# CHAPTER II

## DESCRIPTION OF THE EXPERIMENTAL SET UP

This chapter describes the experimental set up used in the dielectric studies reported in this thesis.

### 2.1 The Cell

The schematic diagram of the cell[1] used is given in fig.2.1a. It consists of two aluminium coated glass plates which serve as the electrodes. The separation between them was defined by two narrow strips of mylar (or Kapton for temperatures above 170°C). The thickness of the spacers used ranged from 12.5 $\mu m$ to 100 $\mu m$, depending on the material investigated and the geometry of the set up. Care was taken to eliminate the contribution of the mylar to the total capacitance of the cell by positioning the mylars/ Kaptons outside the active area of the cell which was about 1 sq.cm. A bevel, made on the shorter side of one of the plates, was used in filling the sample. The two electrodes were offset along the length and the extending area was used to make electrical contacts. The cell was held rigidly in a copper frame (see Fig.2.1a) shaped like a rectangular 'G' clamp. To avoid uneven pressing of the cell by the brass screws, a flat copper plate was used to cover the glass plates. Rectangular slots made in the frame and in the

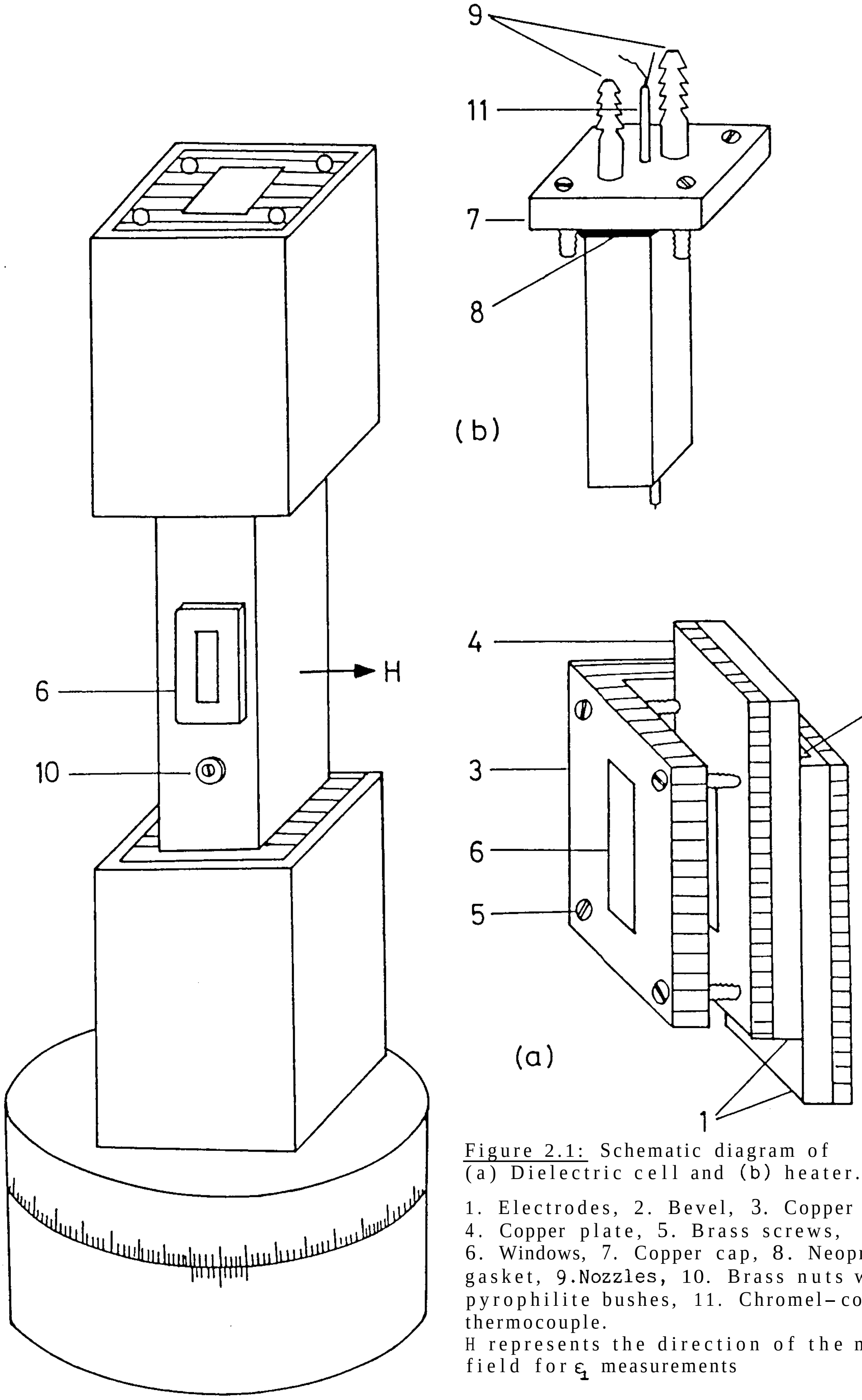

Figure 2.1: Schematic diagram of (a) Dielectric cell and (b) heater.

1. Electrodes, 2. Bevel, 3. Copper clamp, 4. Copper plate, 5. Brass screws, 6. Windows, 7. Copper cap, 8. Neoprene gasket, 9. Nozzles, 10. Brass nuts with pyrophilite bushes, 11. Chromel-constantan thermocouple.
H represents the direction of the magnetic field for $\epsilon_1$ measurements

copper plate served to check the alignment of the sample by visual observation between crossed polarisers. This cell allowed us to carry out measurements even at temperatures as high as 220°C. Also, it has the advantage of requiring only a small quantity of sample.

