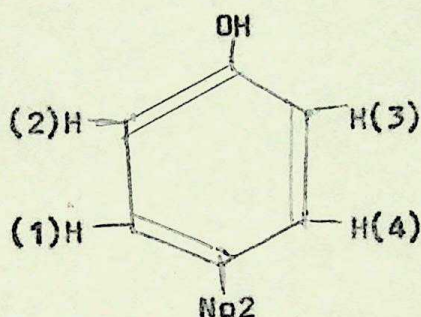


4. EXPERIMENTAL DETAILS AND RESULTS :

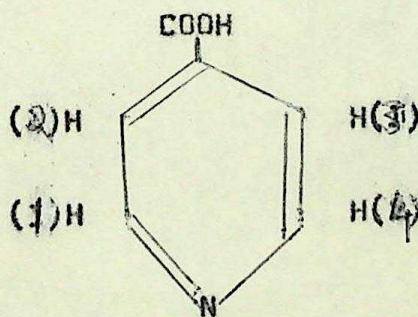
4.1 MOLECULE'S STUDIED :

The following compounds all of which were commercially available were studied in Lyotropic nematic liquid crystal solvent and Thermotropic nematic liquid crystal solvent as mentioned below:

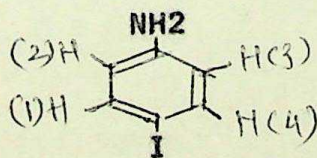
- 1) P-Nitrophenol ($C_6H_5NO_2$) in Lyotropic nematic liquid crystal solvent.



- 2) Isonicotinic Acid ($C_6H_5NO_2$) in Lyotropic nematic liquid crystal solvent.



- 3) 4-Iodo Aniline (C_6H_6NI) in Thermotropic nematic liquid crystal solvent.



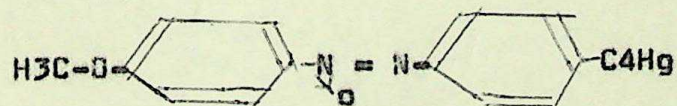
4.2 SOLVENTS USED :

1) Lyotropic nematic liquid crystal solvent used consists the following ingredients with % by weight composition :

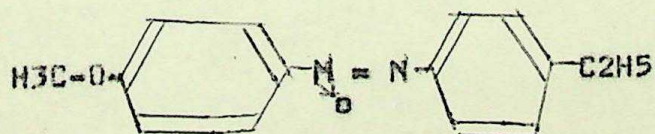
<u>Compounds.</u>	<u>% by weight composition.</u>
Heavy water (D ₂ O)	52.1
Decanol-OD	0.9
Decyl Amine Hydrochloride	42.2
Sodium sulphate	2.5
Solute	2.3

This phase is identical as that of Khetrapal, Patankar et.al.(16),(18). Which is nematic at room temperature.

2) Thermotropic nematic liquid crystal used is Merck's phase V which is mixture of 65 mole % Merck's phase IV.



and 35 mole % P-ethyl-P'-methoxy-azoxybenzene.



with nematic range of temperature -5 to 75°C. and can work even at room temperature. Addition of the solute further lowers the solid to nematic transition temperature.

4.3 PREPARATION OF THE SAMPLES:

Heavy water used in preparing the Lyotropic phase was 99.5 % deuterated supplied by Heavy Water Division, Bhabha Atomic Research Centre, Trombay, Bombay. E.Merck's sodium sulphate, Decanol-OD and phase V. Decyl Amine Hydrochloride was synthesized by Dr. Patankar and used after well drying. The above mentioned solutes were A.R. Grade Chemicals supplied by E.Merck Germany and used without any further purification.

For preparing Lyotropic nematic liquid crystalline samples, two tubes of equal length (about 7.5 mm) having B₁₀ male and Female joints and constriction of about 1.5 to 2 mm in one of the tubes were used. The components of the phase were weighed in appropriate portions by single pan micro balance. The solute was also weighed with the phase ingredients. The tubes were joined with high vacuum grease and centrifuged to and fro until a uniform phase was formed. About 12 to 15 times centrifuging was normally enough to ensure thorough mixing. Heating of the sample tube to about 50°C helps dissolution of the components. The sample then transferred in a 5 mm NMR sample tube.

