

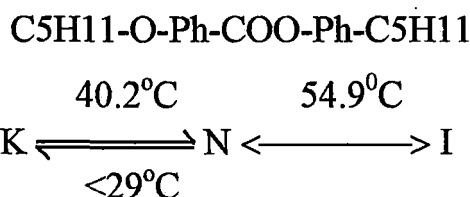
CHAPTER-7

*Magnetic susceptibility, bend and splay elastic constants of four
nematogens.*

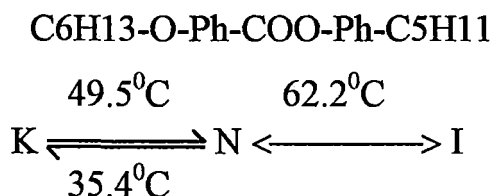
In this chapter I report the temperature variation of magnetic susceptibility anisotropy values for four nematogens. The bend and splay elastic constants of two nematogens have also been reported. The experimental data for magnetic anisotropy have been analysed to calculate the order parameter of the nematogens.

The liquid crystalline compounds studied with their chemical names, chemical structure and transition temperatures are given below:

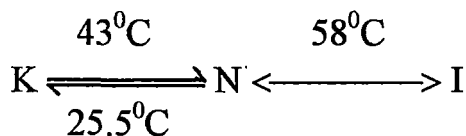
- I. 4-n-pentyl phenyl-4-n' pentyloxy benzoate.
(ME 5O.5 in short).



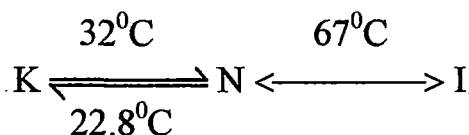
- II. 4-n-pentyl phenyl-4-n' hexyloxy benzoate.
(ME 6O.5 in short).



- III. 3E-n-butane-phenyl-(4-cyclohexane-4'-n-propane)-ether
(3CPOd(3)1 in short).



- IV. 3E-n-butane-phenyl-(4-cyclohexane-4'-n-pentane)-ether
(5CPOd(3)1 in short).



ME 50.5 and ME 60.5 were obtained from E. Merk, U. K. The other two chemicals were donated to us by Hoffmann La Roche, Switzerland. All the chemicals were used without further purification. The transition temperatures were determined by observing their textures under polarising microscope using Mettler FP 80/82 thermosystem. The transition temperatures agreed with the values supplied by the manufacturers. The nematogens ME 50.5 and ME 60.5 have been used frequently in liquid crystalline mixtures, which shows induced smectic A_d phases [1-5]. The density and refractive indices of both the compounds in their mesophase have been determined by Adamski [7]. The density and refractive indices of ME 60.5 have also been reported by other workers [1,8]. Das et al [2,3] have also studied these nematogens and calculated order parameters from x-ray diffraction data.

The refractive indices and elastic constants of the compound 3CPOd(3)1 have been reported by Schadt et al [9,10]. The density and refractive indices of both 3CPOd(3)1 and 5CPOd(3)1 have been determined by Nath et al [11,12]. They have also determined order parameters and other molecular parameters from the x-ray diffraction studies of these two nematogens [11].

Magnetic susceptibility, density and elastic constants of the nematogens were determined following the procedure given in Chapter-2.

The experimental values of density and χ_{\parallel} , the magnetic susceptibility along the director, at different temperatures for ME 50.5 are Tabulated in Table 7.1. The calculated values of $\Delta\chi$ and order parameters are also shown in the Table. The value of $\Delta\chi$ for perfectly ordered sample was determined by Haller's extrapolation method (Chapter 2) and this value is also given in Table 7.1. The corresponding density, χ_{\parallel} , $\Delta\chi$ and $\langle P_2 \rangle$

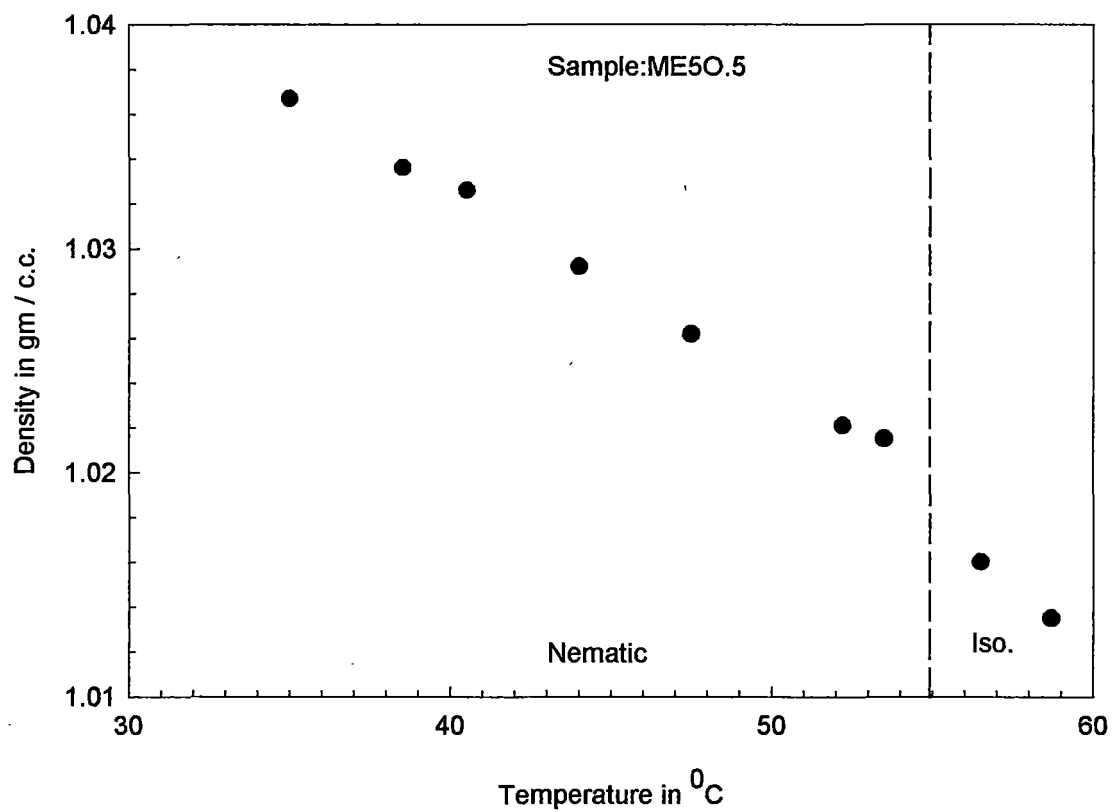


Figure 7.1. Density values as a function of temperature.