## 2.2 Heater

A schematic diagram of the heater is shown in Fig.2.1b. It consisted of a long rectangular copper tube. The length of the heater was deliberately made very large compared to the size of the dielectric cell to ensure that there are no temperature gradients in the sample. Its cross sectional size in the central position was minimised in order to obtain as high a magnetic field as possible. Nichrome heater wire was wound at both ends of the heater. The hylam sheets covering the entire surface of the heater body provided very good thermal insulation. It was made sure that the cell was always positioned at the centre of the heater when it was introduced into it from the top. The heater could be rotated about a vertical axis and its position could be read to an accuracy of 0.1° on a circular scale attached to its bottom. With this arrangement the cell could be rotated exactly by 90°, thereby enabling us to make both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ measurements (in the nematic phase) using the same sample. The heater was sealed by tightening a copper cap with a neoprene **'O'** ring. Two brass nuts were fixed in the body of the heater on the sides with windows. These were insulated from the heater by pyrophilite bushes. Two screws could be made to move forward or backward in the nuts in order to make or break electrical contact with the electrodes without disturbing the sealed environment. The brass nuts were connected to the measuring instrument (Impedance Analyser) via coaxial cables. The heater assembly was placed on a platform which was provided with levelling screws. The purpose of this arrangement is two-fold:

(i) to ensure that the heater is perfectly normal with respect to the direction of the magnetic field and

(ii) to adjust the height of the heater relative to the pole-pieces of the magnet such that the cell is situated exactly at the centre of the pole-pieces. Before the commencement of any experiment the heater was flushed with dry nitrogen for about ten minutes through a pair of nozzles provided at the top of the heater cap. This prevented oxidation and deterioration of the sample at high temperatures.

## 2.3 TEMPERATURE CONTROL AND MEASUREMENT

The electrical power to the heater was supplied by a stabilised DC power supply. To probe the temperature of the sample a chromel-constantan thermocouple was selected as both these elements are non-magnetic materials. The thermocouple was used in conjunction with a digital multimeter (Keithley, Model No. 195A). Using similar probes at various positions inside the heater, it was initially ascertained that the sample did not experience any noticeable temperature gradients. By varying the current through the heater at a controlled rate, the temperature of the sample could be changed at any desired rate. Typically, during the measurement of the static dielectric constant, temperature was varied at a rate of about 4°C/hour, this rate being much slower (1-2°C/hour) near a phase transition. The temperature of the sample was maintained to better than ±25 mK during dispersion measurements.

## 2.4 TMEPERATURE CALIBRATION OF THE CELL

Several liquid crystalline materials that were of good chemical purity were used for the temperature calibration of the cell. The names of the compounds as well as their nematic-isotropic transition temperatures as measured with the polarizing microscope fitted with a programmable hot stage are listed in Table 2.1. The thermal variation of static dielectric constant $\varepsilon_{\parallel}$ (the measuring field $\vec{E} \parallel \vec{n}$, the director) near the nematic-isotropic transition is studied for each compound. $\varepsilon_{\parallel}$ versus thermo emf plots are given in Figures 2.2-2.5. A slow heating rate (~4-5°C/hr.) was adopted for the measurement. The thermo emf measured at the transition for each compound is also given in Table 2.1. The plot of the temperature

## TABLE 21

Compounds used in the temperature calibration of the dielectric cell and their nematic-isotropic transition temperatures

| S.No. | Name of the compound | Actual temperature (°C) by Mettler | DMM reading (mV) |
|---|---|---|---|
| I | 4'-n-Pentyl 4-cyano biphenyl (5CB)[2] | 34.29 | 2.075 |
| 2 | 4-Cyano cyclohexyl-4'-ethyl cyclohexane (CCH$_2$)3 | 48.51 | 3.006 |
| 3 | 4-Nitrophenyl 4'-n-octyloxy benzoate ($\bar{8}$.O.NO$_2$)[4] | 68.24 | 4.251 |
| 4 | 4'-n-Octyloxy 4-cyano biphenyl (8OCB)[2] | 80.35 | 5.069 |
| 5 | 4-n-Hexyloxy phenyl 4'-cyanobenzoate (CN.O.$\bar{6}$)[5] | 95.89 | 6.095 |
| 6 | 4-Biphenylyl-4"-n-propyl benzoate (B3B)[6] | 108.58 | 7.005 |
| 7 | 4-Biphenylyl-4"-n-nonyloxy benzoate (B9OB)[6] | 127.86 | 8.33 |
| 8 | 4-Undecyloxy phenyl-4'-(4"-cyanobenzyloxy) benzoate (I IOPCBOB)[7] | 160.05 | 10.631 |

