CHAPTER III

STUDIES ON DIELECTRIC PERMITTIVITY OF LIQUID CRYSTALS AND THEIR ORDER PARAMETERS.

Introduction:-

Measurments of the anisotropy of dielectric permittivity of liquid crystals in mesophase provide, apart from being of practical importance, information on molecular properties and structure of these substances. The knowledge of dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ parallel and perpendicular to the long molecular axis helps us to select a liquid crystal for a specific electro-optical display device.

The dielectric anisotropy of nematic liquid crystals and the effects of electric and magnetic fields on dielectric properties have been the subject of many investigations. The principal dielectric constants for a series of alkoxy derivatives of azo and azoxy benzenes have been reported by Maier and Meier.[1] The dispersion over a range of microwave and audio frequencies has been studied by Maier and Saupe[2] and Axmann et al.[3,4] Car and his coworkers[5,6,7] have made an extensive study of molecular ordering due to electric and magnetic fields and also the dielectric loss.

The first theory relating the components of the dielectric permittivity tensor of ordered liquid crystal $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ to the dipole moment μ, mean polarizability $\bar{\alpha}$ and the polarzability anisotropy $\Delta\alpha$ of the molecules was developed by W.Maier and G. Meier.[8] They treated the liquid crystal to be a continuous isotropic medium. The local field inside the medium and the effective dipole moment was determined on the basis of Onsager[9] model of spherical cavity of a volume equal to the mean volume per single molecule in liquid crystal. The relevent equations connecting the dielectric permittivities with the order parameter according to Meier and Maier is given by.

$$\epsilon_{\parallel} = 1 + 4\pi N h F\left[\bar{\alpha} + \frac{2}{3}\Delta\alpha S + \frac{F\mu^2}{3kT}\left\{1-(1-3\cos^2\beta)\right\}S\right] \quad \cdots(1)$$

$$\epsilon_{\perp} = 1 + 4\pi N h F\left[\bar{\alpha} - \frac{1}{3}\Delta\alpha S + \frac{F\mu^2}{3kT}\left\{1+\frac{1}{2}(1-3\cos^2\beta)\right\}S\right] \quad \cdots(2)$$

$$\Delta\epsilon = 4\pi N h F\left[\Delta\alpha - \frac{F\mu^2}{2kT}(1-3\cos^2\beta)\right]S \quad \cdots(3)$$

N = The number of molecules/c.c.

h = $\frac{3\bar{\epsilon}}{2\bar{\epsilon}+1}$ cavity field factor.

F = $\frac{1}{1-\bar{\alpha} f}$ reaction field factor

f = $\frac{4\pi N(2\bar{\epsilon}+2)}{3(2\bar{\epsilon}+1)}$

μ = dipole moment of free molecule.

$\Delta\alpha$ = polarizability anisotropy.

$\Delta\epsilon$ = dielectric anisotropy.

β = angle formed by the permanent dipole moment of a molecule with the long axis.

S = The degree of orientational ordering of the long axis of the nematic molecules.

$\alpha_{\parallel}$ is the polarizability along the long axis of the molecule and $\alpha_{\perp}$ is the polarizability in the direction normal to the axis.

From the measurements of dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ parallel and perpendicular to the long axis of the molecule de Jue and Lathouwers[10] observed that in the case of liquid crystals with small dipole moment, the average dielectric constant $\bar{\epsilon}=\frac{1}{3}(\epsilon_{\parallel}+2\epsilon_{\perp})$ practically coincides with the dielectric constant ϵ_{iso} in the isotropic phase. This fact, they pointed out was an indicatio that Maier and Meier's, equations 1, 2 and 3 gives qualitatively the correct picture of dielectric properties of liquid crystals with small dipole moment. For lack of polarizability anisotropy and dipole moment, they could not evaluate the order parameter of the liquid crystals. The object of the present studies is to evaluate the order parameter S of liquid crystals of both strongl and weakly polar molucules from the measurements of dielectric anisotropy using Maier and Meier's equations and to compare these S values with those obtained from birefringences.

Experimental

The dielectric properties of the samples which were studied as follows:

PCH-3, PCH-5, PCH-7, D-302, D-402, D-501, D-55 bought from E Merck.

CPBB, CPPOB from Eastman Kodak.

E-4, E-5, E-7 from B.D.H. Chemicals.

Mixtures E-5 is composed of pentylcyanobiphinyl, 5-CB, 7-CB, 5-OCB, 7-OCB, 8-OCB, in the proportion of 45:24:10:9:12. The nemati range is - 8 degree C - 50 degree C.

The structural formulae and the nematic isotropic transitio temperatures of the other liquid crystals are given in chapter II

All the samples were used for the experiment without any further purification. The transition temperatures of these liquid crystals were checked under a hot stage polarizing microscope of [illegible] mettler.

Measurement of the dielectric permmittivity.

The static dielectric constants were measured at frequencies 1 kHz and 10 kHz using a GR - 1620 capacitance bridge.

A parallel plate capacitor with stainless steel electrodes of dimension 2 cm x 1 cm separated by a 1mm teflon spacer, served as the sample holder. The temperature of the sample was measured with a thermocouple. The thermocouple was mounted directly on one of the electrodes so that exact temperature of the electrodes can be obtained. A magnetic field of 10 K gauss was used to align the liquid crystal molecules parallel and perpendicular to the electrode surfaces. The temperature of the sample holder was maintained constant within 0.2 degree C by means of a thermostat.

The cell was calibrated using freshly distilled toluene and chlorobenzene and the values agree to 0.1% of the standard value.[11] The resistivities of the samples were above 10^{10} Ohms cm. Dispersion was not observed for any of the samples at 10 kHz.

All the measurements of dielectric permittivities were carried out while cooling the liquid crystal. This process helps in the alignment of the samples also the compounds C P B B and C P P O B being monotropic the anisotropic property could be observed only while slow cooling from isotropic state.

Results and Discussions

The experimental values of the dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ of the liquid crystals studied in the nematic state and ϵ_{iso} in the isotropic phase are given in the Tables. 3.1(a) to 3.1(l). The values of the average dielectric constant $\bar{\epsilon} = \frac{1}{3}(\epsilon_{\parallel} + 2\epsilon_{\perp})$ are also included in these tables. Variation of the dielectric anisotropy with temperature is shown in the figures 3.1 (a) - 3.1(l).

The values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ obtained in this study for phenyl cyclohexanes are found to be in fair agreement with those obtained by Pohl et al.[12] Also the dielectric anisotropy of E - 7 nematic mixture given by Raynes[13] is similar to the values of the present investigation.

From the Figures 3.1 (a) to 3.1(c) and 3.1 (h) to 3.1(l) it can be seen that the average dielectric constant $\bar{\epsilon}$ is always less than the dielectric constant ϵ^{*}_{iso} at $T < T_{NI}$ extrapolated in the nematic range from $T \geq T_{NI}$ in all the PCH liquid crystals, mixtures E-4, E-5, E-7 and the cyanophenyl benzoates. These results are in agreement with the dielectric permittivities reported earlier for alkyl cyanobiphenyl, P aminobenzonitriles[14] and some other liquid crystals[15] which have got strong dipole moment.

The suggestion for the higher value of the dielectric constant at the nematic isotropic transition given by Schadt is due to a second order flexo electric effect. However the

Table 3.1 (a)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$, and ϵ_{iso} at nematic and isotropic phases for FCH - 3.

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ_{iso}	$\bar{\epsilon}$
43	16.58	6.90		10.1266
43.5	16.21	7.02		10.0833
44	15.98	7.06		10.033
44.5	15.74	7.25		10.08
45	15.51	7.49		10.1633
46			10.62	
47			10.65	
49			10.71	

