CHAPTER 6

DETERMINATION OF THE ABSOLUTE ORIENTATIONAL ORDER PARAMETER USING INFRARED DICHROISM: APPLICATION TO CBOOA

6.1 Introduction

The director $\hat{n}$ defines the __average__ direction of orientation of the long axes of the molecules. However, the molecules themselves deviate from this mean direction 'because of thermal fluctuations. At any given instant, the orientation of a molecule with respect to a laboratory fixed coordinate system x, y, z, with $\hat{n}$ along a, may be described by the three Eulerian angles ψ, φ and θ.[1] Due to the cylindrical symmetry of the uniaxial smectic A and nematic phases and the occurrence of nearly free rotation of the molecules about their long axes[2-4] in these phases, all values of ψ and φ are equally probable. The orientation of a given molecule is therefore completely specified by the angle θ and the probability of such an orientation can be described by a normalized distribution function $f(\cos \theta)$. The equivalence of the directions $\hat{n}$ and $-\hat{n}$ allows one to expand this distribution function into a series of Legendre polynomials of even order.[5] Thus

$$f(\cos \theta) = \sum_{\substack{l \text{ even}}} \frac{2l + 1}{2} \left\langle P_l(\cos \theta) \right\rangle P_l(\cos \theta) \qquad (1)$$

The coefficients $\langle P_l(\cos\theta)\rangle$ are defined as the orientational order parameters of the system, the angular brackets denoting an ensemble average over all the molecules. The first two of these, $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ are normally found adequate for describing the long range orientational order of the system. For complete order, $\langle P_2(\cos\theta)\rangle = \langle P_4(\cos\theta)\rangle = 1$, while for complete disorder, $\langle P_2(\cos\theta)\rangle = \langle P_4(\cos\theta)\rangle$ 0.

The temperature dependence of the orientational order parameter, $\langle P_2(\cos\theta)\rangle$, normally denoted as S, has been measured using a number of techniques such as optical birefringence,[6,7] infrared and ultraviolet linear dichroism,[8,9] diamagnetic anisotropy,[10,11] NMR[12-15] and ESR.[16] The value of S in the nematic phase is found to be strongly temperature dependent and it drops discontinuously to zero at the nematic-isotropic transition. In the smectic A phase, S is not as strongly temperature dependent as in the nematic phase. When the smectic A phase goes over directly to the isotropic liquid, a discontinuous change in S is observed at the transition.

When the smectic A phase is followed by a nematic phase, the behaviour of S at the smectic A-nematic transition depends on the order of this transition. When the transition is of the first order, S shows a discontinuous change and when it of the second order, it varies continuously

but it may show a discontinuity in slope.

The temperature variation of S in the nematic phase has been explained qualitatively by a mean field theory by Maier and Saupe,[17] though the quantitative departure is considerable *in many* specific cases. The introduction of higher order terms in the Maier-Saupe potential function has been suggested to account for these discrepancies.[18,19] This theory has been extended to the smectic A phase by McMillan[20] and qualitative agreement with experiment has been obtained.

Following an initial suggestion by McMillan that the smectic A-nematic transition in CBOOA may be of the second order,[21] considerable experimental[22-25] and theoretical[26] work has been devoted towards understanding the nature of this transition. The orientational order parameter has therefore been studied by a number of authors. We briefly review the methods used by them.

(a) Diamagnetic anisotropy: If χ_1, and χ_2 are the principal diamagnetic susceptibilities of the molecule referred to its own principal axes and $\Delta\chi$, the diamagnetic anisotropy per unit volume of the nematic medium, the orientational order parameter is given by[27]

$$S = \frac{\Delta\chi}{n(\chi_1 - \chi_2)} \tag{2}$$

where n is the number of molecules per unit volume.
We see from the above expression that the absolute
value of S may be determined if we can determine χ_1
and χ_2, and this requires a knowledge of the
crystal structure. Hardouin et al.[22] have measured
AX for CBOOA but have not been able to obtain χ_1
and χ_2 so that only the relative orientational
order parameter is obtained from their studies.