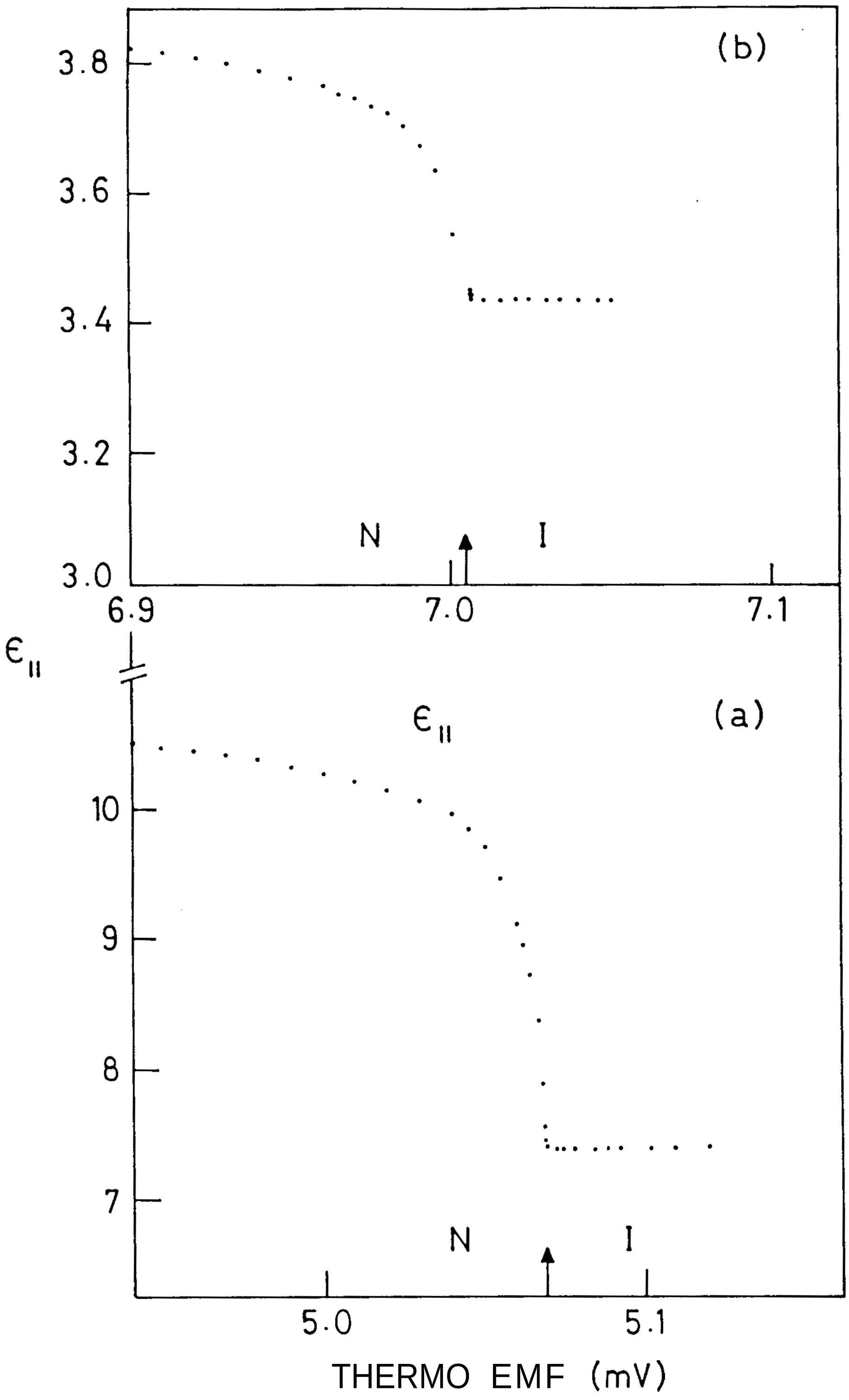

Figure 2.2

Temperature variation of dielectric constant $\varepsilon_{\parallel}$ near the nematic-isotropic transition for (a) 4'-n-octyloxy-4-cyanobiphenyl (8OCB) and (b) 4-biphenylyl-4"-n-propyl benzoate (B3B).

