# CHAPTER 8

## A NEW DIFFERENTIAL TECHNIQUE FOR THE STUDY OF DICHROIC SPECTRA USING UNPOLARIZED RADIATION

### 8.1 Introduction

Infrared dichroic studies on host and guest molecules in liquid crystals is a well established and useful method for probing the structure and orientational ordering of mesophases. Such investigations were usually performed in the past using polarized radiation and homogeneously aligned samples[1-3] where the director *is* parallel to the walls of the sample cell. The need for polarized radiation and the consequent reduction in available energy are two of the main disadvantages of this technique. A simpler method is to use unpolarized radiation in conjunction with a homoeotropically aligned sample[4] whose director is normal to the cell walls. Two other distinct advantages of the latter technique were pointed out by us in Chapter 6 where we applied it to the determination of the absolute orientational order parameter in the smectic A and nematic phases of CBOOA.

In this chapter, we describe a new double-beam differential technique for observing the dichroic spectra in liquid crystals using unpolarized radiation. Unlike in previous cases, this method allows the effective dichroic spectrum to be recorded in a single scan. We present the

differential dichroic spectrum (DDS) *of* n-heptyl cyano-
biphenyl (7CB) and compare it with the behaviour expected
of many distinct group vibrations in 7CB. From the DDS
intensity of the $-C \equiv N$ band, we obtain the temperature
dependence of the relative orientational order parameter
in the nematic phase of 7CB. The differential method is
also preferable in the study of anisotropic solute molecules
oriented in a liquid crystal, as it facilitates complete
compensation for host absorption bands. This enables one
to examine the dichroism of solute absorption bands free
of interference even from intense, overlapping host bands.
We present illustrative results for p-nitrotoluene (PNT)
dissolved in a nematic mixture.

## 8.2 Principle of the method

The principle *of* DDS is quite straightforward.
Identical sample cells are kept in the two channels of
a double-beam spectrometer. The reference channel contains
a homoeotropically aligned nematic ample while the other
channel contains the sample in ita isotropic phase. A
spectral scan under these conditions directly yields the
ratio $T_{iso}/T_{nem}$, where $T_{iso}$ and $T_{nem}$ are the transmitted
percentage intensities of the isotropic and nematic samples,
respectively. If we denote their corresponding absorbances
as $A_{iso}$ and $A_{nem}$, the apparent absorbance computed from

the spectrum would bet the 'dichroic difference' D
where,

$$D = A_{iso} - A_{nem} . \qquad (1)$$

The 'dichroic ratio', R, is defined[4] as

$$R = A_{nem}/A_{iso} . \qquad (2)$$

If the vibrational transition moment of an absorption
band makes an angle a with the long axis of the molecule,
it is easily shown that (Appendix C)

$$1 - R = S(1 - \tfrac{3}{2}\sin^2 \alpha) , \qquad (3)$$

where S is the orientational order parameter of the liquid
crystal. From eqs. (1)-(3), it follows that $D \propto S$ .
Thus from any given band in the DDS it is possible to
determine the relative variation of S as a function of
temperature. Conversely, if $A_{iso}$ and the absolute value
of S are known from other measurements, DDS can be used
to determine a far any absorption band.

It is interesting to note From the above that for
tho 'magic' angle $\alpha_o \sim 54°44'$, $D \equiv 0$. Such a band will
be absent in DDS irrespective of the temperature of the
nematic sample. For any other band, as $D \propto S$, the
largest signals would be obtained at the lowest attainable
temperature of the nematic sample. Also, D is positive

If $\alpha < a_\parallel$ while it is negative for $\alpha_0 < a$ . Hence the observed sign of D in DDS indicates the effective dichroic behaviour of any absorption band.

The present; technique measures the difference between two absorbance values directly; hence it is inherently more sensitive and accurate than if $A_{iso}$ and $A_{nem}$ were to be measured separately. This is especially so for bands whose $a$ is very close to $\alpha_0$.