For preparing Thermotropic nematic liquid crystal sample, the 5 mm NMR Sample tube weighed with single

pan micro balance. E. Merck's phase V about 350 mgm. added in the tube and accurately weighed. The solute of 20 mgm. added so that 20 mole % solution is formed and mixture was heated in a water bath carefully to the transition temperature till a homogeneous isotropic solution was obtained. The solution was then cooled to the probe temperature. To obtain concentration uniformity in the nematic phase, the solution was stored horizontally at the probe temperature for several hours before recording the spectra.

4.4 Recording of the Spectra :

The NMR spectra of the solute molecules in liquid crystal solvent show relatively sharp lines in thermotropic as compared with Lyotropic nematic liquid crystal solvents. In the proton magnetic resonance (PMR) spectra, these sharp lines are superimposed over a broad background arising due to the protons in the solvent molecules. Sometimes, the spectra due to solvent protons may be too broad to be noticeable under the normal working conditions. The reason for the appearance of the broad lines due to solvent lies in the fact that they contain a large number of protons. For example, in solvent phase V, there are Thirty-Six protons and hence the number of nuclear Zeeman levels

would be 2^{36} . The allowed transitions among such levels would be enormous and the intensity of each of the individual transition may be too low to be observed. The overlap of various transitions produce a broad background. On the other hand, it puts an upper limit on the number of interacting nuclei in the molecule that can be studied, and on the other hand, it is because of this situation only that the solute protons give well resolved and sharp lines, undisturbed by those due to solvent molecules. It is well known fact that when solute dissolved in thermotropic nematic liquid crystal solvent is put in NMR magnetic field, it gets oriented such that its longest chain axis or optic axis is parallel to the direction of external magnetic field. However, for most of the lyotropic nematic liquid crystals, the optic axis is perpendicular to the direction of external magnetic field. In the conventional usual NMR spectrometers such as varian HA60, HA100, T-60, XL-60, XL-100 Bruker WH-60, WH90 Perkin Elmer's R-32 where permanent magnets are used, the spinning-sample axis is perpendicular to the field produced which destroys the orientation of solute dissolved in thermotropic phase. Hence sample should not be spun. For Lyotropic phase solution, spinning do not destroy the orientation but it gives very sharp spectral lines. In case of Bruker WH 270 MHZ F.T.NMR

spectrometer used for present work, the electromagnet is used and spinning of the sample in both thermotropic as well Lyotropic phases do not destroy the solute orientation and hence the sample spinning at the speed of 20 Hzs. helps in getting very low line width.

4.5 P-NITROPHENOL IN LYOTROPIC PHASE :

4.5.1 Introduction :-

Six membered ring systems with heteroatoms, occur widely in nature and play important role in natural and biological processes. The study of their geometry particularly in the liquid crystal phase is, therefore, of considerable importance. Such investigations using NMR spectroscopy in thermotropic solvents for Phenol by Diehl et.al.(51), Polar mono-substituted benzenes and para substituted phenols in Lyotropic phase by Long Jr. et.al.(52) by using potassium laurate mesophase at 29°C is well known. It was thought worthwhile to study Para-nitrophenol in Decyl Amine Hydrochloride Lyotropic mesophase. Investigations in different types of Lyotropic liquid crystals as compared to above study (52) may throw some light on solvent-solute interactions which may be of considerable importance; the effects of polar group on the orientation of aromatic compound also gives important information about its structural change due to different solvents. The present investigation of P-Nitrophenol in Decyl

