CHAPTER-8

General discussions and conclusion.

In this dessertation I have presented experimental data for ten pure nematogic compounds and three binary mixtures. The study includes x-ray diffraction, refractive indices, density, magnetic susceptibility and Freedericksz transition measurements and analysis of data to calculate orientational order parameters $<P_2>$ (from x-ray diffraction, refractive index and magnetic susceptibility data), apparent molecular length (l_{ap}) or layer thickness in the mesophase, birefringence (Δn), magnetic susceptibility anisotropy ($\Delta\chi$), bend and splay elastic constants and their ratios. All the binary mixtures studied have induced (or enhanced) smectic A_d phases and one has re-entrant nematic phase as well.

The ten pure component nematogens studied can be subdivided into five groups of two members each, from the structural point of view. Table 8.1 presents the five groups with their structural details and the short name of the members of each group. All compounds have two rings with or without a link between them. Four groups of compounds have one phenyl and one cyclohexyl ring, while only one group has two phenyl rings. In three groups the rings are connected through COO link, while in the other groups the rings are directly connected.

Regarding terminal parts, all the compounds have at least one alkyl or alkoxy chain at one end. Two group of compounds have alkyl or alkoxy chains at both ends. In the remaining three groups -CN, -NCS or $-OCH_2CHCHCH_3$ form the other terminal part.

The main features of the results of my experiments for all the pure compounds are tabulated in brief in Table 8.2. I have not tabulated the order parameter values obtained for these nematogens from different experimental studies, since such comparisons have been done in the chapters concerning the related chemicals.

Table 8.1

Structural details of the compounds studied.

Group No. (Short Chem.names)	Left terminal part	Left* ring	Link	Right* ring	Right terminal part
Group I (CPPCC,CPBCC)	n-alkyl	Cy	COO	Ph	CN
Group II (BPPCC,PPPCC)	n-alkyl	Cy	COO	Ph	n-alkoxy
Group III (10CPS,12CPS)	n-alkyl	Cy	-	Ph	NCS
Group IV (3CPOd(3)1, 5CPOd(3)1)	n-alkyl	Cy	-	Ph	$-OCH_2CHCHCH_3$
Group V (ME5O.5, ME6O.5)	n-alkoxy	Ph	COO	Ph	n-alkyl

* Cy stands for cyclohexyl

Ph stands for phenyl

However, one common feature is that the order parameters determined from x-ray diffraction studies agreed well with the Maier-Saupe calculated values, while the $\langle P_2 \rangle$ values calculated from refractive index and magnetic susceptibility data are always much smaller than the theoretical values near the nematic-isotropic transition temperatures. This lowering seems to be more pronounced for the $\langle P_2 \rangle$ values from refractive index measurements. The possible causes for this discrepancy may be director fluctuations or imperfect alignment of sample in the bulk (in refractive index studies the sample were aligned by surface treatment, whereas, in the other experiments a magnetic field was applied for bulk alignment of the samples) near the transition temperature. It should also be mentioned that the data analysis to calculate $<P_2>$ involve many different assumptions for different experimental techniques, hence there is no reason why two different techniques should yield exactly same order parameter values. From Table 8.2, it can be seen that the ratio of apparent molecular length (l_{ap}) to model molecular length (L) is about 1.4 form the two cyano compounds of Group I. This is in accordance with previous observations on cyanobiphenyl compounds [1,2]. Therefore, the molecules CPPCC and CPBCC form dimers in the mesophases. For Group III molecules with isothiocyanato (-NCS) group there seems to be some association, since the value of l_{ap}/L is little larger than 1.2. The Group II molecules (BPPCC and PPPCC) also show some association in mesophase, having l_{ap}/L between 1.09 to 1.15. However, Group IV and V molecules do not seem to form association in the nematic phase, since for these compounds the apparent molecular lengths are equal to the model lengths.

The refractive indices (n_e) and birefringence of Group III molecules are the largest. It is not surprising since these compounds contain sulphur in -NCS group as well as a phenyl ring. The refractive index (n_e) of Group I molecules are somewhat larger than that of Group II molecules though the birefringence of the two groups seem to be same. The increase in the value of n_e for Group I molecules compare to Group II is due to the -CN terminal part in the Group I molecules.

Regarding magnetic susceptibility ($\chi_{\parallel}$), we again find that the Group III molecules containing isothiocyanato (-NCS) group have the largest value