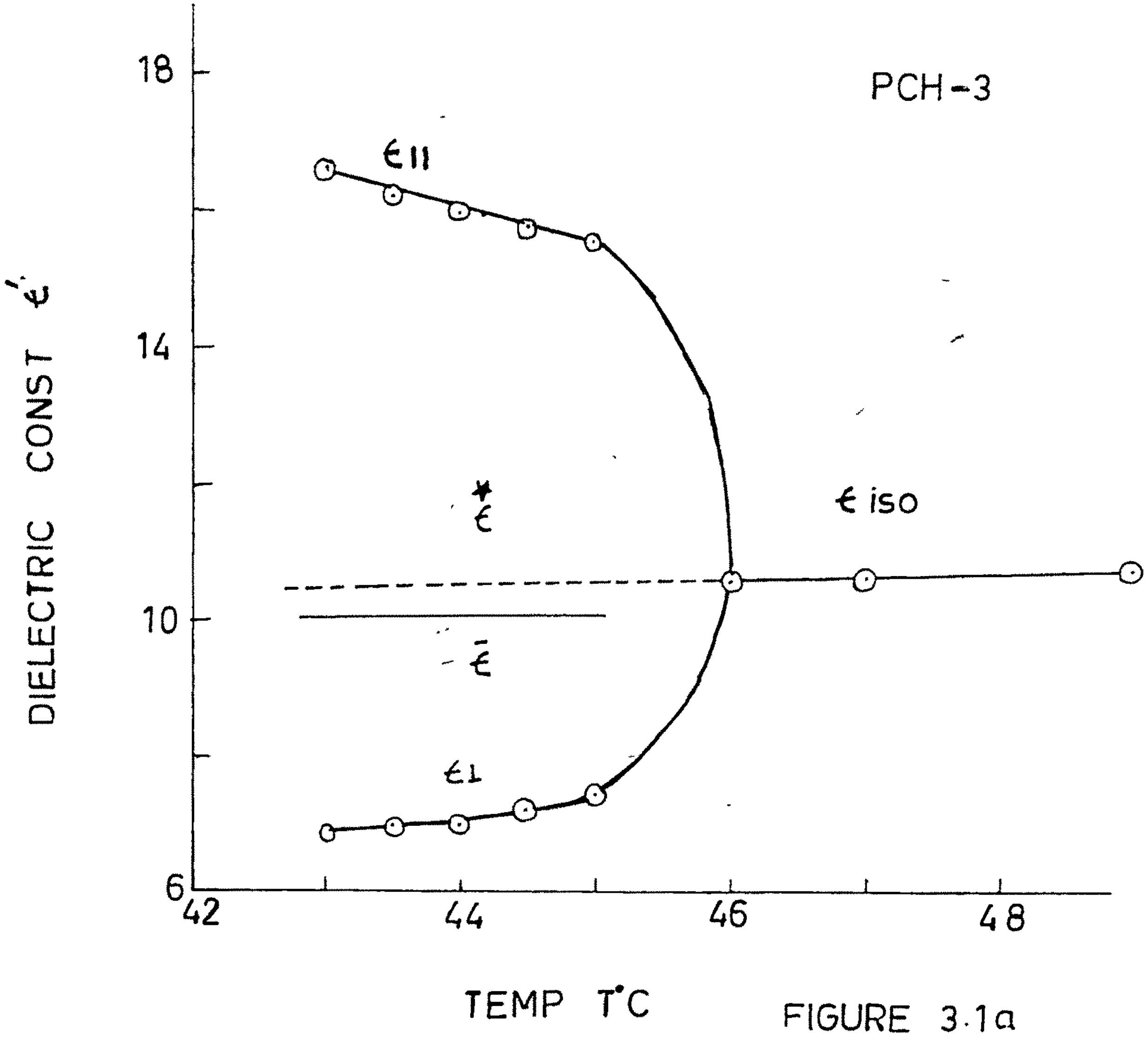

PCH-3
ϵ॥
ϵ^*
$\bar{\epsilon}$
ϵ⊥
ϵ iso
18
14
10
6
42
44
46
48
DIELECTRIC CONST ϵ'
TEMP T°C

FIGURE 3.1a

Table 3.1 (b)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for FCH - 5

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
33	14.74	4.81		8.12
35	14.51	4.97		8.15
39	14.38	5.20		8.26
43	14.23	5.40		8.34
48	13.92	5.69		8.43
52	13.32	6.08		8.49
56 iso			8.93	
58			9.02	
60			9.06	

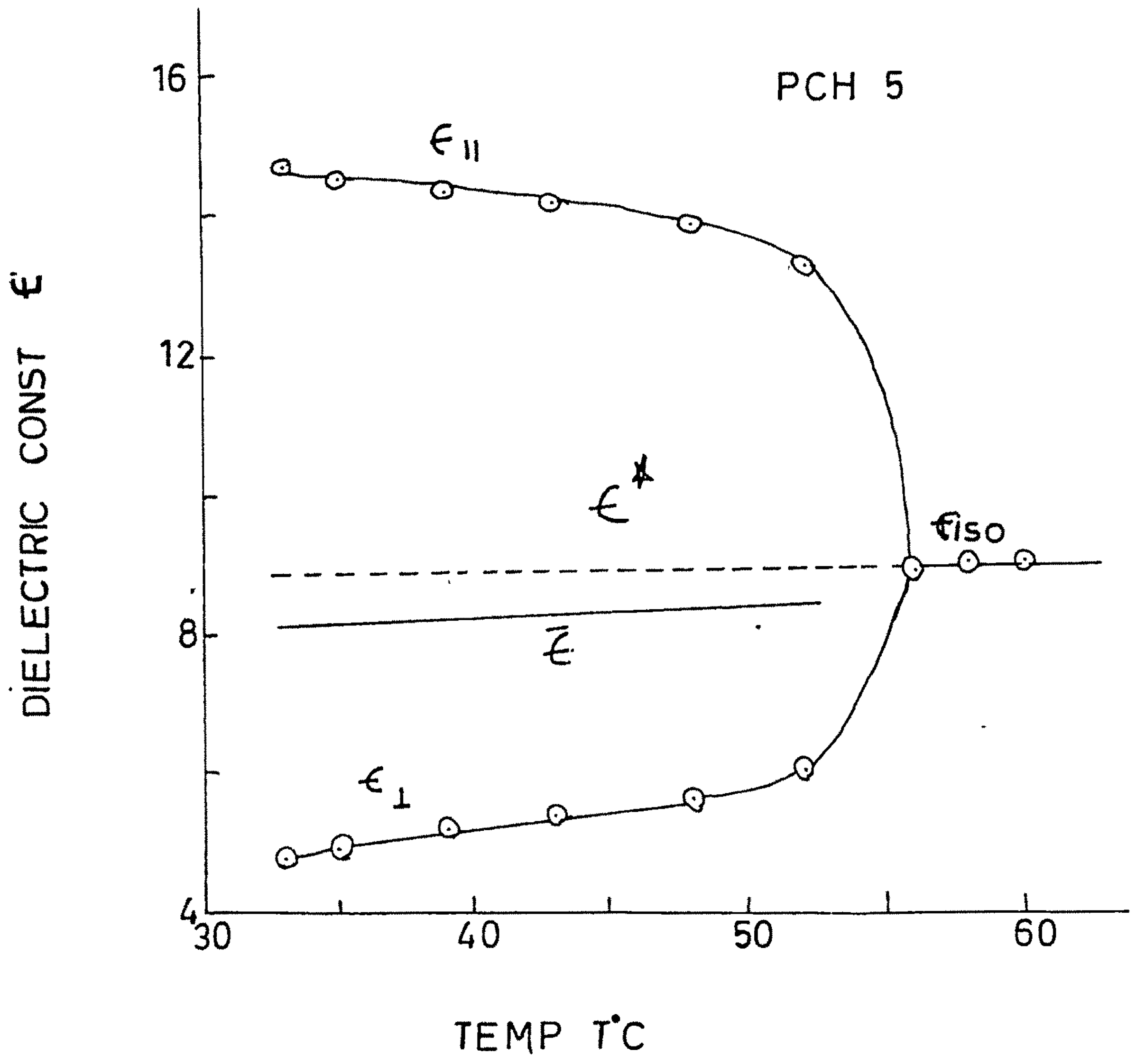

PCH 5
$\epsilon_{\parallel}$
ϵ^{*}
ϵ_{iso}
$\bar{\epsilon}$
$\epsilon_{\perp}$
DIELECTRIC CONST ϵ
16
12
8
4
30
40
50
60
TEMP T°C

fig. 3.1 b

Table 3.1 (c)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for FCH-7.

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
31	12.85	4.18		7.07
35	12.63	4.30		7.0766
39	12.53	4.41		7.1666
43	12.37	4.53		7.1433
48	12.21	4.80		7.27
52	12.03	5.11		7.4166
56	11.74	5.71		7.72
59			8.69	
61			8.76	
63			8.82	

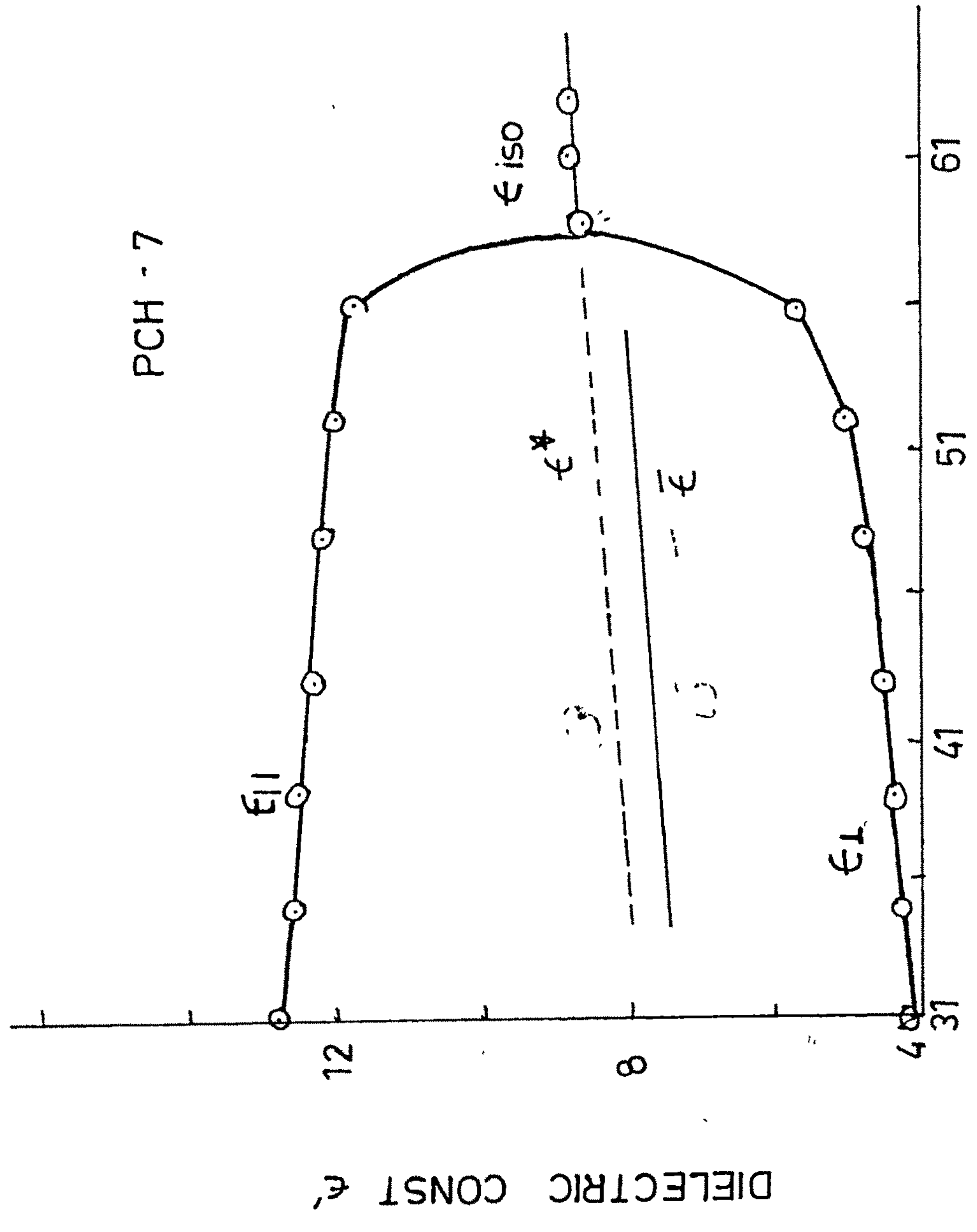


fig. 3·1c

Table 3.1 (d)

Temperature variation of $\epsilon_{\parallel}, \epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for D 302.