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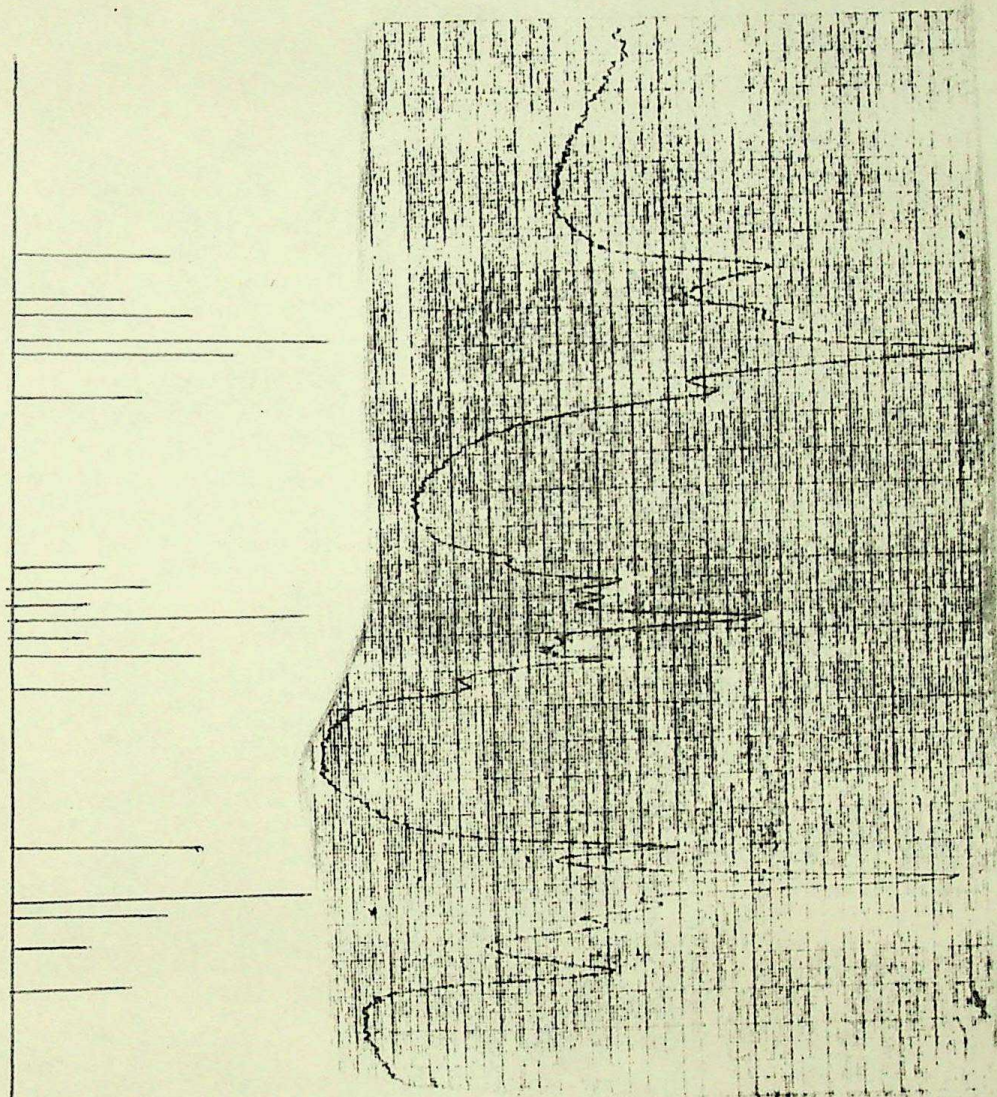
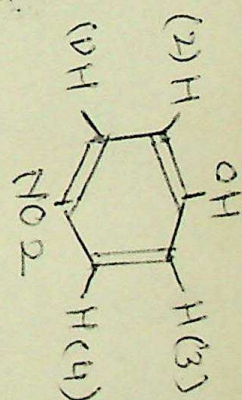


Fig-4.1

Figure 4.1

Experimental and calculated spectra of P-Nitrophenol in
Lyotropic phase.

A) Composition of Solutions :

Components.	Per cent (by weight)
1) Heavy water	52.1
2) Decyl Amine Hydrochloride	42.2
3) Decanol-OD.	0.9
4) Sodium Sulphate	2.5
5) P-Nitrophenol.	2.3

B) Spectrometric conditions :

Spectrometer	Bruker WH 270 F.T.NMR/
Spectrometer Frequency	270 MHzs.
Average line width	4 Hzs.
Temperature	48°C
RMS error	0.025 Hzs.
Maximum error	1.3 Hzs.
Number of transients collected	200
Sweep width	927 Hzs.

Amine Hydrochloride Lyotropic Mesophase at 48°C compares the previous results and gives the solute-solvent interactions along with the effects of temperature. A typical spectrum along with experimental details is shown in Fig. 4.1. It shows 18 well defined lines with the spread of about 927 Hzs.

