CHAPTER - V

ELECTRON PROTON

RESONANCE STUDIES IN

SOME LIQUID CRYSTALS

AND CONCLUSION

Magnetic resonance spectroscopy is an important tool used very extensively by several researchers to investigate the molecular ordering in Liquid crystals. The orientational order of the molecules are obtained directly from the line position and spacings, the magnetic interactions which are responsible for the spectra are anisotropic. In oriented liquid crystals the anisotropies are averaged by molecualr tumbling to a value which is determined by the mean molecular orientation. The theoretical description of the nuclear spin and electron spin resonance techniques are the same, the general aspects of their applications in the study of liquid crystalline systems will be treated in the same way. The mesogenic molecules are diamagnetic, hence the Nuclear Magnetic Resonance, NMR spectroscopy can be performed directly on these systems whereas in Electron Paramegnetic Resonance EPR, doping with paramagnetic probe is required for EPR investigations.

Magnetic Resonance spectra can be interpreted as plots of radio-frequency power absorbed as a function of frequency at a constant field. In practice sweeping the field of constant frequency to satisfy the resonance conditions in NMR is performed, while in EPR the first derivative of absorption curve is recorded rather than the absorption itself. It is always possible however to express the field in frequency units and this makes the theoretical interpretation more direct.

ELECTRON PARAMAGNETIC RESONANCE :

The Electron Paramagnetic Resonance is based on electron spin and it's magnetic moment. The atoms, ions or molecules having an odd number of electron (paramagnetic) exhibit characteristic magnetic properties which arise from spinning or orbiting action of the unpaired electrons about the nucleus when strong magnetic field is applied to the unpaired electrons. The electron dipoles or magnetic moments of the electrons are aligned either parallel or antiparallel to the direction of the external magnetic field. The electron will precess about the axis of the magnetic field at a frequency proportional to both the applied magnetic field and the electron magnetic moment. When a second and weaker radio frequency alternating magnetic field with frequency of precession of the electron is applied at right angles to the fixed magnetic field, resonance occurs. At resonance, the absorption of energy from the rotating field causes the spin of the electrons to flip from the lower enerry level to the higher energy level. The two levels are seperated by

$$E = hv = 2\mu H \quad \dots\dots\dots\dots\dots\dots (1)$$

For a field of 3400 gauss the precession frequency is approximately 9500 MHZ (X-band).

FREE RADICAL OR SPIN PROBE :

The liquid crystalline compounds are not generally paramagnetic. This technique is therefore limited to the solute molecules which contain unpaired electron spin. The concentration of the solute required for EPR is considerably less than that required for NMR work. The concentration less than 10^{-3} gives observable spectra, the ultimate reason for the increased sensitivity being the large the value of Bohr magnetron. The sensitivity can be practicaly advantageous in probing liquid crystals. Since many of the properties of this state are strongly dependent on dissolved foreign substances. EPR studies of nematic liquid crystals show that the required concentration of the paramagnetic probe do not significantly alter such properties such as the nematic-isotropic phase transition temperature or the width of the transition. Another advantage of EPR is that the Hamiltonian interactions are intermolecular. This indicates that the effects of neighbouring solvent molecules do not enter the expression even in viscous materials where the absence of motional narrowing makes NMR studies prohibitive because of intermolecular interactions. The spin probes commonly used are diphenylpicrylhydrazyl (DPPH), tetracyanoethelene ion (TCNE), Vanadyl acetylacetonate (VAAC).

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LITERATURE SURVEY:

Carrington and Luckhurst [1] were the first to report the use of EPR in liquid crystals. They employed diphenylpicryl-hydrazyl (DPPH) and tetracyanoethelene (TCNE) spin probes in their investigations on p-azoxyanisole. Several workers have employed EPR to study the molecular order in liquid crystals [2-12].

Fryburg et al [2] used Vandyl acetyl acetonate (VAAC) which contains Vo^{+2} radical. The analysis with these probes were complicated and no jump was observed for polymesomorphic phase change, instead a continuous curve was obtained. Luckhurst and Setaka [8], Later Rao [9], Sabatini [10] studied EPR using nitroxide probe. The analysis with these probes were simple. The orientational order parameter for polymesomorphic phase is a step type functional jump rather continuous. This shows that nitroxide spin probe is most appropriate for EPR studies. The order parameter was estimated by the author using ultrasonic velocity, density and refractive indices measurements The results of which are presented in chapter III and IV respectively. However the order parameter can also be estimated from EPR measurements, so the author has made an attempt to estimate the order parameter employing EPR and make a comparative study about the validity of all these estimations. EPR measurements were carried out, and the order parameter variation with temperature were estimated.

1. p-(p'-n pentyloxybenzoyloxy)nitrophenon

2. p-(p'-n hexyloxybenzoyloxy)nitrophenon

3. p-(p'-n heptyloxybenzoyloxy)nitrophenon

using the steroidal nitroxide spin 3-(2'-spiro-3'N oxyl 4'-4'dimethyl oxazolidine)5-cholestane.