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
51	3.282	4.545		4.1236
54.5	3.280	4.515		4.1033
60	3.295	4.473		4.0805
66	3.302	4.416		4.0445
72	3.337	4.261		3.9532
77	3.357	4.190		3.9121
80	3.467	4.048		3.85
84.5			3.852	
88			3.831	
90			3.821	

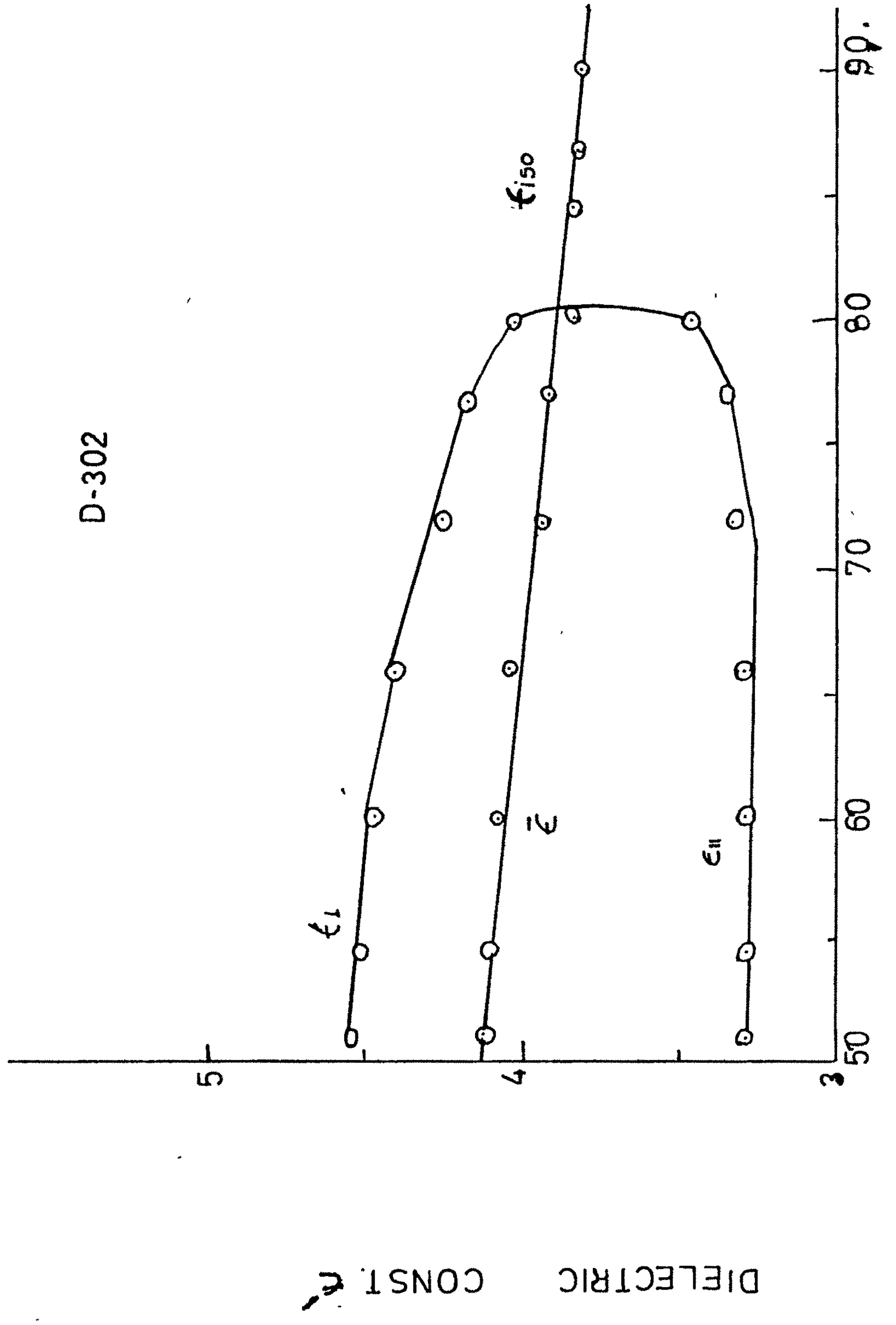

D-302
$\epsilon_\perp$
$\bar{\epsilon}$
$\epsilon_\parallel$
ϵ_{iso}
5
4
3
50
60
70
80
90
TEMP T°C
DIELECTRIC CONST. ε

fig. 3·1d

Table 3.1 (c)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for D402.

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
40	3.2720	4.4947		4.0871
52	3.2355	4.3607		3.9856
59.5	3.2483	4.2246		3.8992
69	3.3229	4.0941		3.8370
73	3.3572	4.0179		3.7977
77			3.7435	
80			3.7143	
85			3.6798	
88			3.6548	

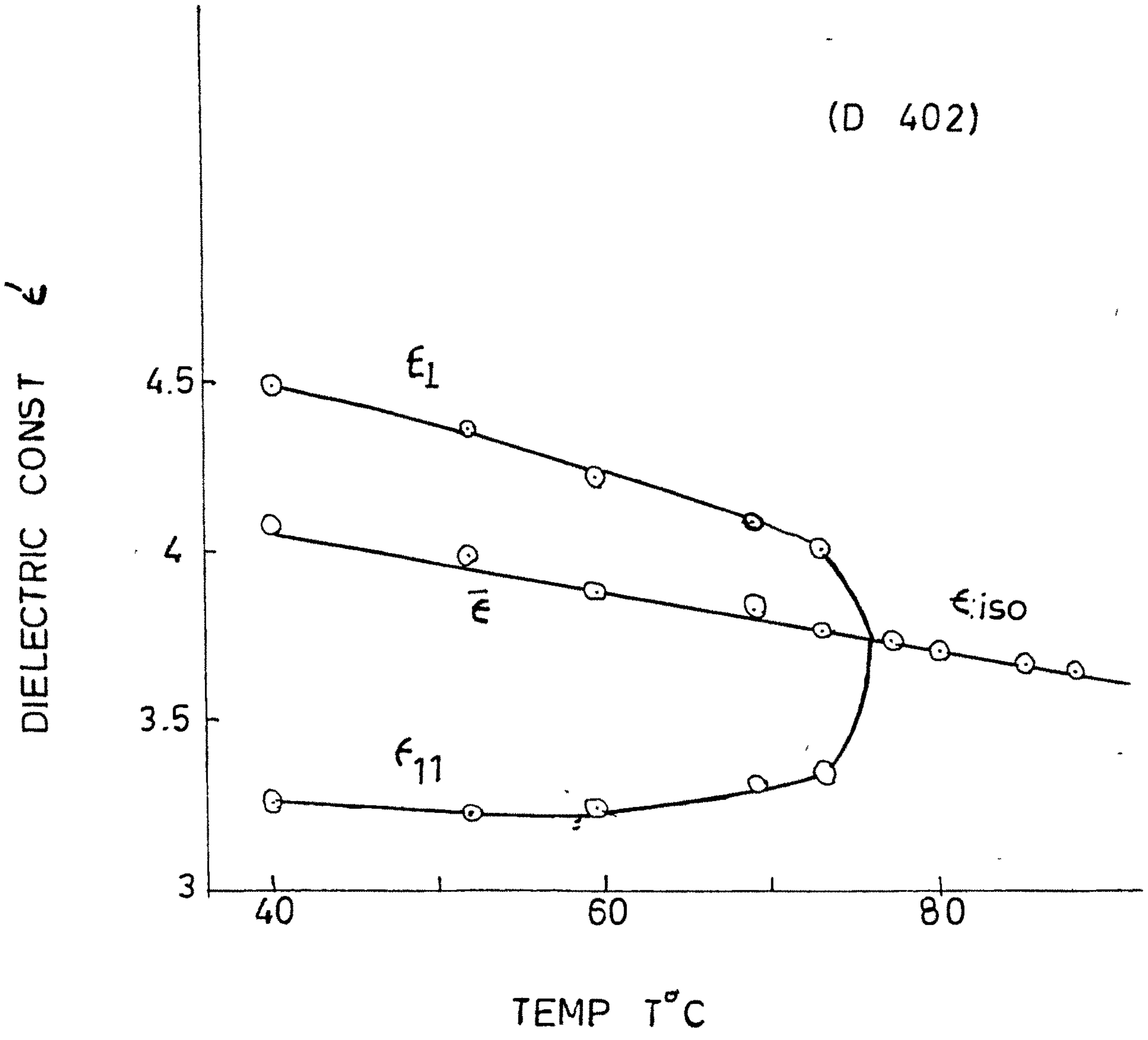

(D 402)
DIELECTRIC CONST ϵ'
4.5
4
3.5
3
40
60
80
TEMP T°C
ϵ_1
$\bar{\epsilon}$
ϵ_{11}
ϵ_{iso}

fig. 3·1e

Table 3.1 (f)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for D-501.

