ELECTRIC AND MAGNETIC FIELD EFFECTS IN LIQUID CRYSTALS

Thesis Submitted to the

UNIVERSITY OF MYSORE

for the Degree of

DOCTOR OF PHILOSOPHY

By

PRAKASH P. KARAT

Liquid Crystals Laboratory

Raman Research Institute

Bangalore 560006 (INDIA)

May 1977

DECLARATION

I hereby declare that the thesis was composed by me independently and that it has not formed the basis for the award of any Degree, Diploma, Associate-ship, Fellowship or other similar title.

PRAKASH P. KARAT

'CERTIFIED'

S. Chandram

CERTIFICATE

I certify that this thesis ha@ been composed by Mr. Prakash P. Karat based on investigations carried out by him at the Liquid Crystals Laboratory, Raman Research Institute under my supervision. The subject matter of this thesis has *not* previously formed the basis of the award of any degree, diploma, associateship, fellowship or other similar title.

Professor S. Chandrasekhar
Liquid Crystals Laboratory
Raman Research Institute
BANGALORE 560006

CONTENTS

PREFACE

This thesis describes some investigations on the effects of magnetic and electric fields on nematic liquid crystals. These investigations may be classified broadly into four parts:

(a) New methods of optical detection of field induced deformations (Chapters II and VI) ;

(b) Study of tho elastic constants in relation to long range orientational order (Chapters III and IV) ;

(c) Study of the elastic constants in relation to short range order (Chapter V) ;

(d) Static and dynamic effects of electric fields (Chapters VII and VIII) .

In Chapter I we give a general introduction to the subject with particular reference to the investigations reported in the rest of the thesis.

In Chapter II, we present a new method of determining the twist elastic constant (k_{22}) of nematic liquid crystals. In the usual configuration in which the nematic is homogeneously aligned

between two glass plates with the director anchored
to the walls at either end, a small twist deformation
in the medium cannot be detected optically when light
is incident normal to the sample plane because *the*
electric vector merely follows the director (.Mauguin
1911). This is a consequence of the large birefringence
of the medium for this direction of propagation, so
that the phase retardation per unit length is very
large compared to the twist par unit length. Under
such circumstances, the 'adiabatic theorem' holds good.
It is shown that the transition from the undistorted
to the distorted state can be observed optically if
the birefringence is small. To reduce the effective
birefringence an experimental set up is described in
which light is allowed to enter the sample obliquely,
i.e., making a very small angle with respect to the
sample plane (instead *of* being normal to it). The
temperature variations of k_{22} of p-azoxyanisole (PAA)
and p-azoxyphenctole (PAP) measured by this method
are presented. Independent measurements on different
samples give consistent results and moreover the data
on PAA agree *well* with those reported earlier,
confirming that this simple method is a reliable one.
The temperature variation of k_{22} of PAA and PAP shows
an S^2 dependence (S being the order parameter) in

conformity with the mean field theory. This new method was used in all the measurements of k_{22} which are described in subsequent chapters.

In Chapter III we present experimental determinations of the splay (k_{11}), twist (k_{22}) and bend (k_{33}) elastic constants and the order parameter (S) as functions of temperature for the 5th, 6th, 7th and 8th homologues of 4'-n-alkyl-4-cyanobiphenyls (nCB)

$$N \equiv C - \langle \text{phenyl} \rangle - \langle \text{phenyl} \rangle - C_nH_{2n+1} \cdot$$
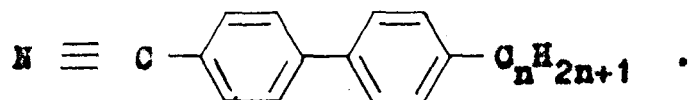
5CB, 6CB and 7CB shew only the nematic phase, while 8CB shows the smectic A phase as well at *lower* temperatures. These compounds are strongly *polar*, room temperature liquid crystals with large positive dielectric anisotropy. X-ray diffraction studies (Leadbetter et al. 1975) ehow that these compounds belong to the class of normal cybotactic nematics wherein small groups with smectic-like *order* are present even in the isotropic phase. Furthermore, the compounds form double layers with interdigitated molecules, because of the antiparallel correlation between the strongly polar nitrile groups attached to one end of the molecule. The results obtained

