

CHAPTER 8

CONCLUDING REMARKS

In the previous chapters the author had discussed in detail the results of his experimental and theoretical studies in the case of the different smectic, nematic and cholesteric liquid crystals. There are certain general features which have emerged from the studies presented in the thesis. In the following are presented some general conclusions and remarks.

Anisotropy of Lorentz field factors

The Neugebauer's approach to the local field, adopted by the author in the theoretical calculations, leads to results which are consistent. In particular, the following points are worthy of remark.

- 1) The ^{values of the} anisotropy of Lorentz field factors generally decrease with increase of temperature and go hand-in-hand with the decrease of the orientational order parameter with increasing temperature.
- 2) In the case of molecules of the homologous series n-alkyl-p-(4-ethoxy benzylidene amino)- α -(methyl cinnamates ,

values of the the/anisotropy of the Lorentz field factors decrease with increase in the number of carbon atoms in the alkyl end group. As a consequence of the numerous possible conformations of the end group, there is a reduction in the anisotropy of the polarization field. In most of the cases, the anisotropy arises mainly from the central rigid portion of the molecule.

3) The maximum values of the anisotropy of the Lorentz field factors in the nematic phase for the different compounds discussed here, are compared with the values in the case of some of the extensively studied compounds like p-azoxyanisole and p-methoxy benzylidene p-butylaniline¹. From the values shown in Table 8.1, it may be noticed that, they are of the same order of magnitude in the case of the cinnamates, N-(4-hexyloxy benzylidene)-p-toluidine (HBT)² and MBBA which have identical central rigid portion. Further, the values of the anisotropy ($L_o - L_e$) in the case of cinnamates are systematically higher in the smectic mesophase as is to be expected from the more ordered nature of this phase.

4) It may be pointed out that the Lorentz field factors are not calculable theoretically. L_e and L_o are parameters which describe the anisotropic local field.

The factors follow from Neugebauer's theory which assumes that the molecules consist of point polarizable units. On the other hand, the molecules have a finite shape and hence it is not easy to make any theoretical calculations of these factors in the different mesophases.

Optical anisotropy and orientational order

The orientational order parameters at different temperatures are calculated from the formula $S = (\alpha_e - \alpha_o) / (\alpha_{||} - \alpha_{\perp})$, where $\alpha_{||} - \alpha_{\perp} (= \Delta\alpha)$ is the optical anisotropy. It was assumed by the earlier investigators that the optical anisotropy may be calculated by making use of the index data for the crystalline phase and assuming some type of form factor for the Lorentz field. Such a calculation, using the index data for the crystals, is strictly valid only if in the crystalline phase all the molecules are arranged such that their axes of the polarizability ellipsoid are parallel to one another. Actually however, it is very rare for molecules to be arranged parallel to one another in the crystalline phase and hence one has to calculate $\Delta\alpha$ either from the anisotropy of the bond polarizabilities or from the known values of the optical anisotropy of molecules having similar molecular structure.

Table 8.1: Anisotropy of Lorentz field factors in the nematic phase for the different compounds studied

Compounds	T_{NI} in K	$(T_{NI}-T)$ in K	$L_o - L_e$
p-azoxyanisole(PAA)	408.2	40	0.074
p-methoxy benzylidene -p-butylaniline (MBBA)	317.2	22	0.071
4,4'-bis(hexyloxy)azoxy benzene	400.0	30	0.074
4,4'-bis(heptyloxy)azoxy benzene	395.0	26	0.125
N-(4-hexyloxy benzylidene)- p-toluidine	348.0	17.3	0.075
n-alkyl-p-(4-ethoxy benzylidene amino)- α - methyl cinnamates			
Ethyl ester	396.0	40	0.085
Propyl ester	394.8	40	0.075

Further, it is necessary to remember that the optical anisotropy ($\Delta \alpha$) of the molecule itself may alter with temperature owing to the flexible nature of the different chemical linkages in the molecule. In particular, it must be pointed out here that, at higher temperatures when there is greater facility of rotations of groups about single C-C bonds, the optical anisotropy is likely to decrease. In this respect, it may be remarked that a single orientational order parameter for the whole molecule will be an approximation in the case of molecules which have facility of rotation of end groups (see Marcelja³). The calculations carried out by the author in the case of homologous cinnamates confirm the well known⁴ zig-zag alternation in the S factors for the successive members of the homologous series.