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
43	3.4125	4.4595		4.1105
47	3.3583	4.4137		4.0619
51	3.3685	4.2837		3.9786
55	3.3182	4.2423		3.9343
60.5	3.3372	4.1875		3.9041
65	3.3560	4.1244		3.8682
70	3.4083	3.9952		3.7996
74			3.8101	
76			3.7936	
78			3.7727	
80			3.7563	
85			3.7110	

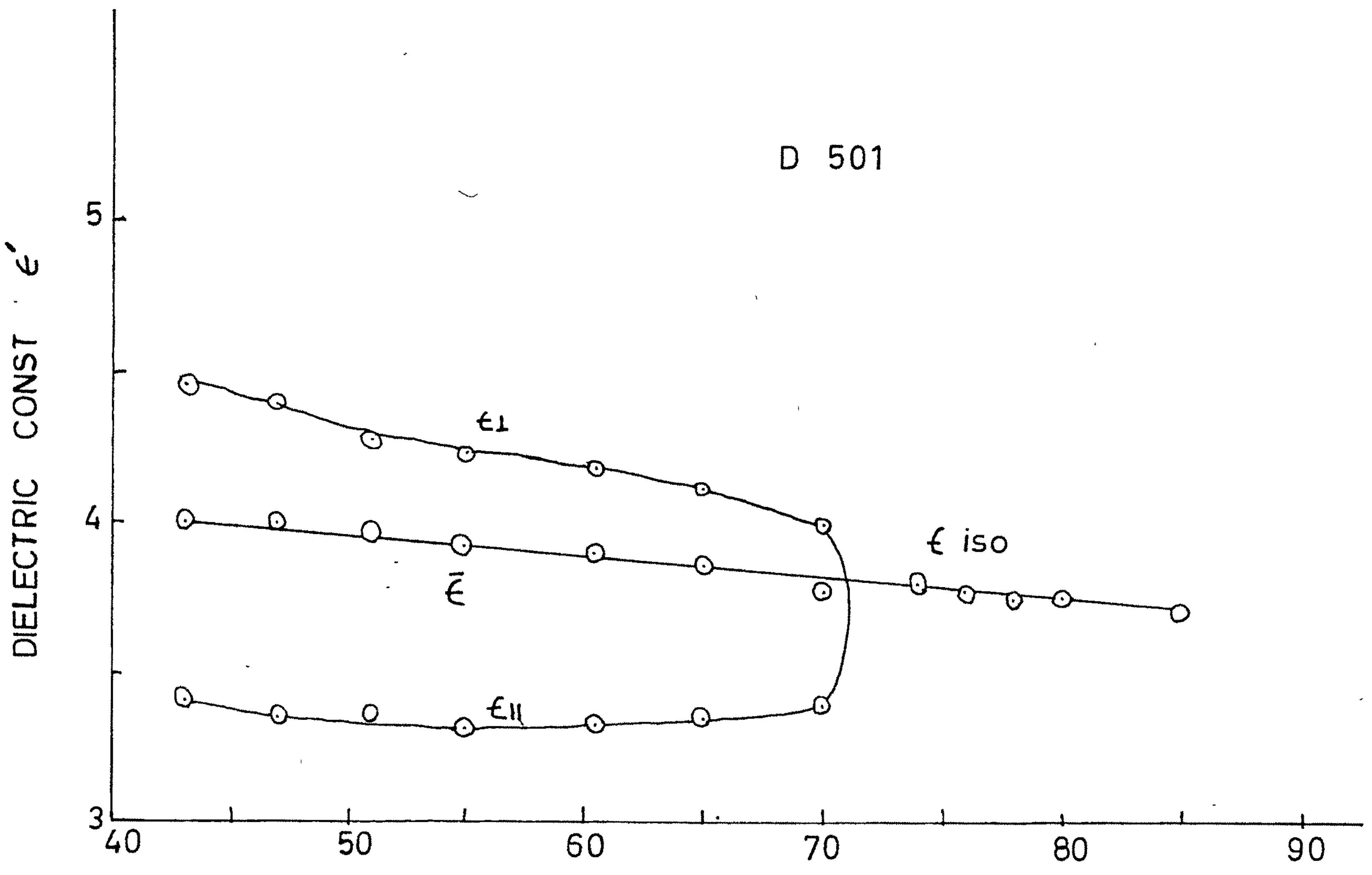

D 501
DIELECTRIC CONST ε'
5
4
3
40
50
60
70
80
90
TEMP T°C
ε⊥
$\bar{\epsilon}$
ε∥
ε iso

fig. 3·14.

Table 3.1 (g)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for D55

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
37.5	2.940	3.419		3.259
40	2.958	3.396		3.25
42	2.958	3.382		3.240
44	2.984	3.351		3.229
46	2.997	3.313		3.208
50			3.226	
52			3.217	
54			3.208	

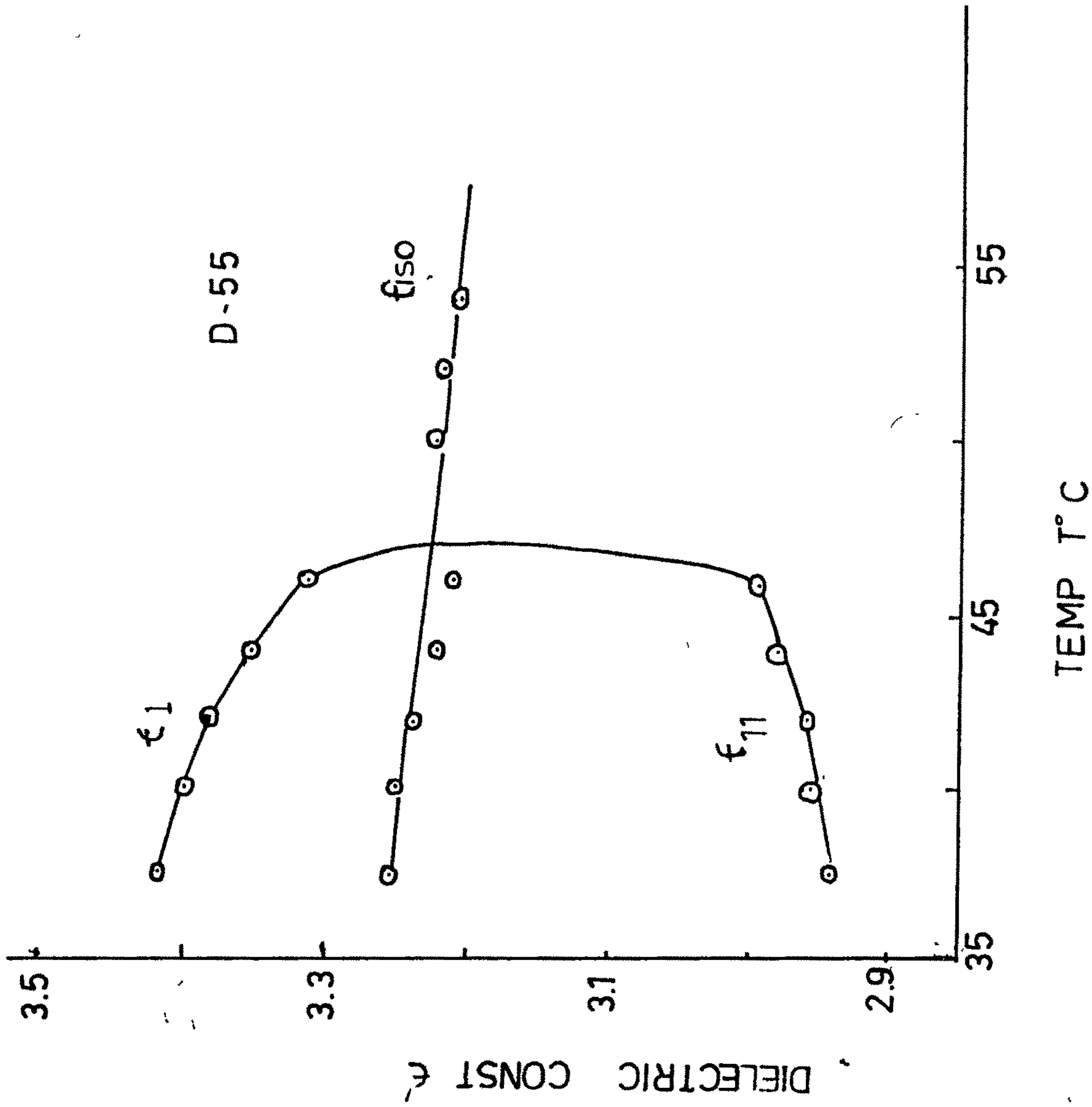

D-55
ϵ_{iso}
ϵ_1
ϵ_{11}
3.5
3.3
3.1
2.9
35
45
55
TEMP T°C
DIELECTRIC CONST ϵ

fig3ig

Table 3.1 (b)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for CPBB

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
62			12.234	
56			12.398	
52			12.540	
49			12.561	
46			12.582	
43			12.512	
42.	17.933	8.434		11.6003
40.	19.947	8.048		12.0143
38	20.689	7.743		12.0583
36.5	21.035	7.680		12.1317
35	21.552	7.594		18.8957
34	21.547	7.427		12.1337