by us show some interesting features. In the first
place k_{33} and to some extent k_{11} deviate from the S^2
dependence. They increase more rapidly as the
temperature is decreased. On the other hand k_{22}
shows the S^2 dependence (except in the case of 8CB,
which will be discussed in the fifth chapter). These
results can be interpreted to mean that the temperature
variations of the longitudinal and transverse corre-
lotion lengths ($\xi_{\parallel}$ and $\xi_{\perp}$) are unequal. However
the ratios of the elastic constants in 5CB, 6CB and
7CB are practically the same (it any given relative
temperature (T_{NI} - T). This suggests that the tempe-
rature variation of short range order is similar in
these compounds, although the absolute values of the
short range order are not ths same.

Rear T_{NI}, k_{33} shows the odd-even effect whereas
S shows alternation only for the first three members
studied and increases from 7CB to 8CB. The latent
heat of transition (ΔH), k_{11} and k_{22} show the same
trend as S. ~~(figuraxxbx~~ Moreover near T_{NI}, k_{33} is less
than k_{11} for 8CB which is a most unusual result. These
observations can be interpreted by assuming that the
ratio ($\xi_{\parallel}/\xi_{\perp}$) near T_{NI} decreases between 7CB and 8CB.

Measurements of k_{11} and S have also been made

on another series *of* now compounds prepared recently
in our chemistry laboratory (Sadashiva 1976), viz.,
trans-p-n-alkoxy-α-methyl cyanophenyl cinnamates
(nOMCPC)

N≡C—⬡—O—C—C—CH₃ ... O ... C ... H ... ⬡ ... O ... C₉H₁₉
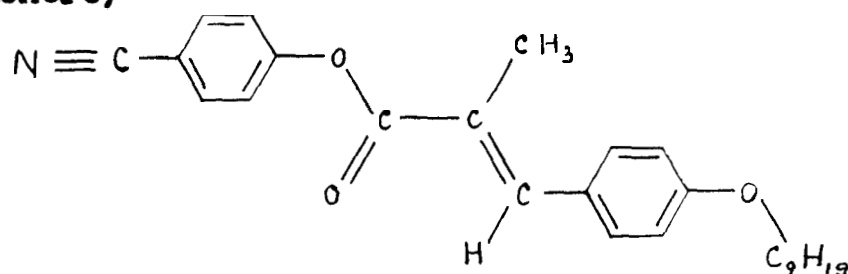
These esters are colourless, chemically stable and
possess high viscosity in the nematic phase. They
also have a nitrile group attached to one end of the
moleaule and exhibit strong positive dielectric
anisotropy. He have studied the second, third,
fourth and eighth, ninth and tenth homologues *of* thfo
series. (The other members were not investigated
because they have a short nematic range, and, further-
more. most of them are monotropic). Of these 10 OMCPC
shows a monotropic smectic A phase. The results on
this series, discussed in Chapter IV, are more compli-
oated than in the case of cyanobiphenyls. For instance,
S and Δ H increase considerably between 4 OMCPC and
8 OMCPC. k_{33} and to a smaller extent k_{11} also exhibit
an upward jump between these two members. However
T_{NI} and k_{22} do not show any such jump. Moreover the

ratios of elastic constants at the same relative temperature differ considerably among the different compounds studied. Both k_{11} and k_{22} broadly follow an S^2 dependence in the second, third, fourth and eighth homologues with the exception of k_{22} of 4 OMCPC which exhibits a significantly slower variation. On the other hand k_{33} varies more rapidly with temperature In all cases.

As yet, no X-ray data *are* available on the compounds. Since the molecules are strongly polar, it is probable that they form double molecular layers, as in the case of other polar molecules (McMillan 1973, Leadbetter et al. 1975). It is observed that the melting point of the crystal decreases steadily between second and fourth members in the series, and shows a large increase between the fourth and fifth homologues. Thereafter kt again decreases steadily till the ninth member. If is possible that the crystal structure changes between fourth and fifth members and the nature sf short range order may also be different between the lower ($\leqslant 4$) and higher ($\geqslant 5$) homologues. This may explain the trends in the physical properties that are described above.