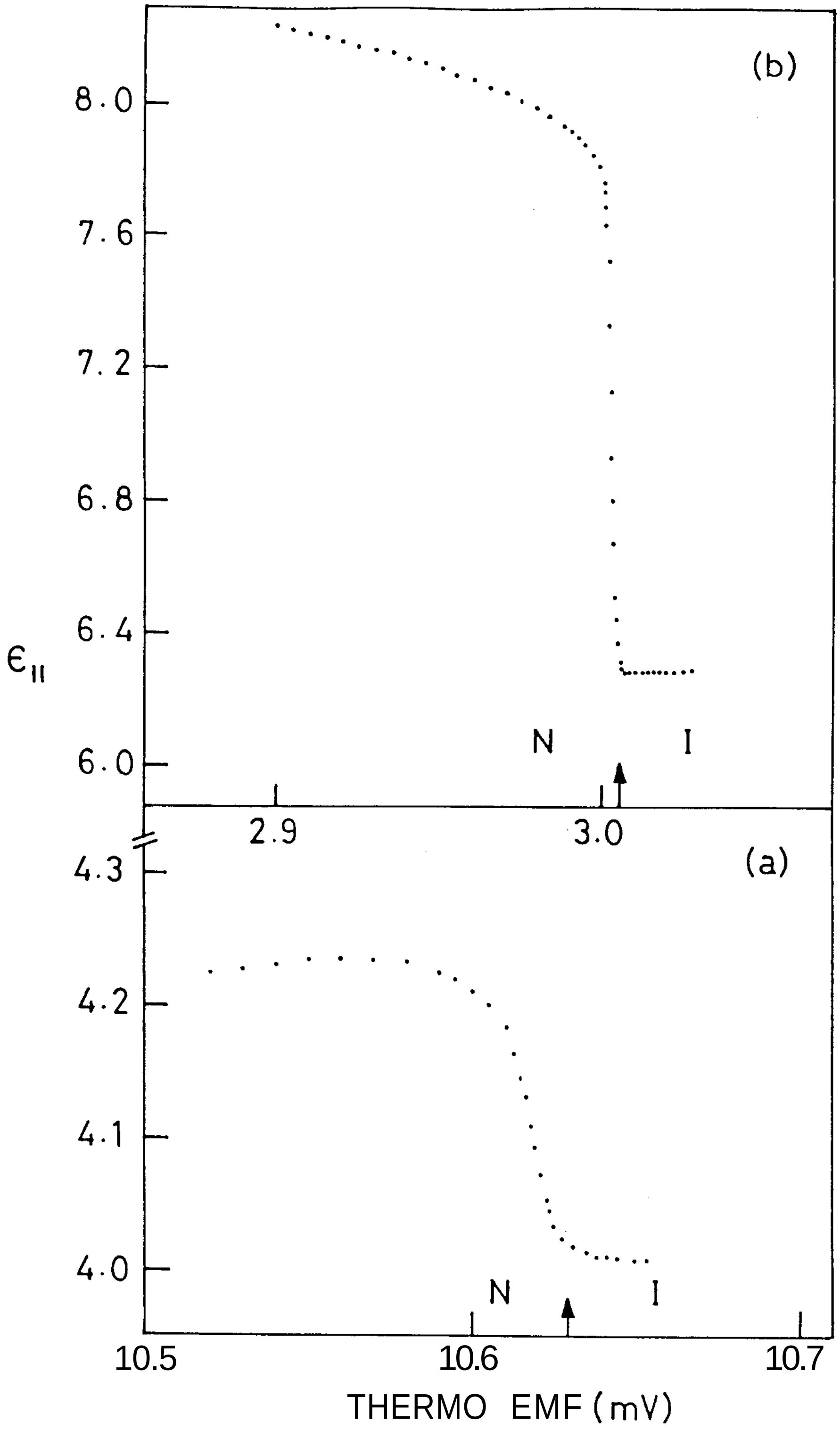

Figure 2.3

Temperature variation of dielectric constant $\epsilon_{\parallel}$ near the nematic-isotropic transition for (a) 4-undecyloxy phenyl-4'-(4"-cyanobenzoyloxy) benzoate (11OPCBOB) and (b) 4-cyano cyclohexyl-4'-ethyl cyclohexane ($CCH_2$)

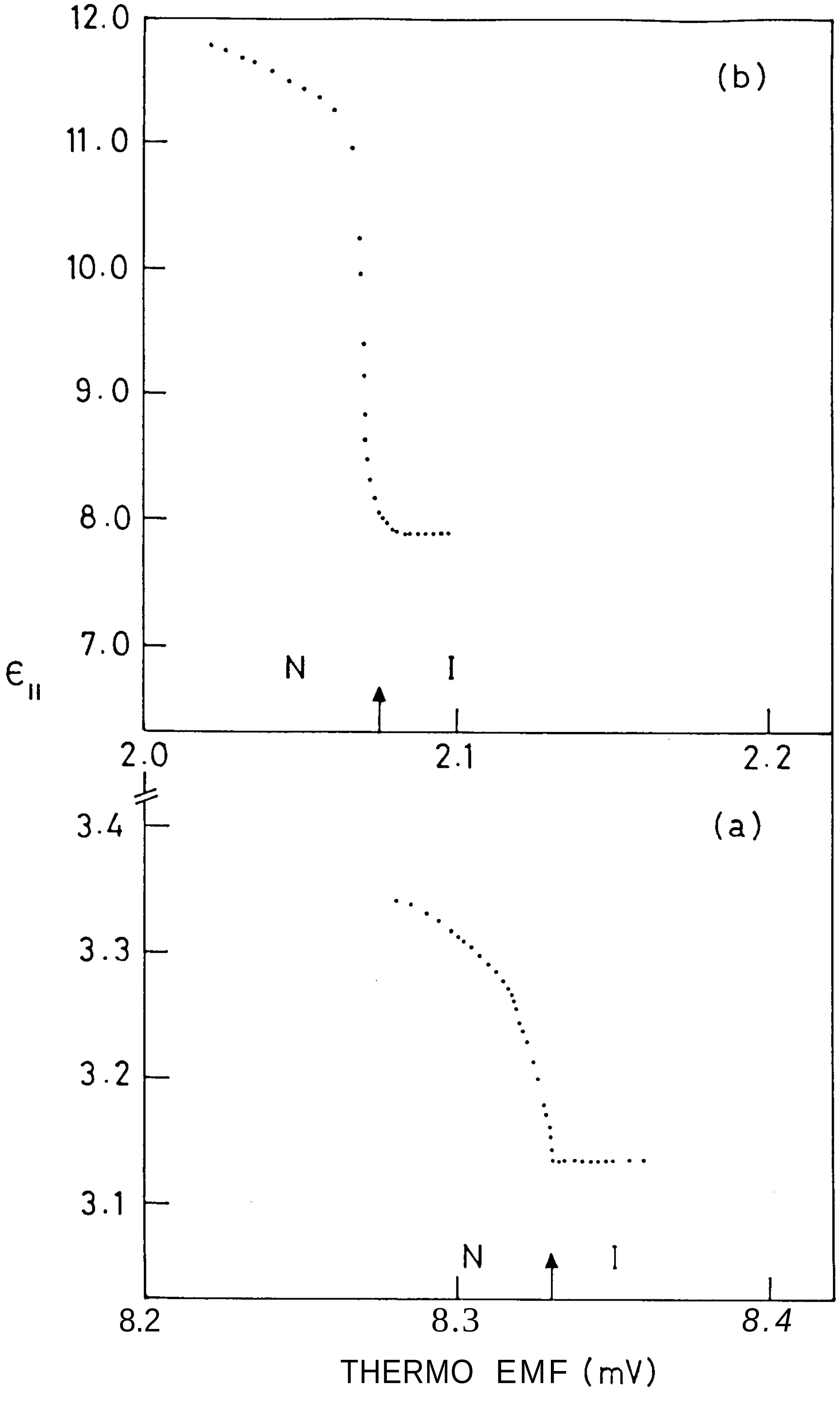

Figure 2.4

Temperature variation of dielectric constant $\epsilon_{\parallel}$ near the nematic-isotropic transition for (a) 4-biphenylyl-4"-n-nonyloxybenzoate (B9OB) and (b) 4'-n-pentyl-4-cyano biphenyl (5CB)