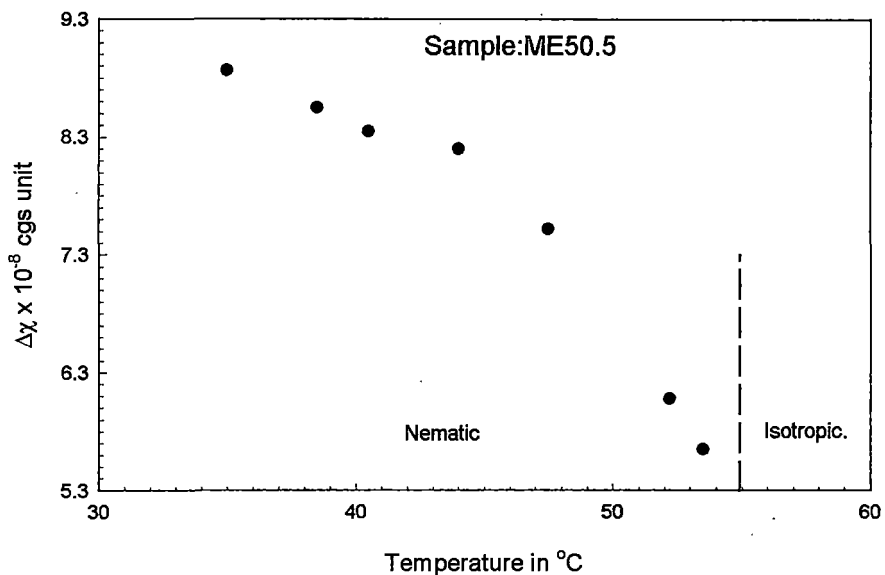


Figure 7.2. Temperature variation of the anisotropy of the diamagnetic susceptibility ($\Delta\chi$).

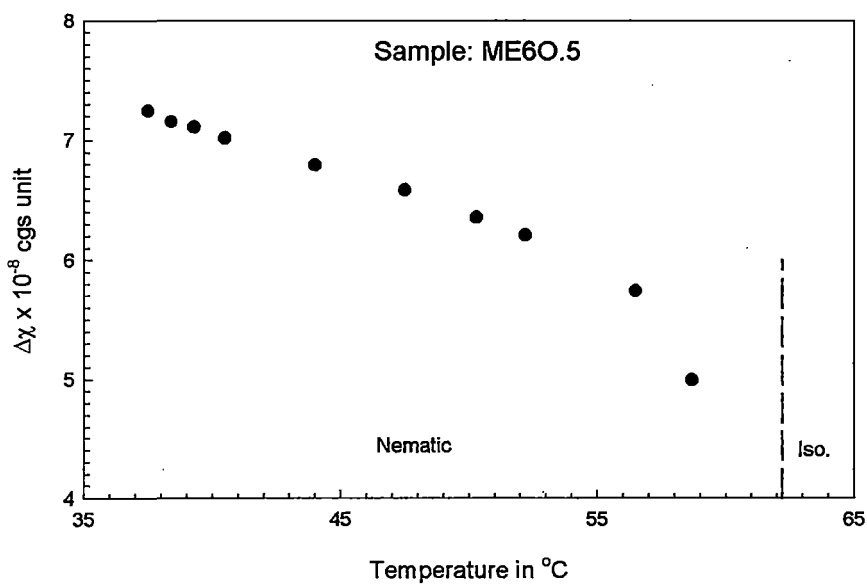


Figure 7.3. Temperature variation of the anisotropy of the diamagnetic susceptibility ($\Delta\chi$).

