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HYDROXYL GROUP ROTATION AND HYDROGEN BONDING IN PYROGALLOL

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Wide line PMR spectra of pyrogallol were recorded in the temperature range of 77 K–384 K at 7.5 MHz. Hydrogen bonds are found to be strong enough to resist the molecular motion. The reduction in the proton second moment (S_2) with temperature suggests change in the composition of pyrogallol.

1. *Introduction*

The present study was undertaken in an attempt to study the hydroxyl groups reorientation in trihydroxy benzene. This study enables to check the rigidity of the lattice of molecule at 77 K.

Pierre Backer et al. [1] reported the molecular structure of pyrogallol. Their X-ray investigation revealed that the hydrogen bonding in the molecule is strong and the bonding bifurcates.

Pyrogallol molecule has the lattice constants as follows

$$a = 13.18 \pm 0.04\ \text{Å}, \quad b = 3.85 \pm 0.01\ \text{Å}, \quad c = 13.60 \pm 0.04\ \text{Å},$$

$$\text{B} = 125°9' \pm 0°5', \quad V = 559\ \text{Å}, \quad \text{Z} = 4, \quad \text{space group} = \text{P}\ 21/\text{C}, \quad d\,\text{theoretical} = 1.493.$$

The proton positions in the molecule are tabulated in Table I.

There are interactions between hydroxyl groups (Lester P. Kuhn et al. [2]). High resolution NMR studies [3] showed that the introduction of the hydroxyl group at the ortho position in phenol has effect upon the hydroxyl group which is strongly hydrogen bonded.

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TABLE I

Table showing positional coordinates of hydrogen atoms

No. of hydrogen atoms \ Coordinates	X	Y
H_1	0.81813	3.05757
H_2	3.03334	0.50722
H_3	2.12419	−1.44647
H_4	−1.05779	−2.17869
H_5	−2.39475	−0.90125
H_6	−1.07128	2.16776

2. *Theoretical calculations*

(a) Rigid lattice proton second moment

The intramolecular $S_2^{(1)}$ contribution to the proton second moment (S_2) has been calculated using the modified Van Vleck's [4] powder relation. $S_2^{(1)}$ was found to be 5.94 G^2. Intermolecular $S_2^{(2)}$ contribution to S_2 has been calculated using Smith's approximation formula [5]. $S_2^{(2)}$ was found to be 1.93 G^2.

Hence the rigid lattice S_2 is $S_2^{(1)}+S_2^{(2)}$ i. e. 7.87 G^2.

(b) Calculation of reduction in proton second moment for the intramolecular motion of hydroxyl groups

Gupta et al. [6] reported that the reduction in the value of rigid lattice S_2 for the intramolecular rotation of substituent group can be estimated by the equation

$$\langle \Delta\omega^2 \rangle_{\text{rot}} = \langle \Delta\omega^2 \rangle_{\text{RL}} \left[\frac{3\cos^2 r_{JK}-1}{2}\right]^2,$$

where r_{JK} is the angle between the radius vector J and K and rotation axis, $\langle \Delta\omega^2 \rangle_{\text{rot}}$ is the rotational S_2 and $\langle \Delta\omega^2 \rangle_{\text{RL}}$ is the S_2 at rigid lattice. This holds only when OH group is not hindered by the interaction of other heavy substituent groups.

3. *Experiment and result*

Broad line NMR spectra were recorded using Varian's variable frequency spectrometer having a 12″ magnet system at TIFR, Bombay. The spectra were recorded at 7.5 MHz. Modulation amplitude was kept small. Proton second moments were derived from the derivative traces by using the trapezium rule. Proton second moment (S_2) vs temperature curve is shown in the figure.

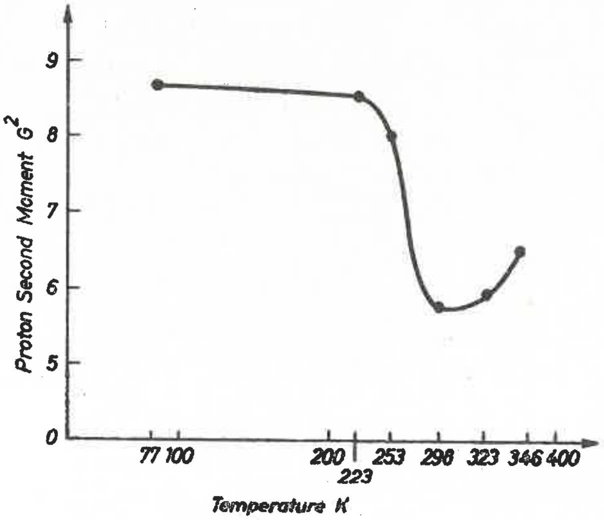

Fig. 1. Figure showing variation of proton second moment with temperature

4. *Discussion*

Theoretically calculated value of the rigid lattice S_2(7.87 G^2) agrees favourably with the experimental S_2 at 77 K (8.68 G^2). The lattice is, therefore, rigid at 77 K. The S_2 roughly remains at the rigid lattice value upto temperature 253 K. After 253 K the S_2 slightly decreases. The hydrogen bonds bound the successive layers of the molecule, it therefore seems unlikely that the molecular motion is taking place.

The possibility of intramolecular rotation of hydroxyl groups arises. But the observed S_2 at 298°K is incompatible with the calculated S_2 (3.74 G^2) for hydroxyl groups motion. Kuhn et al. [2] observed free and bonded OH bonds in parogallol. Triol conformation permits two intramolecular H bonds. Oxygen atom (O) can act as an acceptor for 2 OH groups and H bond is as strong as that formed when O accepts only 1 H. Artsdalen et al. [7] while studying the PMR spectra of molten alkali metal acetate solutions of polyhydric alcohols and phenols, observed that aromatic triols show strong interaction. In phloroglucinol molecule Agarwal et al. [8] found intramolecular hydroxyl group motion. The reason, that in pyrogallol, the intramolecular motion is not observed, may be that the rotation of hydroxyl group at the ortho position is hindered by the interactions with strongly hydrogen bonded hydroxyl group. Balterhan et al. [3] also indicated that the substitution at the ortho positon in phenol has greater interaction with the strongly hydrogen bounded hydroxyl group, than the substitution at the para position. Hence there is no free motion of hydroxyl groups. Therefore, as the temperature rises, hydroxyl group gains a tendency to rotate. But this tendency is nullified by the interaction with strongly hydrogen bonded hydroxyl group at the ortho position. The result is that the hydroxyl group at the ortho position tends to depart from planarity. This departure from planarity with the rise in temperature may be the reason that the S_2 slightly decreases by about 2 G^2.

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