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NUCLEAR QUADRUPOLE RESONANCE ZEEMAN STUDIES OF p-BROMOBENZENESULFONYL
CHLORIDE AND p-BROMOANILINE HYDROCHLORIDE

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ABSTRACT
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An NQR Zeeman study of ^{79}Br in p-bromobenzenesulfonyl chloride and p-bromoaniline hydrochloride has been carried out at room temperature. The principal field gradient directions and asymmetry parameters have been determined. The data have been used to estimate the double bond character of the C-Br bond in these molecules and the results have been compared with previously reported values for various para substituted bromobenzenes.

I. INTRODUCTION

Investigation of the Zeeman effect of the bromine NQR lines in a single crystal of a compound of bromine enables one to determine, in favorable cases, the orientation of the principal axes of the electric field gradient tensor at the bromine nucleus and the asymmetry parameter.²

2. T. P. Das and E. L. Hahn, Solid State Physics (Academic Press, New York, 1958), Suppl. 1.

It has been shown³ that in the case of a compound where bromine is essentially

3. R. Bersohn, J. Chem. Phys. **22**, 2078 (1954).

covalently bonded to an sp^2 hybridized carbon atom the fractional double-bond character in the C-Br bond, corresponding to resonance between structures I and II

may be estimated from the asymmetry parameter and the quadrupole coupling constant. This fraction, according to the above viewpoint, may also be taken as the fractional π bond character of the C-Br bond. Such studies have been carried out for a few bromobenzene derivatives including p-bromophenol,^{4,5} p-bromoaniline,^{4,6} p-dibromobenzene,⁷ 2,6-dibromoaniline,⁶ 1,3,5-tribromobenzene⁸

4. K. V. S. Rama Rao and C. R. K. Murty, J. Phys. Soc. Japan, **25**, 1423 (1968).

5. P. Bucci, P. Cecchi and A. Colligiani, J. Chem. Phys. **50**, 530 (1969).

and 2,4,6-tribromoaniline.⁶ Similar studies have also been carried out on some substituted chlorobenzenes.^{9,10} Estimates¹⁰ of the extent of the π -bond character obtained in this way range from 2 to 10% for the C-Cl bonds

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6. P. Bucci, P. Cecchi, A. Colligiani and R. Meschia, *Boll. Sci. Fac. Chim. Ind. Univ. Bologna* 23, 307 (1965).
  7. P. Bucci, P. Cecchi and A. Colligiani, *J. Am. Chem. Soc.* 86, 2513 (1963).
  8. P. Bucci, P. Cecchi and A. Colligiani, *Ric. Sci.* A8, 1144 (1965).
  9. G. E. Peterson and P. M. Bridenbaugh, *J. Chem. Phys.* 46, 2644 (1967);
G. E. Peterson, N. Stead and P. M. Bridenbaugh, *J. Chem. Phys.* 47, 2262 (1967).
  10. E. A. C. Lucken, Nuclear Quadrupole Coupling Constants (Academic Press, New York, 1969), pp. 176, 205.
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but are uniformly much lower (2-4%) for C-Br bonds. However, no molecules with strongly electron attracting groups para to bromine have yet been studied and it was felt that the double-bond character might be somewhat enhanced in such molecules because electron withdrawing groups should stabilize the molecule.

We have therefore made room temperature single crystal NQR Zeeman studies of the ⁷⁹Br resonance in p-bromobenzenesulfonyl chloride and in p-bromoaniline hydrochloride since the -NH₃⁺ and -SO₂Cl groups are recognized as strongly electron withdrawing groups. The bromine NQR frequencies for these molecules have been reported previously.¹¹

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11. P. J. Bray, *J. Chem. Phys.* 22, 950 (1954); K. V. S. Rama Rao and C. E. K. Murty, *Ind. J. Pure Appl. Phys.* 4, 334 (1966).
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II. MATERIALS AND CRYSTAL DATA

Both compounds were obtained from Aldrich Chemical Company. p-Bromobenzenesulfonyl chloride (m. p. 75°C) is very soluble in benzene and seed crystals were grown by slow evaporation of a saturated benzene solution at room temperature. After two or three days some of the seeds were large enough to suspend in the saturated solution and sizable (2 x 1 x 1cm) crystals were obtained by allowing these to grow. Large crystals of p-bromoaniline hydrochloride were obtained in a similar way from aqueous solutions.

Large single crystals of p-bromobenzenesulfonyl chloride were also grown from the melt by the method of Tammann.¹² A Pyrex tube 7-1/2" long,

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12. G. Tammann, Metallography (Chemical Catalog Co., New York, 1925).

1/2" in diameter and tapered to a point over the lower half was filled and slowly lowered through a tube furnace (2mm/hour) held 10° above the melting point of the crystals. Large, transparent single crystals were obtained in about two days.

The following crystallographic data are reported by Groth:¹³ p-benzenesulfonyl chloride is monoclinic prismatic with axial ratios

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13. P. Groth, Chemische Krystallographie, Verlag Wilhelm Engelmann, Leipzig, Vol. 4, pp. 176, 314.