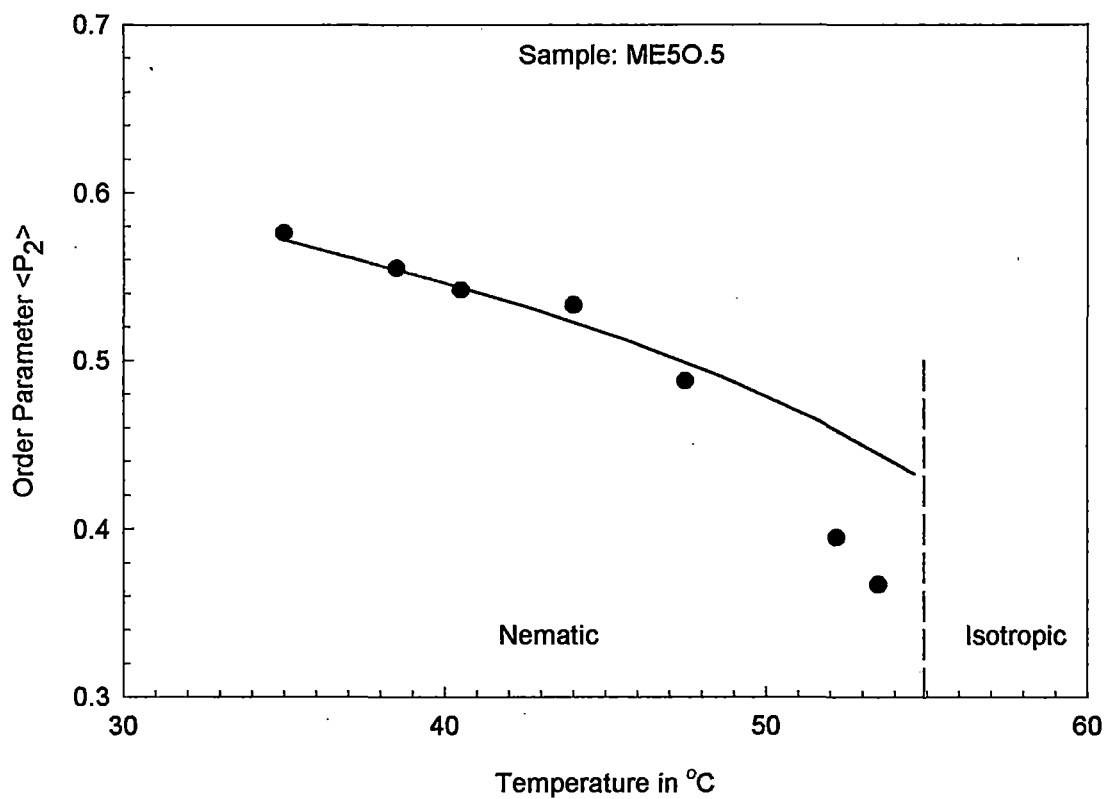


Figure 7.4. Temperature variation of Order Parameter $\langle P_2 \rangle$. Continuous curve corresponds to Maier-Saupe theoretical values.

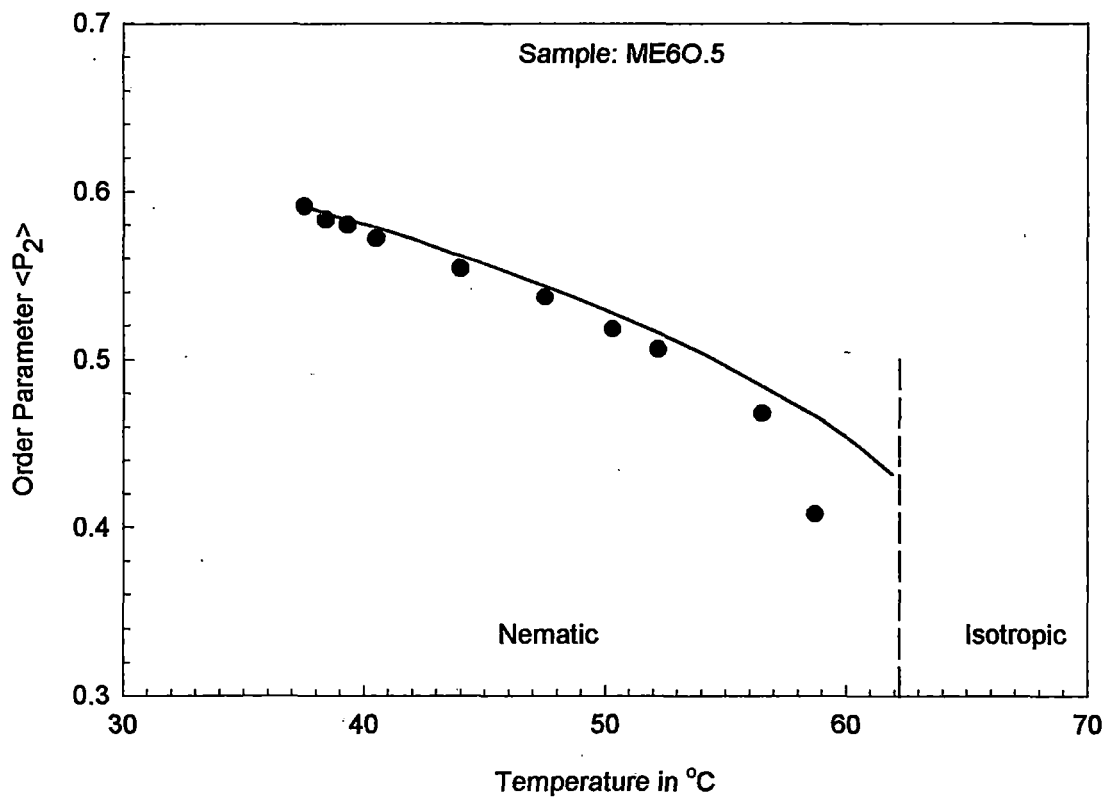


Figure 7.5. Temperature variation of Order Parameter $\langle P_2 \rangle$. Continuous curve corresponds to Maier-Saupe theoretical values.

values for 6O.5 are given Table 7.2. The density values are those interpolated from the data of Das et al [1]. The temperature variation of density of ME 5O.5 is shown in Figure 7.1. Figures 7.2 and 7.3 show the temperature variations of $\Delta\chi$ for ME 5O.5 and ME 6O.5 respectively. Our magnetic susceptibility values for ME 6O.5 are in good agreement with those obtained by Ibrahim and Haase [8]. The temperature variation of order parameters of ME 5O.5 and ME 6O.5 are shown in Figures 7.4 and 7.5 respectively. The theoretical Maier-Saupe order parameter values are also shown in the Figures. The agreement between our experimental values and Maier-Saupe calculated values of $\langle P_2 \rangle$ is good except near the nematic-isotropic transition temperature. This type of behaviour of the order parameters calculated from magnetic susceptibility is quite common (see for example Chapter 3 and Chapter 4 of this thesis). The order parameter values of ME 6O.5 are some what larger than those obtained by Das et al [1] from refractive index data. However, Das et al [2] calculated $\langle P_2 \rangle$ from x-ray diffraction data for ME 6O.5 and found values which are slightly larger than the present $\langle P_2 \rangle$ values obtained from magnetic susceptibility.

