

The chemical interpretation and the temperature dependence of the ^{14}N nuclear quadrupole resonance of aniline and several derivatives

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Received November 10, 1967

The ^{14}N nuclear quadrupole resonance frequencies of aniline, *o*- and *p*-phenylene diamine, and *p*-chloro-, *p*-bromo-, and *p*-iodo-aniline were measured with a super-regenerative oscillator over a temperature range from 77 to 292 °K. The temperature dependence is analyzed. The chemical interpretation of the quadrupole coupling constants and asymmetry parameters is described.

Canadian Journal of Chemistry, 46, 3595 (1968)

Introduction

Regenerative spectrometers (1, 2), using either magnetic field or frequency modulation (3, 4), have been used to measure ^{14}N nuclear quadrupole resonance (n.q.r.). The super-regenerative spectrometer has been used extensively to measure halogen n.q.r. (5-7); it has a greater sensitivity than the regenerative spectrometer, and the frequency modulation causes a smaller amplitude modulation. Consequently a super-regenerative spectrometer was used to measure the ^{14}N n.q.r. in aniline and several aniline derivatives. The ^{14}N n.q.r. frequencies in *p*-chloro- and *p*-bromo-aniline, and *p*-phenylene-diamine at 77 °K, have been measured with a regenerative spectrometer (8); these were remeasured with the super-regenerative spectrometer. The temperature dependence of the ^{14}N n.q.r. frequencies in aniline, *p*- and *o*-phenylene-diamine, *p*-iodo-, *p*-bromo-, and *p*-chloro-aniline was studied between 77 and 292 °K.

Experimental

The super-regenerative spectrometer shown in Fig. 1 was self-quenched and frequency modulated sinusoidally (9). The signal was recorded using narrow band amplification and phase-sensitive detection (10, 11). The frequency sweep speed was 0.5 kc per min; the time constant was 8 s. The frequencies were determined using a calibrated BC 221 M frequency meter, standardized against the

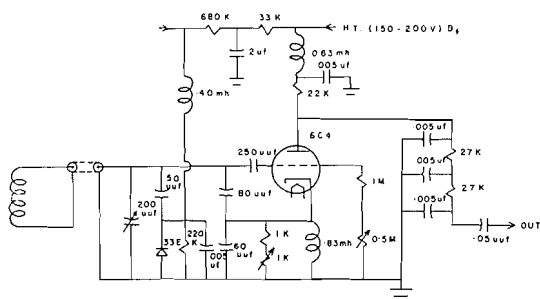


FIG. 1. Circuit diagram of the super-regenerative oscillator based on that of Narath, O'Sullivan, Robinson, and Simmons (9), but self-quenched. Modulation frequency 120 c.p.s. sine wave. Quench frequency 10-15 kc depending on the circuit parameters; thus in Fig. 2 the value was 13 kc.

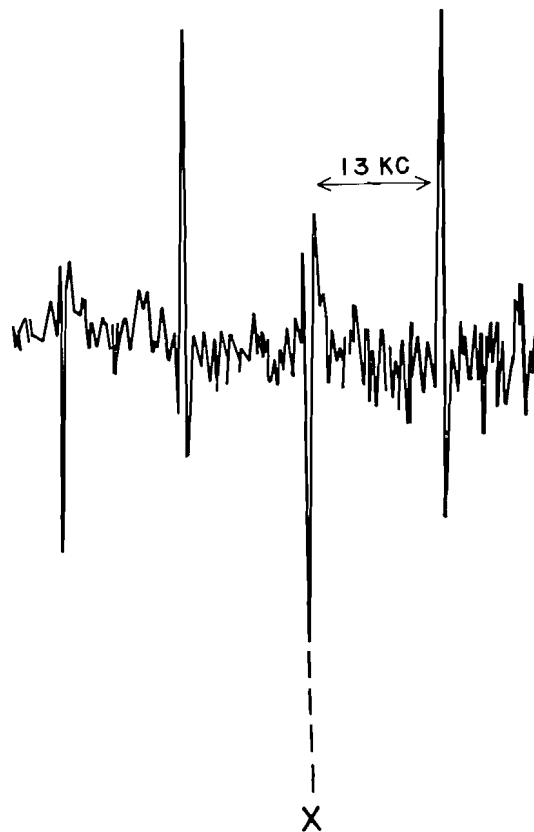


FIG. 2. ν_+ spectrum of *p*-chloro-aniline at 77 °K with a quench frequency of 13 kc.

WWV station frequency. The samples and resonance coil were immersed in liquid nitrogen or the appropriate slush (12) for low temperature measurements. All the samples were recrystallized from suitable solvents, and carefully melted into the sample tube, to avoid decomposition. Samples of 12, 18, or 40 cc were used depending on the signal strength and temperature. The recorded spectrum of the ν_+ line of *p*-chloroaniline at 292 °K is shown in Fig. 2; all the spectra were too weak to measure by oscilloscope display.

When a signal is recorded, the frequency of one line from the super-regenerative spectrometer coincides with the actual resonance frequency of the sample. Thus if the unknown signal is at (a) in Fig. 3(i) when the spectrometer sweeps through the signal, a spectrum such as Fig. 2 is obtained, since a super-regenerative spectrometer gives numerous side bands. One of the lines in the spectrum is selected as test line X (Fig. 2), and the spectrum is run through to the center of X. The spectrometer is then locked to this fixed frequency. The BC 221 M is tuned through this frequency to give the super-regenerative oscillator spectrum Fig. 3(ii) in which the fixed signal occurs as a side band. The quench frequency is then changed, a new BC 221 M spectrum obtained, and the n.q.r. signal frequency corresponds to the line (a) which does not shift. Each n.q.r. frequency was checked by fixing the frequencies of several different test lines X, in all cases the results were within the experimental error of ± 0.5 kc. This error is due to the difficulty of fixing the exact center of a line.