In Chapter V we describe some studies on the critical divergence of k_{22} and k_{33} near the A-N transition.

In particular we have made measurements on
8CB, 10 OMCPC, p-cyanobenzylidene-p-n-octyloxyaniline
(CBOOA) and octyloxy cyanobiphenyl (8 OCB). To
increase the nematic range we prepared two mixtures
of 8 OCB and 7CB. de Gennes ha8 shown that in these
cases the twist and bend constants can be expressed
as $k_{11} = (k_{11})_0 + C_2(T - T^*)^{-\gamma}$ when $(k_{11})_0$ is the
'normal' elastic constant (in the absence of corre-
lations). $T^* = T_{AN}$ if the transition is strictly
second order. In all the compounds studied except
8CB, the values of γ is around 0.6. *For* 8CB in which
the A-N is distinctly first order $\gamma \sim 1.0$. However
it must be emphasized that a quantitatively meaningful
estimate of the critical exponent requires the measure-
ment to be carried out within a *few* millidegrees of
the transition. In the present sfudy the measurements
were not made to *this* degree of *precision* and the value
of γ obtained here cannot be regarded as accurate
enough to throw any light on the question of whether
the A-S transition exhibits helium like or classical
mean field behaviour. (Indeed this objection is probably
valid in many of the previous studies, e.g., Cheung et
al.1973, Delaye et al. 1973).

In Chapter VI we present measurements of the
threshold for a twisted nematic cell (TN cell). The

TN cell has gained importance in recent years because of its use in display devices. The theory of the TN cell was developed by Leslie (1970), who derived an expression for the threshold magnetic field (H_L) beyond which deformation occurs in the sample. It is well known that when viewed through parallel polarizers kept parallel or perpendicular to the director st either bounding surface, the optical threshold (H_0) is always greater than H_L (Gerritsma et al. 1971). This is again due to the adiabatic theorem referred to earlier. We show that H_L can be determined optically, if the set up is sensitive to 8—11 changes in the birefringence of the sample. Using this method, we have determined the threshold H_L accurately. Using k_{11}, k_{22} and k_{33} values (from Chapter III), we have checked that Leslie's expression for the critical field agrees well with the observed value. Further, we have shown that $H_L x_0$ (x_0 being the sample thickness) is independent of sample thickness proving that H_L is the true Leslie threshold. This is the first verification of Leslie's theory for the twisted nematic cell.

The next two chapters discuss some electric field effects. It is well known that nematic liquid crystals have a low frequency dielectric relaxation ($\sim$ MHz) which is Bus to the reorientation of the

dipoles about an axis normal to the director. This
relaxation can be understood In terms of the nematic
potential, which a molecule has to overcome in trying
to rotate about its short axis (Meier and Saupe 1966).

In Chapter VII we present a study of this low
frequency relaxation by observation of the Freedericksz
threshold both in the k_{33} and k_{11} geometries.   The
principle is to measure the critical magnetic field
corresponding to the Freedericksz transition in the
presence of on alternating stabilising electric field.
The electric field is along the undistorted director axis and
the magnetic field normal to it. As the frequency
of the electric field approaches the frequency of
relaxation the critical magnetic field (H_c) decreases
considerably and tends to approach H_o. In the case of
6CB, even for frequencies higher than the relaxation
frequency, $H_e > H_o$ (the value in zero electric field),
i.e., the dielectric anisotropy remains weakly positive.
However in the case of 9 OMCPC, beyond a particular
frequency f_o (depending upon the temperature) H_e beams
less than H_o indicating that $\triangle \epsilon$ has changed sign.
The graph of log f_R (relaxation frequency) Vs. $\frac{1}{T}$ gives
a slope which Is proportional to the total activation
energy Q. For 9 OMCPC, Q was estimated to be 1 eV.
We have also made observations of the Freedericksz

threshold in the k_{11} geometry due to an electric
field (with no magnetic field *present)*. In the case
of 9 OMCPC a critical field does not pertain to a
pure Freederickss transition at very high frequencies
($>$1 MHz) since electrohydrodynamic instability makes
a strong contribution. Indeed as the electric field
is increased beyond the threshold value striations
analogous to 'Williams domains' are seen. The domain
width has the same order of magnitude as the sample
thickness. Possible mechanisms for this high frequency
instability are discussed briefly.

