NQR investigations in crystalline 2,5–dichloroacetanilide

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Abstract. Two close NQR lines were observed in 2,5-dichloroacetanilide at room temperature at 34·606 MHz and 35·212 MHz as well as at liquid nitrogen temperature at 34·832 MHz and 35·791 MHz, using a self–quenched super-regenerative spectrometer. Analysis of the Zeeman effect on the two lines using a cylindrical single crystal reveals that the crystal belongs to either orthorhombic or monoclinic system. There are two crystallographically equivalent but physically non-equivalent directions for the principal field gradient Z axes making an angle of 77° for both resonance lines. The unit cell contains either two or a multiple of two molecules. There is an in-plane bending of the two C–Cl bonds by 1°. The ionic, single bond and double bond characters of C–Cl bonds for both chlorines are almost equal and are in the ratio 25 : 74 : 1.

Keywords. Nuclear quadrupole resonance ; Zeeman effect ; super-regeneration; single crystals ; in-plane bending ; bond characters ; dichloroacetanilide.

1. Introduction

Two NQR lines were observed at room temperature as well as at liquid nitrogen temperature in the title compound. X-ray diffraction data of any kind (detailed or partial) or morphological data are not available for this crystal. Hence the Zeeman effect of the NQR lines in single crystals is investigated to obtain possible information regarding the nature of the crystalline unit cell in this respect. As suitable size single crystals could not be grown from solution, cylindrical single crystals grown from melt using Bridgemann technique were used to conduct the present investigation.

2. Experimental details

2,5-dichloroacetanilide is a solid at room temperature with a melting point of 133° C. The compound was obtained from K and K Laboratories Inc., New York, U.S.A. The commercial sample was purified and single crystals grown from the melt. The crystal shows a well-defined cleavage plane parallel to the growth axis.

Zeeman effect studies were carried out on the two resonance lines. For each line the zero splitting loci were obtained and analysed to yield the directions of the principal electric field gradient Z-axes and asymmetry parameters η. The experimental technique used and the method of analysis have already been reported. Venkatacharyulu and Premaswarup 1974).

3. Results

With the crystal mounted so that its growth axis is parallel to the *rf* axis of the tank coil, two zero splitting loci could be observed for the low frequency (LF) as well as the high frequency (HF) line. For convenience, the loci corresponding to the LF line are labelled as 11 and 12 while those of HF line as 21 and 22. The observations were repeated in two different crystals grown under different conditions and reproducible results were obtained. The four observed loci are analysed by the method of least squares to yield the directions of the principal electric field gradient (EFG) axis and the asymmetry parameters. The observations are presented in table 1. In view of the low asymmetry parameter, the accuracy in the determination of the X and Y axes is expected to be about $\pm\ 20°$ and hence no data are given about these axes. The ϕ scale is so chosen that for the cleavage plane $\phi = 0°$.

4. Discussion

4.1. *Crystal system*

The number of crystallographically equivalent but orientationally inequivalent directions (when they are in general as well as special positions) and the relationship between them for crystals of different classes has been reported earlier (Narayan *et al* 1975).

Table 1. Directions of the principal EFG Z-axes and values of η (growth axis parallel to *rf* axis).

	θ (deg)	ϕ (deg)	η
LF resonance line			
Z_{11}	125	115	0·04
Z_{12}	48	114	0·04
HF resonance line			
Z_{21}	125	115	0·02
Z_{22}	48	113	0·06

The existence of two loci indicates the possible symmetry for the crystal as tetragonal, orthorhombic or monoclinic. In general, if the crystal belongs to tetragonal symmetry, 8 loci should be observed, but in the special case where the Z axes lie in the *ab* plane, there will be only 2 loci, but in such a case the angle between the two Z's will be 90°. Since the angle in the present case is 77°, this is ruled out here. With an orthorhombic system, a set of two crystallographically equivalent but physically inequivalent directions will be obtained when both of them are in any one of the crystalline principal planes *ab*, *bc* or *ca*. In such a case the three crystalline axes will be along the internal and external bisectors of the angle formed by the two directions and the directions perpendicular to both these bisectors. These three directions calculated for the two sets of Z's are given in table 2.