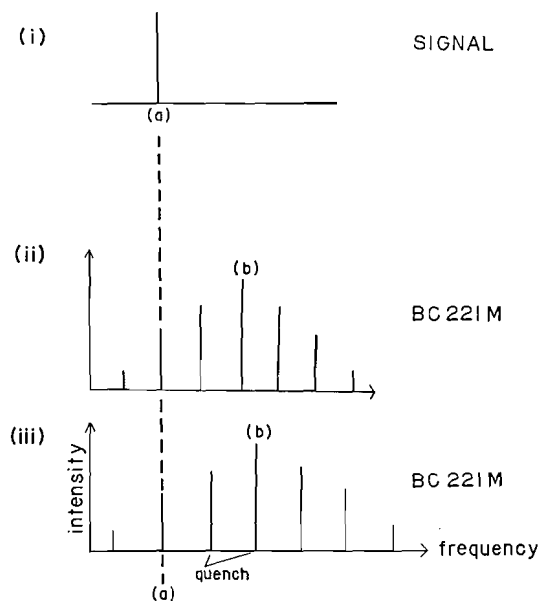


Fig. 3. The unknown signal frequency is at (a) in (i), the line spectrum is as Fig. 2, and X is the chosen line; (ii) shows the BC 221 M spectrum from sweeping through X; (iii) shows the BC 221 M spectrum at a different quench frequency; (b) marks the center line of the spectrum.

Since the method does not depend on the stability of the center band to varying quench frequency, it is possible to change the sensitivity of the spectrometer at a chosen quench frequency, by varying the various circuit parameters.

With B_+ at 250 V the voltages at the circumference of the coil and coil center were 4.0 and 2.5 V; at 200 V they were 3.0 and 2.0 V and at 150 V they were 2.0 and 1.5 V, respectively, with the 15 cc sample coil, of internal diameter 2.5 cm, wound from 18 gauge copper wire; the number of turns in the coil govern the coil's frequency.

Results and Discussion

1. The resonance frequencies, ν_+ and ν_- , the quadrupole coupling constants, e^2Qq/h , and the asymmetry parameters η , at 77 °K

These values are listed in Table Ia.

The resonance frequencies ν_+ and ν_- , at various other temperatures are also given, and shown in Figs. 4, 5, and 6 for aniline, *p*-chloro- and *p*-bromo-aniline, and *o*-phenylene-diamine. The calculated coupling constants and asymmetry parameters are temperature dependent, but are given at 77 °K (Table Ia); they are easily calculated for any other temperature using

$$[1a] \quad e^2Qq/h = \frac{2}{3}(\nu_+ + \nu_-)$$

and

$$[1b] \quad \nu_{\pm} = \frac{3e^2Qq}{4h} \left(1 \pm \frac{\eta}{3} \right)$$

respectively.

A strong piezoelectric effect occurs in *p*-iodoaniline below 195 °K (13, 14) so the resonance

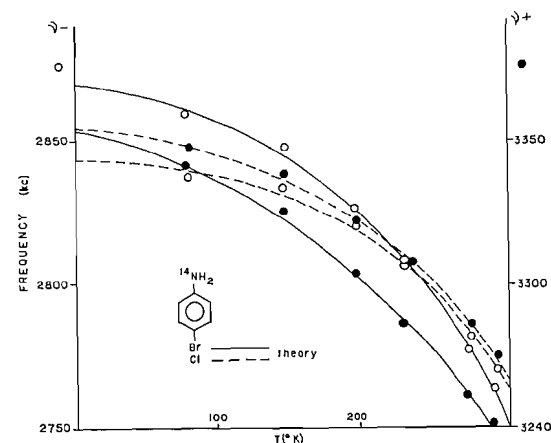


Fig. 4. The experimental points for the ν_+ and ν_- lines of *p*-chloro- and *p*-bromo-aniline, together with the calculated lines.

Note that the ν_- axis is calibrated on the left, and the ν_+ axis on the right.

TABLE Ia

The ^{14}N n.q.r. frequencies ν , coupling constants e^2Qq/h and asymmetry parameters η , and the temperature dependence of the ν^*

| Molecule | e^2Qq/h (kc) at 77 °K | η (%) at 77 °K | Line | Frequency in kc ± 0.5 kc at temperature (°K) | | | | | | |
|-----------------------------|-------------------------------|---------------------------|----------|--|-------------------------|--------|-------------------|-------------------------|--------|--------|
| | | | | 77 | 143 | 195 | 228 | 250 | 275 | 292 |
| Aniline | 3933 | 26.9 | ν_+ | 3243.2 | 3234.5 | 3211.2 | (210) (3201.7) | line vanished at 228 °K | | |
| | | | ν'_+ | 3184.2 | 3176.2 | 3160.5 | 3146.0 | 3134.0 | | |
| | | | ν_- | 2720.4 | 2716.0 | 2710.0 | 2704.3 | 2699.0 | | |
| | | | ν'_- | 2650.0 | 2640.0 | 2618.0 | 2594.3 | 2578.0 | | |
| | | | | | | | | | | |
| <i>o</i> -Phenylene-diamine | 3773 | 33.1 | ν_+ | 3150.6 | 3142.8 | 3134.0 | | | 3107.5 | |
| | | | ν'_+ | 3131.6 | 3121.5 | 3109.1 | | | 3074.0 | |
| | | | ν_- | 2536.0 | 2533.8 | 2525.5 | | | 2500.0 | |
| | | | ν'_- | 2497.3 | 2492.3 | 2484.2 | | | 2455.0 | |
| | | | | | | | | | | |
| <i>p</i> -Phenylene-diamine | 3910 | 26.4 | ν_+ | 3190.5 | Weak broad signals only | | | | | |
| | | | ν_- | 2674.4 | | | | | | |
| <i>p</i> -Chloro-aniline | 4116 | 24.3 | ν_+ | 3337.5 | 3328.5 | 3311.5 | 3296.7 | | 3275.0 | 3264.5 |
| | | | ν_- | 2836.5 | 2833.0 | 2819.8 | 2805.5 | | 2780.7 | 2769.4 |
| <i>p</i> -Bromo-aniline | 4134 | 23.3 | ν_+ | 3341.7 | 3325.5 | 3303.5 | 3286.0 | | 3261.3 | 3351.1 |
| | | | ν_- | 2859.0 | 2848.2 | 2826.9 | 2808.0 | | 2776.4 | 2763.7 |
| <i>p</i> -Iodo-aniline | 3766 | 33.1 | ν_+ | | Piezoelectric effect | | | | 3136.0 | |
| | | | ν_- | | | | | | 2512.0 | |