The values of splay and bend elastic constants of ME 5O.5 at different temperatures are given in Tables 7.3 and 7.4 respectively. Tables 7.5 and 7.6 show the values of splay and bend elastic constants respectively. The values of critical magnetic field and the sample thicknesses are also recorded in the respective Tables. The temperature variation of splay elastic constants for ME 5O.5 and ME 6O.5 are shown in Figures 7.6 and 7.7 respectively. Similarly, the temperature variation of bend elastic constants for ME 5O.5 and ME 6O.5 are shown in Figures 7.8 and 7.9 respectively. All the four Figures show normal behaviour, i.e.,

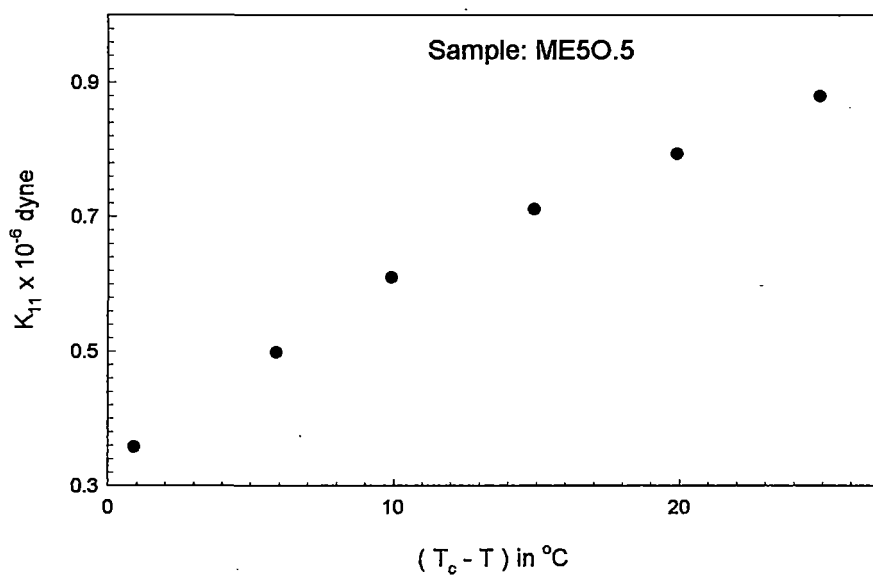


Figure 7.6. Splay elastic constant (K_{11}) as a function of relative temperature ($T_c - T$).

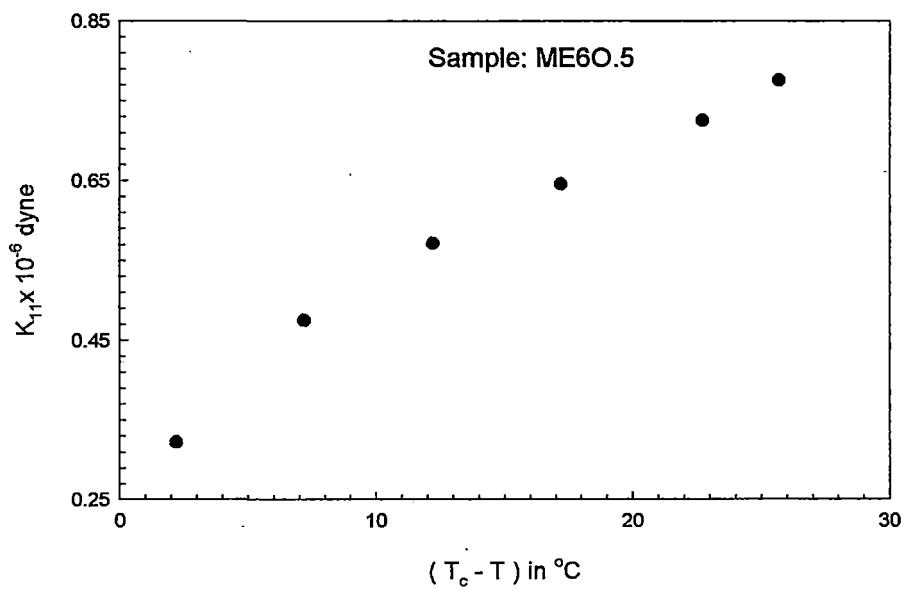


Figure 7.7. Splay elastic constant (K_{11}) as a function of relative temperature ($T_c - T$).

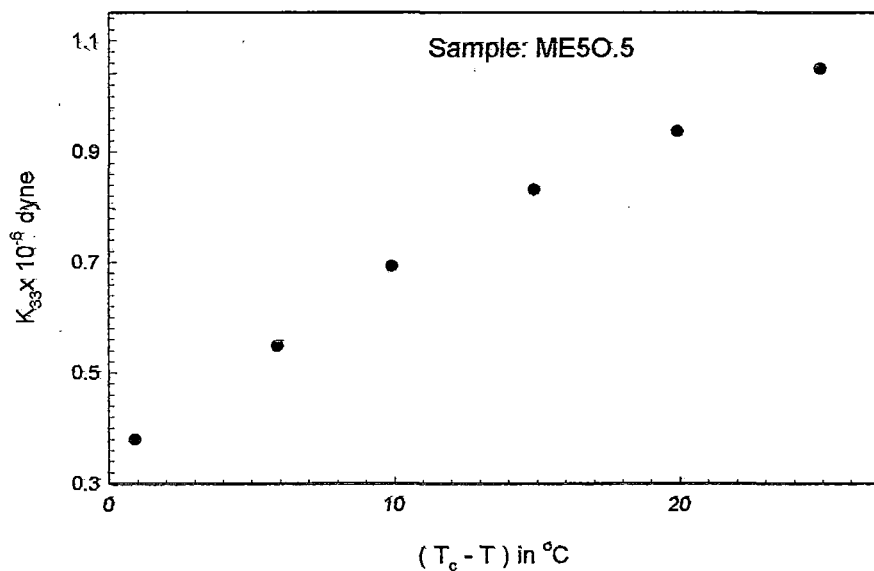


Figure 7.8. Bend elastic constant (K_{33}) as a function of relative temperature ($T_c - T$).