ANALYSIS OF SPECTRUM :

When the ordering potential or the director defined by order parameter is parallel to the magnetic field, the coupling constant a, for any nucleus is a radical dissolved in liquid crystalline phase obtained from the experimental motionally averaged spectrum is defined as

$$\overline{a} = a + (2/3) \sum_{i,j} A'_{ij} S_{ij} \quad \dots\dots\dots\dots 3$$

where a is the scalar coupling constant i.e the isotropic hyperfine parameter measured in the isotropic phase; A is the an isotropic hyperfine tensor and S is the ordering matrix which described the solute alignment. The G factor in the mesophase is given by an equation analogous to the previous equation i.e.

$$g = g' + (2/3) \sum_{i,j} g_{ij} S_{ij} \quad \dots\dots\dots\dots 4$$

If both g and hyperfine tensors are cylindrically symmetric about the same axis the equations (3) and (4) reduce to

$$a = a + A'_{33} \quad S_{33}$$

$$g = g + g'_{33} \quad S_{33}$$

consequently, it is possible to determine the element of the ordering matrix for such paramagnetic solutes which include the popular spin probe Vanadyl acetyl acetonate Nitroxide radi-

cals. Although the nitrogen hyperfine tensor is cylindrically symmetric the g tensor deviates considerably from cylindrical symmetry and for probe shown in figure 5.1 the principal components are

$$g_x = 2.0089$$
$$g_y = 2.0058$$
$$g_z = 2.0021$$

The principal coordinate system is shown in figure 5.1. In case of liquid crystals PBNP, H6BNP, H7BNP in this spin probe, the molecular model reveals that although the Z-axis is likly to be the principal axis of the ordering matrix, this is not so for X and Y axis.

Since the symmetry axis of the nitrogen hyperfine tensor is parallel to the Z-axis orthogonal to the Oxazolitine ring, then the change in the coupling constant or alignment gives the principal component S directly i.e. the hyperfine shift calculated from (3) gives directly the order parameter S

$$S_{33} = \overline{a} - a / A'_{33} = <a> - a / A_{11} - a$$

where a is coupling constant obtained from the experimental motionally averaged spectrum in the nematic phase. A and A' are the parallel and perpendicular components of the hyperfine tensor. The g tensor does not possess cylindrical symmetry, but one can expect the ordering matrix to be cylindrically symmetric about the long axis which is parallel to the plane of oxazolidine ring, consequently g shift is $g' - g = Sg$

and the ratio $(\bar{a}-a)/(\bar{g}-g)$ should be independent of temperature
which was already demonstrated by Luckhurst and his Coworkers
[8]. The hyperfine shift, therefore, is given by

$$a' - a = \bar{P}_2 \; A_{33} \; / \; 2$$

where $\bar{P}_2$ denotes the ordering matrix elements for the long axis.
This equation can be used to calculate the degree of solute
alignment (S) which reflects the degree of order of pure
mesophase. The nature of the EPR spectrum dissolved in
nitroxide probe is illustrated in figures 5.2 through 5.6. The
scalar nitroxide coupling constant is found to be 46.44 MHz in
the isotropic phase of the liquid crystals. The tensor
components $A_{11} = A_{33}$ is taken from literature for the radical
used in this work which is 75.2 MHz. Hence the measurements of
the nitrogen coupling constant at different temperature are
used to calculate the orientation order parameter of the liquid
crystals PBNP, H6BNP and H7BNP. The results obtained are shown
in Table 5.1. The variation of the order parameter is
represented in Figure 5.6 through 5.8. From the figures, it is
clear that the order parameter increases as the temperature
decreases, the normal behaviour in liquid crystals. The order
parameter obtained from EPR agrees very well with the results
obtained from birefringence experiments.

CONCLUSION :

As has been observed, the liquid crystals exhibit a distinct state which lies intermediate between the solid crystalline state charactarized by a perfect order and the isotropic liquid state-charactarized by disorder. The order parameter defined in terms of the distribution functions involving spacial and orientational coordinates is difficult to determine. However, the order parameter, defined as the ensemble average of second order Legender polynomial, $P_2(Cos\theta)$, can be obtained from several experiemnts. The temperature variation of the order parameter provides a valuable test for the various theoritical models suggested for liquid crystals. In addition to the ultrasonic velocity measurements, it is expected that the nature of the forces responsible for liquid crystals may also be understood. In view of this, the order parameter using various experimental models has been evaluated.

The order parameter estimated from ultrasonic velocity and density data is included in Chapter III - section B, from refractive indices in Chapter IV and from EPR in Chapter V. It can be observed that the order parameter estimated from ultrasonic velocity and density differs appreciably from order parameter estimated from refractive indices and EPR measurement. The reason appears to be that, the order parameter derived from ultrasonic data involves the application of several theories like Maier-Saupe and Chandrsekhar theories which are

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actually based on diffrent assumptions. The constant B in equation (19) of Chapter III - Section B, was assumed to be invariant through out the mesophase. This appears to be the another reason. However, through this method gives a rough estimation of the order parameter, it has the advantage of providing a fast estimation of the order parameter variation with temperature from the available ultrasonic velocity and density data. The order parameter obtained from referactive indices employing Vuks' and Neugebauer's theories and from Electron paramagnetic Resonance are differing slightly and so the results obtained are comparable with each other. Similar behaviour was observed by other researchers [14,15] and hence the validity of these theories can be established.