4.5.2 Analysis of the Spectrum :-

The spectrum is symmetric about its centre meaning that there is no chemical shifts between the various protons. The geometry of the molecule guessed and the necessary dipolar coupling constants were estimated from the spectral lines. The set of dipolar couplings used as the starting parameters for part-I of the LAOCOONOR programme. The chemical shifts and the indirect spin-spin couplings were taken from literature (52). The final analysis was achieved with the help of part-II of the LAOCOONOR programme on I.I.Sc. Bangalore computer centre. In the iterative analysis, only the chemical shift and the direct dipolar coupling constants were iterated upon. The experimental and the calculated intensities of the allowed transitions are given in table 4.1.1. Values of the Final parameters obtained are reproduced in table 4.1.2.

Experimental and calculated line frequencies with
calculated line intensities for P-Nitrophenol in Decyl Amine
hydrochloride Lyotropic Nematic Phase at 40°C.

Experimental line Frequency (Hzs)	Calculated line Frequency Hzs	Calculated Relative Line intensity.
463.278	463.270	1.150
448.571	448.570	0.953
404.449	404.445	1.328
380.918	380.915	4.028
350.032	350.030	1.538
300.028	300.025	0.953
85.302	85.300	1.906
51.475	51.470	1.545
29.414	29.410	1.328
-29.414	-29.410	1.328
-51.475	-51.470	1.545
-85.302	-85.300	1.906
-301.498	-300.025	0.953
-351.503	-350.030	1.538
-379.447	-380.915	4.028
-402.979	-404.445	1.328
-454.454	-448.570	0.953
-463.278	-463.270	1.150

4.5.3 Molecular Geometry :-

The molecule is planar with C_{2v} symmetry and $AA'BB'$ spin system. There are four different proton-proton direct dipolar couplings. They provide the two order parameters and two distance-ratios needed to specify the molecular order and shape of the proton skeleton. The relations between the dipolar couplings, the two independent ratios of the inter-proton distances along with two order parameters reported in the literature were used (31) and are reproduced below :

$$\frac{r_{14}}{r_{23}} = \left(\frac{D_{23}}{D_{14}} \right)^{\frac{1}{3}} \quad (4.1)$$

$$D_{12} \left(\frac{r_{12}}{r_{23}} \right)^5 - D_{13} \left[\left(\frac{D_{23}}{D_{14}} \right)^{\frac{1}{3}} + \left(\frac{r_{12}}{r_{23}} \right)^{5/2} \right] = -D_{23} \left(\frac{D_{23}}{D_{14}} \right)^{\frac{1}{3}} \quad (4.2)$$

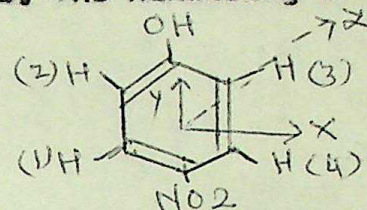
$$\left(\frac{r_{13}}{r_{23}} \right)^2 = \left(\frac{D_{23}}{D_{14}} \right)^{\frac{1}{3}} + \left(\frac{r_{12}}{r_{23}} \right)^2 \quad (4.3)$$

$$S_{xx} = -\left(\frac{4\pi}{h} \right)^2 \frac{1}{8H^2} D_{23} \cdot r_{23}^3 \quad (4.4)$$

$$S_{yy} = -\left(\frac{4\pi}{h} \right)^2 \frac{1}{8H^2} \frac{r_{12}^3 \left[D_{12} - (D_{23}/4) \left(\frac{r_{12}}{r_{23}} \right)^{-5} \left\{ (D_{23}/D_{14})^{-1/3} - 1 \right\}^2 \right]}{\left[1 - \left(\frac{1}{4} \right) \left(\frac{r_{12}}{r_{23}} \right)^{-2} \left\{ (D_{23}/D_{14})^{-1/3} - 1 \right\}^2 \right]} \quad (4.5)$$

TABLE 4.1.2

Spectral parameters of P-Nitrobenzene oriented in Decyl Amine Hydrochloride Lyotropic Nematic phase. The numbering of protons is as shown in following structure.