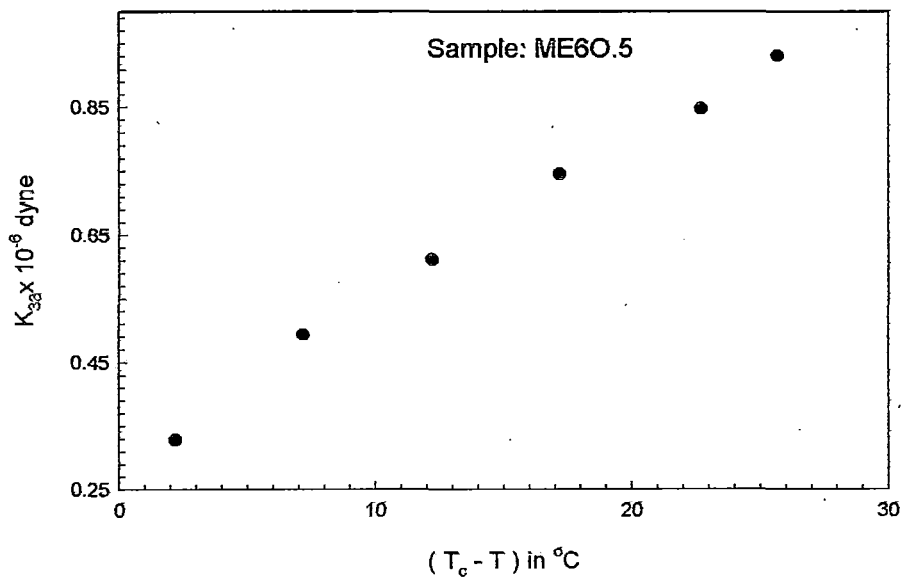


Figure 7.9. Bend elastic constant (K_{33}) as a function of relative temperature ($T_c - T$).

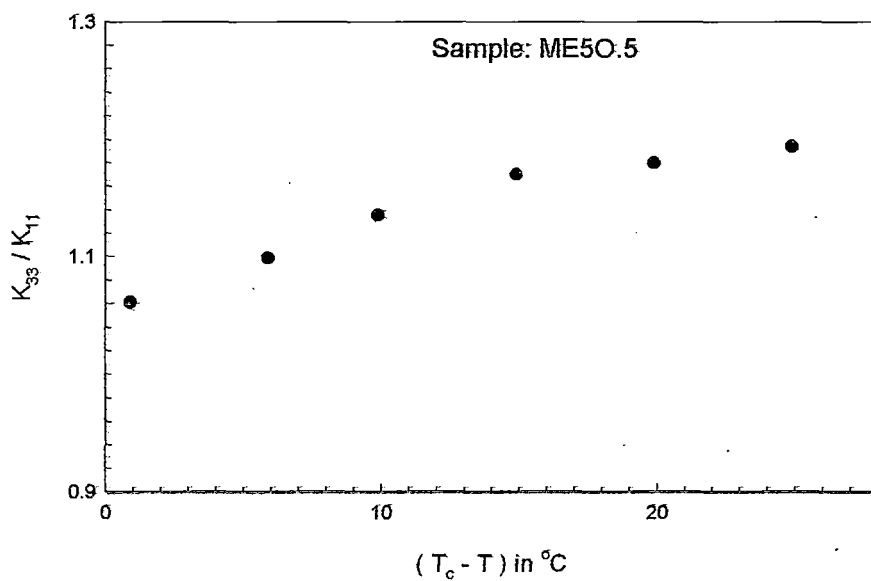


Figure 7.10. Bend to Splay elastic constant ratio (K_{33}/K_{11}) as a function of relative temperature ($T_c - T$).

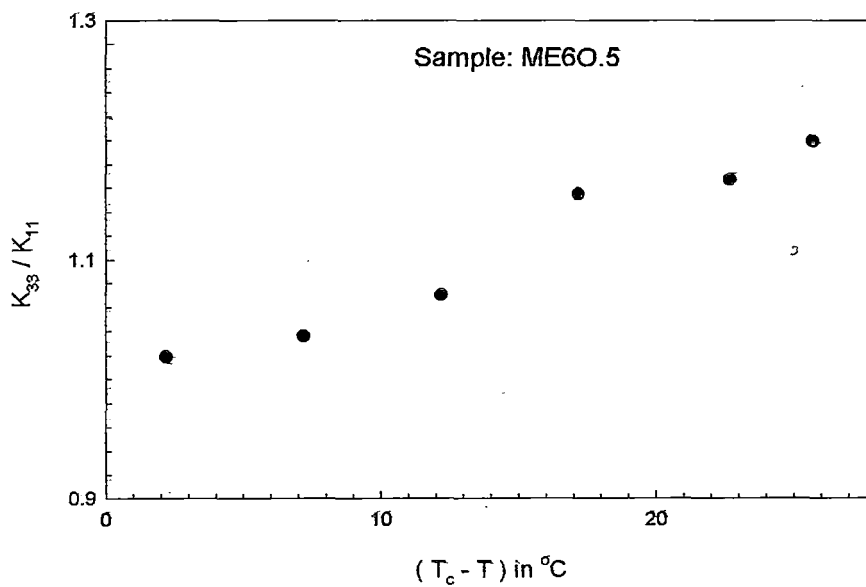


Figure 7.11. Bend to Splay elastic constant ratio (K_{33}/K_{11}) as a function of relative temperature ($T_c - T$).

elastic constants are increasing with decreasing temperatures. The bend to splay elastic constant ratios for ME 5O.5 and ME 6O.5 are given in Table 7.7 and shown in Figures 7.10 and 7.11 respectively. The K_{33}/K_{11} ratios for both the nematogens are greater than 1 at all temperatures and also increase with decreasing temperatures. This behaviour is quite common in normal nematogens. It is well known [13] that if any alkoxy part in a mesogenic compound is replaced by corresponding alkyl chain, then K_{33}/K_{11} ratio is larger in the alkoxy compound than that in the alkyl compound. It can be seen that if the alkoxy chain in ME 5O.5 is replaced by corresponding alkyl chain then the resulting compound is ME 5.5, whose K_{33}/K_{11} values are given by Bradshaw et al.[13]. One can see that the K_{33}/K_{11} value of ME 5.5 are smaller than those of ME 5O.5 if comparisons are made at the same relative temperature ($T_c - T$). For example at $T_c - T = 24.9^\circ\text{C}$, the K_{33}/K_{11} ratio for ME 5O.5 and ME 5.5 are 1.194 and 1.145 respectively.