(b) <u>Optical birefringence</u>: If α_e and α_o are the
principal polarizabilities of the nematic medium, and
$\alpha_{||}$ and $\alpha_\perp$ are the principal molecular polarizabilities,
the order parameter is given by[27]

$$S = \frac{\alpha_e - \alpha_o}{\alpha_{||} - \alpha_\perp} \qquad (3)$$

Using the Vuks relation[28,7] for the internal
field, we have,[29]

$$S = \frac{3(n_e + n_o)}{4\pi n(\alpha_{||} - \alpha_\perp)\,(n^2 + 2)}\,\triangle n \qquad (4)$$

where n_e and n_o are the extraordinary and ordinary refractive

indices and $\bar{n}^2 = (n_e^2 + 2n_o^2)/3$ and $\Delta n = n_e - n_o$ is the birefringence.

Huang et al.[29] have measured the birefringence in the nematic phase of CBOOA. Here, because of the lack of refractive index data in the crystalline phase they have not been able to determine $\alpha_{||}$ and $\alpha_{\perp}$, and hence they obtained only the relative values of S.

Also, since homogeneously aligned smectic A samples are difficult to produce, this method is not convenient for determining the orientational order in smectic A phases.

(c) **Nuclear Magnetic Resonance-Quadrupolar Splitting**: The quadrupolar splitting ΔH in the nematic and smectic phases, of nuclei with spin $I \geqslant 1$ is proportional to the order parameter, the constant of proportionality being sensitive to the electric field gradient tensor at the nuclear site.[30]

Cabane and Clark[15] have measured the quadrupolar splitting of the central nitrogen atom in the nematic and smectic A phases. However, they are unable to obtain the absolute value of the order parameter due to the lack of knowledge of the electric field gradient tensor at the site of the nitrogen atom.

We note that all these studies have been able to

determine the relative *variation* of the orientational
order parameter. The absence of measurements in the solid
phase or inadequate information about the molecular
structure has rendered it impossible to determine the
absolute value in all these cases.

In this chapter we present the results of our
studies *of* the absolute orientational order parameter in
CBOOA using infrared dichroism.

6.2   Principles of the method

In determining S from infrared studies, one needs
a vibrational transition moment in the molecule, which
makes a known angle a with the long axis of the molecule.
Using a homogeneously aligned sample and polarized radiation,
S can be evaluated from the two Integrated absorption
coefficients,[27,31] $A_{||}$ and $A_{\perp}$, the subscripts $||$ and $\perp$
denote, respectively, the cases where the incident radiation
is polarized parallel and perpendicular to the direction
of alignment of the sample. A simpler technique which
avoids the need *for* polarized radiation utilizes homoeo-
tropically aligned samples.[32] In this case, when the
incident radiation propagates along the uniaxial direction
of the sample, the, choice of a specific direction of the
electric vector becomes superfluous. An additional
advantage is that aligned smectic A samples can be obtained

more easily in the homoeotropic configuration. In contrast, it is necessary to cool the nematic phase in the presence of an external field,[33] in order to obtain a homogeneously aligned smectic A sample.

When a homoeotropically oriented sample is used, the 'dichroic' ratio, R, can be defined as the ratio of the integrated absorption of the band in the liquid crystal to that in the, isotropic phase. Then, it is relatively straightforward to show that

$$R = 1 - S(1 - \frac{3}{2} \sin^2 \alpha) \tag{5}$$

and hence,

$$S = (1 - R)/(1 - \frac{3}{2} \sin^2 \alpha) \quad . \tag{6}$$

This result is derived in Appendix C.

In evaluating R from the experimental data, one must ratio the integrated absorption of the band in the liquid crystal with that in the isotropic phase and not just the respective peak absorption coefficients. Also, the experimental absorption profile has to be corrected for the effects of finite spectral slit width, Following Ramsay's procedure[34] we represent the true absorption profile by a Lorentzian function. The corrected integrated absorption strength is then calculated from the transmittance curve using the experimentally observed values of the peak

absorption coefficient, the Width of the absorption profile at half peak height as well as the spectral slit width of the instrument. It is known that for suitably isolated bands, the Lorentzian function modified by the Finite spectral slit width, can satisfactorily approximate the experimental absorption profiles.[34]

The experimental value of R, R(exp), would in general be different from the true value because the refractive indices of the liquid crystal differ from that of the isotropic phase. Moreover, the polarization field in the liquid crystal is expected to be anisotropic. Hence we *write,*

$$R = \bigwedge R(exp) \tag{7}$$

where, $\bigwedge$ is the appropriate correction factor. Following Saupe and Maier,[27] it is shown in Appendix D that in our case,

$$\bigwedge = \frac{n_o(n^2 + 2)^2}{n[n_o^2 + 2 + \underline{a}(n_o^2 - 1)]^2} , \tag{8}$$

here. n_o is the refractive index of the liquid crystal for the ordinary rag, n is the refractive index of the isotropic liquid and $\underline{a}$ is a temperature dependent factor which takes account of the anisotropic polarizability of the liquid crystalline medium.[27] The refractire indices relate to the pertinent wavelength range, excluding the contribution from the absorption band of interest.