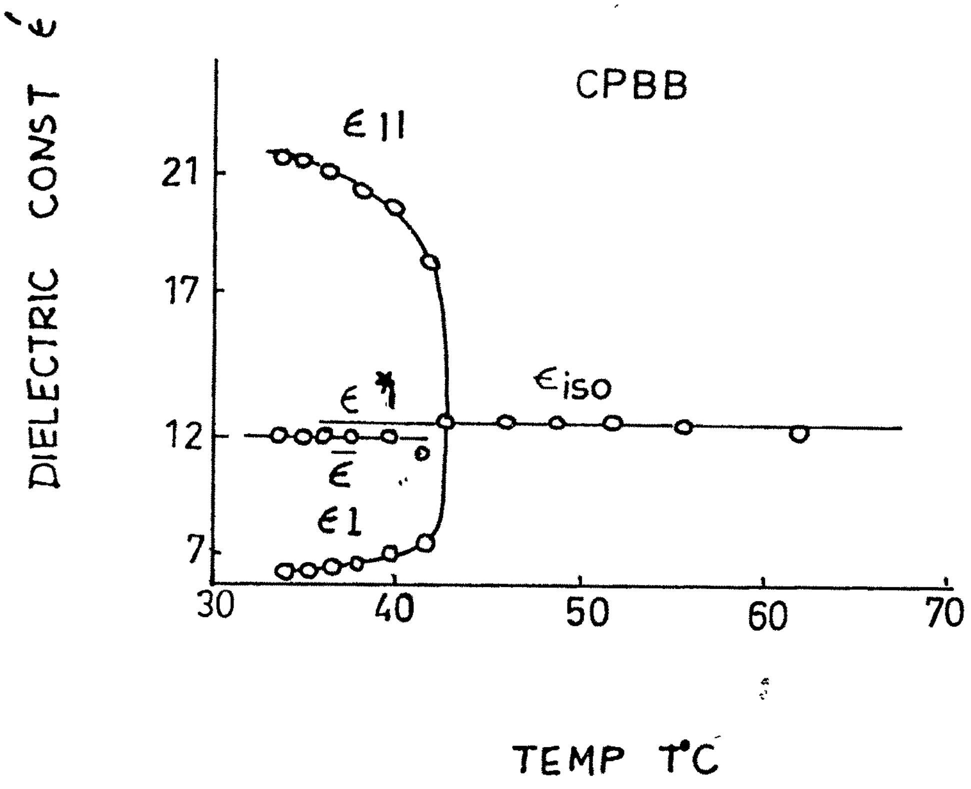

CPBB
ε ||
ε *
ε iso
ε̄
ε ⊥
DIELECTRIC CONST ε'
21
17
12
7
30
40
50
60
70
TEMP T°C

fig 3·1h

Table 3.1 (i)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for CPFOB.

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
93			8.843	
90			8.897	
87			9.100	
85			9.150	
82.5			9.168	
80			9.088	
77.5	13.319	6.692		8.901
75.5	13.961	6.410		8.927
73	14.536	6.215		8.9887
70.5	14.964	6.053		9.0233
67.5	15.344	5.811		8.9887

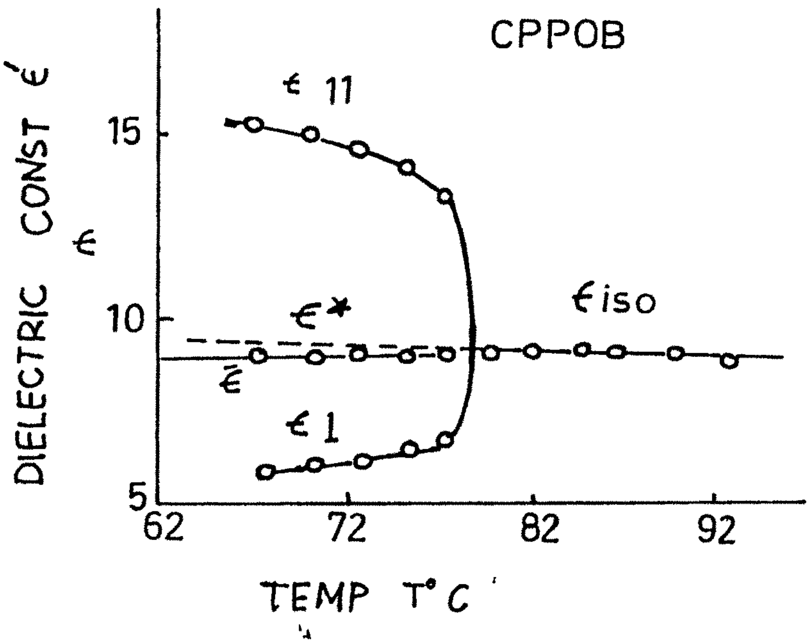

CPPOB
DIELECTRIC CONST ε′
ε
ε 11
εiso
ε*
ε̄
ε 1
5
10
15
62
72
82
92
TEMP T°C

fig 3·1(i)

Table 3.1 (j)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for E4

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
29	17.8666	5.7077		9.7607
35	17.7035	5.8244		9.7841
40	17.4898	5.9470		9.7946
45	17.0416	6.1375		9.7722
50	16.5517	6.4541		9.8200
55	15.2750	6.8952		9.6885
62.5			10.3517	
64			10.4011	
65			10.3517	
70			10.2922	
75			10.1196	

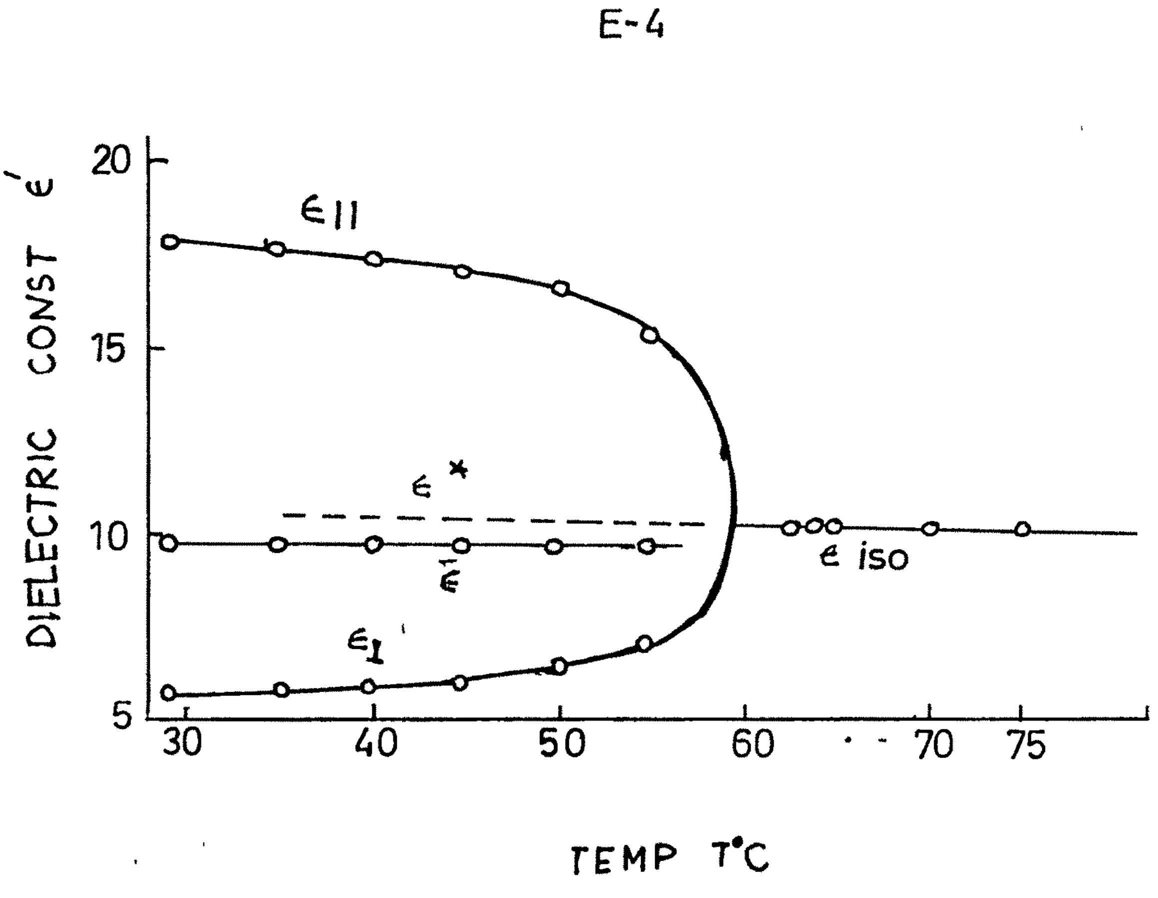

E-4
DIELECTRIC CONST ε'
20
15
10
5
ε∥
ε*
ε'
ε iso
ε⊥
30
40
50
60
70
75
TEMP T°C

fig 3-1j

Table 3.1 (k)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for E5.