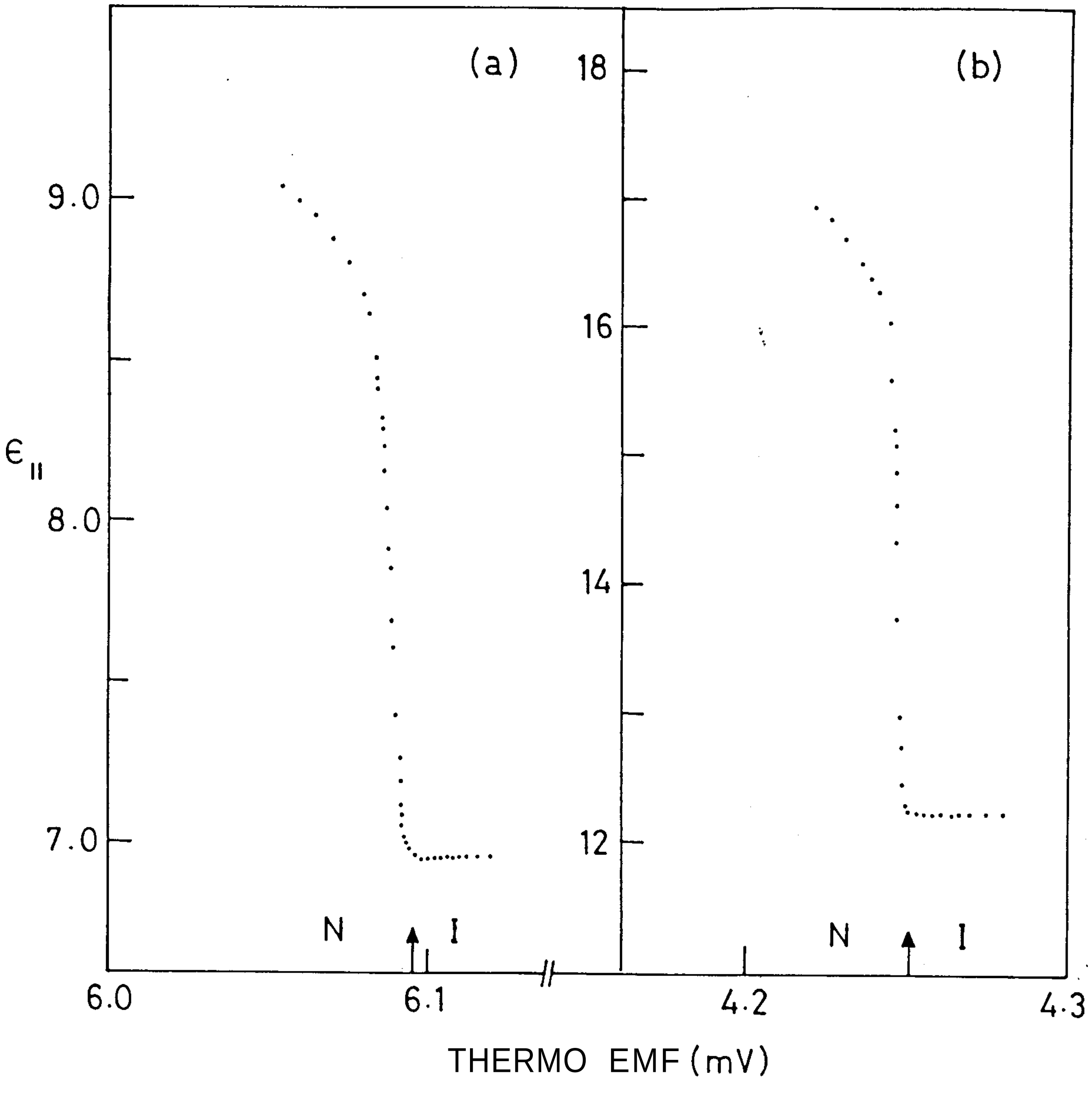

Figure 2.5

**Temperature variation of dielectric constant $\epsilon_{\parallel}$ near the nematic-isotropic transition for** (a) 4-n-hexyloxyphenyl 4'-cyanobenzoate **(CN.0.6) and** (b) 4-nitrophenyl 4'-n-octyloxybenzoate ($\bar{8}$.O.$NO_2$), of transition as measured using the Mettler hot stage (in °C) against the thermo emf (in mV) at the transition as measured by the dielectric study is shown in fig.2.6. The data were fitted to a polynomial expression of the type,

$$T = A_0 + A_1X + A_2X^2$$

(where T = the temperature in °C and X is the thermo emf in mV.)

Using a linear least square fit programme, the values obtained for the constants $A_0$, $A_1$ and $A_2$ are 1.2216, 16.2543 and -0.1246 respectively.