*Since $\nu_{\pm} = 3e^2Qq/4h(1 \pm \eta/3)$, the two lines ν_+ and ν_- coalesce when η is zero. The equations $e^2Qq/h = \frac{2}{3}(\nu_+ + \nu_-)$ and $(\eta/2)(e^2Qq/h) = \nu_+ - \nu_-$ allow e^2Qq/h to be calculated, with the average of ν_+ and ν_- used.

The frequency of *p*-iodo-aniline lies below that for *p*-bromo-aniline in contradiction to the predicted frequency in (8).

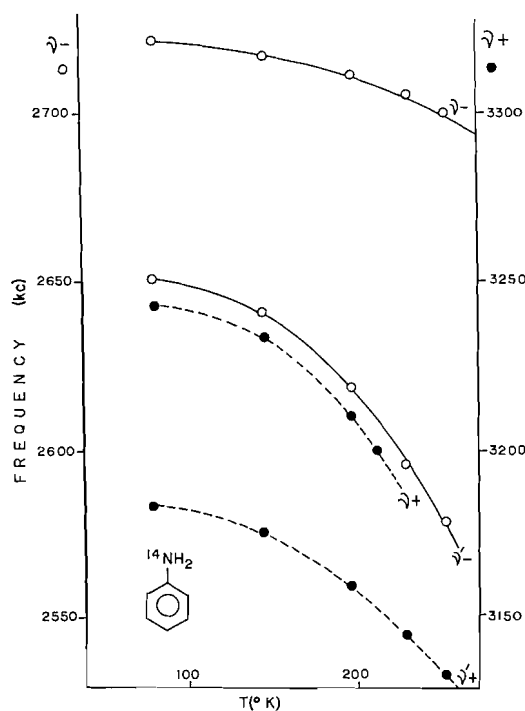


FIG. 5. The temperature dependence of the ν_+ , ν'_+ , ν_- , and ν'_- lines of aniline.

Note that the ν_- axis is calibrated on the left and the ν_+ axis on the right.

was only detected at 292 °K. The *p*-chloro- and *p*-bromo-aniline frequencies agree with those previously reported (8).

The signal line-width increased as the temperature decreased. While a super-regenerative oscillator cannot give absolute line-width measurement, it does give the right order of line-width (15). The line-width was not a function of the cooling procedure or rate, or of the time the sample was maintained at a given temperature;

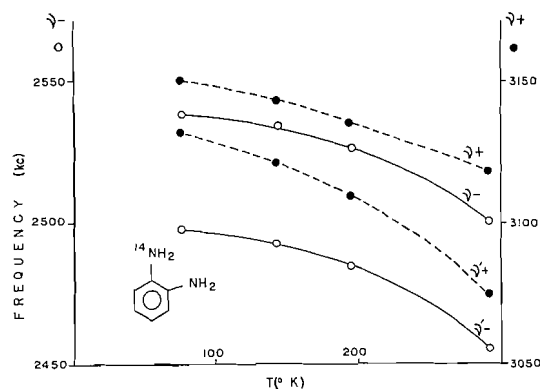


FIG. 6. The temperature dependence of the ν_+ , ν'_+ , ν_- , and ν'_- lines of *o*-phenylene-diamine.

Note that the ν_- axis is calibrated on the left and the ν_+ axis on the right.

therefore it is not due to crystal strain. The same phenomenon has been observed in NH_3 (16) and ethylene-diamine (17) and was attributed to magnetic dipole-broadening caused by the large proton magnetic moment (16, 17)¹.

TABLE Ib
Some typical signal-to-noise ratios for
o-phenylene-diamine, *p*-chloro- and
p-bromo-aniline

| Line | Sample volume (cc) | S/N for $B_+ = 150$ V at temperatures ($^{\circ}\text{K}$) | | |
|-----------------------------|--------------------|--|-----|-----|
| | | 77 | 196 | 292 |
| <i>o</i> -Phenylene-diamine | | | | |
| v_+ | 18 | 4 | 7 | 10 |
| | 40 | 5 | 9 | 13 |
| v_- | 18 | 0 | 6 | 13 |
| | 40 | >1 | 7 | 17 |
| <i>p</i> -Chloro-aniline | | | | |
| v_+ | 12 | 5 | 10 | 11 |
| | 40 | 7 | 16 | 17 |
| v_- | 12 | 0 | 2 | 5 |
| | 40 | >1 | 3 | 8 |
| <i>p</i> -Bromo-aniline | | | | |
| v_+ | 40 | 9 | 9 | 9 |
| v_- | 40 | >1 | 3 | 8 |

The signal-to-noise ratio, S/N , decreased with decreasing temperature, except for the *p*-bromo-aniline v_+ line in which S/N remained constant. The S/N are shown in Table Ib for v_{\pm} lines of *p*-chloro-aniline and *o*-phenylene-diamine at 77, 196, and 292 $^{\circ}\text{K}$. The apparent decrease in S/N is partly due to line broadening.

The v_+ line of aniline is a doublet up to 210 $^{\circ}\text{K}$; at 228 $^{\circ}\text{K}$ the higher line vanishes; there was no phase change, and the lower v_+ line and the v_- doublet continued a smooth frequency change with increasing temperature.