An estimate of $\bigwedge$ thus requires a knowledge of n_o, n and $\underline{a}$. In the case of p-azoxyanisole, by extrapolating the available refractive index data[35] to 4.50 μ, we find that the estimated deviation of $\bigwedge$ from unity is well within 2% over a mesomorphic range of 40°C and this diffe- rence is even lees at lower temperatures. Although the refractive indices of CBOOA are not known in the wave- length region of interest, we may assume that they do not differ significantly from the case of p-azoxyanisole. This is a reasonable assumption because in both cases, the refractive indices are being extrapolated to a wavelength range far away from %hedispersion region, which lies in the ultraviolet or the short wavelength end of the visible region. On this basis, the possible corrections to the experimental values of the order parameter in CBOOA are also expected to be within about 2%. As this correction is less than our experimental uncertainties, it is not included in our determination of S. Thus, within the experimental accuracy, the present study leads to the absolute values of S in the liquid crystalline phases of CBOOA, whereas the earlier studies[15,22,29] yielded only the relative values of S.

6.3 Experimental

The spectra were recorded using the Leitz double, beam prism spectrograph. The spectra were scanned on the

expanded wavelength scale to facilitate more accurate
measurements of the linewidths.

Nematic liquid crystalline samples, aligned in the
homoeotropic configuration were prepared following the
method described in chapter 2. The nematic samples showed
good extinction under crossed polarizers. Also, upon cooling
to the smectic A phase, the homoeotropic alignment was
still preserved with no apparent degradation whatsoever.
NaCl windows were used and the sample thickness was kept at
$\sim$ 20 μ using a mylar spacer.