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a:b:c = 0.820:1:2.079 and $\beta = 96^\circ 47'$ while p-bromoaniline hydrochloride is monoclinic prismatic with axial ratios a:b:c = 0.5167:1:1.8878 and $\beta = 107^\circ 42'$. The crystal structures have not been reported.

III. APPARATUS AND METHOD

The bromine NQR frequencies were detected using a self-quenched super-regenerative oscillator of the Lecher-line type operating between 200 and 400 MHz. Part of the output of the oscillator was fed to the oscilloscope through an audio wide-band amplifier and part to a Princeton Applied Research Model JB-4 lock-in amplifier whose output was in turn fed to a Varian G-10 recorder. The frequency modulation was achieved by attaching a metal strip to a loudspeaker diaphragm energized by a 39Hz signal generator and power amplifier.

The large single crystals of each substance which had been grown from solution were ground carefully to fit exactly in a hollow Plexiglass crystal holder. This was fitted with a disc graduated at 1° intervals and could be rotated about a horizontal axis (angle ϕ) in a cylindrical hole in a box fixed to the shielding of the Lecher lines.

The Zeeman field was provided by a pair of Helmholtz coils 11" in diameter and 5" apart which could be rotated about a vertical axis (angle θ); a calibrated disc attached to the coils was graduated in 1° intervals. The coils were supplied from a constant current power supply (Alpha Scientific Laboratories, Model AL 100) and gave a field of 50 gauss/ampere.

Application of the magnetic field splits each doubly-degenerate level of ^{79}Br (or ^{81}Br) into two levels and four resonance lines are observed; the splitting depends on the orientation of the field relative to the principal axes of the electric field gradient tensor. The theory has been developed¹⁴ and it is found that for special orientations of

14. C. Dean, Phys. Rev. 96, 1053 (1954).

the magnetic field the resonance frequency corresponding to the α' transition $E_{-1/2} \rightarrow E_{-3/2}$ becomes equal to that for the α transition $E_{+1/2} \rightarrow E_{+3/2}$ and that these lines coalesce to a single line when

$$\sin \theta_0 = [2/(3 - \eta \cos 2\phi_0)]^{1/2} \quad (1)$$

where θ_0 , ϕ_0 are the polar coordinates of the magnetic field with respect to the field gradient principal axes X, Y, Z and η is the asymmetry parameter. In this way a cone about the Z axis can be drawn for values of θ_0 , ϕ_0 which satisfy Eq. 1. This zero splitting cone is circular for $\eta = 0$ and elliptical for $\eta \neq 0$.

The zero splitting loci were obtained in these experiments by setting θ at 5° intervals from 0° to 180° and rotating the magnetic field ϕ to coalescence at each setting. Rotation of the magnetic field corresponds to a change in θ and rotation of the crystal corresponds to a change in ϕ ; θ is here the polar angle of the magnetic field with respect to the rf axis (rotation axis of crystal) and $\phi = 0$ is fixed when the pointer of the crystal holder is parallel to the laboratory fixed horizontal. A second set of points was obtained by setting the magnetic field at 5° intervals and rotating the crystal to coalescence. The two sets of points (about 55 points altogether) plotted together on a stereographic net gave a uniform distribution of points on the loci as shown in Fig. 1 for p-bromobenzene-sulfonyl chloride and in Fig. 2 for p-bromoaniline hydrochloride.

Approximate values of θ_z , ϕ_z and η (where θ_z is now the orientation of the principal Z axis of the field gradient with respect to the rotation axis of the crystal and ϕ_z is its orientation relative to a direction perpendicular to this axis and in the horizontal laboratory plane) were obtained from the stereographic projection in each case by the following procedure. If η is small, as is true here, and the correct value of ϕ_z is subtracted from all the observed ϕ values of a given zero splitting locus the Z axis will be at the rim of the polar diagram. Half the points will then lie on the upper hemisphere and half on the lower hemisphere and these two sets of points will overlap on the net if ϕ_z is guessed correctly. The plot thus obtained, if rotated in the plane of projection by an angle θ_z , will bring Z into coincidence with the polar axis; also, the points should now lie symmetrically distributed about the polar axis. An approximate value of the asymmetry parameter can be obtained from this final plot by use of the equation

$$\eta = 3(\sin^2 \theta_X - \sin^2 \theta_Y) / (\sin^2 \theta_X + \sin^2 \theta_Y) \quad (2)$$

where θ_X , θ_Y are the values of θ where the locus intersects $\phi = 0$ and $\phi = 90^\circ$, respectively.

Accurate values of θ_z , ϕ_z and η were obtained using a least-squares method programmed for the CDC-3600 computer.¹⁵ The parameters

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15. K. V. S. Rama Rao and M. T. Rogers, unpublished results.

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obtained in this way are shown in Table I along with the approximate values obtained by the method outlined above.

The ^{35}Cl resonance in p-bromobenzenesulfonyl chloride was also observed at liquid nitrogen temperature using a frequency-modulated self-quenched oscillator previously described.¹⁶ The resonance frequency observed was in good agreement with the value reported previously.¹⁷

16. J. A. Ryan and M. T. Rogers, J. Phys. Chem. 72, 1340 (1968).

17. P. J. Bray, J. Chem. Phys. 21, 2226 (1953).

However, the intensity was too low to permit a room temperature Zeeman analysis.