## 2.5 Sample Alignment

In general, a strong magnetic field was used to orient the sample. A homogeneous or planar alignment (measuring field $\vec{E} \perp \vec{n}$) gave $\varepsilon_\perp$ while a homeotropic alignment ($\vec{E} \parallel \vec{n}$) gave $\varepsilon_\parallel$ (see fig.2.7). Since it is well known that alignments of liquid crystals are strongly influenced by surface conditions, the glass plates constituting the electrodes were selected after careful scrutiny. They were first cleaned with a detergent (Teepol, BDH Ltd.) and then with freshly prepared chromic acid. Both homeotropic and homogeneous alignments were achieved by applying a magnetic field of about 2.4 Tesla which was more than twice the saturation field for the thickness of the sample used (50-100 μm).[8] The magnet

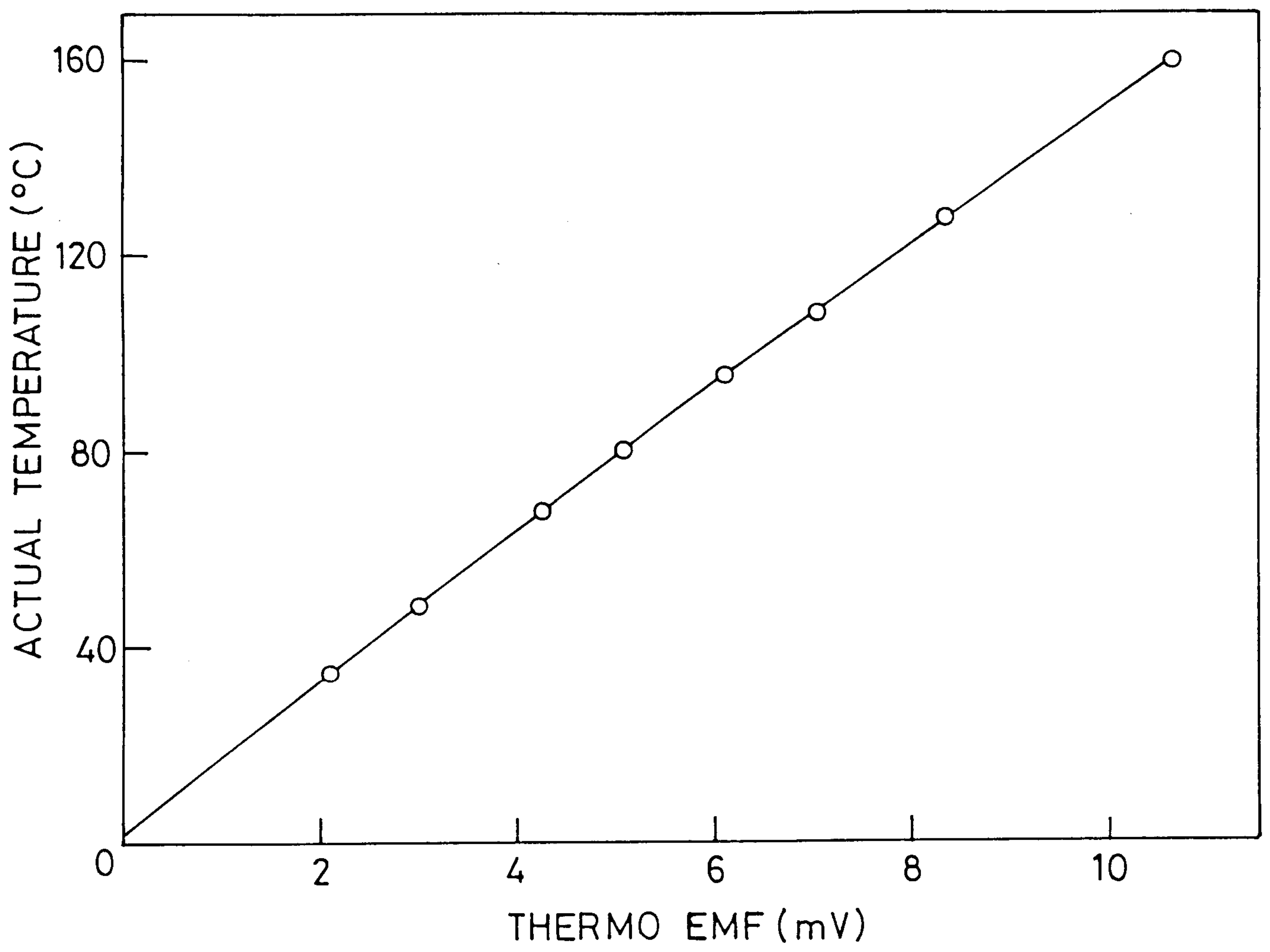

Figure 2.6

Temperature calibration curve of the dielectric ce using the compounds listed in Table