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
31	19.5601	6.3904		10.7803
35	19.1767	6.5300		10.7589
38	18.9017	6.6940		10.7632
41	18.4750	6.9244		10.7746
44	17.9964	7.1928		10.794
47	17.2702	7.5869		10.8147
51			11.1553	
55			11.1970	
60			11.1851	
65			11.1591	
68			11.1100	

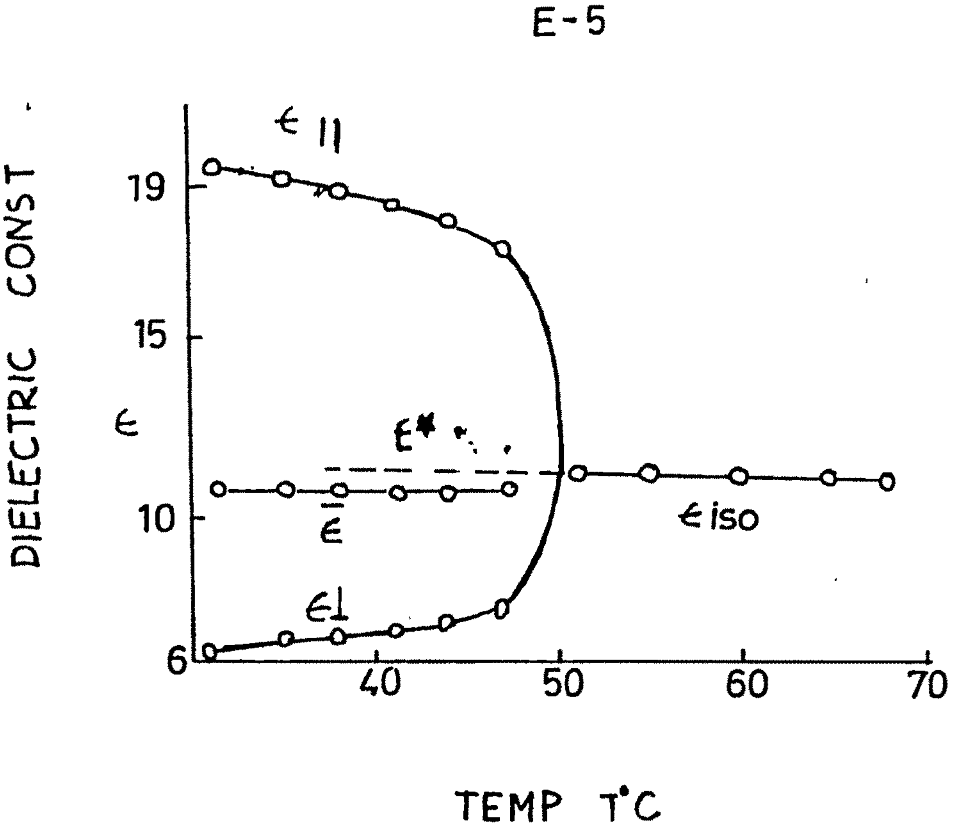


fig 3-1k

Table 3.1 (1)

Temperature variation of $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\bar{\epsilon}$ and ϵ iso at nematic and isotropic phases for E-7

Temp degree C	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ iso	$\bar{\epsilon}$
24	19.5836	5.5488		10.2271
30	19.0425	5.6892		10.1403
35	18.6773	5.8089		10.0984
40	18.2208	6.0050		10.0769
45	17.7369	6.2080		10.0510
50	17.0601	6.5491		10.0528
55	16.1613	7.2163		10.1980
60			10.5802	
62			10.6150	
65			10.5553	
70			10.4952	
76			10.3511	

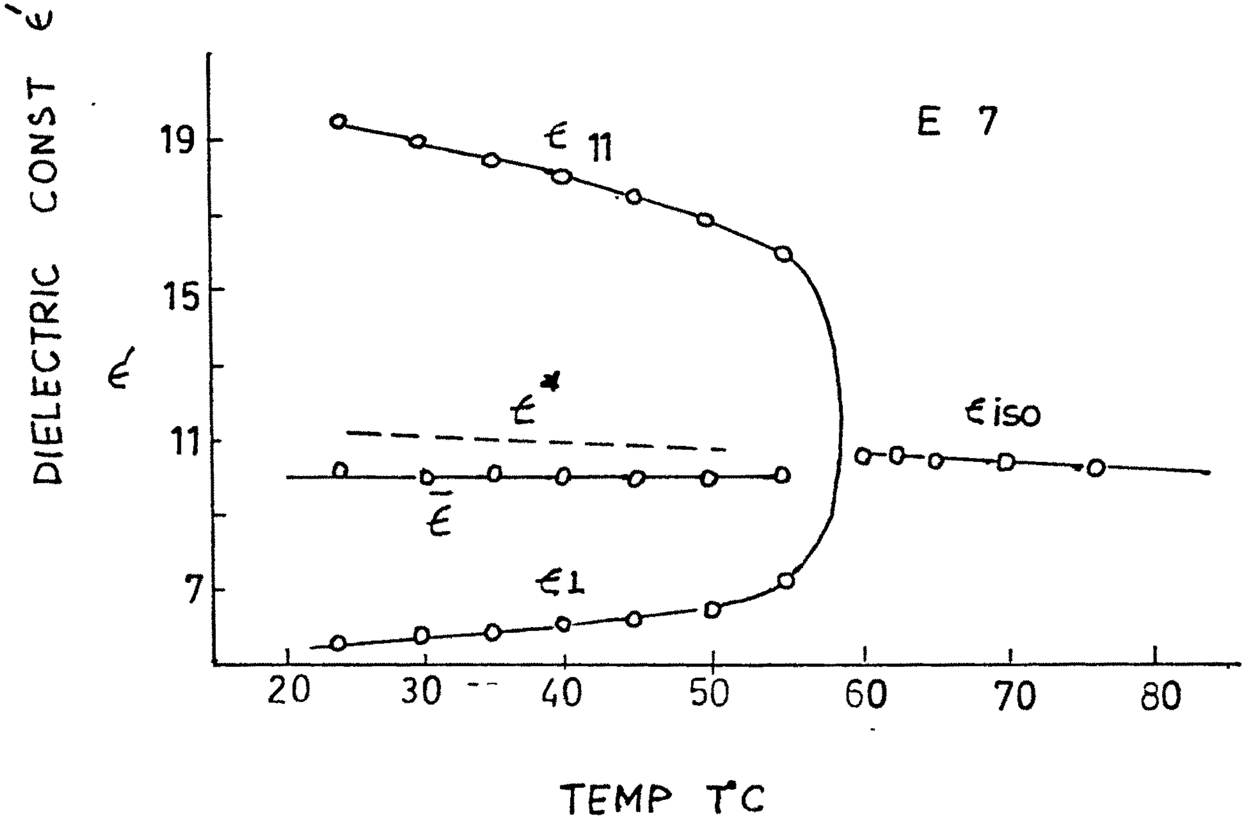
E 7
DIELECTRIC CONST ε'
ε
19
15
11
7
ε 11
ε*
$\bar{\varepsilon}$
ε⊥
εiso
20
30
40
50
60
70
80
TEMP T°C

fig 3.1 l

explanation given by Madhusudana and Chandrasekhar[16] is that the increase in the dielectric constant of the isotropic phase arises from the decrease in the antiferroelectric short range order at T_{NI}.

For liquid crystals having small and zero dipole moment it was shown by de Jeu et al[10] that $\bar{\epsilon}$ coincides with the dielectric constant ϵ_{iso} at the clearing temperature. From figures 3,1 d to 3.1 g it can be noted that the average dielectric constants in the nematic phase for the alkyl/alkoxy phenylcyclohexane carbonxylate liquid crystals practically coincide with the dielectric constants in the isotropic phase. These smaples have a small dipole moment.

The dipole moments μ of the liquid crystals were determined in dilute solution of benzene and are included in the Tables 3.2.

$$\mu^2 = \frac{9kT}{4\pi\mathcal{N}} \frac{(\epsilon_0 - \epsilon_\alpha)(2\epsilon_0 + \epsilon_\alpha)}{\epsilon_0(\epsilon_\alpha + 2)^2}$$

0.1 cc of sample was mixed with 0.9 cc of benzene. The refractiv index of the solution n_d was observed, $\epsilon_\alpha = n_d^2$

The dielectric permittivity of the solution ϵ_0 was also found. is the temperature of the solution given in kelvin, k is th Boltzmann's constant.

$\mathcal{N}$ is the number of molecules per cc of the solution = $\frac{N}{M}\rho$

N=Avogadro's number. ρ is the density of the sample at th particular temperature.

The order parameter was calculated using the Maier ar Meier's formula given by the equation (3). The angle β betwe the resultant moment and the long axis of the molecules of the liquid crystals for alkyl cyanophenyles were negligible. Also the β value for the mixtures E-4 and E-7 containing 55 to 70% of P - alkyl cyanobiphenyl were very small and assumed to be zero. In case of samples D - 302, D - 402, D - 501 and D - 55 the β value was calculated from the alkoxy group moment and ester group moment reported in the literature.[17] The angle β for CPBB and CPPOB was estimated from the P - heptyl P cyanobiphenyl $\mu_D = 4.55$ and ester group moment of $\mu_D = 1.7$ making an angle of 66 degree with the paraaxis. The value of the angle β for each sample is included in the tables 3.2.

For the samples PCH-3, PCH-5, PCH-7, CPBB, CPPOB, E-4, E-7 we find from the Tables 3.2 (a, b,c,h,i,j and k) that the values of the order parameters calculated from experimental results o dielectric anisotropy $\Delta\epsilon$ using Maier and Meier's equation (3 comes out to be much less than that obtained from birefringence o other

methods. Similar results were reported earlier in the case of cyanobiphenyls and cyanophenyl heptyl benzoate.[18]

Thus the results show that Maier and Meier's theory fo dielectric constants in anisotropic media of strongly pola molecules fails to give consistent results with the experimenta values. This is due to the fact that only long range order wa considered in Maier and Meier's theory, existance of short rang

TABLE 3.2 (a)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter S for FCH-3.

T C.	$\Delta\epsilon$	S from ref.ind.	S from $\Delta\epsilon$
43	9.68	.61	.20
43.5	9.19	.60	.19
44	8.92	.58	.18
44.5	8.49	.57	.18
45	8.02	.55	.17

$\mu_D = 4.27$ $\beta \sim 0^\circ$

TABLE 3.2 (b)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter S for FCH - 5.

T C.	$\Delta\epsilon$	S from ref.ind.	S from $\Delta\epsilon$
33	9.93	.65	.32
35	9.54	.63	.31
39	9.18	.61	.30
43	8.83	.56	.29
48	8.23		
52	7.24		

$\mu_D = 4.27$ $\beta \sim 0^\circ$

TABLE 3.2 (c)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter S for PCH - 7.