To ensure that the decrease in S/N at 77 $^{\circ}\text{K}$ was not due to saturation effects, the measurements were carried out with a wide range of B_+ . The S/N was constant for B_+ from 200 V to 125 V, below which it decreased markedly. Similar results were obtained by varying other circuit parameters. Measurements were carried out on 12, 15, 18, and 40 cc samples in several differently wound coils. The S/N of the v_+ line increased with increased sample quantity, but still decreased by a factor of 10–15 at 77 $^{\circ}\text{K}$; the v_- line was enhanced sufficiently by the 40 cc sample to

permit measurement at 77 $^{\circ}\text{K}$. In view of the voltages involved in the coil it is not likely that saturation is responsible for the decrease in S/N . The S/N is actually improved by a large B_+ which causes larger coil voltages. However, the decrease in S/N with decreased temperature is important since, if common, it may prove a major obstacle to ^{14}N super-regenerative n.q.r.

2. The ^{14}N n.q.r. temperature dependence of *p*-chloro- and *p*-bromo-aniline

The principal axes of ^{14}N in *p*-bromo-aniline were established by a Zeeman study of a single crystal (8); the crystal structure is unknown. However, the crystal structure of *p*-chloro-aniline is known (18); the molecules are almost planar. Since chlorine and bromine are similar atoms, it can be assumed that the crystal structures and ^{14}N principal axes will be the same in *p*-bromo- and *p*-chloro-aniline. The temperature dependences of the ^{14}N n.q.r. frequencies can then be treated theoretically, although the assumption may cause minor errors.

Molecular torsional motions average the field gradient, thereby decreasing it with increasing temperature (19, 20). The ^{14}N n.q.r. frequencies and their temperature dependence are (21)

$$[2] \quad v_+ = \frac{3e^2Q}{4h} q \left\{ \left(1 + \frac{\eta}{3} \right) (1 - 2\overline{\theta_x^2} - \overline{\theta_y^2}) - \frac{2}{3} \eta (\overline{\theta_z^2} - \overline{\theta_y^2}) \right\}$$

and similarly for v_- . The q and η are the stationary system values for the maximum field gradient component and the asymmetry parameter, and $\overline{\theta_x^2}$ etc. are the root-mean-squares of the angular displacements about three principal axes. Only if $\overline{\theta_z^2} \gg \overline{\theta_y^2}$ would the second term be large; the η values² in these substituted anilines are about 25%. Thermal data from X-ray crystallography (18) exclude this possibility in *p*-chloro-aniline; we assume this is also true in *p*-bromo-aniline. Therefore [2] becomes

$$[3] \quad v_+ = v_{+0} (1 - 2\overline{\theta_x^2} - \overline{\theta_y^2})$$

and similarly for v_- with the coefficients reversed; $v_{\pm 0}$ are given by [1] and are the frequencies that would be observed in the absence of torsional

¹This cause has been questioned, see ref. 48.

²The axes are: z perpendicular to ring, y along C—N bond, and x mutually perpendicular to z and y .

oscillations. The vibrational force constant is, quantum mechanically,

$$[4] \quad K = 4\pi v^2 \theta$$

where θ is the moment of inertia, and v the torsional vibrational frequency, hence

$$[5] \quad v_+ = v_{+0} \left\{ 1 - \frac{hv_x}{K_x} \left[\coth \left(\frac{hv_x}{kT} \right) \right] - \frac{hv_y}{2K_y} \left[\coth \left(\frac{hv_y}{kT} \right) \right] \right\}$$

where x and y denote the field gradient axes; v_- is similarly defined with x and y interchanged.

The terms $v_{\pm 0}$, v , and θ are temperature dependent under constant pressure (22, 23) but in a molecular crystal $v_{\pm 0}$ and θ are constants (24, 25) and only the volume dependence of v has to be considered. Thus

$$[6] \quad v = v(T) = v(0)(1 - \alpha T)$$

where $v(0)$ is the vibrational frequency at an arbitrary zero of temperature and α an empirical constant particular to the axis considered (26); T is the temperature. The α accounts for the thermal expansion of the lattice, the anharmonicity in the torsional vibrations, and neglect of low frequency vibrational modes. Combining [5] and [6] gives

$$[7] \quad v_+ = v_{+0} \left\{ 1 - \left(\frac{hv_x(0)}{K_x(0)(1 - \alpha_x T)} \right) \cdot \left[\coth \left(\frac{hv_x(0)(1 - \alpha_x T)}{kT} \right) \right] - \left(\frac{hv_y(0)}{2K_y(0)(1 - \alpha_y T)} \right) \cdot \left[\coth \left(\frac{hv_y(0)(1 - \alpha_y T)}{kT} \right) \right] \right\}$$

and similarly for v_- .

The θ were calculated from X-ray data (18) using average bond lengths (19). The McGill IBM 7044 computer was programmed for a least-square fit of the experimental v_+ and v_- against v_{+0} , v_{-0} , $v_x(0)$, $v_y(0)$, α_x , and α_y ; these parameters are listed in Table II. The standard deviation for both compounds is ± 2 kc. The torsional frequencies fall into the correct frequency region and in the correct order for the relative atomic weights, as can be seen by comparison with other torsional frequencies in Table II.