Parameters	Values in Decyl Amine Hydrochloride phase at 48°C.	Values in Potassium Laurate phase at 29°C (52)
$\nu_2 - \nu_1$	365.25	386.372
J12 = J34	10.10 (a)	10.10
J13 = J24	0.20 (a)	0.20
J14	3.08 (a)	3.08
J23	2.65 (a)	2.65
D12 = D34	266.64	182.82
D13 = D24	21.891	15.02
D14	27.225	18.79
D23	27.222	18.74
$\frac{r_{12}}{r_{23}}$	0.591	0.589
$\frac{r_{13}}{r_{23}}$	1.163	1.060
$\frac{r_{14}}{r_{23}}$	1.003	1.000
Sxx	-0.00596 (b)	-0.00615
Syy	-0.01205 (b)	-0.01217
Szz	+0.01801	+0.01832
No. of lines assigned	18	18
R.M.S. error	0.02	0.03

Note : a) Taken from (52).

b) Sij values are calculated assuming an r23 distance of 4.2892 Å.

The values of $\frac{r_{14}}{r_{23}}$ and r_{12}/r_{23} thus obtained along with those derived by other workers (52) are reported. Thermotropic data for this compound is not available but the necessary investigations are in progress by the author.

The table 4.1.2 shows that the values obtained by the author and that given (52) are some what in agreement, the deviation is due to effect of temperature and solute-solvent interaction.

4.6 ISONICOTINIC ACID IN LYOTROPIC PHASE :

4.6.1 Introduction :-

Monoazines such as pyridine, Pyridine-N-Oxide, 5-Hydroxy-pyridine, form an important class of heterocyclic compounds, widely occurring in nature. These ring systems occur in alkaloids, vitamins and other pharmaceutical chemicals. Nicotinic Acid and Isonicotinic Acid are of heterocyclic compounds which play very important role in medical drugs. The study of the structure of Isonicotinic Acid is therefore of very important particularly in oriented media. Isonicotinic Acid has not been studied either in thermotropic or lyotropic liquid crystalline media. The results are compared with 5-Hydroxypyridine (53) studied in Lyotropic nematic liquid crystal media.