The Bendler's equations are also capable of explaining the pretransitional effects observed in the isotropic phase near the isotropic-mesomorphic phase transition, since satisfactory fit was obtained for the experimental data and of the thermal expansion coefficient and temperature coefficient of adiabatic compressibility. The physical parameters such as adiabatic compressibility, molar sound velocity, molar volume and Lennard Jone's critical exponent are all consistant in explaining the liquid crystalline behaviour.

TABLE 5.1					
TEMPERATURE VARIATION OF ORDER PARAMETER S IN PBNP,H6BNP AND H7BNP.					
PBNP		H6BNP		H7BNP	
Reduced Temperature T/T_c	ORDER PARAMETER (S)	Reduced Temperature T/T_c	ORDER PARAMETER (S)	Reduced Temperature T/T_c	ORDER PARAMETER (S)
0.8387	0.6042	0.8923	0.5720	0.8571	0.6320
0.8709	0.5050	0.9154	0.5790	0.8929	0.6304
0.9032	0.5900	0.9308	0.5540	0.9107	0.6289
0.9274	0.5780	0.9462	0.5590	0.9289	0.6204
0.9435	0.5559	0.9615	0.4917	0.9464	0.5772
0.9597	0.5280	0.9760	0.4440	0.9643	0.5090
0.9677	0.4840	0.9840	0.4178	0.9732	0.4730
0.9758	0.4601	0.9924	0.3744	0.9912	0.3702