IV. RESULTS AND DISCUSSION

Two zero splitting loci have been found for each of the compounds studied. It was shown by rotating the crystals about three mutually perpendicular axes, in turn, that there were no more than two loci for either crystal. Twinning, which would lead to extra field gradients, was shown to be absent by using several different crystals and by examination under the polarizing microscope. In p-bromobenzenesulfonyl chloride the rotation axis was the b axis of the monoclinic crystal hence the two observed C-Br directions are bisected by the ac plane and make an angle of $73^\circ 46'$ with each other.

Quadrupole coupling constants were calculated from the observed values of the ^{79}Br NQR frequencies and the asymmetry parameters using the equation¹

$$e^2 Q q_{zz} = 2h\nu(1 + \eta^2/3)^{-1/2} \quad (3)$$

where η , the asymmetry parameter, is taken from Table I, ν is the observed frequency and q_{zz} is the principal value of the electric field gradient tensor.

Approximate values of π , the pi-bond character or double-bond character of the C-Br bond, were obtained in each case from the above quantities by the equation³

$$\pi = (2\nu/3\nu_p)\eta \quad (4)$$

where $\nu_p = (e^2 q_{zz} Q)_0 = 769.62$ MHz is the quadrupole coupling for the free ^{79}Br atom. The values so obtained, along with values computed by us using this same equation and values in the literature for some other para substituted bromobenzenes, are shown in Table II. The orbital contraction factor $(1 + \epsilon)$ has been omitted from Eq. 4 since the simpler equation is probably more reliable as a result of a cancellation of effects (ref. 10, p. 145).

It may be noted from Table II that the fractional double-bond character of the C-Br bond does appear to increase (to ~4%) with strongly electron withdrawing para substituents such as $-\text{NH}_3^+$ and $-\text{SO}_2\text{Cl}$ relative to the smaller values (~1.5 - 2.5%) observed with strongly electron donating substituents such as $-\text{NH}_2$ and $-\text{OH}$. It is interesting that this also holds for an ortho nitro substituent ($\pi = 0.04$) but less so for a meta nitro substituent ($\pi = 0.03$).¹⁸ We have listed Hammett σ parameters¹⁹ for the

18. K. V. S. Rama Rao and C. R. K. Murty, J. Phys. Soc. Japan 21, 1627 (1966).

19. C. D. Ritchie and W. F. Sager, Progress in Physical Organic Chemistry, V. Gold, ed. (Interscience Publishers, New York, 1964).

substituents of Table II as a measure of the relative electron donating or withdrawing power of these groups in the para position; the values for $-\text{SO}_2\text{Cl}$ and $-\text{NH}_3^+$ are not available but the σ values for $-\text{SO}_2\text{CH}_3$ and $-\text{N}(\text{CH}_3)_3^+$ should be quite similar and are listed in parentheses as estimates.

V. ACKNOWLEDGMENTS

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Table I. Orientations of the principal field gradients and asymmetry parameters.^a

Method	First Locus			Second Locus		
	θ_z	ϕ_z	η	θ_z	ϕ_z	η
p-Bromobenzenesulfonyl chloride^b						
Approximate	126°	91°	0.06	52°	90°	0.07
Least-squares	126°30'	90°	0.05	52°44'	90°	0.08
p-Bromoaniline hydrochloride						
Approximate	79°	118°	0.11	78°	65°	0.10
Least-squares	79°57'	117°57'	0.12	78°13'	65°17'	0.09

^a θ_z, ϕ_z are the polar and azimuthal angles of the principal field gradient relative to the rotation axis of the crystal ($\theta = 0^\circ$) and the laboratory horizontal ($\phi = 0^\circ$).

^bThe rotation axis is the b-axis of the monoclinic crystal.

Table II. NQR parameters for some para substituted bromobenzenes.

Substituent	$\nu(^{79}\text{Br})$	$e^2q_{zz}Q$	η	π	σ	Ref.
-Br	267.89 ^a	535.60	0.045 ^b	2.1	+0.23	7
-OH	264.78	529.56	0.053	2.4	-0.37	4,5
-NH ₂	265.57	531.14	0.029	1.3	-0.66	4,6
-SO ₂ Cl	278.92	557.84	0.080	3.9	(+0.72) ^c	This work
-NH ₃ ⁺	273.60	545.72	0.090	4.3	(+0.82) ^d	This work

^aAll observed frequencies are for room temperature.

^bThe probable error in the asymmetry parameters is about ± 0.02 for substances with small η values.

^cValue is the Hammett σ constant for -SO₂CH₃ as a para substituent in substituted benzenes.

^dValue is that for -N(CH₃)₃⁺.

Captions for Figures

Fig. 1. Zero splitting loci for p-bromobenzenesulfonyl chloride.

Fig. 2. Zero splitting loci for p-bromoaniline hydrochloride.

Fig.1. Zero splitting loci for p-bromobenzenesulfonyl chloride.

Fig.2 . Zero splitting loci for p-bromoaniline hydrochloride.