Table 8.2

Physical properties of the nematogens studied

Name of the compound		$T_{NI} = T_c$ in ^{0}C	X-ray diffraction		Refractive index at T_c- 5°C		Mag. Susceptibility at T_c- 5°C		Elastic const. at $(T_c$-5)°C	
			l_{ap} in Å	l_{ap} / L	n_e	Δn	$-\chi_{\parallel} \times 10^{-7}$ (cgs unit)	$\Delta\chi \times 10^{-8}$ (cgs unit)	$K_{33} \times 10^{-6}$ (dyne)	K_{33}/K_{11}
Group I	CPPCC	70.0	22.66	1.39	1.552	0.076	6.90	3.7	0.64	1.14
	CPBCC	68.3	24.42	1.42	1.553	0.075	6.80	3.6	0.41	1.02
Group II	BPPCC	72.6	20.87	1.09	1.531	0.075	6.32	2.6	0.26	0.86
	PPPCC	75.0	24.26	1.15	1.535	0.065	6.45	2.9	0.59	0.98
Group III	10CPS	50.7	31.7	1.23	1.632	0.098	7.15	3.0	0.44	0.92
	12CPS	52.5	33.9	1.21	1.614[d]	0.121[d]	7.63[e]	2.9[e]	0.40[e]	0.99[e]
Group IV	ME5O.5	54.9	-	-	-	-	6.53	6.8	0.52	1.09
	ME6O.5	62.2	24.5[a]	1.00[a]	1.061[f]	0.074[f]	6.81	5.5	0.42	1.03
Group V	3CPOd(3)1	58.0	16.8[b]	0.98[b]	1.504[b]	0.068[b]	6.50	6.0	1.27[c]	1.14[c]
	5CPOd(3)1	67.0	19.1[b]	1.00[b]	1.535[b]	0.097[b]	6.99	4.7	0.83[c]	1.01[c]

[a] - value taken from reference [1]. [b] - value taken from reference [9]. [e] - at temperature T_c - 1.5^{0}C.

[c] - value taken from reference [10]. [d] - at temperature T_c - 4^{0}C.

(magnitude) of $\chi_{\parallel}$. Again, this may be due the presence of sulphur. All other molecules have the value of $\chi_{\parallel}$ in the range 6.3 to 6.9 x 10^{-7} c.g.s unit. The Group I molecules with cyano group and Group IV molecules with two phenyl rings have larger value of $\chi_{\parallel}$. The Group II molecules with only one phenyl ring have the lowest $\chi_{\parallel}$ values. Regarding magnetic susceptibility anisotropy ($\Delta\chi$), the Group IV (with two phenyl rings) and Group V (with one phenyl ring connected to alkenyl chain at one end) have largest anisotropies. These large $\Delta\chi$ may be the effect of enhanced dislocation of π electrons over two phenyl rings (Group IV) or between phenyl ring and the alkenyl chain (Group V). This may also be the reason for the birefringence values of the compounds in these two groups (Group IV and Group V) to be quite large. For all other molecules the $\Delta\chi$ values are much smaller.

The values of bend elastic constants at T_c - 5^0C are also shown in Table 8.2. The largest values are of the two alkenyl compounds (Group V). For all pairs of molecules in each group, the K_{33} values decrease with increasing length of alkyl or alkoxy chain, as is expected. The only exception is in Group II, PPPCC has larger K_{33} values compared to BPPCC even if it has longer alkyl or alkoxy chain at both ends. This is due to the fact that PPPCC has a smectic phase at low temperatures and its nematic phase x-ray diffraction pattern shows sign of cybotactic groups (Chapter 3, Plate 3h). The bend to splay elastic constant ratios are greater than one for Group I, IV and V compounds. It is well known that this ratio are larger for molecules having large polarity. Since Group I molecules have a phenyl ring and a cyano group they have large values of K_{33} /K_{11}. The alkenyl compounds (Group V) and Group IV compounds (with two phenyl rings) have also large polarities, hence their K_{33} /K_{11} values are larger than one.

This ratio also should decrease with increasing chain lengths within each group. Except for Group II and III it seems to be the case. In Group II, PPPCC has larger values of K_{33}/K_{11} than BPPCC, since it has cybotactic groups in its nematic phase. In the Group III (10CPS and 12CPS) the comparison cannot be made, since for 12CPS elastic constants could be measured at only one temperature, 1.5°C below the transition temperature.

Mixture studies.

As mentioned earlier three binary mixtures have been studied by me. Two binary mixtures of a terminal polar compound (5CB) and a non polar compound (ME 5O.5 or ME 6O.5) show induced smectic A_d phase and have been studied extensively before by other workers in our laboratory [3,5]. They observed that the orientational order in these mixtures show a minimum in the same composition range where the smectic A_d phase is most stable. They obtained the $<P_2>$ values from x-ray diffraction and refractive index studies. I measured the magnetic susceptibilities of these two mixtures at different compositions and calculated order parameteres from these data. My data fully corroborates the earlier observations regarding $<P_2>$ being minimum at the composition where smectic A_d phase is more stable.

The other binary system studied by me has both the components terminal polar compounds (12OCB and 7CBB, both having -CN group at one end). This mixture has been previously studied by Dabrowski et al.[6] and show an enhanced smectic A_d phase as well as a re-entrant nematic phase in a certain composition range. I have studied in detail a particular mixture ($x_{7CBB} = 0.917$) of this binary system, which showed both re-entrant nematic and smectic A_d phases. I studied density, refractive indices and x-ray diffraction patterns of this particular mixture. My study seems to indicate that the re-entrant nematic to smectic A_d phase transition for this mixture is continuous. I have also measured variation of layer thickness with both temperature and composition for the mixtures of 7CBB and 12OCB. The main observation is that while the temperature variation of layer thickness at a particular composition is negligible, the composition variation of layer thickness shows a broad maximum near equimolar concentration. This behaviour has been qualitatively explained in Chapter 6, assuming formation of homo dimers (12OCB +12OCB) and hetero dimers (7CBB+12OCB). A calculation which will presumably explain the variation of layer thickness quantitatively in this system as well as in a related system (7CBB+7OCB), which has been studied in our laboratory, [7] is in progress.

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