The values of density, χ_{\parallel} , $\Delta\chi$, and $\langle P_2 \rangle$ at different temperatures for 3CPOd(3)1 and 5CPOd(3)1 are tabulated in Tables 7.8 and 7.9 respectively. The values of $\Delta\chi$ for $\langle P_2 \rangle = 1$ are obtained by Haller's extrapolation method (Chapter 2) and are shown in the Tables. The density values shown in the Tables are interpolated from the density values given by Nath et al.[12]. The temperature variation of $\Delta\chi$ for 3CPOd(3)1 and 5CPOd(3)1 are shown in Figures 7.12 and 7.13 respectively. The values of $\Delta\chi$ changes discontinuously at the clearing temperature as it should for nematogens. Figures 7.14 and 7.15 show the temperature variation of order parameter for 3CPOd(3)1 and 5CPOd(3)1 respectively. The order parameter values calculated from Maier-Saupe theory are also shown in the figures. Again, the agreements are very good except near the nematic to

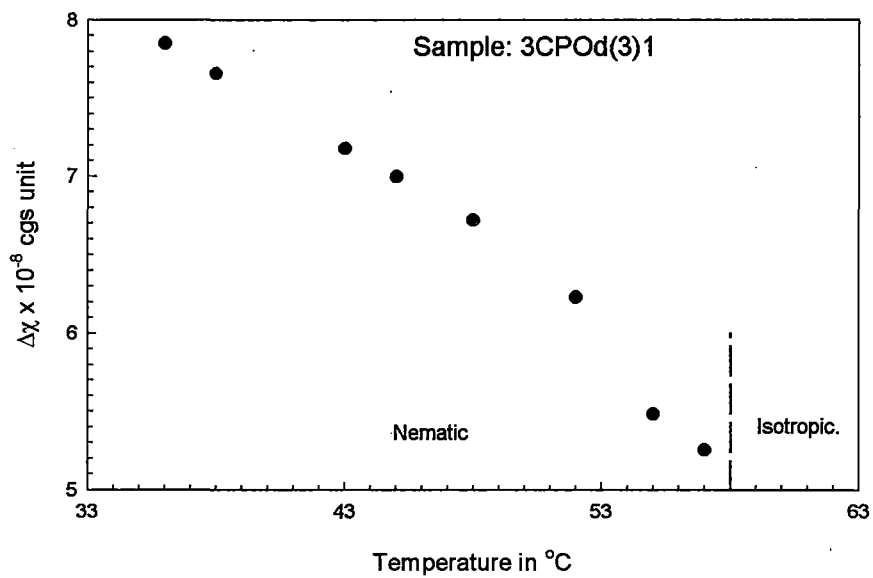


Figure 7.12. Temperature variation of the anisotropy of the diamagnetic susceptibility ($\Delta\chi$).

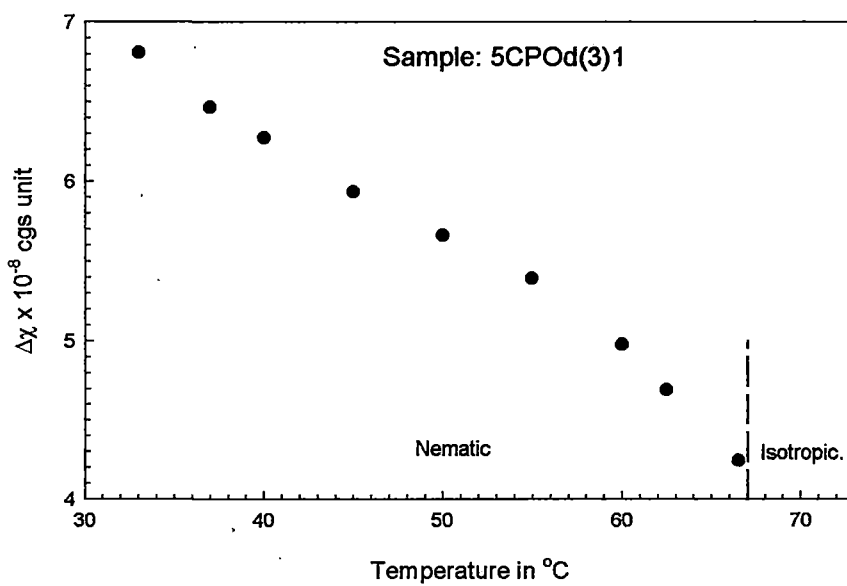


Figure 7.13. Temperature variation of the anisotropy of the diamagnetic susceptibility ($\Delta\chi$).

