoaniline (DA)					
Br(o)	225.975	222.375 <sup>c)</sup>	6.9		3
	227.190	223.740 <sup>c)</sup>			
4-bromoaniline (BA)					
Br(p)	221.862	219.210 <sup>c)</sup>			8
4-chloroaniline (CA)					
Cl(p)	34.468	33.762 <sup>c)</sup>	4.9		4, 5, 9
2,4,6-trichloroaniline (TCA)					
Cl(o)	34.925	34.516 <sup>f, g)</sup>			This work <sup>h)</sup>
	34.977				10
Cl(p)	35.177	34.707 <sup>f)</sup>			
	35.591	34.958 <sup>f)</sup>			
	35.780	35.274 <sup>f)</sup>			

a) The values at room temperature. b) At 294 K. c) At 295 K. d) At 299 K. e) At 296.6 K. f) At 296.6 K. g) Approximately twice the intensity of the other line. h) The frequencies at 296.6 K.

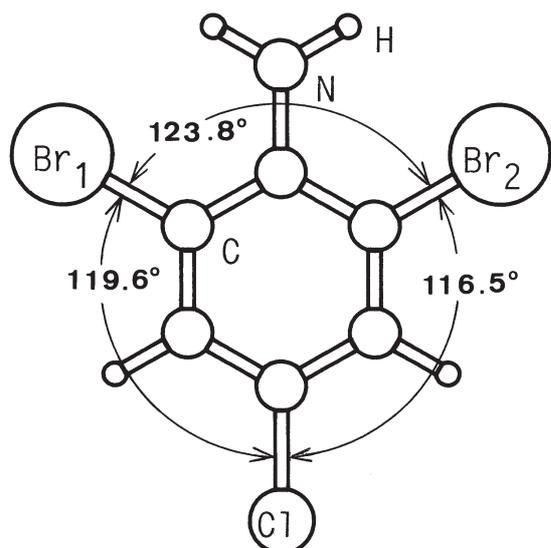


Fig. 3. Angles between the C - Cl bonds in 4-chloro-2,6-dibromoaniline.

$$U_p = |e^2 Q q h^{-1}| / |e^2 Q q h^{-1}|_{\text{atom}} = (1-i)(1-s) - i/2,$$

and

$$3 = 2 U_p. \quad (4)$$

Here  $|e^2 Q q h^{-1}|_{\text{atom}}$  is the atomic coupling constant (104.74 MHz for  $^{35}\text{Cl}$  and 643.03 MHz for  $^{81}\text{Br}$ ).<sup>19, 20)</sup>  $s$  is the fractional  $s$  character of the C - X bond and is usually assumed to be 0.15 for the C - X bond.<sup>18)</sup> The bond characters in the halogenated derivatives of aniline are summarized in Table 4.

Table 4. Mean coupling constants, mean asymmetry parameters

Compound	Atom	$\langle e^2 Q q h^{-1} \rangle_{\text{av}}$	$\langle \nu_{\text{av}} \rangle$	$i/\%^{a)}$	$i/\%$
CDBA	Br(o)	454.42	6.5	15.0(16.8)	3.1
	Cl(p)	70.23	5.0	23.5(24.3)	2.1
BDCA	Cl(o)	71.08		(23.8)	
	Br(p)	464.18		(15.1)	
TBA	Br(o)	455.02	7.4	14.7(16.5)	3.5
	Br(p)	461.19	4.0	13.4(15.6)	1.9
DBA	Br(o)	455.76	7.4	16.5(18.4)	3.2
BA	Br(p)	436.36	2.9	19.0(19.8)	1.3
TCA	Cl(o)	70.20		(24.7)	
	Cl(p)	68.53		(26.0)	
CA	Cl(p)	67.51	4.9	26.4(27.6)	

a) The values in parentheses are calculated by neglecting the bond character.

Comparison of CDBA with BDCA and DBA reveals that the substituent at the para-position does not affect the  $p$  density on the Br atoms at the ortho-positions. The excess electrons on the C atoms at the ortho- and para-positions which are estimated to be about  $0.03e^{21)}$  is considered to hinder the  $p$  electron on the Br atom from transferring to the C atom. The values calculated by neglecting the bond character are also shown in Table 4, since the character of the C - X bond at the ortho- or para-position is not so significant.