TABLE II
The theoretically calculated terms of [7]*

| Parameter | Molecule | |
|---------------------------------|---|---|
| | <i>p</i> -ClC ₆ H ₄ NH ₂ | <i>p</i> -BrC ₆ H ₄ NH ₂ |
| v_{+0} (kc) | 3351.1 | 3362.5 |
| v_{-0} (kc) | 2850.3 | 2879.8 |
| $v_x(0)$ (cm ⁻¹) | 57.83 | 36.16 |
| $v_y(0)$ (cm ⁻¹) | 192.61 | 125.81 |
| α_x (deg ⁻¹) | 1.024×10^{-3} | 4.622×10^{-4} |
| α_y (deg ⁻¹) | 1.901×10^{-3} | 1.548×10^{-3} |

Comparable results

| Molecule | Parameter | Value (cm ⁻¹ at 300 °K) | Reference |
|---|-----------|------------------------------------|-----------|
| <i>p</i> -Cl ₂ C ₆ H ₄ | v_z | 94 | 28 |
| | v_x | 54 | |
| | v_y | 27 | |
| (CH ₂) ₆ N ₄ | v | 69.5 | 25 |
| | | or 72 | |
| NH ₃ | v_a | 234 | 15 |
| | v_b | 362 | |
| ND ₃ | v_a | 213 | 15 |
| | v_b | 260 | |
| NF ₃ | v_a | 50 | 30 |
| | v_b | 30 | |
| C ₂ H ₆ | v | 275 | 29 |
| | v | 200 | |
| CH ₂ Cl | v | 1355 | 29 |
| | v_{Br} | 13.0 | |

| Molecule | Parameter | Value (deg ⁻¹) | Reference |
|--|-----------|----------------------------|-----------|
| ⁶³ Cu ₂ O | α | 1.31×10^{-4} | 31 |
| ⁶⁵ Cu ₂ O | α | 1.30×10^{-4} | 31 |
| (CH ₂) ₆ N ₄ | α | 3.5×10^{-4} | 25 |

* $v_{\pm 0}$ are the quadrupole resonance frequencies at zero torsional vibration; $v_x(0)$ and $v_y(0)$ are the torsional vibrational frequencies at an arbitrary zero of temperature; α_x and α_y are empirical constants, and x and y are the field-gradient principal axes.

The temperature coefficients, α_x and α_y , are quite large but in the same region as those previously reported for ⁶³Cu₂O, ⁶⁵Cu₂O (31), and (CH₂)₆N₄ (25). Thus the slope of any curve increases in the low temperature region.

The curves derived using these parameters are shown in Fig. 4, together with the experimental points, which deviate from the curves at the low temperature end. This may be due to ignoring v_z , which is present in *p*-dichloro-benzene (28). Including v_z would require θ_z^2 to be included in [3] and consequently θ and v_z in [4] through [7]. When a more extensive study of the temperature dependence is available, and the directions of the field-gradient principal axes are known together with the moments of inertia, a more comprehensive discussion will be possible.

3. The coupling constants and asymmetry parameters, e^2Qq/h and η for ^{14}N

Table Ia shows that for ^{14}N :

(a) A smaller e^2Qq/h is associated with a larger η ; the percentage change in η is five times that in e^2Qq/h : this is reasonable in view of the theoretical results for q_{aa} , q_{bb} , and q_{cc} (Table III) since a larger q_{aa} gives a larger e^2Qq/h and smaller η . The q_{aa} , q_{bb} , and q_{cc} are general expressions for any three mutually perpendicular q , such that $|q_{aa}| > |q_{bb}| > |q_{cc}|$. At any particular atom the q will be q_{xx} , q_{yy} , and q_{zz} , and the identification of the q_{aa} , etc., with the q_{xx} , etc., will be *particular to that atom* (Table III).

(b) The η and e^2Qq/h for *p*-iodo-aniline are anomalous; the values were calculated from the 292 °K frequencies, instead of the 77 °K frequencies, but the *p*-chloro- and *p*-bromo-aniline values at 292 °K are still higher for e^2Qq/h and lower for η than *p*-iodo-aniline. Hydrogen bonding between the $-\text{NH}_2$ and I, intermolecularly, would explain the large η and small e^2Qq/h , but the ^{127}I n.q.r. resonance at 261.14 mc does not support such an idea (27, 32).

(c) The e^2Qq/h and η for aniline (3933 kc; 26.9%) and *p*-phenylene-diamine (3910 kc; 26.4%) are surprisingly close in view of their different chemical properties. The e^2Qq/h and η of *o*-phenylene-diamine (3777 kc, 33.0%) are very different due perhaps to steric effects, or "direct field" effects between adjacent $-\text{NH}_2$ groups (33) which are absent in aniline and *p*-phenylene-diamine.

4. Theory

Preliminary calculations using the simple Hückel molecular orbital theory (34) and the extended Hückel method (35) led to our decision to analyze the results in terms of the bond electronegativity equalization method with Hückel molecular orbital π -bond treatment, BEEM- π (36).

BEEM- π is fully discussed elsewhere (40). The σ -orbitals in the molecule are treated by the bond electronegativity equalization method in which the orbital electronegativities as functions of their own occupancy and the occupancy of other orbitals on the same atom are equalized in a two centered bond (41-43). Thus the σ -core is changed from the free atom state, and this affects the σ -orbital parameters of the Hückel molecular orbital method, which change the

charge density distributions, and alter the σ -orbital occupancies. Thus the σ and π orbitals are interrelated, and the procedure is taken to self-consistency for the σ and π orbitals (40).

The parameters in the BEEM- π calculations for the π -orbital are

$$[8] \quad \alpha_x = \alpha_0 + h_x \beta_0$$

$$[9] \quad \beta_{cx} = k_{cx} \beta_0 \quad \text{i.e. } k_{\text{CN}} = 0.8$$

in which α is the coulomb integral and β the resonance integral, the subscripts x and 0 signifying the hetero-atom and the benzene carbon where $h_c = 0$ and $k_c = 1$, where $h_{\text{N}} = 1.5$, $k_{\text{CN}} = 0.8$, $h_{\text{Cl}} = 2.0$, and $k_{\text{CCl}} = 0.4$ (44). The σ -bond parameters were the usual valence state orbital electronegativities and their parameters (41).

BEEM- π has been successfully applied to predicting the ^{35}Cl n.q.r. frequencies in a series of conjugated molecules (40). In this paper it is applied to *p*-chloro-aniline.