T C.	$\Delta\epsilon$	S from ref.ind	S from
31	8.67	.58	.31
35	8.33	.55	.30
39	8.12	.50	.29
43	7.84	.49	.29
48	7.41		
52	6.92		
56	6.03		

$\mu_D = 4.39$ $\beta \sim 0^\circ$

TABLE 3.2 (d)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter S for D - 302

T C.	$\Delta\epsilon$	S from ref.ind.	S from $\Delta\epsilon$
51	-1.2631	.75	.69
54.5	-1.2352	.72	.68
60	-1.1780	.71	.67
66	-1.1131	.66	.64
72	-0.9244	.60	.55
77	-0.8333	.53	.50
80	-0.5809		

$\mu_D = 2.17$ $\beta \sim 72^\circ$

TABLE 3.2 (e)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter S for D - 402

T°C.	$\Delta\epsilon$	S from ref.ind.	S from $\Delta\epsilon$
40	-1.2227	.73	.74
52	-1.1252	.67	.72
59.5	-0.9763	.62	.64
69	-0.7711	.53	.53
73	-0.6607	.46	.46

$\mu_D = 2.08$ $\beta \sim 72^\circ$

TABLE 3.2 (f)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter S for D - 501

T°C.	$\Delta\epsilon$	S from ref.ind.	S from $\Delta\epsilon$
43	-1.13	.73	.73
47	-1.088	.72	.72
51	-1.01	.71	.68
55	-0.9241	.68	.64
60.5	-0.8503	.63	.60
65	-0.7684	.59	.55
70	-0.5869	.49	.43

$\mu_D = 2.23$ $\beta \sim 68^\circ$

TABLE 3.2 (g)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter S for D - 55

T°C.	$\Delta\epsilon$	S from ref.ind.	S from $\Delta\epsilon$
37.5	-0.479	.67	061
40	-0.438	.65	.57
42	-0.424	.61	.55
44	-0.367	.53	.47
46	-0.317		

$\mu_D = 1.99$ $\beta \sim 66^\circ$

TABLE 3.2 (h)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter S for CPBB.

T°C.	$\Delta\epsilon$	S from ref.ind.	S from $\Delta\epsilon$
42	9.499		
40	11.899	.52	.32
38	12.946	.56	.34
36.5	13.354	.59	.35
35	13.959	.61	
34	14.120		

$\mu_D = 5.1$ $\beta \sim 25^\circ$

TABLE 3.2 (i)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter for CFFOB.

T °C.	$\Delta\epsilon$	S from ref.ind.	S from $\Delta\epsilon$
77.5	6.627		
75.5	7.551		
73	8.321	.49	.28
70.5	8.911	.52	.30
67.5	9.533	.56	.32

$\mu_D = 5.59$ $\beta \sim 30$ degree.

TABLE 3.2 (i)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter S for E - 4.

T °C.	$\Delta\epsilon$	S from ref.ind.	S from $\Delta\epsilon$
29	12.1589		
35	11.8791	.65	.23
40	11.5428	.63	.23
45.	10.9041	.60	.22
50	10.0976	.57	.21
55	8.3798	.52	.18

$\mu_D = 5.1$ $\beta \sim 0$ degree.

TABLE 3.2 (ii)

Temperature variation of the Dielectric anisotropy $\Delta\epsilon$ and order parameter S for E - 7.

T °C.	$\Delta\epsilon$	S from ref.ind.	S from $\Delta\epsilon$
24	10.2270	.72	.16
30	10.1403	.69	.15
35	10.0983		
40	10.0769		
45	10.0509	.60	.14
50	10.0527		
55	10.1979		

$\mu_D = 4.5$ $\beta \sim 0°$

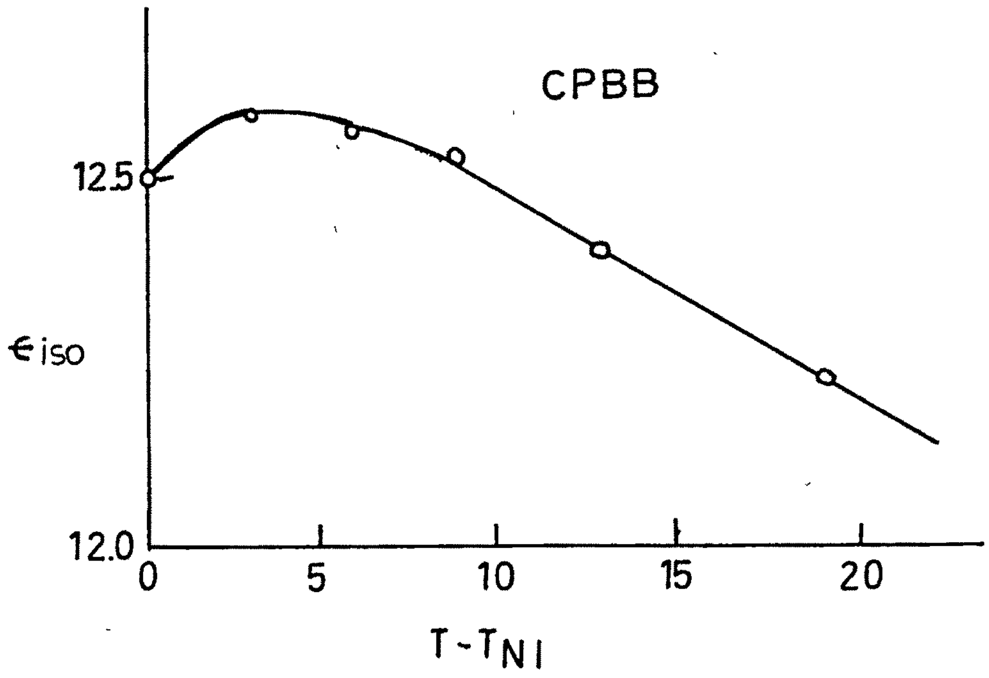
order was completely ignored. Madhusudan in his theory proposed the existance of antiferro electric short range order in nematic phase of strongly polar molecules. Such short range antiparallel ordering in strongly polar nematic liquid crystals might cause a large decrease in $\epsilon_{\parallel}$ resulting in a decrease in the dielectric anisotropy $\Delta\epsilon$ and thus a decrease in the order parameter.

From the tables 3.2 (d, e, f, g) it can be seen that the values of the order parameter calculated from the values of the dielectric anisotropy $\Delta\epsilon$ polarizability anisotropy $\Delta\alpha$ and dipole moment μ using the Maier and Meier equation for the alkoxyphenyl trans - 4′ alkylcyclohexane carboxylates, compare very well at all temperatures with those obtained from refractive index methods. Similarly for alkylphenyl trans - 4′ alkylcyclohexane carboxylates the order parameter S from the Maier and Meier equation also agree well with those obtained from the refractive index methods though the former values are only slightly less than the latter. The slight discrepancy may be due to the estimation of the angle β made by the resultant moment with the long axis of the molecule So, it appears that for liquid crystals having dipole moment of about 3D or so the Maier and Meier equation with dielectric anisotropy provides another method for the determination of the order parameter.

The decrease in $\epsilon_{\parallel}$ as proposed by Madhusudan and Chandrasekhar due to short range antiferoelectric dipole corelation of the permanent dipole moment in less polar nematic might not affect the dielectric anisotropy and hence the order parameter very effectively.

It is now well known that at the nematic isotropic phase transition the long range nematic ordering vanishes, but short range ordering still persists well into isotropic phase influencing some physical properties such as magnetic birefriengence, Kerr constant, light scattering, dielectric permittivety etc. just near the transition temperature. We have observed such pretransitional effect in dielectric permittivity of two monotropic liquid crystals CPBB and CPPOB and three thermotrophic liquid crystals E-4, E-5 and E-7.

The pretransitional effects in dielectric permittivity in the liquid crystals are shown in Fgure 3.3 (a-l). When temperature dependance of dielectric permittivity ϵ_{iso} over wide range of temperature is illustrated. It can be clearly seen that there is peak in ϵ_{iso} value a little above the transition temperature T_{NI}. Similar pretransitional effects in dielectric constant in nematics with Cyano end groups were reported by Bradhaw, and Raynes[20] and Thoen J and Menu[21] G. Normally the ϵ_{iso} should monotonically increase with decrease of temperature in proportion to μ^2/kT upto the transition temperature T_{NI}. But instead, a maximum in ϵ_{iso} is observed a little above T_{NI} and then decreases as T_{NI} is approached. The reduced contribution to dielectric permittivity ϵ_{iso} from dipole moment μ is attributed to apparent reduction in μ value due[22] to the formation of dimers in anti