In Chapter VIII we present some new types of
optical patterns due to electrohydrodynamic instabilities
in nematic MBBA. The usual method of observing these
domains is to use the 'sandwich' geometry, the
direction of observation being along the electric field.
We have used a geometry in which the direction of
observation is along the initial undistorted director
axis and normal *to* the applied eleotric field. Just
above the threshold voltage, if appears that the
vortices are in the plane containing the electric
field and the direction of observation. With increase
of the voltage the patterns observed become complicated
and three dimensional flow patterns are seen. The
domain widths are approximately half the electrode

separation. However the threshold voltage is much larger than that in the usual sandwich geometry. An explanation is given of the origin of this type of flow pattern.

Another interesting observation presented in this Chapter is the, effect af electric fields on nematic droplets of MBBA suspended in its isotropic phase. The drops which appear spherical at zero field, become ellipsoidal with its major axis normal to the field. For very high fields the droplets acquire highly distorted, rapidly changing shapes. These deformations are observed both in DC and low frequency AC fields. As the frequency is increased, the deformation decreases and for high frequency ~ 5 KHz no deformation Is seen. The origin of this type of distortion is again electrohydrodynamic, but a detailed theory of the observe4 behaviour still remains to be developed.

Some of the results discussed in this thesis are reported in the following publications:

1. Some electrohydrodynamic distortion patterns in a nematic liquid crystal (N.V. Madhusudana, P.P.Karat and S. Chandrasekhar) - Current Science 42(5) , 147-149 (1973).

2. Experimental determination of the twist elastic
constant of nematic Liquid crystals (N.V.Madhusudana,
P.P. Karat and S. Chandrasekhar) - Presented at the
International Liquid Crystals Conference, Bangalore
December 1973 - Pramana Suppl. 1, 225-236 (1975).

3. Some new types of electrohydrodynamic *flow* patterns
in nematic liquid Crystals (P.P. Karat, N.V.
Madhusudana) - Presented at the International Liquid
Crystals Conference, Bangalore, December 1973 -
Pramana Suppl. 1, 285-288 (1975).

4. Elastic and optical properties of some 4'-n-alkyl-4-
cyanobiphenyls (P.P. Karat and N.V. Madhusudana) -
Molecular Crystals & Liquid Crystals 36, 51 (1576).

5. Elasticity and orientational order in some 4'-a-
alkyl-4-cyanobiphenyls: Part II (P.P. Karat and N.V.
Madhusudana) - Mol.Cryst.Liquid Crust. (In press).

6. Verification of Leslie's expression for the threshold
field for a twisted nematic cell (P.P. Karat and
N.V.Madhusudana) - Mol.Cryst.Liquid Cryst. (in press).

7. A study of the dielectric relaxation in nematic
liquid crystals using the Freedericksz transition
technique (P.P. Karat and N.V. Madhusudana) - Mol.
Cryst. Liquid Cryst. (in press).

References

Cheung, L., Meyer, R.B. and Gruler, H. 1973
Phys. Rev. Lett. 31, 349.

de Gennes, P.G. 1972 Solid State Commun. 10, 753.

Delaye, M., Ribotta, R. and Durand, G. 1973 Phys. Rev.
Lett. 31, 443.

Gerritsma, C.J., De Jeu, W.H. and Van Zanten, P. 1971
Phys. Lett. 36A, 389.

Leadbetter, A.J., Richardson, R.M. and Colling, C.N.
1975 J. de Physique 36, C1-37.

Leslie, F.M. 1970 Mol. Cryst. Liquid Cryst. 12, 57.

Mauguin, M.C. 1911 Bull. Soc. Miner. Crist. 34, 77.

McMillan, W.L. 1973 Phys. Rev. A7, 1419.

Meier, G. and Saupe, A. 1966 Mol. Cryst. 1, 515.

Sadashiva, B.K. 1976 Mol. Cryst. Liquid Cryst. 35, 205.