The chlorine atom can be assumed to be in several different hybridized states. If it uses only *p*-orbitals in bonding it will be $\text{sp}_x\text{p}_y\text{p}_z$, if it is trigonally hybridized³ (an extreme condition which is chemically unlikely) it will be $\text{tr.tr.tr.}\pi$, and if there is a certain percentage of *s*-character in the σ -orbital to the carbon atom in the ring, it will lie between these extreme positions. The results for *p*-chloro-aniline in Table IIIc demonstrate the sensitivity of the ^{35}Cl n.q.r. frequency to the hybridization of the ^{35}Cl . A pure p_σ orbital gives 50.75 Mc, a pure trigonal orbital gives 33.69 Mc, while 20% *s*-character in the σ -orbital gives 42.22 Mc. The respective asymmetry parameters are 2.5, 3.7, and 3.0% respectively. The experimental results are 34.15 Mc for the frequency and $6 \pm 3\%$ for the asymmetry parameter (37). Thus 28% *s*-character in the σ -orbital would predict the frequency, and presumably the asymmetry, exactly.

Since the BEEM- π theory is successful in predicting ^{35}Cl n.q.r. frequencies, it should be equally successful in predicting ^{14}N n.q.r. frequencies. However, at the ^{35}Cl atom the site axes coincide with the ring system axes, which in the planar molecule define the molecular axes; thus the only variable in the theory is the *s*-character of the chlorine σ -orbital.

³The nomenclature is discussed in refs. 49, 7, and 41-44.

This condition holds for the ^{35}Cl atom in *p*-chloro-aniline even when there is an angle of $25^\circ 18'$ between the π -orbital of the ^{14}N in the NH_2 group and the z -axis of the ring (38). The angle between the plane of the ring and the plane of the NH_2 unit is thus $39^\circ 21'$. Consequently BEEM- π calculations were repeated for such a non-planar *p*-chloro-aniline, in which the resonance integral β_{CN} was altered to its value for a $25^\circ 18'$ loss in overlap between the ^{14}N - π -orbital and the ring π -orbital. It is seen that the ^{35}Cl frequency and asymmetry parameter are quite insensitive to such changes.

At the ^{14}N atom on the other hand several variables can all affect the ^{14}N n.q.r. frequency and asymmetry parameter.

(a) *The Hybridization at the Nitrogen*

The actual σ -bond hybridization is unknown; thus the angle HNH for *p*-phenylene-diamine is $109^\circ 4'$ in CCl_4 solution (39) suggesting that the NH bonds are almost tetrahedral in hybridization (25% s -character) while the N—C bond will have 50% s -character in the ^{14}N σ -orbital. In the other molecules it is reported to be 112° for the angle HNH, so that the N—H σ -orbital has more s -character and the N—C σ -orbital less s -character than in *p*-phenylene-diamine. The exact hybridization governs the resolution into $sp_xp_y p_z$ occupancies, hence the values of q_{xx} , q_{yy} , and q_{zz} and consequently the e^2Qq/h and η , as seen above for ^{35}Cl , and as discussed by Das and Hahn (47). In all the BEEM- π calculations the ^{14}N is assumed to be exactly tr.tr.tr. π hybridized, and only the occupancy of these orbitals is considered as a variable.

(b) *The Angle between the z-Axis of the Ring and the π Orbital of ^{14}N in the $-\text{NH}_2$ Group*

The absence of X-ray data on the molecules makes it difficult to select the correct principal molecular axes and the site axes at the ^{14}N . In the BEEM- π calculations it is initially assumed that the molecular and site axes are the same; thus the molecule is planar and the results in Table IIIa are obtained. It will be noticed that the asymmetry parameters are about one tenth of the experimental and that e^2Qq_{ai}/h is around -5.6 Mc, well below the predicted -7.4 Mc (45). Also the frequency

$$[10] \quad \nu = (e^2Qq_{\text{ai}}/h)q_{zz}$$

is experimentally in the order *p*-chloro-aniline >

aniline > *p*-phenylene-diamine > *o*-phenylene-diamine. The BEEM- π planar molecule predicted order is *p*-phenylene-diamine > aniline > *p*-chloro-aniline > *o*-phenylene-diamine. The resonance integral β_{CN} is 0.80 in these calculations.

The angle between the molecular ring z -axis and the ^{14}N π -orbital in aniline is $25^\circ 18'$ (38). Thus if it is assumed that this angle is the same in *o*-phenylene-diamine, *p*-phenylene-diamine, and *p*-chloro-aniline, then BEEM- π calculations can be performed to give Table IIIb. The terms in this table are primed to signify that there is a $25^\circ 18'$ angle between the ^{14}N π -orbital and the π -orbital of the ring. It is immediately obvious that the theoretical asymmetry parameters η' are now in the same region as the experimental (Table I), while the $e^2Qq'_{\text{ai}}/h$ are all near the expected -7.4 Mc. An assumed angle slightly less than $25^\circ 18'$ for any of the molecules would bring η'_{theory} and η_{exp} into agreement, and e^2Qq_{ai}/h nearer to -7.4 Mc. In Table IIIb the resonance integral β_{CN} is held at 0.80.

If the e^2Qq_{ai}/h for ^{14}N were absolutely established as -7.4 Mc it would be possible to use it to find the angles needed to give η_{theory} in agreement with η_{exp} and to predict the frequency. However, the uncertainty in e^2Qq_{ai}/h , and that discussed in (a), together with the choice of the resonance integral parameter β , make such calculations invalid.