6.4   Results and discussion

The infrared absorption band used in our study of
the orientational order is the localized, $-C\equiv N$ stretching
mode arising from the nitrile group at one end of the
CBOOA molecule. This is a distinct and strong vibrational
band, almost free from any overlap with neighbouring lines
and having its transition moment nearly parallel to the
long axis of the molecule. The molecular structure of CBOOA
is shown in Fig. 3.1. Owing to the lack of any specific
knowledge concerning the statistical distribution of the
different possible conformations of the octyl tail in the
mesophases, we take the long axis of the CBOOA molecule as
the line passing through the centres of the two benzene
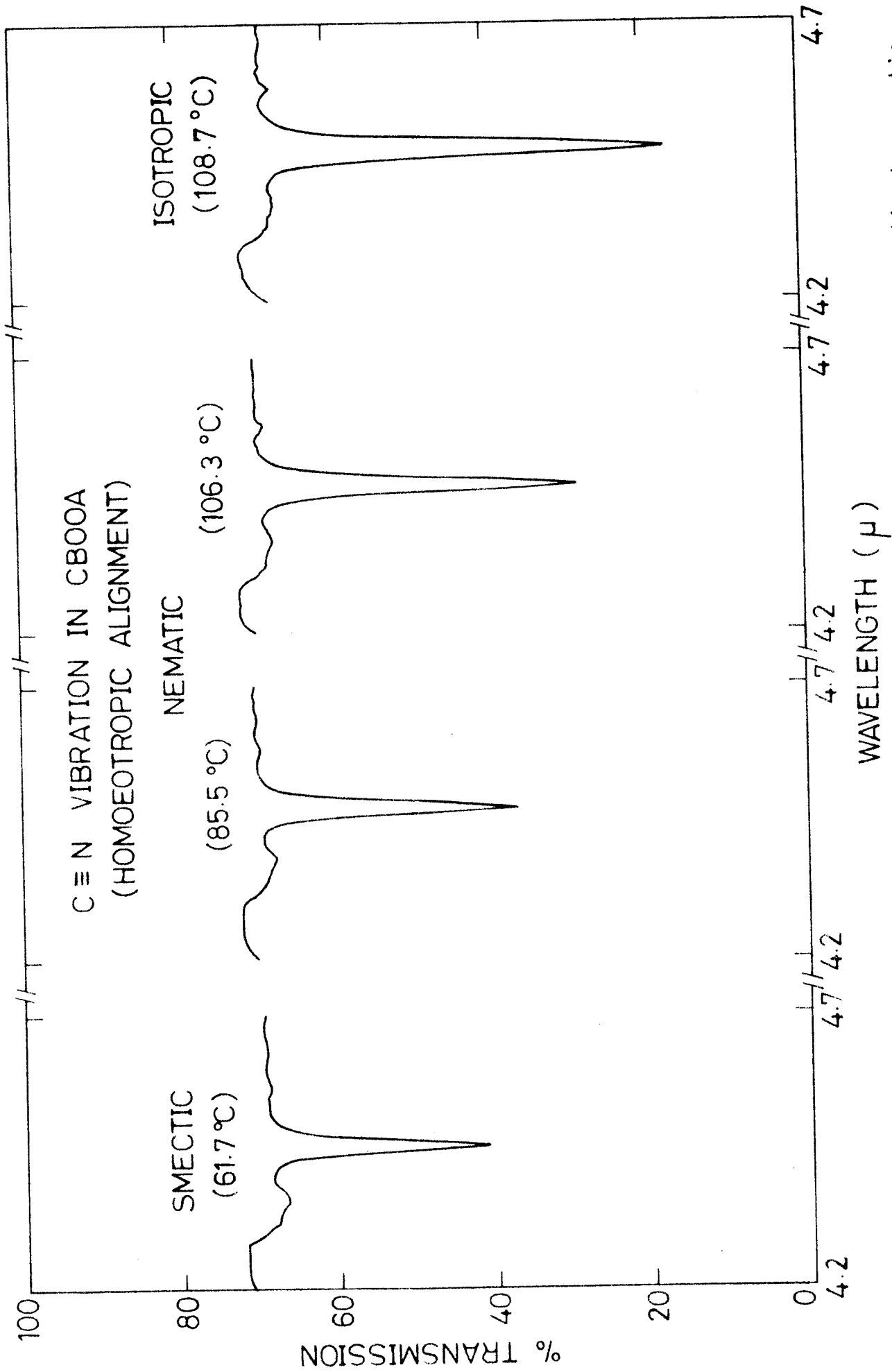rings. On this basis, the angle a between the transition

FIGURE 6.1: Absorption strength of the -C≡N stretching mode of CBOOA in the smectic A, nematic and isotropic phases. Below 73°C, the smectic A phase is supercooled. The liquid crystalline samples were homoeotropically aligned. The sample temperature corresponding to each trace is also shown.

moment of the $-C\equiv N$ stretching mode and the long axis of
the molecule is estimated to be $\sim 10°$.   This estimate of
α is in close agreement with the values assumed in other
similar cases where good agreement with experimental data
was obtained.[36,37]

Using a homoeotropically aligned sample and unpolarized
radiation in conjunction with %he experimental geometry
mentioned above, the absorption strength of this band was
studied as a function of temperature.   Figure 6.1 shows the
typical results obfained.   As the temperature is increased,
the degree of ordering of the molecules is expected to
decrease.   In view of the near parallelism of the $-C\equiv N$
transition moment with the *long* axis of the molecule, the
absorption strength should hence increase with increasing
temperature and this is consistent with the observed
behaviour.   At the transition to the isotropic phase, the
absorption strength showed a discontinuous increase corre-
sponding to a discontinuous change in the molecular ordering
st the nematic-isotropic transition.

