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Wide line NMR study of some hydrogen bonded solids

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By wide line NMR study anomolous behaviour of ortho compounds due to hydrogen bonding was observed in case of orthochlorobenzoic acid. Departure from planarity was observed in the case of hydrogen bonded crystal structure of catechol. In case of L-Alanine group rotation at higher temperature was possible after breaking hydrogen bond. Transitional jumping of proton was observed in N-H-N hydrogen bond of imidazole. In *p*-amino benzoic acid rotation of NH_2 group becomes more rapid with rise of temperature. Wave length shift due to hydrogen bonding was responsible for reduction in the second moment values in case of α and β naphthol

1 INTRODUCTION

The present paper reviews nuclear magnetic resonance studies which have been aimed specifically at investigating hydrogen bonded solids. Hydrogen atom can in certain circumstances link two other atoms together Hydrogen bonding is an interaction between a covalently bound *H* atom with some tendency to be donated and a region of high electron density on an electronegative atom or group of atoms which can accept the proton. Typical proton donor groups include hydrogen bond covalently to electronegative atoms such as oxygen. nitrogen, sulphur, halogen and in special cases carbon, phosphorus.

Hydrogen bonding occurs in all states of aggregation but our concern with low resolution NMR spectra necessarily limits us to solids only. Low resolution NMR technique can provide much information about hydrogen bonded solids. Richards (1956). Many organic compounds have been studied in recent past by wide line NMR whose molecules are linked together by means of hydrogen bonds to gain information regarding molecular or group rotation in the solids and to find out the rigidity of crystal lattice at higher temperature.

2 EXPLANATION FOR ORTHO EFFECT

In several reported investigations hydrogen bonding has been offered as an explanation for anomalous behaviour of many aromatic *O*-compound as compared with *m* and *p*-isomers Agarwal & Gupta (1974) indicated that second moment calculated from NMR derivative curves for *O*-chloro benzoic acid is less than that of *m*-bromo benzoic acid. This discripency in the result may be due to the ortho effect because Smyth (1927) and Smallwood (1950) have observed that the dipolemoments for ortho compounds were somewhat lower than that of their expected valve. It may be noted here that hydrogen bonding exists in the crystal structure of *O*-chlorobenzoic and as reported by Fergusson & Sin (1961).

Another explanation for ortho effect which is also called anomalous behaviour of *O*-compounds due to hydrogen bonding was given by Hunter (1950). *O*-nitro phenol differs from its *m* and *p*-isomers in having lower melting and boiling points, lower solubility in water etc. In other words the phenolic characteristics are to a considerable extent suppressed as a result of the hydrogen bond structure of *O*-nitrophenol.

3. EXPLANATION FOR DEPARTURE FROM PLANARITY OF CATECHOL MOLECULE

X-ray investigations by Brown (1966) revealed that the pairs of catechol molecules are linked together by means of the hydrogen bonds. Catechol molecule is expected to be fairly dense as the hydrogen bonds draw the molecule together. The calculated values of the second moment by Agarwal (1974) roughly remains at the rigid lattice value upto 312°K. After 312°K the second moment value was slightly decreased. Due to strong hydrogen bonding present in the crystal structure it seems unlikely that molecular rotation is taking place. The possibility of intramolecular rotation of hydroxy group arises. Lloyd *et al* (1952) found two OH vibration frequencies for the catechol, one corresponding to bonded hydroxyl group and other corresponding to the free hydroxyl group. It may be possible that free hydroxyl group may start rotation at higher temperature while other hydroxyl group remains strongly hydrogen bonded. But the observed value of second moment at 355°*K* (7.0 gauss) as calculated by Agarwal (1974) does not agree with the value in the range (3.89-4.79) for such type of stationary rotating interactions. The reason that the rotation of hydroxyl group was not observed is that rotation of hydroxyl group at the ortho position is hinderd by the interaction with other strongly hydrogen bonded hydroxyl group. Only the departure from planarity with the rise of temperature may be the reason that second moment was slightly decreased at higher temperature. So departure from planarity may be due to the presence of hydrogen bonding in the Catechol. This has alsoo been supported by Roberts (1955).