The optical anisotropy of the molecules consisting of two aromatic rings as in PAA, MBBA, HBT and cinnamates have roughly equal values as shown in Table 8.2. In all these cases the central rigid portion of the molecules consists of structurally similar pair of aromatic rings bridged by specific groups; the central rigid portion contributes most to the optical anisotropy.

There are, however, molecules which are weakly

Table 8.2: Optical anisotropy of the liquid crystalline compounds studied

Compounds	$\Delta \alpha$	Central bridge group	Reference Number
p-azoxyanisole(PAA)	25.6	$\begin{array}{c} \text{N}=\text{N} \\ \\ \text{N}-\text{O} \end{array}$	1
p-methoxy benzylidene-p-butylaniline(MBBA)	23.7	$\begin{array}{c} \text{C}=\text{N} \\ \\ \text{H} \end{array}$	1
4,4'-bis(hexyloxy)azoxy benzene	29.3	$\begin{array}{c} \text{N}=\text{N} \\ \\ \text{N}-\text{O} \end{array}$	5
4,4'-bis(heptyloxy)azoxy benzene	29.4	$\begin{array}{c} \text{N}=\text{N} \\ \\ \text{N}-\text{O} \end{array}$	5
N-(4-hexyloxy benzylidene)-p-toluidine	23.6	$\begin{array}{c} \text{C}=\text{N} \\ \\ \text{H} \end{array}$	2
n-alkyl-p-(4-ethoxy benzylidene amino)- α -methyl cinnamates			
Ethyl ester	25.0		
Propyl ester	25.1		
Butyl ester	25.8		
Amyl ester	25.1		
Hexyl ester	24.6	$\begin{array}{c} \text{C}=\text{N} \\ \\ \text{H} \end{array}$	6
Heptyl ester	24.1		
Octyl ester	24.3		
Nonyl ester	24.2		

optically anisotropic, e.g., the cholesteryl compounds. In particular, the cholesteryl oleyl carbonate studied by us has an optical anisotropy roughly about $2 \times 10^{-24} \text{ cm}^3$. The physical origin of this small value is to be sought for in the sprawling nature of the chemical linkages of the cholesteryl group.

Molecular orientation in optical textures

The present studies on the textures exhibited by dodecyl benzene sulfonic acid, sodium dodecyl benzene sulfonate and the mixtures have proved conclusively the nature of the molecular orientation in 'batonnets' and 'droplets'. The interference method used to study these textures promises to be a powerful technique for the determination of birefringence and molecular orientation in different kinds of textures. The wealth of data and results presented, serve to show that the molecular structure and the flexible nature of the molecules give rise to spectacular effects with regard to the textures and birefringence. There is plenty of further scope for similar work with other compounds.

References

1. Chatelain, P., C.R. Acad. Sci. Paris 203, 1169 (1936);
203, 266 (1936).
2. Subramhanyam, H.S., Thesis, University of Mysore,
Mysore, India, 1977.
3. Somashekar, R. and Krishnamurti, D., Proceedings of
the Nuclear Physics and Solid State Physics
Symposium, Pune, Vol. 20C, p 366 (1977).
4. Marcelja, S., J. Chem. Phys., 60, 3599 (1974).
5. Karat, P.P. and Madhusudana, N.V., Mol. Cryst.
Liq. Cryst., 36, 51 (1976); 55, 119 (1979).
6. Somashekar, R., Revannasiddaiah, D., Subramhanyam, H.S.,
Madhava, M.S. and Krishnamurti, D.,
Mol. Cryst. Liq. Cryst., 45, 243 (1978).
7. Krishnamurti, D. and Somashekar, R.,
Mol. Cryst. Liq. Cryst., (In press) 1981.