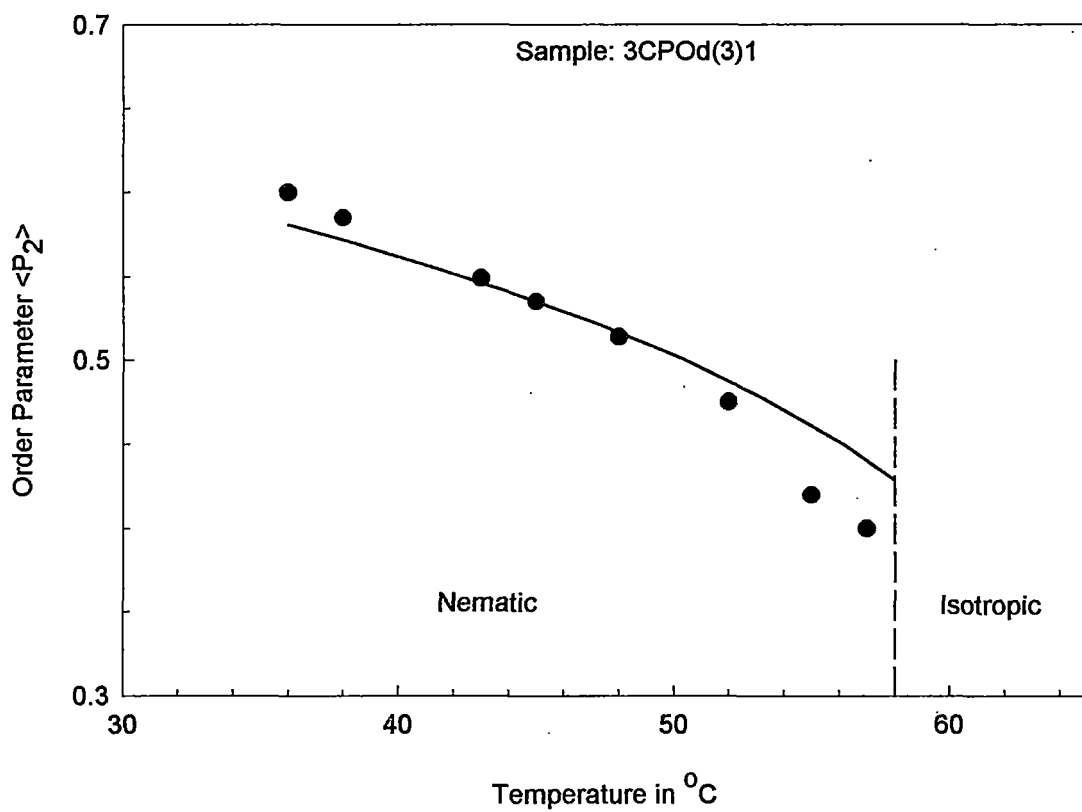


Figure 7.14. Temperature variation of orientational order parameter $\langle P_2 \rangle$ obtained from magnetic susceptibility measurement.

Continuous curves correspond to Maier-Saupe theoretical values.

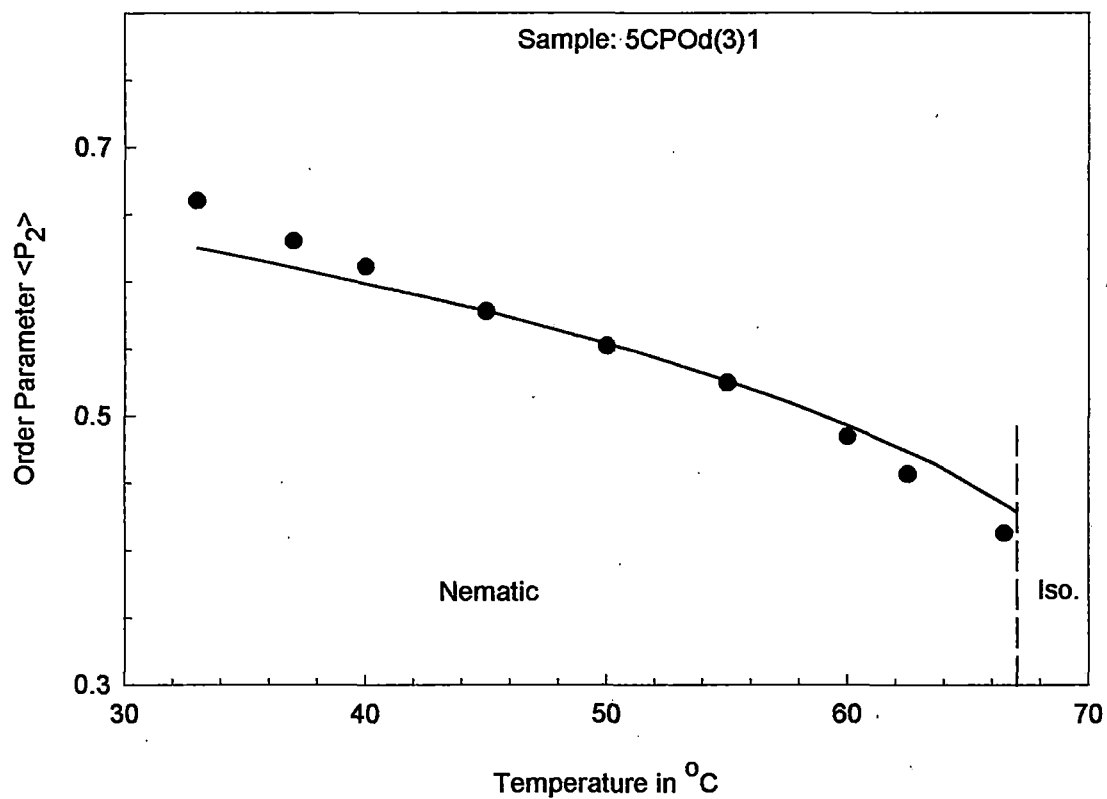


Figure 7.15. Temperature variation of orientational order parameter $\langle P_2 \rangle$ obtained from magnetic susceptibility measurement.

Continuous curves correspond to Maier-Saupe theoretical values.

isotropic transition temperature. The present order parameter values for both the nematogens are slightly lower than the $\langle P_2 \rangle$ values calculated from x-ray diffraction data [11], but are somewhat greater than those determined from refractive index data [11]. This trend in order parameter values obtained from different techniques is also well known and has been discussed in a previous Chapter (Chapter-3) in some detail. The bend and splay elastic constant for 3CPOd(3)1 have been reported earlier [9.10] and those for both 3CPOd(3)1 and 5CPOd(3)1 have been measured in our laboratory [13]. The K_{33}/K_{11} ratio for both the nematogens are greater than 1 and the temperature variation of elastic constants have no abnormal behaviour.

Table 7.1

Experimental values of the density (ρ), magnetic susceptibility (χ), susceptibility anisotropy ($\Delta\chi$), and the order parameter $\langle P_2 \rangle$.

Sample: ME50.5

Temp. in °C	Density (ρ) in gm/cc	$-\chi_{\parallel} \times 10^{-7}$ c.g.s.unit	$\Delta\chi \times 10^{-8}$ c.g.s.unit	order parameter $\langle P_2 \rangle$
35	1.0367	6.40	8.9	0.576
38.5	1.0336	6.42	8.5	0.555
40.5	1.0326	6.44	8.3	0.542
44	1.0292	6.45	8.2	0.533
47.5	1.0262	6.49	7.5	0.488
52.2	1.0221	6.59	6.1	0.395
53.5	1.0215	6.62	5.6	0.367
56.5	1.0186	6.99 = $\bar{\chi}_{\text{iso}}$		

$$\Delta\chi_0 = 1.54 \times 10^{-7} \text{ c.g.s.unit ;}$$

Table 7.2

Experimental values of the density (ρ), magnetic susceptibility (χ), susceptibility anisotropy ($\Delta\chi$), and the order parameter $\langle P_2 \rangle$.