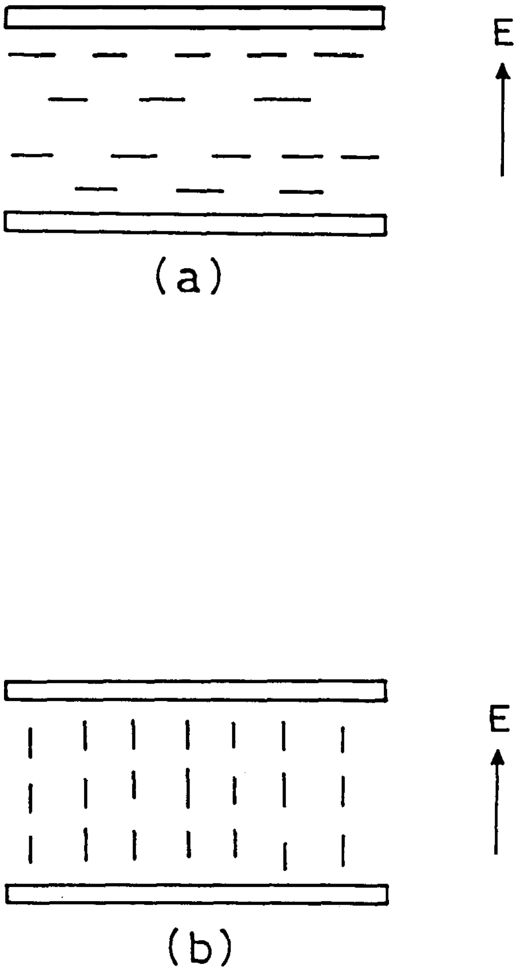

Figure 2.7

Schematic representation of (a) homogeneous and (b) homeotropic structures used was BRUKER (Model No. B-E25) with tapered cobalt-iron pole-pieces. The sample alignment in the smectic A phase was obtained by slowly cooling the well aligned nematic in the presence of the magnetic field. In case of isotropic-smectic A transitions, the alignments were obtained by means of surfactants, octadecyl triethoxy silane and polymide Resin (ZLI-2650) being used for homeotropic and homogeneous alignments respectively.

## 2.6 MEASURING SET UP

The dielectric constants were measured using a Hewlett-Packard Impedance Analyser (4192A). The functioning of the Impedance Analyser is based on an autobalance bridge measurement circuit. The capacitance measurement function of the analyser is based on vector-voltage-current ratio measurement method. Even at low oscillator voltage levels, high precision capacitance measurements could be carried out over a wide range of frequencies, viz., 5 Hz-13 MHz. Capacitance measuring range was 0.1pF-100 mF with a basic accuracy of 0.1% over the entire range. At the lower end of its frequency spectrum (up to 10 KHz), the value of the set frequency could be read to an accuracy of 1 mHz while in the range of 10 MHz, to an accuracy of 1 Hz. The oscillator level could be set to as low a value as 5 mV rms.

In order to minimize the effect of parasitic capacitance on the measured values, a suitable method was adopted which basically involves representing all measurement errors as four residual parameters R, X, G and B in the fashion (1) R+JX and (2) G+JB. The former was corrected by a "zero short" operation while the latter with "zero open" operation. The values thus obtained in different frequency ranges were stored in the memory of the impedance analyser in different registers and could be recalled later. The recalling of the parameters enabled automatic lead capacitance correction during the measurements.

Most of the work described in this thesis (Chapters III, IV, VI and VII) were carried out by collecting the data manually. However in order to improve the quality of the data and to perform speedier and automatic measurements in real time, a personal computer (Hewlett-Packard 86B) was used for the measurements described in chapter V. Schematic diagram of the experimental set up used for these studies is shown in Fig.2.8. The diagram is self-explanatory. The data acquired was stored on floppy diskettes for analysis which could be carried out later. A display monitor and an on-line plotter provided the graphics output as and when the information was being collected.

## 2.7 MEASUREMENT OF DIELECTRIC CONSTANTS

The temperature dependence of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ was investigated