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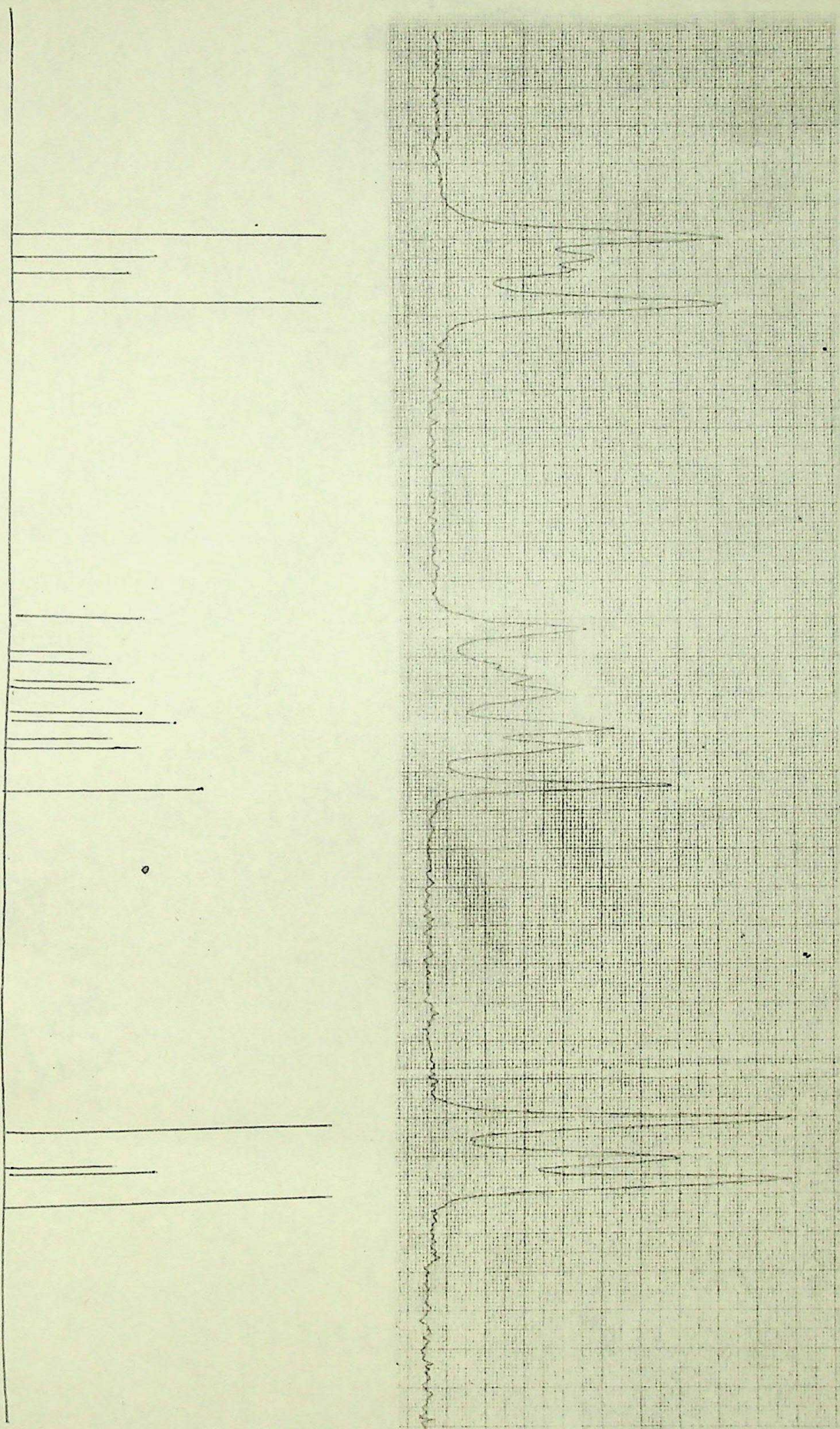
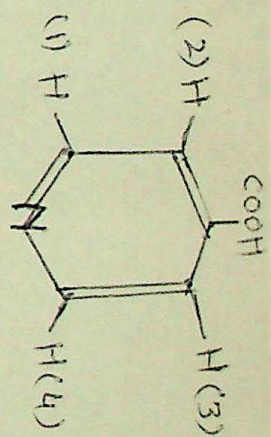


Fig. 4.2.

Figure 4.2

Experimental and calculated spectra of Isonicotinic Acid oriented in Lyotropic phase.

A) Composition of Solutions :

Components.	Per cent (by weight)
1) Heavy water	52.2
2) Decyl Amine Hydrochloride	42.2
3) Decanol-OD	0.9
4) Sodium sulphate	2.5
5) Isonicotinic Acid	2.2

B) Spectrometric conditions :

Spectrometer	Bruker WH 270 F.T.NMR.
Spectrometer Frequency	270 MHz.
Average line width	4 Hzs.
Temperature	21°C
RMS error	0.03 Hzs.
Maximum error	2.3 Hzs.
Number of transients collected.	160
Sweep width	352 Hzs.

4.6.2 Experimental details and spectral Analysis :-

The spectrum of Isonicotinic Acid is shown in Fig.4.2.1 along with some experimental details. It essentially consists three groups of lines having total spread of about 352 Hzs. with well defined 18 lines and the spectrum is symmetric about the centre. The COOH proton in Isonicotinic Acid exchanges rapidly in the Lyotropic medium and hence the system has only four interacting protons with AA'BB' spin system and C_{2v} molecular axis symmetry.

The geometry of the molecule guessed and the necessary dipolar couplings were estimated from the spectral lines. The set of dipolar couplings used as the starting parameters for part-I of the LAOCOONOR programme. The chemical shifts and the indirect spin-spin couplings were assumed similar to 5-Hydroxypyridine (53) as no isotropic data for this compound is available. The final analysis was achieved with help of part II of the LAOCOONOR using computer. In the iterative analysis only the chemical shift and direct dipole-dipole coupling constants along with indirect spin-spin coupling constants were iterated upon. The experimental and the calculated frequencies along with the calculated line intensities are given in table 4.2.1. The values of the final parameters obtained are reported in table 4.2.2.