Sample: ME6O.5

Temp. in °C	Density (ρ)* in gm/cc	$-\chi_{\parallel} \times 10^{-7}$ c.g.s.unit	$\Delta\chi \times 10^{-8}$ c.g.s.unit	order parameter $\langle P_2 \rangle$
37.5	1.0193	6.69	7.2	0.591
38.4	1.019	6.70	7.1	0.583
39.3	1.018	6.70	7.1	0.580
40.5	1.016	6.71	7.0	0.572
44.0	1.014	6.72	6.7	0.554
47.5	1.012	6.74	6.6	0.537
50.3	1.009	6.75	6.4	0.518
52.2	1.007	6.76	6.2	0.506
56.5	1.004	6.79	5.7	0.468
58.7	1.001	6.84	4.8	0.408
63.7	0.992	$7.18 = \bar{\chi}_{iso}$		

$$\Delta\chi_o = 1.226 \times 10^{-7} \text{ c.g.s.unit ;}$$

* Interpolated values from reference [1].

Table 7.3

Experimental values of splay elastic constant (K_{11}) for various ($T_c - T$) values.

Sample ME50.5

$T_c = 54.9^\circ \text{C}$, Sample thickness = 162 μm , H_c = Threshold magnetic field

$T_c - T$	H_c in Gauss	$\Delta\chi \times 10^{-8}$ cgs unit	$K_{11} \times 10^{-6}$ dyne
0.9	495	5.5	0.36
5.9	515	7.1	0.50
9.9	535	8.0	0.61
14.9	564	8.4	0.71
19.9	580	8.9	0.79
24.9	595	9.3	0.88

Table 7.4

Experimental values of Bend elastic constant (K_3) for various ($T_c - T$) values.

Sample ME50.5

$T_c = 54.9^\circ \text{C}$, Sample thickness = 162 μm , H_c = Threshold magnetic field

$T_c - T$	H_c in Gauss	$\Delta\chi \times 10^{-8}$ cgs unit	$K_{33} \times 10^{-6}$ dyne
0.9	510	5.5	0.38
5.9	540	7.1	0.55
9.9	570	8.0	0.69
14.9	610	8.4	0.83
19.9	630	8.9	0.94
24.9	650	9.3	1.05

Table 7.5

Experimental values of splay elastic constant (K_{11}) for various ($T_c - T$) values.

Sample ME6O.5

$T_c = 62.2^\circ \text{C}$, Sample thickness = 162 μm , H_c = Threshold magnetic field

$T_c - T$	H_c in Gauss	$\Delta\chi \times 10^{-8}$ cgs unit	$K_{11} \times 10^{-6}$ dyne
2.2	515	4.6	0.32
7.2	550	5.9	0.47
12.2	580	6.4	0.57
17.2	600	6.7	0.64
22.7	620	7.1	0.72
25.7	630	7.3	0.78

Table 7.6

Experimental values of Bend elastic constant (K_3) for various ($T_c - T$) values.

Sample ME6O.5

$T_c = 62.2^\circ \text{C}$, Sample thickness = 162 μm , H_c = Threshold magnetic field

$T_c - T$	H_c in Gauss	$\Delta\chi \times 10^{-8}$ cgs unit	$K_{33} \times 10^{-6}$ dyne
2.2	520	4.5	0.33
7.2	560	5.9	0.49
12.2	600	6.4	0.61
17.2	645	6.7	0.74
22.7	670	7.1	0.85
25.7	690	7.3	0.93

Table 7.7

Experimental values of the Frank elastic constant ratio (K_{33} / K_{11}) at different relative temperatures ($T_c - T$).

Sample: ME5O.5		Sample: ME6O.5	
$T_c - T$	K_{33} / K_{11}	$T_c - T$	K_{33} / K_{11}
0.9	1.06	2.2	1.02
5.9	1.10	7.2	1.04
9.9	1.13	12.2	1.07
14.9	1.17	17.2	1.15
19.9	1.18	22.7	1.17
24.9	1.19	25.7	1.20

Table 7.8

Experimental values of the density (ρ), magnetic susceptibility (χ), susceptibility anisotropy ($\Delta\chi$), and the order parameter $\langle P_2 \rangle$

Sample: 3CPOd(3)1

Temp. in $^{\circ}\text{C}$	Density (ρ)* in gm/cc	$-\chi_{\parallel} \times 10^{-7}$ c.g.s.unit	$\Delta\chi \times 10^{-8}$ c.g.s.unit	order parameter $\langle P_2 \rangle$
36	0.973	6.37	7.8	0.600
38	0.971	6.39	7.6	0.585
43	0.967	6.42	7.2	0.549
45	0.965	6.43	7.0	0.535
48	0.963	6.45	6.7	0.514
52	0.958	6.48	6.2	0.475
55	0.955	6.53	5.5	0.420
57	0.951	6.55	5.2	0.400
60	0.945	$6.90 = \bar{\chi}_{\text{iso}}$		

$$\Delta\chi_0 = 1.308 \times 10^{-7} \text{ c.g.s.unit ;}$$

* Interpolated values from reference [22].

Table 7.9

Experimental values of the density (ρ), magnetic susceptibility (χ), susceptibility anisotropy ($\Delta\chi$), and the order parameter $\langle P_2 \rangle$

Sample: 5CPOd(3)1

Temp. in °C	Density (ρ)* in gm/cc	$-\chi_{\parallel} \times 10^{-7}$ c.g.s.unit	$\Delta\chi \times 10^{-8}$ c.g.s.unit	order parameter $\langle P_2 \rangle$
33.0	0.963	6.85	6.8	0.660
37.0	0.962	6.87	6.5	0.630
40.0	0.959	6.88	6.3	0.611
45.0	0.955	6.90	5.9	0.578
50.0	0.950	6.92	5.7	0.552
55.0	0.946	6.94	5.4	0.525
60.0	0.942	6.97	5.0	0.485
62.5	0.939	6.99	4.7	0.457
66.5	0.930	7.02	4.2	0.413
70.0	0.925	$7.30 = \bar{\chi}_{iso}$		

$$\Delta\chi_o = 1.03 \times 10^{-7} \text{ c.g.s.unit ;}$$

* Interpolated values from reference [22].

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