Front the corrected integrated absorption strengths[34]
and Eq. (6), the variation of S can be determined if $\bigwedge$ is
assumed to be almost unity and these results are shown in
Fig. 6.2.   It can be seen *that* the values of S determined
in this study at the A-N and N-I transitions, are, respectively,
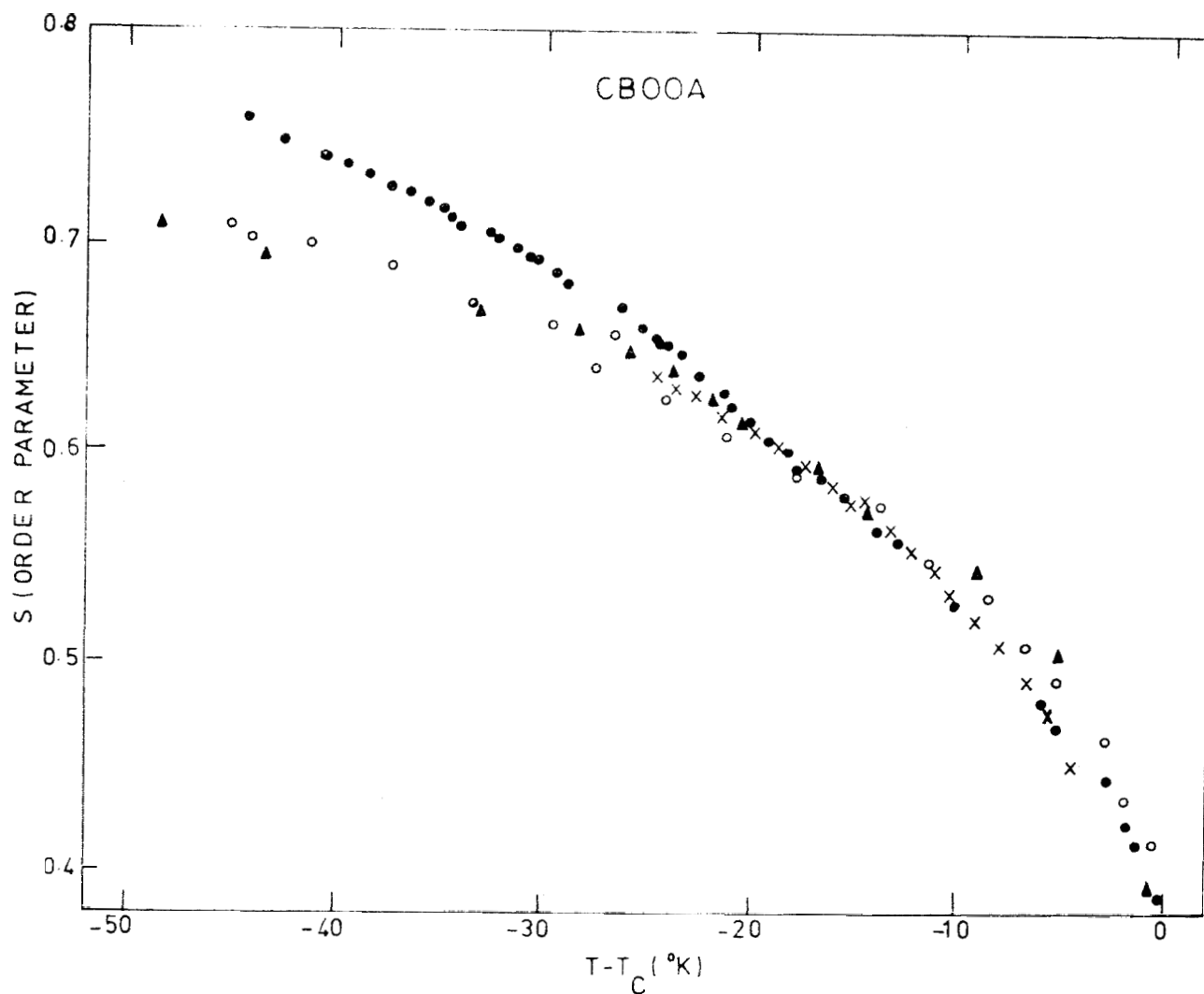0.62 and 0.41;   these are close to the typical values found

FIGURE 6.2: Variation of S in the smectic A and nematic phases of CBOOA. Open circles denote the values determined in this study. The variation of S determined from three other studies is also shown after each set of data is normalized to the present data at $T-T_c=-19°K$; T_c corresponds to the respective N-I transition temperature in each case. The ▲▲▲▲ triangles are from diamagnetic anisotropy data (Ref. 22); filled circles, NMR results (Ref. 15); crosses, birefringence results (Ref. 29).

near these transitions.[14,20,38] This tends to support
our assumption that in the present case, $\wedge$ does not differ
appreciably from unity. The S values are estimated to be
accurate to within the experimental scatter, which is less
than 5%.