I   II —

III   IV —

V

$A_{xx} = 6G$

$A_{yy} = 6G$

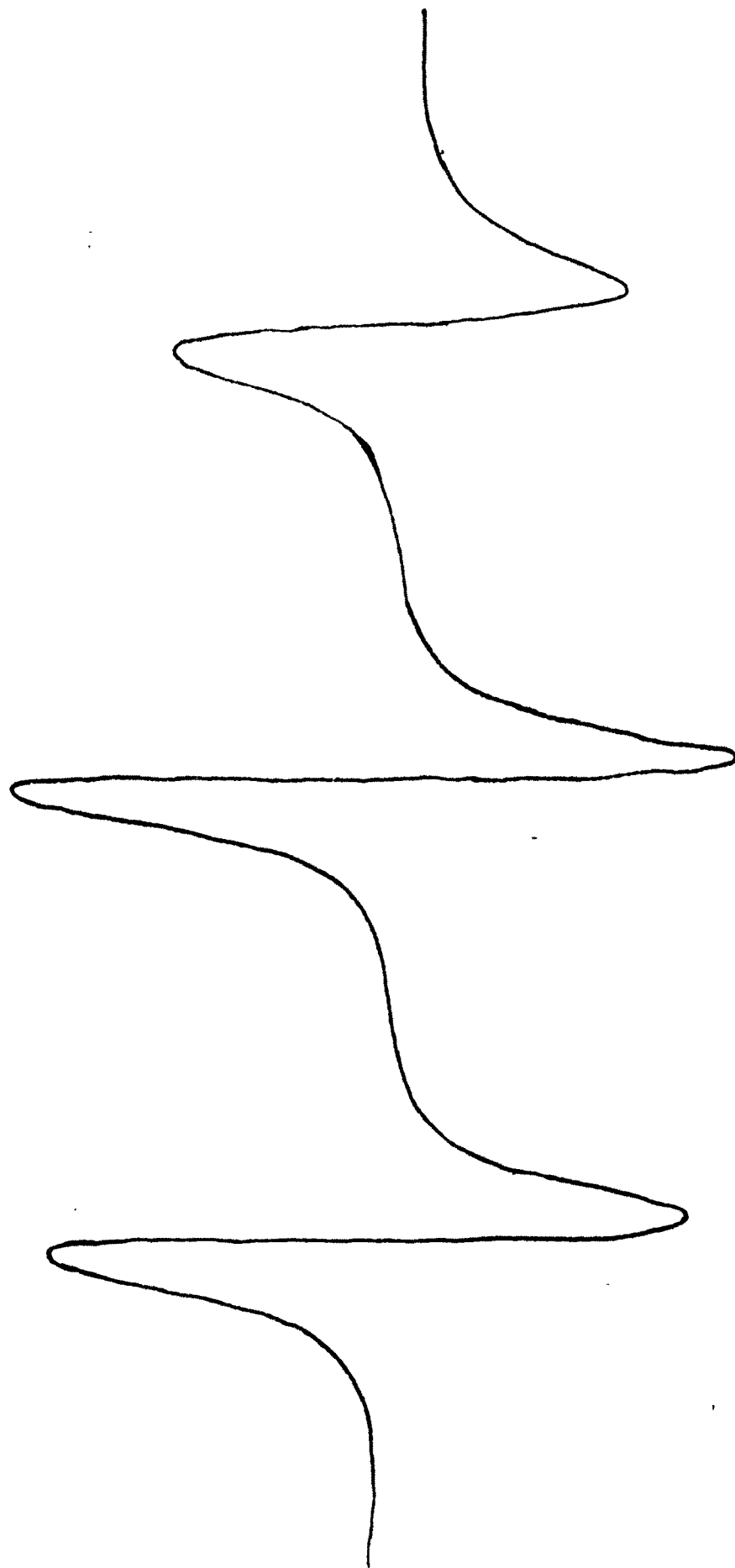$A_{zz} = 32G$