fig,3-3 a

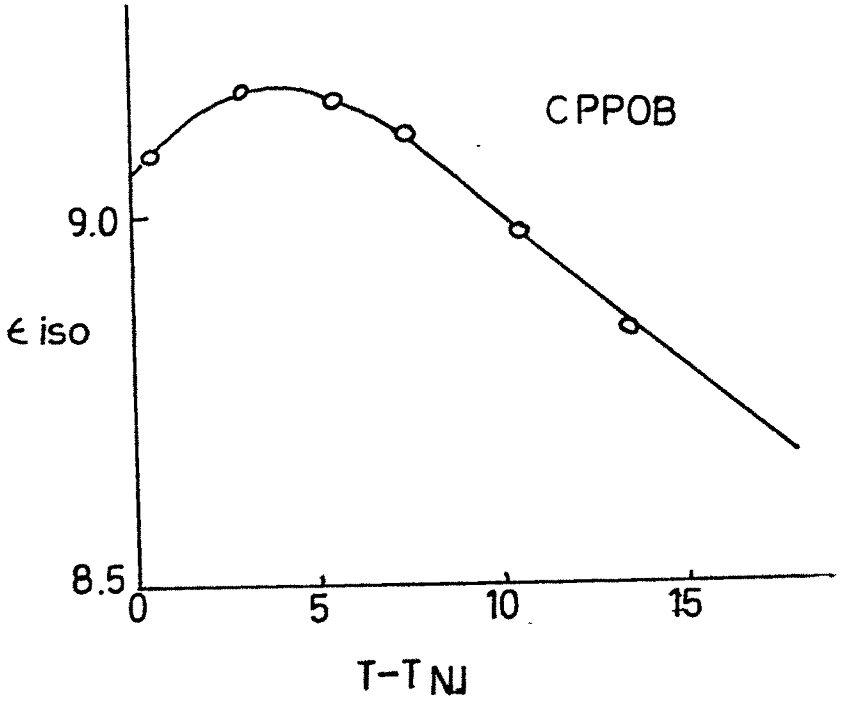


fig. 3.3 b

E 4

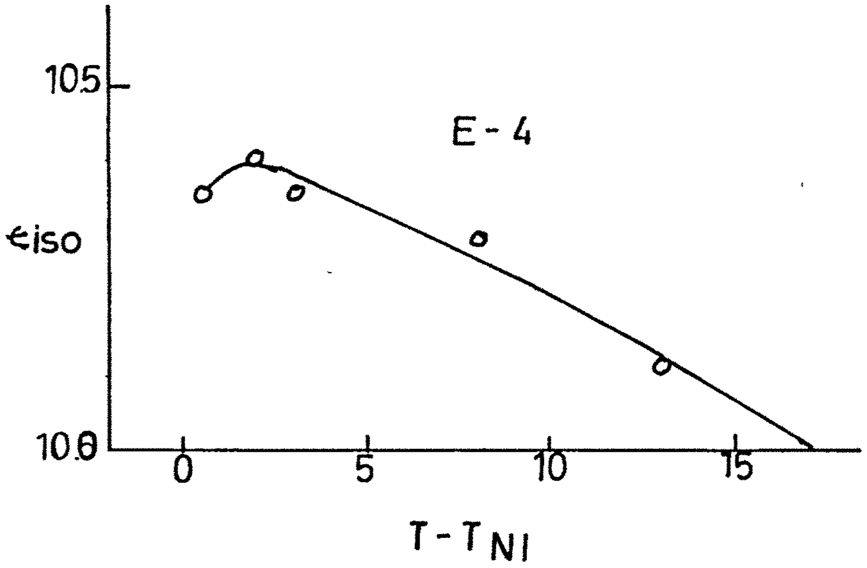


fig 3·3c

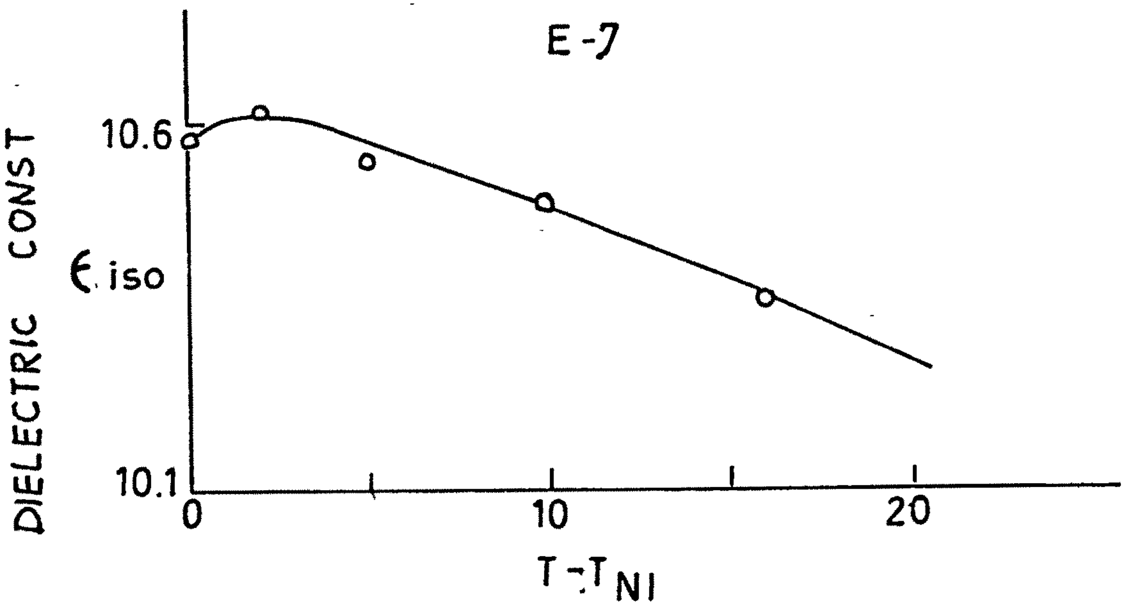


fig 3-3d

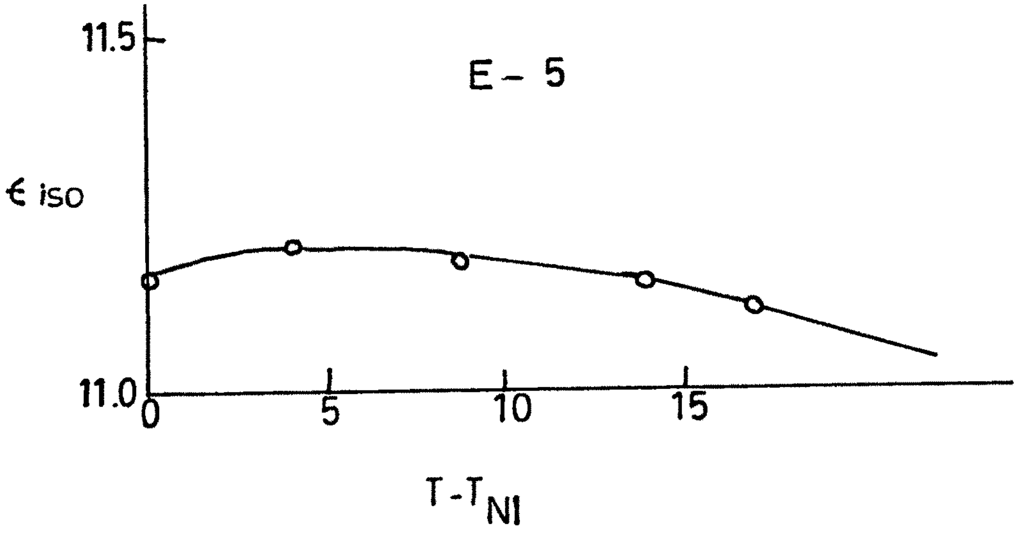


Fig 3·3e

parallel local ordering. The pretransitional ϵ_{iso} near T_{NI} showing a maximum may be due to appreciable concentration of dimers in a dynamic monomer dimer equilibrium[23].

REFERENCES.

1. Maier, W. and Meier, G., Z Naturforsch 16 A 470 (1961), 16 A, 1200 (1961) 16 A, 262 (1961)

2. Meier, G. and Saupe, A. Mol. Cryst., 1, 4 (1966)

3. Weise, H. and Axmann, A. Z. Naturforsch 21 A, 1316 (1966).

4. Axmann A. Mol. Cryst. 3, 471 (1968).

5. Carr., E.F., Hoar, E.A. and Mac Donald. W.J. Bull Amer. Phys. Soc. 13, 222 (1968).

6. Carr, E.G. in Ordered Fluids and Liquid Crystals. Advances in Chemistry series No. 63 American Chemical Society Washington D.C. (1967) Chapter 8.

7. Carr, E.F. Mol. Cryst. Liq. Cryst. 7, 253, (1969).

8. Maier, W. Meier, G. Z Naturforsch. 16 a, 26 (1960).

9. Onsager, J. Amer. Chem Soc. 58, 1486 (1936).

10 De Jeu, W.H. and Lathouwers, Th, W Z Naturforsch 29 a, 905 (1974) 30 a, 79 (1975).

11 C.D. Hodgman, R.c. Weast, R.S. Shanklend, and S.M. Selby, "Hand Book of Chemistry and Physics". The Chemical Rubber Publishing Co. Cleveland. Ohio (1962).

12 Pohl, L. Eidenschink, R, Krause, G. and Erdnann, D. Physics Letts. 60 A, 421 (1977).

13 Raynes, E.P. M.C.L.C. 56, 63 (1979).

14 Schadt, M. J. Chem. Phys. 56, 1994 (1972)

15 Ratna, B.R and Sashidhar, R. Pramana, 6, 278 (1976).

16 Madhusudana, N.V. and Chandrasekhar, S. Pramana Suppl. no. 1, 57 (1975).

17 Minkin, V.I. Osipov, O.A and Zhadanov Y.A. "Dipole moments in Organic Chemistry" Plenum Press, N.Y. London p91 (1970).

18 Sen, S. Brahma, P. Roy S.K. and Roy, S.B. Acta Phys. Polonica.

19 Madhusudan, N.V and Chandrasekhar, S. Proc. International Conf on liquid crystals Bangalou 427 (1973).

20 Bradshaw, M.J. Raynes, E.P. Mol. Cryst. Liq. Cryst. L 72, 73 (1981).

21 Jhoen, J and Minu G. Mol. Cryst. Liq. Crystl 76 (1983).

22 Longa, L. De Jeu, W.H. Phys. Rev. A 26, 1632 (1982).

23 Tay, S.P. Crossley, J. Canad J. Chem. 50, 2031 (1972).