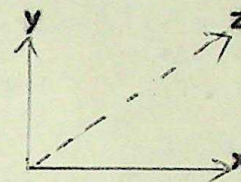
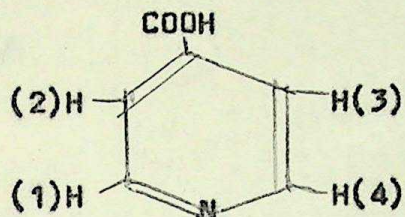
TABLE : 4.2.1

Experimental and calculated line Frequencies with calculated line intensities for Isonicotinic Acid in Decyl Amine Hydrochloride Lyotropic nematic phase at 21⁰c.

Experimental line Frequencies Hzs.	Calculated line Frequencies Hzs.	Calculated relative line intensities.
175.781	175.785	3.525
168.945	168.948	1.983
164.062	164.065	1.625
151.967	151.970	3.525
29.296	29.299	1.782
15.626	15.630	0.682
13.743	13.745	1.224
7.810	7.812	1.498
5.860	5.863	1.226
-5.859	-5.863	1.226
-7.812	-7.812	1.498
-13.671	-13.745	1.224
-15.624	-15.630	0.882
-29.296	-29.299	1.782
-153.320	-151.970	3.525
-165.015	-164.065	1.625
-167.968	-168.948	1.983
-175.781	-175.785	3.525

TABLE : 4.2.2

Spectral parameters of Isonicotinic Acid oriented in Decyl Amine Hydrochloride Lystropic nematic phase. The numbering of protons is as shown in Following structure :



Parameters.	Values in Decyl Amine Hydrochloride phase at 21°C and 270 MHz.	Values of 4-Hydroxy Pyridine in sodium Dodecyl sulphate phase at 32°C and 100 MHz.
$\nu_2 - \nu_1$	340.39	126.80
$J_{12} = J_{34}$	9.0 (a)	9.0
$J_{13} = J_{24}$	1.0 (a)	1.0
J_{14}	1.2 (a)	1.2
J_{23}	2.2 (a)	2.2
$D_{12} = D_{34}$	-49.35	-43.75
$D_{13} = D_{24}$	-14.43	-10.25
D_{14}	-28.26	-19.30
D_{23}	-25.39	-16.55
r_{12}/r_{23}	0.575	0.552
r_{13}/r_{23}	1.139	1.127
r_{14}/r_{23}	0.965	0.952
S_{xx}	0.0165 (b)	0.0112
S_{yy}	0.0061 (b)	0.0049
S_{zz}	-0.0226	-0.0161
Number of lines assigned	18	22
R.M.S. error	0.03	0.05

Note: (a) Taken from ref.(53), (b) S_{ij} values are calculated assuming an $r_{23} = 40274 \text{ Å}^2$

4.6.3 Molecular Geometry :-

The four proton-proton dipolar couplings provide two independent order parameters and the two relative interproton distance ratios required to describe the shape of proton skeleton. The equations relating to the dipolar couplings and the ratios of inter-proton distances reported in section 4.5.3 were used. The derived values of interproton distance ratios, calculated dipolar couplings, assumed indirect spin-spin couplings, chemical shift and order-parameters are reported in table 4.2.2. It is seen that the ratio of $\frac{r_{12}}{r_{23}}$ deviates slightly from corresponding values of pyridine (54) and γ -Hydroxy pyridine (53) may be due to acidic group exchanging instead of hydroxyl group in δ -Hydroxy pyridine and difference in the solute-solvent interactions in the two cases. The order parameter values show that the molecule preferentially orients with the normal to the ring plane perpendicular to the magnetic field direction.