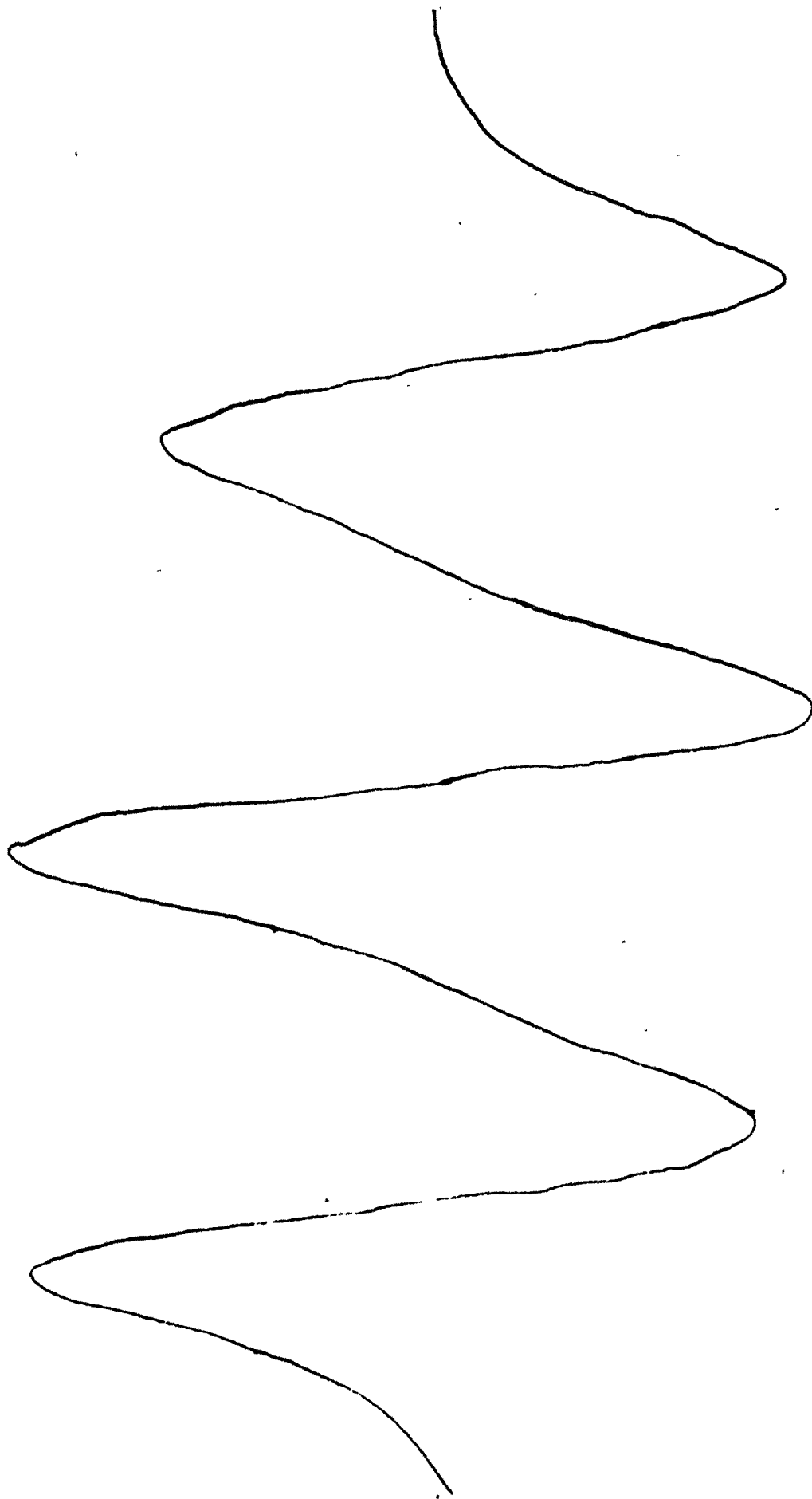$g_{xx} = 2.0089$
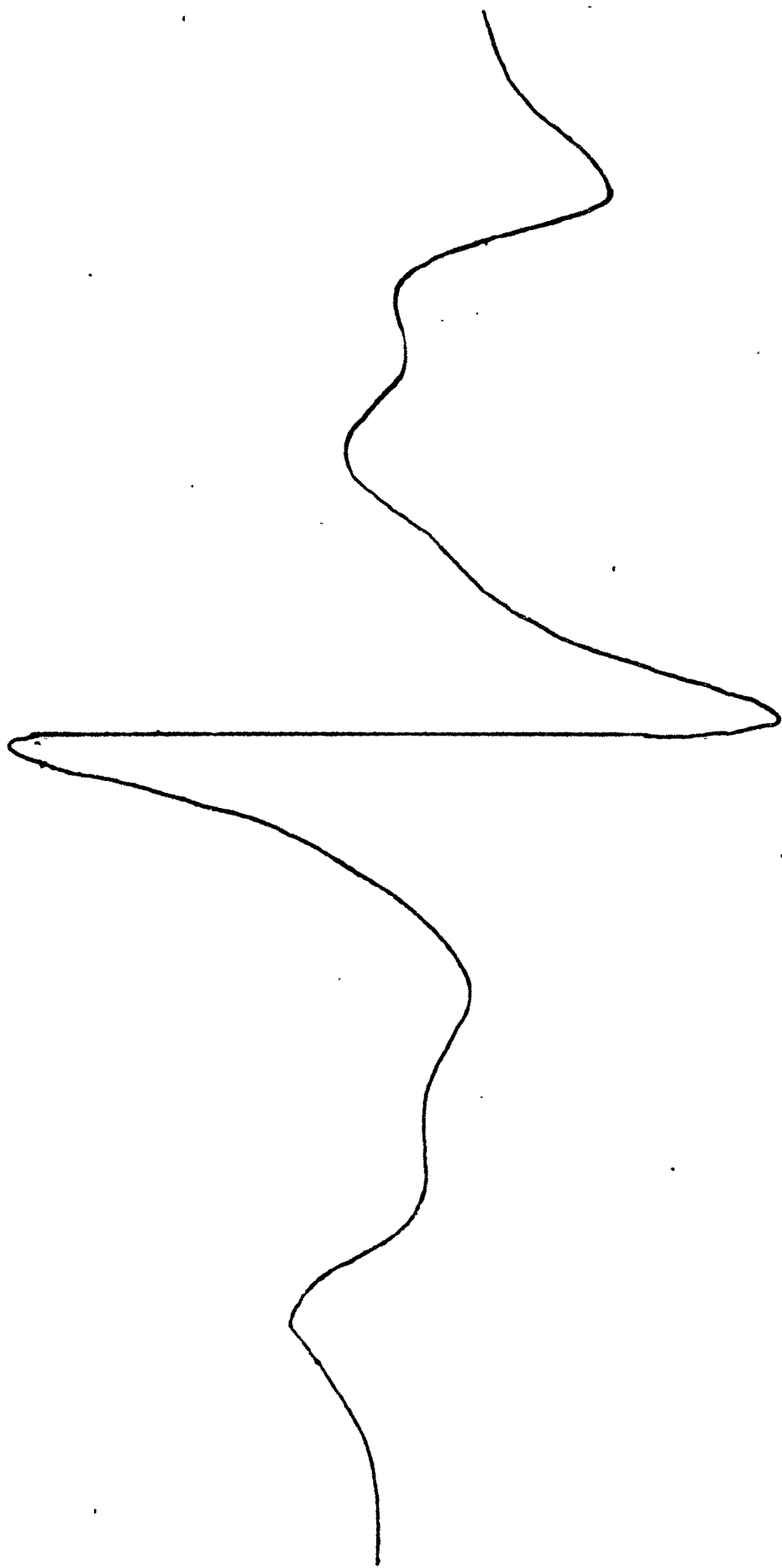
$g_{yy} = 2.0058$