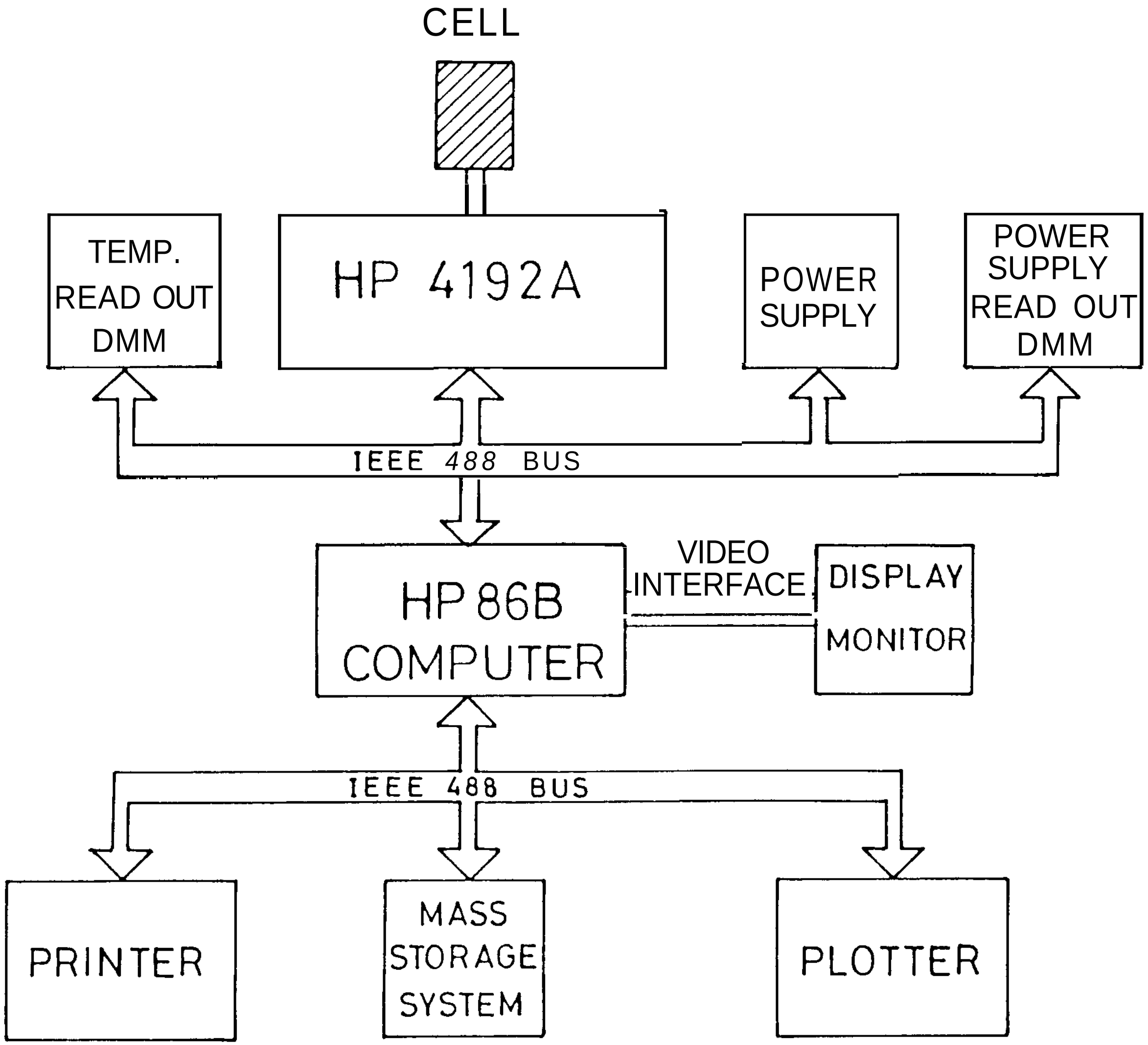

Figure 2.8. Schematic diagram of the experimental set up used for the dielectric studies.

at 1 KHz, this frequency being chosen since it is much below the frequencies of absorption domains and higher than the frequencies at which the conductivity mechanism becomes dominant. As mentioned earlier, a slow and uniform rate of heating/cooling (~4-5°C/hr.) was maintained during the measurement. The oscillator level of the measuring voltage across the sample was kept very low ( 300 mV) so that there was no disturbing influence on the sample. The value of the dielectric constant in the isotropic phase obtained independently from the two geometries matched to within 1%.

## 2.8 MEASUREMENT OF THE DIELECTRIC RELAXATION OF $\varepsilon_{\parallel}$

It is well known that the dielectric constants of liquid crystals are frequency dependent.[9] While $\varepsilon_{\perp}$ exhibits a relaxation in the microwave region only, $\varepsilon_{\parallel}$ shows a relaxation in the low frequency region also. The low frequency relaxation mechanism can be attributed to the reorientation motion of the molecules around an axis perpendicular to their longitudinal axis.

The low frequency dispersion of $\varepsilon_{\parallel}$ was measured using the set up described earlier. At any temperature (maintained constant to within ±25mK) the values $\varepsilon'_{\parallel}$ and $\varepsilon''_{\parallel}$ ($= \varepsilon'_{\parallel} \times D$, D being dielectric loss factor) were determined as function of frequency. $\varepsilon''_{\parallel}$ versus frequency curve (known as loss curve) gave the frequency of relaxation $f_R$ (the frequency corresponding to the $\varepsilon''_{\parallel max}$).

A $\varepsilon'_{\parallel} - \varepsilon''_{\parallel}$ plot, known as the Cole-Cole plot also gives $f_R$ value and indicates the nature of the relaxation.[10,11] A semicircle plot with centre lying on the $\varepsilon'_{\parallel}$ axis denotes a single relaxation time while any deviation indicates a distribution of relaxation times. In all the experiments described in this thesis, the value of $f_R$ obtained from the Cole-Cole plot agreed with that determined from the loss curve to better than 2%. In any case the average value of $f_R$ (determined from these two types of plots) was used for the evaluation of W, the activation energy which can be associated with the reorientation of the molecule about its short axis.

The set up described so far has been used to study the dielectric properties of a variety of liquid crystalline materials. The results of these investigations will be discussed in the following chapters.

## REFERENCES

1 B.R.Ratna, "Dielectric Properties and Short range Order in Liquid Crystals", Ph.D.Thesis, University of Mysore (1978).

2 G.W.Gray, K.J.Harrison, J.A.Nash, J.Constant, D.S.Hulme, J.Kirton and E.P.Raynes, "Liquid Crystals and Ordered Fluids", Vol.2, Eds. J.F.Johnson and R.S.Porter (Plenum Press: New York, London, 1973) p.617.

3 R.Eidenschink, D.Erdmann, J.Krause, L.Pohl, Angew. Chem. **90,** 133 (1978).

4 A.C.Griffin, R.F.Fisher, S.J.Havens, J.Am.Chem.Soc. **100,** 6329 (1978).

5 A. Gobl-Wunsch, G. Heppke and R. Hopf, Z.Naturforsch. **36a,** 213 (1981).

6 B.K.Sadashiva, G.S.R.Subba Rao, Current Science, 44, 222 (1975).

7 Nguyen Huu Tinh, C. Destrade, Mol. Cryst.Liq. Cryst.Lett. 92, 257 (1984).

8 P. G. de Gennes, "The Physics of Liquid Crystals", (Clarendon Press, Oxford, 1974).

9 Von W.Maier and G. Meier, Z.Naturforsch. **16a,** 1200 (1961).

10 N.E.Hill, W.E.Vaughan, A.H.Price, M.Davies, "Dielectric Properties and Molecular Behaviour" (Van Nostrand Reinhold Company: London, New York, Toronto, Melbourne, 1969).

11 C.J.F.Bottcher and P.Bordewijk, "Theory of Electric Polarization", Vol.II (Elsevier Scientific Publishing Company: Amsterdam, Oxford, New York, 1978).