In Table IIIc BEEM- π calculations are performed on *p*-chloro-aniline assuming a non-planar molecule and altering β_{CN} from 0.80, the value for a planar molecule, to 0.72 the value for an angle of $25^\circ 18'$, in the overlap expression, and for $\beta = 0.62$, an arbitrary decrease in β_{CN} . It is obvious that the ^{14}N η' is quite insensitive to the change from 0.62 to 0.72 (both 40%) but sensitive to the change from 0.72 to 0.80 (40% to 30%). The $e^2Qq'_{\text{ai}}/h$ is similarly sensitive to the change of β_{CN} from 0.80 to 0.72 (-8.37 and -7.71 Mc) but only slightly sensitive to the change from 0.72 to 0.62 (-7.71 to -7.35 Mc).

In Table IIIb the order of the predicted frequencies ν is *p*-phenylene-diamine > aniline > *p*-chloro-aniline > *o*-phenylene-diamine, the same order as for a planar molecule calculation. Either an angle change and/or a change in β_{CN} alters such an order. Thus in *p*-chloro-aniline with $\beta_{\text{CN}} = 0.72$, the value of $q_{zz}'(\pi)$ is 0.5339, predicting that *p*-chloro-aniline will have the highest n.q.r. frequency, in agreement with Table Ia.

TABLE III

¹⁴N and ³⁵Cl BEEM- π calculations of the electron densities and field gradients in aniline and several derivatives*

$$\text{Define } \eta = \left| \frac{q_{bb} - q_{cc}}{q_{aa}} \right|, \text{ and } \frac{e^2 Q q}{h} = \frac{e^2 Q q_{aa}}{h}$$

The maximum field gradient is chosen as $|q_{aa}| > |q_{bb}| > |q_{cc}|$.For ¹⁴N, $q_{aa} = q_{zz}$, the ¹⁴N π -orbital; $q_{bb} = q_{xx}$, the ¹⁴N p-orbital tangential to the benzene ring; $q_{cc} = q_{yy}$, the ¹⁴N p-orbital in the C-N bond.For ³⁵Cl, $q_{aa} = q_{yy}$, the ³⁵Cl p-orbital in the C-Cl bond; $q_{bb} = q_{xx}$, the ³⁵Cl p-orbital tangential to the benzene ring; $q_{cc} = q_{zz}$, the ³⁵Cl π -orbital.Full results for *p*-bromo-aniline and *p*-iodo-aniline are not shown as the necessary BEEM- π parameters for Br and I have not yet been completely established (40).

TABLE IIIa

¹⁴N BEEM- π calculations on aniline and several substituted anilines*

| Compound | tr ₁ = tr ₂ | tr ₃ | p _z (π) | p _x | p _y | q _{zz} (π) | q _{xx} | q _{yy} | η (%) | e ² Qq _{at} /h |
|-----------------------------|-----------------------------------|-----------------|--------------------------|----------------|----------------|---------------------------|-----------------|-----------------|------------|------------------------------------|
| Aniline | 1.1559 | 1.1297 | 1.8377 | 1.1559 | 1.1384 | 0.6905 | -0.3321 | -0.3584 | 3.80 | -5.69 |
| <i>o</i> -Phenylene-diamine | 1.1562 | 1.1410 | 1.8259 | 1.1562 | 1.1461 | 0.6747 | -0.3298 | -0.3449 | 2.2 | -5.60 |
| <i>p</i> -Phenylene-diamine | 1.1511 | 1.1339 | 1.8529 | 1.1511 | 1.1396 | 0.7075 | -0.3451 | -0.3624 | 2.4 | -5.53 |
| <i>p</i> -Chloro-aniline | 1.1609 | 1.1179 | 1.8289 | 1.1609 | 1.1322 | 0.6823 | -0.3627 | -0.3197 | 6.3 | -6.03 |

*¹⁴N BEEM- π calculations on aniline and several substituted anilines assuming the molecules to be planar. The resonance integral β_{CN} is 0.80. The calculations are performed on a trigonally hybridized ¹⁴N; tr₁ = tr₂ as these are bonded to H, tr₃ is bonded to C, and p_z(π) is the lone pair orbital. The results are transformed to an s, p_x, p_y, and p_z(π) basis set, and the field gradients q_{xx}, q_{yy}, and q_{zz} calculated from the p_x, p_y, and p_z(π), since (47)

$$q_{zz} = p_z(\pi) - 1/2(p_y + p_x) \quad \text{etc.}$$

The figures under columns 2 through 6 represent electron densities, or occupation numbers, those in columns 7 through 9 represent numbers by which the field gradient in the free atom must be multiplied to give the field gradient in the molecule (47). Thus

$$q_{mol} = q_{at} \quad \text{etc.}$$

TABLE IIIb

¹⁴N BEEM- π calculations on aniline and several substituted anilines*

| Compound | p' _z (π) | p' _x | p' _y | q' _{zz} (π) | q' _{xx} | q' _{yy} | η' (%) | e ² Qq' _{at} /h |
|-----------------------------|---------------------------|-----------------|-----------------|----------------------------|------------------|------------------|-------------|-------------------------------------|
| Aniline | 1.7100 | 1.1559 | 1.2662 | 0.4989 | -0.3322 | -0.1667 | 33 | -7.88 |
| <i>o</i> -Phenylene-diamine | 1.7018 | 1.1562 | 1.2703 | 0.4885 | -0.3292 | -0.1587 | 35 | -7.72 |
| <i>p</i> -Phenylene-diamine | 1.7227 | 1.1511 | 1.2699 | 0.5122 | -0.3452 | -0.1670 | 35 | -7.63 |
| <i>p</i> -Chloro-aniline | 1.7017 | 1.1609 | 1.2595 | 0.4915 | -0.3197 | -0.1718 | 30 | -8.37 |

*¹⁴N BEEM- π calculations on aniline and several substituted anilines assumed to have an angle θ of 25° 18' between the nitrogen lone pair axis and the z-axis of the benzene ring. The resonance integral β_{CN} is maintained at 0.80. The electron densities p', and new field gradients q', are calculated using p'_x = p_x, p'_y = p_y cos θ + p_z sin θ , and p'_z = p_z cos θ + p_y sin θ .