4.7 4 IODO-ANILINE IN THERMOTROPIC PHASE :

4.7.1 Introduction :-

Aniline and its derivatives, have so far resisted many efforts to investigate their structure in

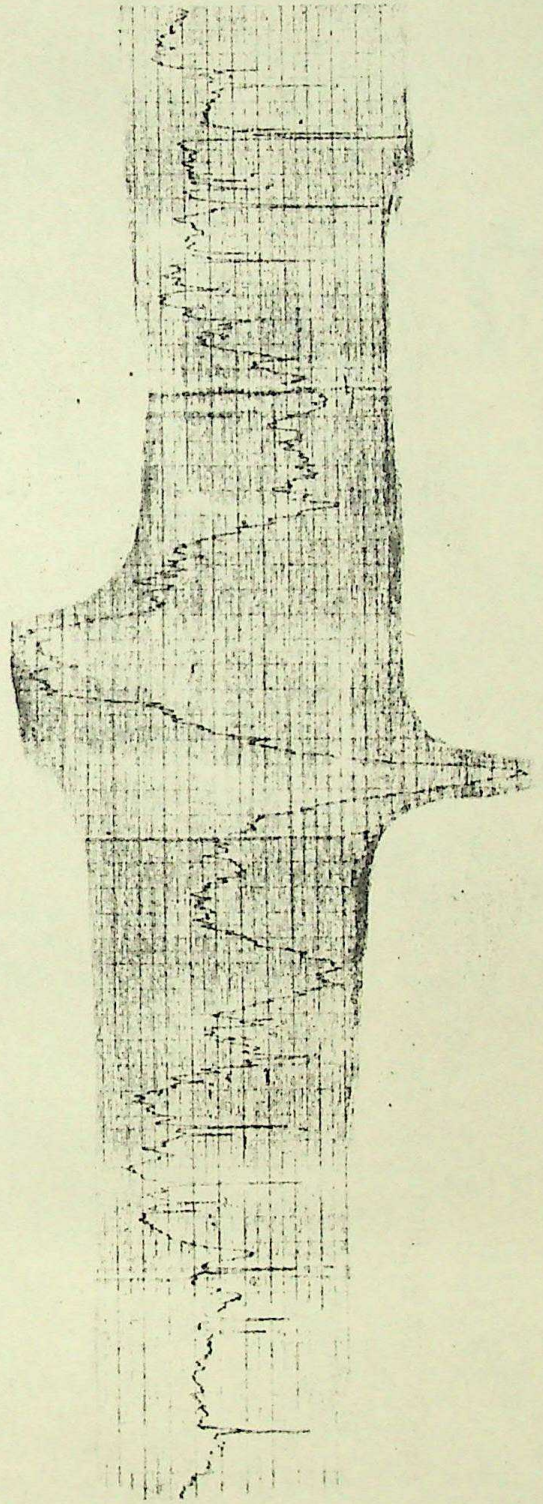


Fig. 413

Figure 4.3

Experimental and calculated spectra of 4-Iodo Aniline oriented in Thermotropic Nematic liquid, crystal phase.

Solvent	Merck phase V
Solute concentration	10 mole percents
Spectrometer	Bruker WH.270 F.T.NMR
Spectrometer Frequency	270 MHzs.
Temperature	19°C
Average line width	5 Hzs.
RMS error	0.25
Maximum error	2.3 Hzs.
Number of transients collected.	120
Sweep width	10.000 Hzs.

thermotropic nematic solvents (55). The early difficulties experienced with this kind of molecule, namely, broad H lines, were attributed to the quadrupole effect of N^{14} nucleus (56). It is found that although the quadrupole effect of N^{14} nucleus is not negligible, the main reason for the line broadening is the effect of water-catalyzed exchange of the NH_2 hydrogens. The nonplanar nature of aniline was deduced from dipole moment studies as long ago as 1936 (57). Structural data for substituted anilines are available from x-rays diffraction studies of the solid (58), from N^{15} NMR studies in the isotropic phase (59,60) and from microwave measurements in the gas phase (61-62). We report below only the recorded spectra of 4-Iodo-Aniline using thermotropic nematic liquid crystal phase. Similar para substituted anilines like para-nitroaniline ($1-N^{14}$), para-nitroaniline ($1-N^{15}$) and para-Bromoaniline ($1-N^{15}$), in thermotropic phase has been studied (63).

4.7.2 Experimental Details :-

Commercially available A.R. Grade 4-Iodo-Aniline used as solute for preparing the sample. The experimental

spectrum and the details are as shown in Fig. 4.3.1. The spectrum has more than 32 lines having total spread of about 10,000 Hzs. The system has six interacting protons with $AA'BB'C_2$ spin system and C_{2v} molecular axis symmetry. The computer analysis being too much complicated the spectra is not analysed. Analysis work is in progress.

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