$g_{zz} = 2.0021$

10 Å
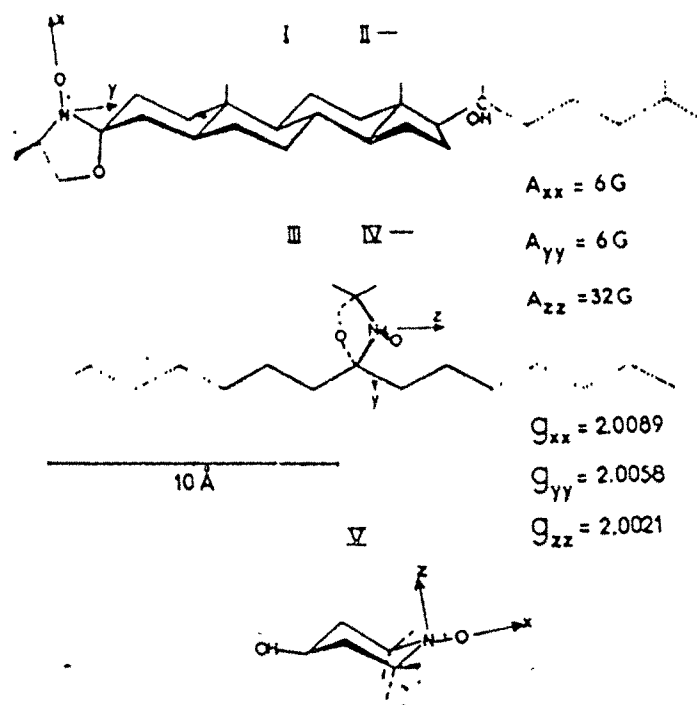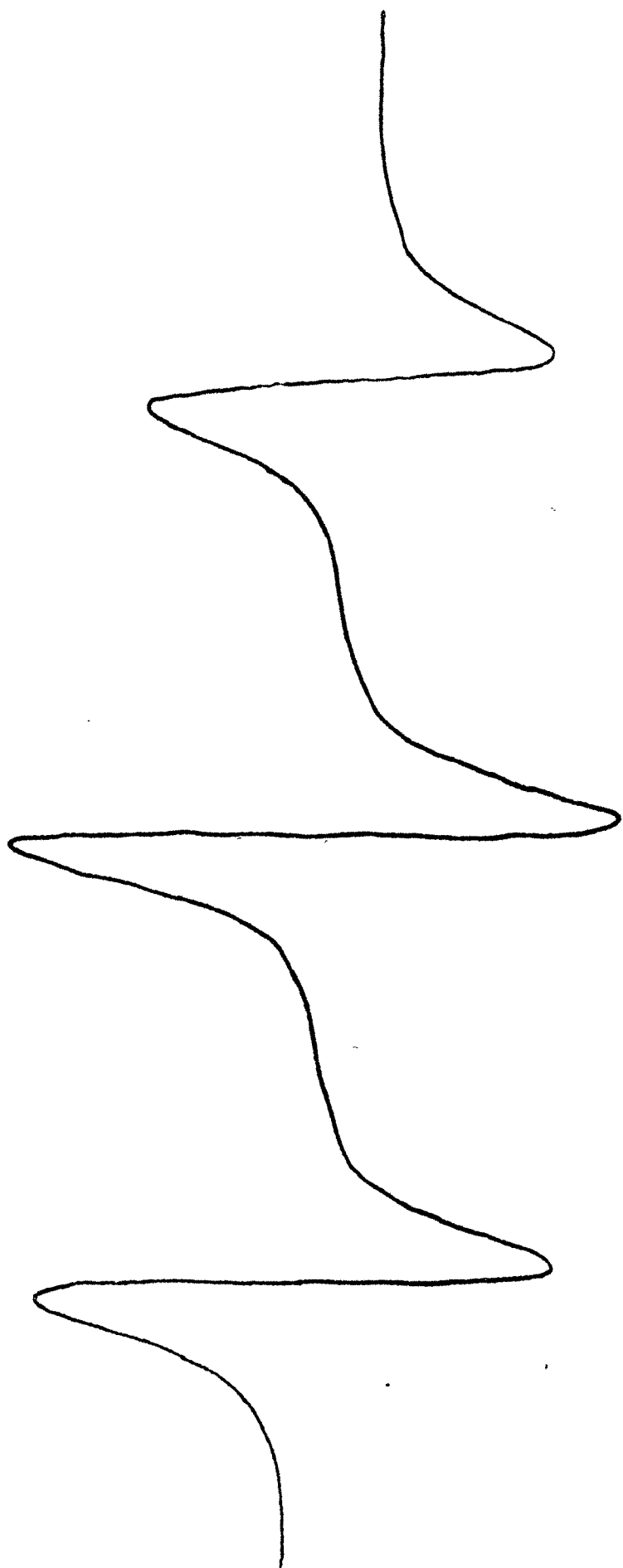
Figure : 5.1