We now compare the results of this study with those
obtained from earlier studies on CBOOA.[15,22,29] From a
study of its birefringence in the nematic phase, Huang
et al. reported[29] that their results did not agree with the
NMR data[15] or the diamagnetic anisotropy results.[22] The
discrepancy was reported to be substantial especially at
temperatures close to the N-I transition. In view of this,
it is of interest to compare the present value8 of S with
the earlier results. Figure 6.2 shows these data normalized
to ours at a relative temperature of $T-T_c = -19°K$; here T_c
denotes the respective N-I transition temperature for each
set of data. The relative temperature chosen here for
normalizing the different sets of data corresponds to the
lowest common point on the temperature scale, where all the
four sets of data relate to the nematic phase, It is seen
that in the nematic phase, the agreement between the diffe-
rent sets of data is reasonably satisfactory, the deviations
being within the typical limits normally encountered while
comparing the values obtained by different methods. The
substantial differences noticed by Huang et al. are attri-
butable to the fact that these authors compared the different

sets of data on a temperature scale referred to the A-N
transition temperature. This tends to produce considerable
discrepancies, especially at higher temperatures, because
the different sets of data are characterized by slightly
different N-I transition temperatures, presumably due to
different amount of impurities in them. Nevertheless,
as McColl[39] has shown the presence of small amounts of
impurities in a nematic phase does not normally affect the
value of the orientational order parameter at the nematic-isotropic
transition. It is thus clear that a proper comparison of
the! orientational order in the nematic phase must he based
on a temperature scaler referred Lo the N-I transition tempe-
rature, although one can, in principle, choose to normalize
the different sets of data at any given temperature within
the nematic range.

In the smectic A phase, the present results agree
closely with the diamagnetic anisotropy data.[22] However,
the NMR experiments[15] show a much steeper increase in S at
lower temperatures, than either of these two sets of data.
The magnetic fields used in both the NMR and the diamagnetic
anisotropy measurements are comparable, being nearly 28 and
23.0 kilogauss, respectively. This indicates that the
apparently higher orientational order obtained from the NMR
measurements is not entirely accounted for by the orienting
effects of the magnetic field. Optically, our samples were
seen to maintain good homoeotropic alignment in the smectic A

phase also. Thus, the origin of the observed differences in the smectic A phase between the NMR results on the one hand and the present results as well as the diamagnetic anisotropy data on the other, remains to be clarified.

The diamagnetic anisotropy results do not depend upon any specific assumptions regarding the molecular Interactions or local field effects. In this light, the agreement between the present data and the diamagnetic anisotropy results over the entire temperature range is a further indication that possible corrections to our data from local field effects are well within our experimental uncertainties.

As remarked earlier, near a second order A-N transition, the orientational order parameter is expected to vary continuously, but it may exhibit a discontinuity in slope. On the other hand, when the A-N transition is distinctly of first order, a discontinuous change in the order parameter is expected at the transition.[20,40] The NMR results of Cabane et al.[15] show that the discontinuity in the order parameter at the A-N transition in CBOOA is loss than 0.3% and an this bawls, they suggest that this transition may be of second order. Our data shown in Pig. 6.2 do not reveal a mensurable discontinuity at; the A-N transition. However, It must be noted that the possible scatter in our data amounts to $\sim$ 5% and 'hence our data do

not permit any conclusions *to* be drawn regarding the order of this transition.

6.5　Conclusion

From the temperature dependent changes in the intensity of the $-C \equiv N$ stretching mode, it has been possible *to* determine the absolute orientational order parameter in both the smectic A and nematic phases of CBOOA. The utilization of a homoeotropically aligned sample avoids the use of a polarizer and consequently improves the accuracy of the measurements. We find that the temperature variation of the order parameter agrees, for the most part, with previous measurements carried out using other techniques.

References

1. H. Goldstein, _Classical Mechanics_ (Addison Wesley Publishing Co., New York, 1950) p. 107.

2. H. Lippman and K.H. Weber, Ann. Phys. (Leipzig) 20, 265 (1957).

3. Z. Luz and S. Meiboom, J.Chem.Phys. 59, 275 (1973). See also Z. Luz, R.C.Hewitt and S. Meiboom, J. Chem. Phys. 61, 1758 (1974).