Hence the crystal may be orthorhombic. Within experimental error the two loci of the LF line coincide with the two loci of the HF line. The loci for the low frequency line are represented in figure 1. This may be due to the fact that the two chlorines are present in positions 2 and 5 respectively in the molecule. Since the two sets of loci are the same for the LF and HF lines, one naturally gets the same sets of internal, external bisectors and common perpendicular. The second choice of the crystal system is monoclinic. If the crystal belongs to the monoclinic system the common bisector will be parallel to *b*-axis.

4.2. *Minimum number of molecules per unit cell*

In the crystal under consideration Z_{12} is parallel to Z_{22} and Z_{11} is parallel to Z_{21} within experimental error. The angle between Z_{11} and Z_{12} is equal to the angle between Z_{21} and Z_{22}, within experimental error the value of which is equal to 77°. The angle between the two LF Z's and the two HF Z's are as given below.

$$Z_{11}Z_{22} = 77° \qquad\qquad Z_{12}Z_{21} = 77°$$

$$Z_{12}Z_{22} = 1° \qquad\qquad Z_{11}Z_{21} = 1°$$

It is therefore clear that the chlorines responsible for the 11 and 21 loci belong to one molecule while those responsible for the 12 and 22 loci belong to the another molecule. There are two sets of molecules in the unit cell, with the molecular planes in each set being parallel among themselves and the two C–Cl bond

Table 2. Directions of internal, external bisectors and common perpendicular for the two sets of Zs.

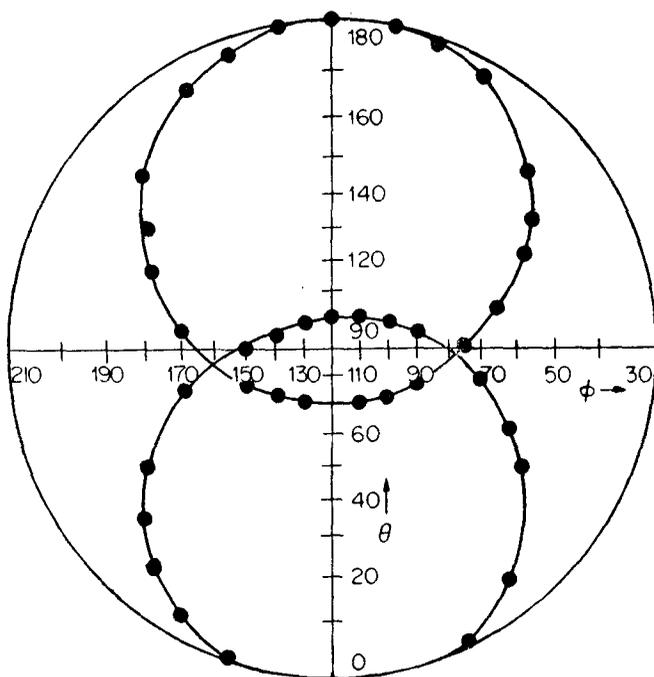|	LF line (in deg.)		HF line (in deg.)	
	θ	ϕ	θ	ϕ
Internal bisector	87	115	86	114
External bisector	177	121	176	126
Common perpendicular	90	25	89	24

Figure 1. Zero splitting loci for the low frequency line.

directions contain an angle equivalent to 77°. The unit cell contains either two or a multiple of two molecules. The experimental data show that although there are two field gradients Z_{11} and Z_{21} their axes lie almost in the same direction. This is so in the case of Z_{12} and Z_{22} also. As a result, these Z's cannot be used themselves to define the plane of the benzene molecule. From the calculations the in-plane bending of the two C–Cl bonds is 1°. In view of the limitation of the experimental accuracy ($\pm$ 1°) we cannot say whether this is genuine bending or due to experimental inaccuracy.

4.3. Bond characters

The bond characters are calculated by the method of Kojima et al (1955) and the values are given in table 3. The proportions of the different characters

Table 3. Percentage bond characters.

Character	LF line	HF line
Double bond	1·45	1·38
Single bond	73·13	74·47
Ionic	25·42	24·15

(ionic, single bond and double bond) are almost the same for the two chlorines. The two chlorines in the molecule are chemically inequivalent as they have different atomic environment. Hence it is not theoretically essential that they should exhibit the same proportion of bond characters. However, the difference, if any, does not seem to be large.

Acknowledgements

References

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