Figure: 5.2

Figure: S-3

Figure: 5.4

Figure: 5.5
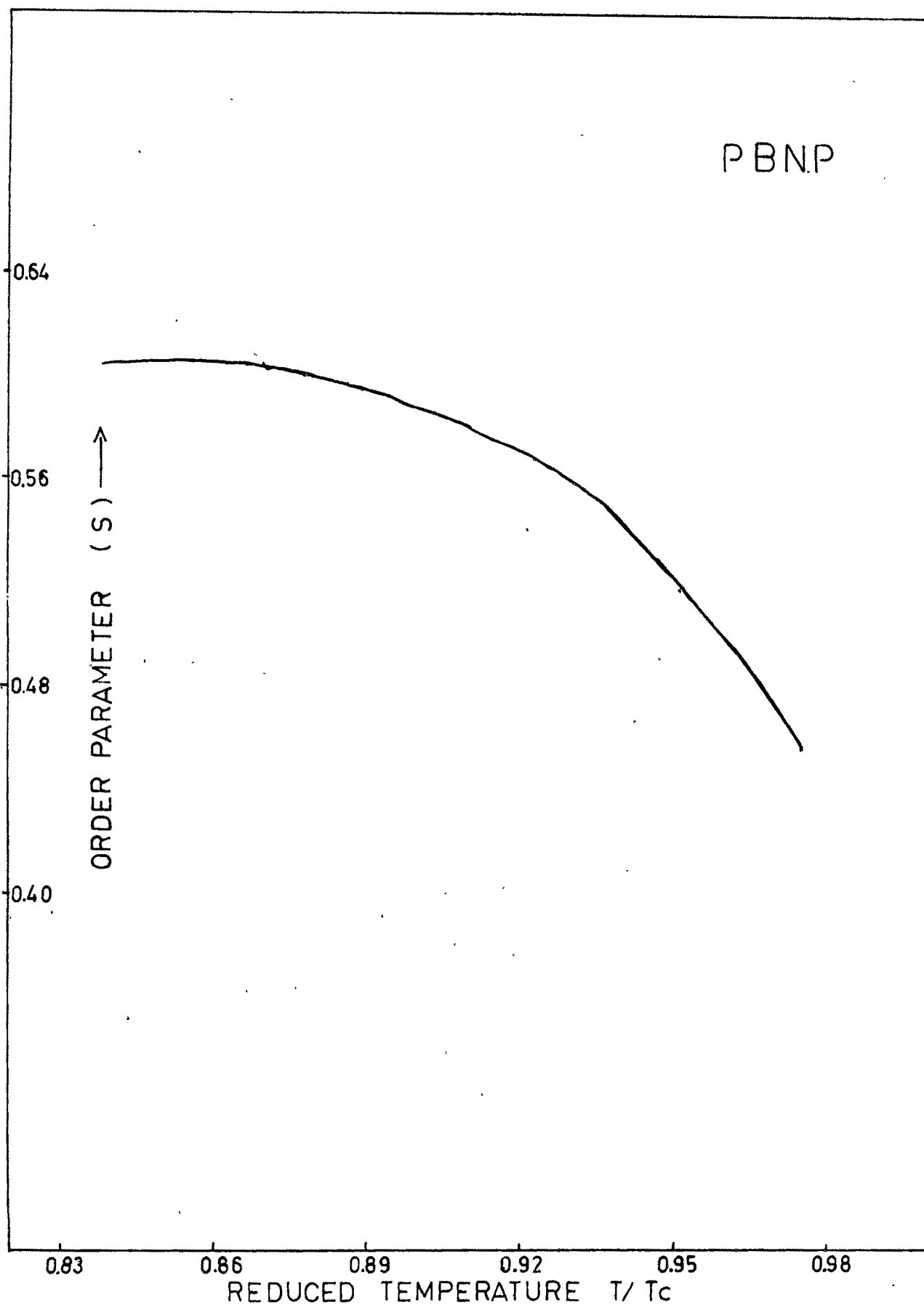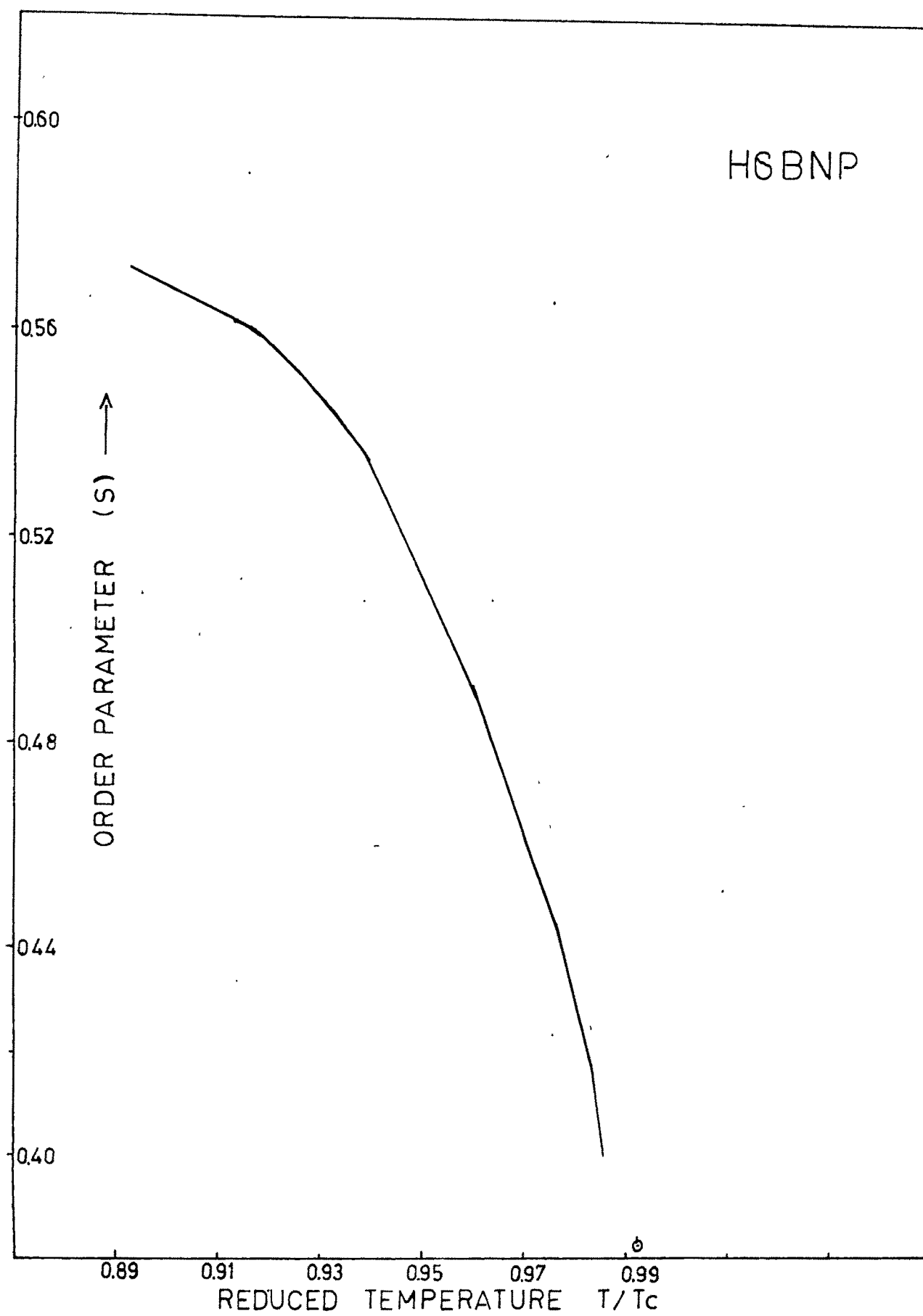
Figure 5.6