4. OBSERVATION ON L-ALANINE

In the *L*-Alinine structure all the three available protons are used to form hydrogen bonds with lengths of 2.83Å, 2.85Å and 2.81Å. One of the hydrogen bonds link the molecule length wise to form columns along *C*-direction. The other two hydrogen bonds link the columns together in three dimension net work. The second moment values calculated from the NMR derivative tracings of *L*-

Alanine was calculated by Agarwal (1973). The lattice has been found to be rigid upto 230°K. Levy & Corey (1941) suggested that the forces resulting from the arrangements of hydrogen bonds are such as to stop the rotation of methyl groups round the C-C axis. Any rotation of the methyl group round the C-C axis would involve a disturbance between the hydrogen spheres. Hence rotation of methyl group was not possible at lower temperature range and reduction in the values of second moment at 352°K was due to torsional oscillation of methyl group.

5. OBSERVATION ON IMIDAZOLE

The crystal of imidazole was studied by Will (1963) and Martines Carrera (1966). The molecule are linked along the C-axis by strong hydrogen bonds at a N-H ... N distance of 2.86Å forming chains along the C-axis.

Many solids show a sudden change in the value of second moments at temperatures which are considerably below the melting point. No such sudden change in the second moments was observed in the case of imidazole by Mirza (1974). Molecular rotation in crystalline imidazole was rendered somewhat difficult as the hydrogen bonds do not allow sufficient reorientation of the molecule. But slight reduction in the value of second moment may be due to switching of position of proton in N-H-N hydrogen bond. The second moments values of the fixed and oscillating N-H-N protons are compared. By second moment values it was inferred by Mirza (1974) that proton oscillates between the two positions in the N-H-N bond.

Infrared studies due to Zimmermann (1959) too have indicated a high mobility of the protons within the hydrogen bridge of imidazole.

6. OBSERVATION ON *p*-AMINO BENZOIC ACID

Lal & Marsh (1967) have reported the crystal structure of *p*-amino benzoic acid. An interesting feature of the crystal structure is the presence of two structurally distinct molecules in the unit cell. Pairs of molecules are held together to form dimers throguh two C-H-O hydrogen bonds arranged about a centre of symmetry. An additional N-H-O hydrogen bond is formed by one of the two kinds of molecules. Hence possibilityof molecular rotation is greatly diminished but bond joining molecule *A* to molecule *B* is weak. The hindrance to the NH_2 group rotation caused by this hydrogen bond may be over come if sufficient thermal energy is imparted to the molecule This will then enable the NH_2 group to rotate about C-N bond as the COOH group in the same molecule being in para position with respect to it cannot substantially effect the rotation of this NH_2 group. The detailed wide line NMR study of the compound was reported by Banerjee (1974). At lower temperature range rotation of NH_2 group was hindered by the COOH group attached to the neighbouring molecule but rotation of NH_2 group becomes more rapid with rise of temperature.

7. EXPLANATION FOR HYDROGEN BOND WAVE LENGTH SHIFT

The formation of a hydrogen bond modifies the electron density around the proton of the group and hence its shielding. In most cases the PMR absorption is displaced downfield causing a hydrogen bonding shift Gupta (1963) have observed slight reduction in the values of the second moment in case of α and β naphthol and explained it to be due to the vibrational motion of the molecule. This sort of motion is associated with the wave length shift due to hydrogen bonding present in naphthol. This was also suggested by Negakura (1957)

8. CONCLUSION

With the help of wide line NMR investigations many phenomena of structural bonding in the crystal structure of the molecules. Anomolous behaviour of O-compounds due to hydrogen bonding was observed in the case of *O*-chlorobenzoic acid. Slight decrease of second moment as observed in catechol may be responsible for departure from planarity due to strongly hydrogen bonded crystal structure of catechol. In *L*-alanine probability of methyl group rotation at low temperature was discarded but group rotation at higher temperature was possible after breaking hydrogen bond

Particular behaviour of imidazole was explained as due to translational jumping of the proton in N-H-N hydrogen bond. In case of *p*-amino benzoic acid rotation of NH_2 group becomes more rapid with the rise of temperature. Slight reduction in the second moment values in case of α and β naphthol was associated with the wave length shift due to hydrogen bonding.

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