
Temperature Dependence of Internal Torsional Frequencies in 2,5-Dichloro Aniline Using Nuclear Quadrupole Resonance Data

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The temperature dependent ³⁵Cl NQR data of 2,5-dichloro aniline was analysed using a two-mode approximation to yield the internal torsional frequencies in this compound. The torsional frequencies lie in the range 28–70 cm⁻¹ and their temperature dependence is non-linear. The two modes obtained lie close to each other and the lower frequency mode obtained around 30 cm⁻¹ agrees closely with the results obtained in similar compounds 2,6-dichloro aniline and 3,4-dichloro aniline. This mode can be identified with motion around an axis perpendicular to the ring.

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1. Introduction

The ³⁵Cl NQR in chloro substituted benzene and its derivatives have been studied [1, 2] to obtain the effect of various substituents. The resonance frequency varies with temperature and is considered to be primarily due to the bond-bending torsional motions. It is possible to study the nature of the torsional motions by looking at the temperature variation of the NQR frequency. The torsional modes in 2,6-dichloro aniline and 3,4-dichloro aniline were obtained [3] from their NQR data using a two-mode approximation. The above two compounds have also been studied by Raman spectroscopy [4]. The temperature variation of the NQR frequency in a similar compound, 2,5-dichloro aniline was carried out by Ramakrishna [5] and the ³⁵Cl NQR data has been used in this work to obtain the internal torsional frequencies and their temperature dependence in this compound.

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2. Temperature dependence of NQR frequencies

The NQR spectra of 2,5-dichloro aniline (2,5-DCA) was obtained by Ramakrishna in the temperature range 77 K to 301 K [5]. He observed two ^{35}Cl NQR lines throughout the temperature range investigated. These two lines could be assigned to the two chlorines in the molecule by using the additive model of substituent effect [6]. The lower frequency line (line 1) may be assigned to the 2-chlorine and the higher frequency line (line 2) to 5-chlorine. The temperature variation of the

TABLE I
Least squares fit parameters and $\langle g \rangle$ corresponding to line I of 2,5-dichloro aniline.

Parameter	4th order polynomial	Brown ($T_0 = 200$ K)	Kushida
A_{-1} [MHz K]	–	–	0.3534×10^2
A_0 [MHz K]	0.3445×10^2	0.3421×10^2	0.3413×10^2
A_1 [MHz K $^{-1}$]	-0.6822×10^{-3}	-0.2219×10^{-2}	-0.7665×10^{-3}
A_2 [MHz K $^{-2}$]	-0.1388×10^{-5}	0.5625×10^{-5}	–
A_3 [MHz K $^{-3}$]	-0.3736×10^{-8}	–	–
A_4 [MHz K $^{-4}$]	-0.1261×10^{-10}	–	–
Δ [MHz]	0.6241×10^{-3}	0.6700×10^{-3}	0.357810×10^{-2}
$\langle g \rangle$	0.00173448	0.0013920	–

TABLE II
Least squares fit parameters and $\langle g \rangle$ corresponding to line II of 2,5-dichloro aniline.

Parameter	4th order polynomial	Brown ($T_0 = 200$ K)	Kushida
A_{-1} [MHz K]	–	–	0.3973×10^2
A_0 [MHz K]	0.3459×10^2	0.3423×10^2	0.3432×10^2
A_1 [MHz K $^{-1}$]	-0.7459×10^{-3}	-0.2471×10^{-2}	-0.8567×10^{-3}
A_2 [MHz K $^{-2}$]	-0.1754×10^{-5}	0.6612×10^{-5}	–
A_3 [MHz K $^{-3}$]	-0.4372×10^{-8}	–	–
A_4 [MHz K $^{-4}$]	-0.1143×10^{-10}	–	–
Δ [MHz]	0.4707×10^{-4}	0.5634×10^{-4}	0.3975×10^{-2}
$\langle g \rangle$	0.0005071	0.0014747	–

NQR frequency [7] can be written in the form suggested by Kushida et al. [8] under high temperature approximation as

$$\nu(T) = A_{-1}/T + A_0 + A_1 T. \quad (1)$$

If the temperature dependence of the torsional frequencies is considered, one obtains the Brown model [9] and the expression

$$\nu(T) = A_0 + A_1(T - T_0) + A_2(T - T_0)^2, \quad (2)$$

where T_0 is an arbitrary temperature in the high temperature region.

The temperature variation of the NQR frequency can also be fit to a general fourth order polynomial of the form

$$\nu(T) = A_0 + A_1T + A_2T^2 + A_3T^3 + A_4T^4. \quad (3)$$

The two ^{35}Cl NQR lines of 2,5-dichloro aniline were least squares fitted to the above three Eqs. (1)–(3) and the results are given in Table I and II. Δ is the root mean square deviation and $\langle g \rangle$ is the average temperature coefficient. It is seen from the Δ values that the fourth order polynomial gives the best fit. This indicates that the temperature variation of the torsional frequencies cannot be neglected in this case.