Figure 5.7
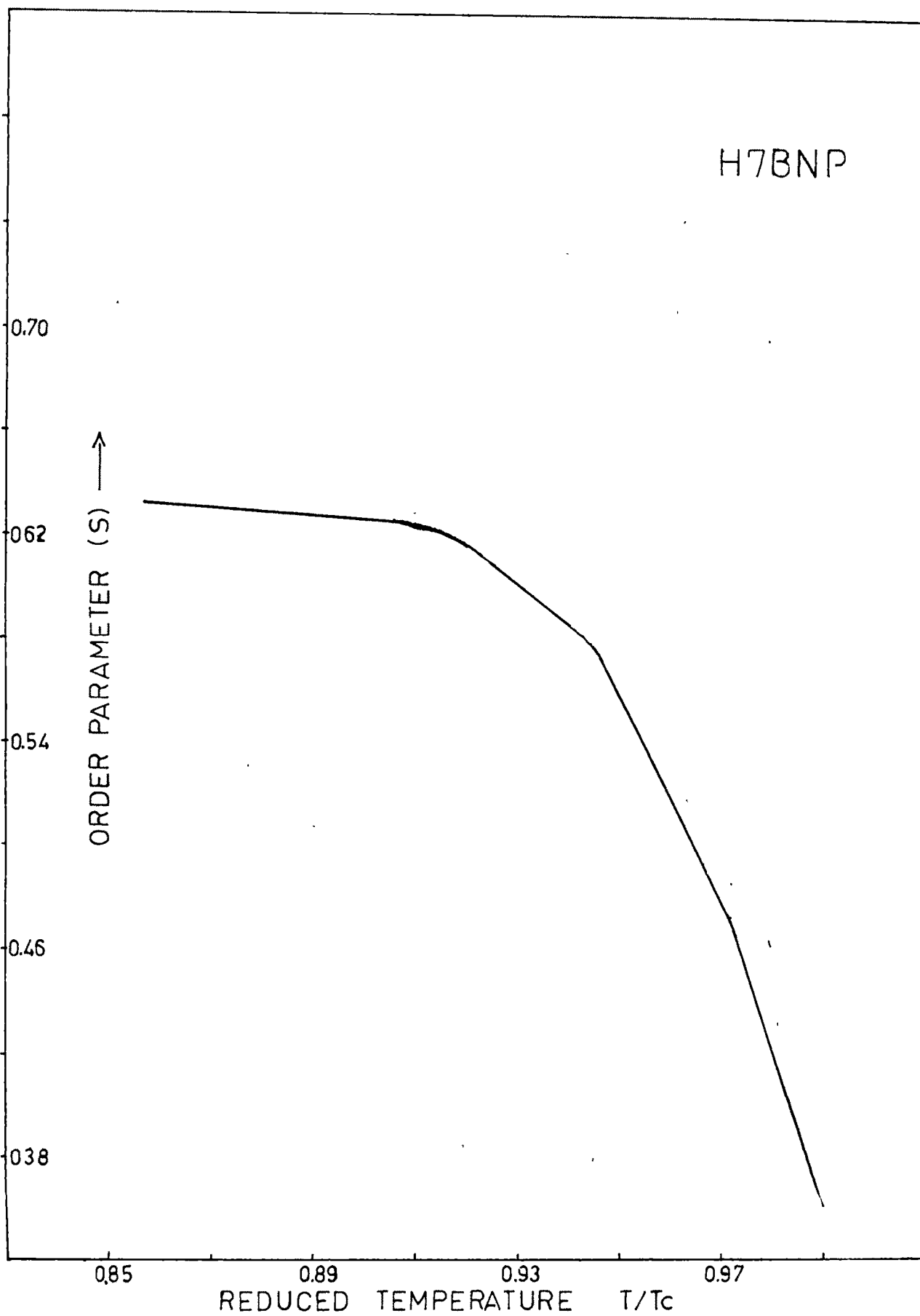
Figure 5.8

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