TABLE IIIc

BEEM- π calculations on *p*-chloro-aniline*

| (i) ³⁵ Cl results for a fixed $\beta_{CN} = 0.80$ and variable hybridization | | | | | | | | | |
|---|--|---------------------------|---------------------------|-----------------|----------------------------|----------------------------|------------------|-------------|-------------------------------------|
| β_{CN} | Hybrid | p _z (π) | p _x | p _y | q _{zz} (π) | q _{xx} | q _{yy} | η (%) | v Mc |
| 0.80 | tr.tr.tr. π | 1.9848 | 2.000 | 1.3784 | 0.2956 | 0.3184 | -0.6140 | 3.7 | 33.69 |
| 0.80 | p _x p _y p _z | 1.9848 | 2.000 | 1.0676 | 0.4510 | 0.4738 | -0.9248 | 2.5 | 50.75 |
| 0.80 | 20% s in p _y | 1.9848 | 2.000 | 1.2230 | 0.3733 | 0.3961 | -0.7694 | 3.0 | 42.22 |
| (ii) Variable β_{CN} and fixed hybridization | | | | | | | | | |
| ³⁵ Cl | | p' _z (π) | p' _x | p' _y | q' _{zz} (π) | q' _{xx} | q' _{yy} | η' (%) | v' Mc |
| 0.72 | tr.tr.tr. π | 1.9845 | 2.000 | 1.3901 | 0.2894 | 0.3127 | -0.6022 | 3.9 | 33.04 |
| 0.62 | tr.tr.tr. π | 1.9841 | 2.000 | 1.3880 | 0.2901 | 0.3139 | -0.6040 | 3.9 | 33.14 |
| ¹⁴ N | | p' _x | p' _z (π) | p' _y | q' _{xx} | q' _{zz} (π) | q' _{yy} | η' (%) | e ² Qq' _{at} /h |
| 0.72 | tr.tr.tr. π | 1.2834 | 1.7454 | 1.1396 | -0.3748 | 0.5339 | -0.1591 | 40 | -7.71 |
| 0.62 | tr.tr.tr. π | 1.2833 | 1.7685 | 1.1339 | -0.3920 | 0.5599 | -0.1679 | 40 | -7.35 |

*(i) The table shows how the resonance frequency for ³⁵Cl is dependent on the hybridization of the chlorine orbitals. Two extreme cases tr.tr.tr. π and sp_xp_yp_z are calculated, and a case with 20% s-character in the C-Cl σ bond (p_z).(ii) With a fixed hybridization assumed for ³⁵Cl and ¹⁴N the effect of changing the resonance integral β_{CN} is considered. The ³⁵Cl is, as expected, very insensitive to such a change, and so is the ¹⁴N. Thus the calculations in Table IIIb are fairly reliable despite the use of an unaltered $\beta_{CN} = 0.80$, derived for planar molecules, in the non-planar molecule calculations.

(c) *The Possible Twisting of the $-\text{NH}_2$ Group out of the Plane of the Ring*

This would change both the site axes, now being at a solid angle to the molecular axes by θ for the angle between the z -axis of the ring and the ^{14}N π -orbital, and by ϕ for the angle between the x axis of the ring and the x axis of the ^{14}N . This would affect the values of q_{aa} , q_{bb} , and q_{cc} simply by the resolution of the orbital densities, and also the π -bonding to the ring and consequently the value of β_{CN} .

(d) *Other Results*

The results for p -bromo-aniline and p -iodo-aniline are not shown in detail in Table III due to the preliminary nature of their BEEM- π parameters (40). The preliminary results give q_{aa}^{Br} as 0.4936 with η at 28% and q_{aa}^{I} as 0.4497 with η at 40%. The predicted e^2Qq_{aa}/h is 8.37 Mc as in p -chloro-aniline. The parameters in the Hückel part of the theory are derived relative to chlorine (44) and are of questionable validity (44) at $h_{\text{Br}} = 1.5$, $k_{\text{CBr}} = 0.3$, $h_1 = 1.2$, and $k_{\text{Cl}} = 0.15$.

5. Conclusion

In view of the uncertainty in the hybridization at the ^{14}N atom, the non-planarity angle θ , the twist angle ϕ , and the resonance integral β_{CN} , no definitive quantitative results can be expected. However, the value of e^2Qq_{aa}/h will not be changed by any of these factors to any significant extent and it can be concluded that e^2Qq_{aa}/h cannot be far from -7.4 Mc (45). There is no justification for assuming it to be -14.0 Mc simply because it is more "appropriate" to some limited calculations (46).

It can be concluded that

(i) The ^{14}N n.q.r. frequencies and asymmetry parameters are explainable if the non-planarity of aniline and its derivatives is considered.

(ii) The BEEM- π theory gives a correct and consistent description of the conjugative effect through the π -system, of the inductive effect through the σ -system, and of the interaction between them. Such σ - π interaction is essential for any successful interpretation of the experimental results.

(iii) The e^2Qq_{aa}/h for ^{14}N is approximately -7.4 Mc.

(iv) Further work awaits more detailed structural analysis.

(v) These results are sufficiently encouraging that work is at present under way to predict the

v precisely; it includes variations in the HNH angle, in θ and ϕ , as well as experimental measurements on 25 other substituted anilines over a wider temperature range. The β_{CN} parameters are being improved and BEEM- π parameters for Br and I verified.

Acknowledgments

This research was supported by the National Research Council of Canada. We wish to thank the Referee most sincerely for his advice and help. We wish to thank Dr. M. Kaplansky for useful discussions. C. T. Yim thanks McGill University for the award of University Graduate Fellowships (1966-1968); D. H. Lo thanks the NRCC for the award of a Studentship (1968-1969). We acknowledge the use of the McGill University IBM 7044 computer and time allotted.

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