3. Torsional frequency calculations

Bayer's theory [7] for the temperature dependence of NQR frequency modified by Tatsuzaki and Yokozawa [10] gives

$$\nu(T) = \nu_0 \left\{ 1 - \frac{3h}{8\pi^2c} \sum_i \frac{\sin^2 \alpha_i}{A_i f_i} \left[\frac{1}{2} + \frac{1}{\exp(hf_i c/kT) - 1} \right] \right\}, \quad (4)$$

where $\nu(T)$ is the NQR frequency at temperature T , ν_0 is the NQR frequency at 0 K and can be obtained from the least squares fit to the fourth-order polynomial. The A_i 's are the moments of inertia. The X-ray crystal structure of 2,5-dichloro aniline has been reported [11] and this was used to obtain the three moments of inertia A_1 , A_2 , and A_3 . Table III lists the principal values A_i , α_i the angle that their respective axes make with the z -axes of the electric field gradient (efg) tensor and the factor $\sin^2 \alpha_i / \sqrt{A_i}$ that multiplies each term in the summation. Of these three terms in the summation, the leading two are retained and the third

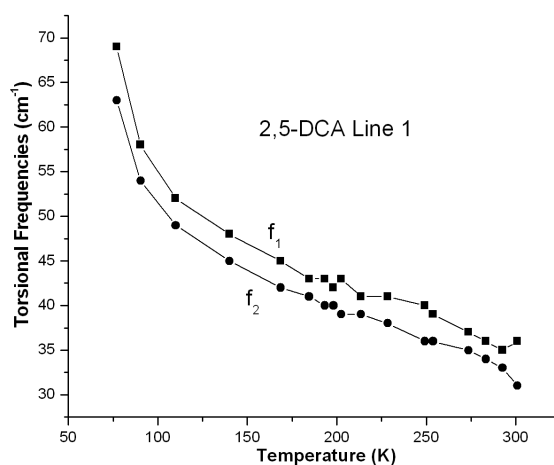


Fig. 1. Temperature dependence of torsional frequencies in 2,5-DCA.

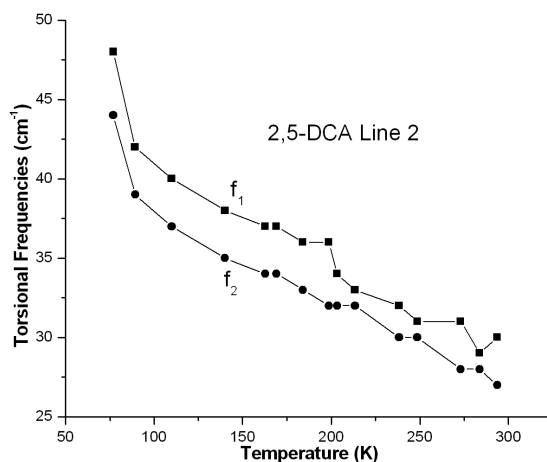


Fig. 2. Temperature dependence of torsional frequencies in 2,5-DCA.

TABLE III

Moments of inertia, angles α_i and weight factors for the Tatsuzaki model.

A_i [g cm ²]	1307.241×10^{-40}		$1546.6926 \times 10^{-40}$		239.4498×10^{-40}	
	α_1	$\frac{\sin^2 \alpha_1}{\sqrt{A_1}}$	α_2	$\frac{\sin^2 \alpha_2}{\sqrt{A_2}}$	α_3	$\frac{\sin^2 \alpha_3}{\sqrt{A_3}}$
Line I 2-Cl	93.38°	2.756×10^{18}	90°	2.542×10^{18}	3.38°	2.24×10^{16}
Line II 5-Cl	93.74°	2.754×10^{18}	90°	2.542×10^{18}	3.74°	2.76×10^{16}

neglected to give the two-mode approximation [12]. In the case of each of the two lines of 2,5-DCA, this approximation yielded two frequencies f_1 and f_2 at each temperature. The temperature dependence of these torsional frequencies is shown in Figs. 1 and 2.

4. Results and conclusions

The temperature dependence of the torsional frequencies in 2,5-dichloro aniline was obtained from the ³⁵Cl NQR data. The torsional frequencies lie between 28 cm⁻¹ and 70 cm⁻¹. The two chlorine atoms in the molecule, lie approximately on a line and hence the two moments of inertia used in the calculations are nearly equal. The torsional frequencies are also close to each other and differ only by 2–4 cm⁻¹ at every temperature. Ramakrishna [5] used a single mode approximation and obtained a value of 40.45 cm⁻¹ and 42.38 cm⁻¹ for the torsional frequencies in this compound. This is in agreement with our results and is a sort

of average frequency. The torsional frequencies in the similar compounds 2,6-dichloro aniline and 3,4-dichloro aniline [3] show a low frequency mode varying between 29 cm^{-1} and 45 cm^{-1} . This is also obtained in 2,5-dichloro aniline and may be assigned to motion perpendicular to the ring in this case, too.

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References

- [1] A. Peneau, L. Guibe, *J. Magn. Reson.* **20**, 422 (1975).
- [2] P.J. Bray, R.G. Barnes, *J. Chem. Phys.* **27**, 551 (1957).
- [3] H.D. Basavegowda, K. Rukmani, *Acta Phys. Pol. A* **111**, 257 (2007).
- [4] M.E. Ramia, M.J. Zuriago, C.A. Martin, *J. Phys C, Solid State Phys.* **21**, 3467 (1988).
- [5] J. Ramakrishna, *Proc. Phys. Soc.* **86**, 595 (1965).
- [6] D. Biedenkapp, A. Weiss, *J. Chem. Phys.* **49**, 3933 (1968).
- [7] H. Bayer, *Z. Phys.* **130**, 227 (1951).
- [8] T. Kushida, G. Benedek, N. Bloembergen, *Phys. Rev.* **104**, 1364 (1956).
- [9] R.J.C. Brown, *J. Chem. Phys.* **32**, 116 (1960).
- [10] I. Tatsuzaki, Y. Yokozawa, *J. Phys. Soc. Jpn.* **12**, 802 (1957).
- [11] T. Sakurai, M. Sundaralingam, G.A. Jeffrey, *Acta Crystallogr.* **16**, 354 (1963).
- [12] M.S. Vijaya, J. Ramakrishna, *Mol. Phys.* **19**, 131 (1970).