4. B. Deloche, J. Charvolin, L. Liebert and L.Strzelecki, J. de Phys. 36, Suppl. 3, C1-21 (1975).

5. E.B. Priestley and P.S. Pershan, Mol. Cryst. Liquid Cryst. , 369 (1973).

6. P. Chatelain, Bul. Soc. Franc. Miner. Cryst. 78, 262 (1955).

7. S. Chandrasekhar and N.V.Madhusudana, J. de Phys. Suppl. 30, C4-24 (1967).

8. W. Maier and G. Englert, Z. Electrochem. 64, 689 (1960).

9. W. Maier and A.Saupe, Z.Physik.Chem.(NF) 6, 327 (1956).

10. A. Saupe and W. Maier, Z.Naturforschg. 16a, 816 (1961).

11. H. Gasparoux, F. Hardouin and M.F. Achard, Pramana Suppl. 1, 215 (1973).

12. R.D. Spence, H.A. Moses and P.L. Jain, J.Chem.Phys. 21, 380 (1953).

13. R.D. Spence, H. Gutowsky and C.H. Holm, **J.Chem.Phys.** 21, 1891 (1953).

14. J.W. Doane, R.S. Parkes, B. Cvikl, D.L. Johnson and D.L. Fishel, Phys. Rev. Lett. **28**, 1694 (1972).

15. B. Cabane and W.G. Clark, Solid State Commun. **13**, 129 (1973).

16. A. Carrington and G.R. Luckhurst, Mol.Phys. **8**, 401 (1964).

17. W. Maier and A. Saupe, Z. Naturforsch. **13a**, 564 (1958), **14a**, 882 (1959); **15a**, 287 (1960).

18. S. Chandrasekhar and N.V. Madhusudana, Acta Crystallogr. **A27**, 303 (1971).

19. R.L. Humphries, P.G. James and G.R. Luckhurst, J.Chem.Soc. Faraday Trans. II, **68**, 1031 (1972).

20. W.L. McMillan, Phys. Rev. **A4**, 1238 (1971).

21. W.L. McMillan, Phys. Rev. **A7**, 1419 (1973).

22. F. Hardouin, H. Gasparoux and P. Delhaes, J. de Phys. **36**, Suppl. 3, C1-127 (1975).

23. D. Djurek, J. Baturic-Rubcic and F. Franulovic, Phys. Rev. Lett. **33**, 1126 (1974).

24. S. Torza and P.E. Cladis, Phys.Rev.Lett. **32**, 1406 (1974).

25. K.C. Chu and W.L.McMillan, Phys. Rev. **A11**, 1059 (1975).

26. B.I. Halperin, T. Lubensky and S.Ma, Phys.Rev.Lett. **32**, 292 (1974).

27. A. Saupe and W.Maier, Z. Naturforschg. **16a**, 816 (1961).

28. M.F. Vuks, Opt. Spectrosc. **20**, 361 (1966).

29. C.C. Huang, R.S. Pindak and J.T. Ho, J.de Phys. **35**, L185 (1974).

126

30. B. Cabane and W.G. Clark, Phys.Rev.Lett. 25, 91 (1 970).

31. W. Maier and G. Englert, Z.Electrochem. 64, 689 (1960).

32. H. Kelkar, R. Hatz and G. Wirzing, Z. Anal. Chem. 267, 161 (1973).

33. G.H. Brown, J.W. Doane and V.D. Neff, $Review-of the Structure and Physical Properties of Liquid Crystals (CRC Press, Cleveland, Ohio, 1971).

34. D.A. Ramsay, J. Amer. Chem. Soc. 74, 72 (1952).

35. M. Brunet-Germain, Mol. Cryst. Liquid Cryst. 11, 289 (1970).

36. S. Jen, N.A. Clark, P.S. Pershan and E.B. Priestley, Phys. Rev. Lett. 31, 1552 (1973).

37. A. Pines and J.J. Chang, Phys. Rev. A10, 946 (1974).

38. W.L. McMillan, Phys.Rev. A6, 936 (1972).

39. J.R. McColl, J. Chem. Phys. 62, 1593 (1975).

40. G.R. Luckhurst and M. Setaka, Mol. Cryst. Liquid Cryst. 19, 179 (1972).