Examining the influence of the halogen atom at the para-position on the charge densities on the halogen atoms at the ortho-positions, there is no appreciable difference in ionic character between CDBA and TBA, though the Cl atoms at the ortho-positions are slightly ionic in TCA than in CDBA. The substitution of the H atom for the Br atom at the para-position in CDBA or TBA increases the charge density on the Br atoms at the ortho-positions. Unfortunately the influence on the C - Cl bonds at the ortho-position cannot be discussed, since there are no NQR data for 2,6-dichloroaniline.

Similarly the ionic character of the C - X bond at the para-position is hardly affected by replacing the halogen atoms at the ortho-positions by other halogen atoms. Comparing TCA with CDBA, the Cl atom in CDBA is less negatively charged than that in TCA, contrary to our expectations. In the derivatives of BA, however, the negative charge on the Br atom is increased by replacing the halogen atoms at the ortho positions with H atoms. The change in charge density is more remarkable in the Br atom at the para-position than the one at the ortho-position. The ionic character of the Cl atom in the derivatives of CA is not so remarkably changed as that of the Br atom in the derivatives of BA. This is probably because the Cl atom is more negatively charged than the Br atom and the electron-attracting ability of the Cl atom is considerably reduced. The results of NQR in the halogenated anilines reveal that the charge-transfer between the atoms bonded to the C atoms at the 2-, 4-, and 6-positions is not so important, so long as there is no large difference in electron-donating or electron-attracting ability between these atoms.

## References

- 1) I.P.Biryukov, M.G.Voronkov, and I.A.Safin, "Tables of Nuclear Quadrupole Resonance Frequencies", Israel

- Program for Scientific Translations, Jerusalem (1969).
- 2) Y.Nakayama, N.Nakamura, and H. Chihara, *J. Magn. Reson.*, 53, 103 (1983).
  - 3) P.Bucci, P.Cecchi, A.Colligiani, and R.Meschia, *Bull. Sci. Fac. Chim. Ind. Univ. Bologna*, 23, 307 (1965); E.A.C.Lucken, "Nuclear Quadrupole Coupling Constants", Academic Press. New York (1969) Chap. 10.
  - 4) D.Sakikara and C.R.K.Murty, *J. Chem. Phys.*, 58, 2955 (1973).
  - 5) K.V.S.Rama Rao, *J. Phys. Soc. Jpn.*, 25, 1423 (1968).
  - 6) V.Nagarajan and C.R.K.Murty, *Current Sci.*, 31, 279 (1962).
  - 7) C.H.Meal, *J. Chem. Phys.*, 24, 1011 (1956).
  - 8) K.V.L.N.Sastry and R.F.Curl, *J. Chem. Phys.*, 41, 77 (1964).
  - 9) V.Rehn, *J. Chem. Phys.*, 38, 749 (1963).
  - 10) M.Mishima and T.Okuda, *J. Mol. Chem.*, 412, 205 (1997).
  - 11) F.N.H.Robinson, *J. Phys. E: Sci. Instrum.*, 15, 814 (1982).
  - 12) P.J.Bray, *J. Chem. Phys.*, 23, 220 (1955).
  - 13) T.Kushida, G.G.Benedek, and N. Bloembergen, *Phys. Rev.*, 104, 1364 (1956).
  - 14) C.Dean, *Phys. Rev.*, 96, 1053 (1954).
  - 15) M.Mishima, *Bull. Shimane Med. Univ.*, 16, 41 (1993).
  - 16) M.Mishima, *Bull. Shimane Med. Univ.*, 14, 21 (1991).
  - 17) M.Mishima, *Bull. Shimane Med. Univ.*, 15, 77 (1992).
  - 18) B.P.Dailey and C.H.Townes, *J. Chem. Phys.*, 23, 118 (1955).
  - 19) V.Jaccarino and J.G.King, *Phys. Rev.*, 63, 471 (1951)
  - 20) V.Jaccarino and J.G.King, *Phys. Rev.*, 94, 1610 (1954)
  - 21) A.Streitwieser, "Molecular Orbital Theory for Organic Chemists", John Wiley & Sons, New York (1961) Chap. 11 p.353.

(Received October, 26, 2001)