As D can be positive ox negative, in practice it is necessary to position the baseline of DDS at or below the middle of the transmitted intensity scale on the chart. For this purpose, we found it convenient to use in the sample channel a wire mesh attenuator with $\sim 40\%$ transmission.
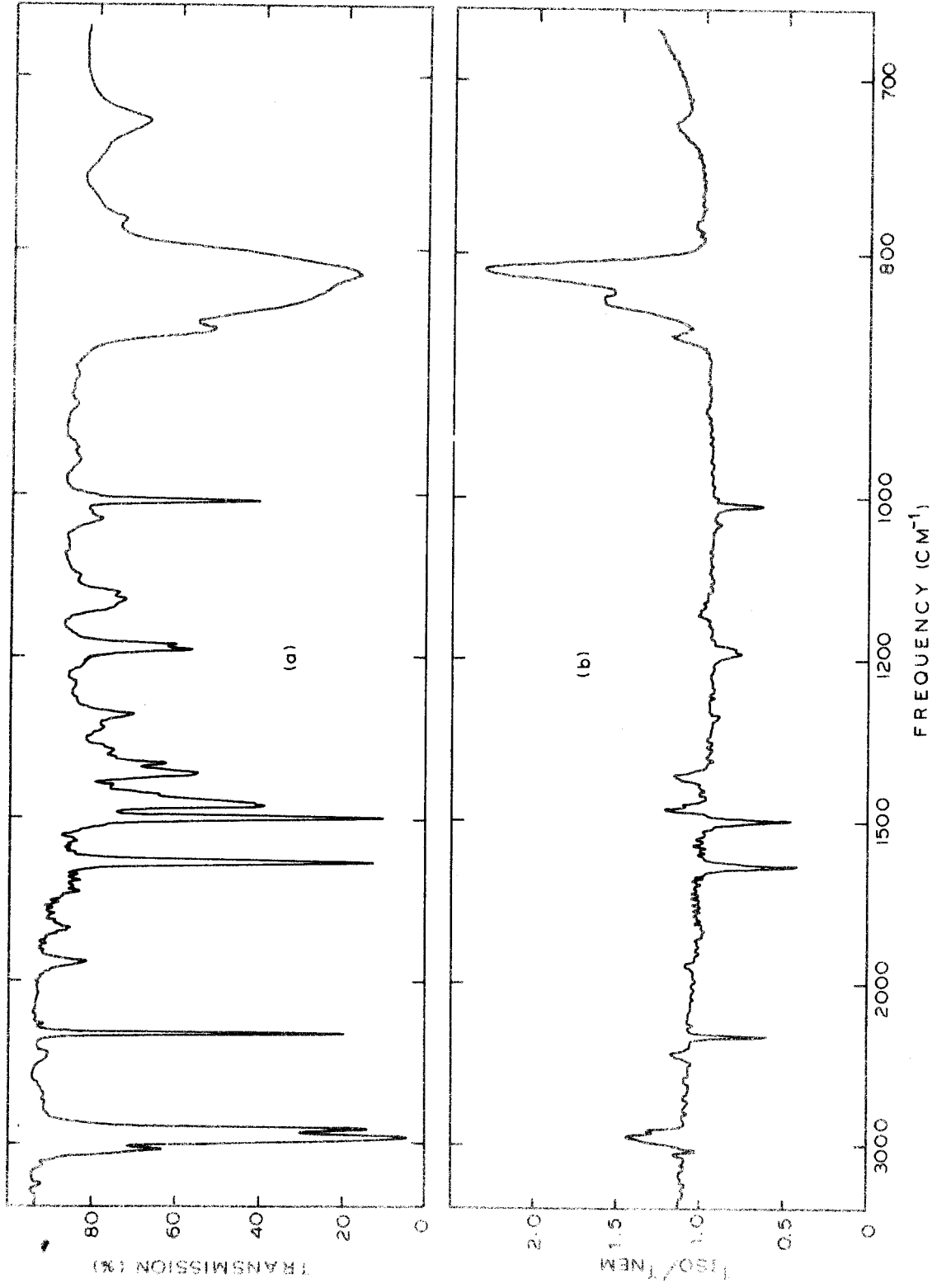
## 8.3  Experimental

The liquid crystals used in these experiments were all synthesized and purified in our chemistry laboratory. The p-nitrotoluene was of commercial grade and it was purified by recrystallization in ethanol. Other details including the method of preparing homoeotropically aligned samples have been described previously.

## 8.4  Results and discussion

Figure 8.1 shows the DDS of 7CB. Also shown for

FIGURE 8.1

(a) Absorption spectrum of (7CB) in the
    isotropic phase;  T = 48°C.

(b) Differential dichroic spectrum of 7CB;
    the temperatures of the nematic and
    isotropic samples are, respectively, 35
    and 48°C.

TRANSMISSION (%)

80

60

40

20

0

(a)

MEM $I/SO_2$

2.0

1.5

1.0

0.5

0

(b)

FREQUENCY (CM$^{-1}$)

700   800   1000   1200   1500   2000   3000

comparison is the normal transmission spectrum of the
isotropic phase. We ascertained that when both samples
were taken to the isotropic phase, the compensation was
exact over the entire spectral range. As noted already,
the DDS has peaks on both sides of the baseline. The
behaviour expected of several distinct group vibrations
is in accord with that observed here. For example, the
-C≡N stretching vibration at $\sim 2240$ cm$^{-1}$ should have its
transition moment along the long axis of the molecule; for
such a vibration D is expected to be positive and this is
what is observed. In contrast, the out-of-plane C-H
bending modes of the aromatic ring which occur in the
range 770-870 cm$^{-1}$ and the CH$_2$ rooking mode at 724 cm$^{-1}$
all show the opposite behaviour as is to be expected. Also,
the mode at 833 cm$^{-1}$ appears well resolved in DDS whereas
St is seen only as a shoulder in the normal transmission
spectrum. In the C-H stretching region, the aromatic C-H
stretch at $\sim 3050$ cm$^{-1}$ exhibits positive D, whereas the
aliphatic C-H stretching nodes at $\sim 2960$ and 2880 cm$^{-1}$
show negative D. The ring C-C skeletal modes at 1615 and
9500 cm$^{-1}$ are both seen to be polarized predominantly along
the long axis of the molecule. The mode at 1008 cm$^{-1}$ may
also be a ring skeletal mode. The methylene and methyl
deformation modes in the range 1380-1490 clearly have the
major component of their transition moment perpendicular
to the long axis. The modes at 1925 and 1810 cm$^{-1}$ are very

probably combinations of ring deformations. These as
also the modes around 1120 and 1290 $cm^{-1}$ are barely seen
in DDS indicating that their $\alpha$ values are all quite close
to $\alpha_0$. Assignments of the modes in the range 1000-1300
$cm^{-1}$ is, however, complicated by the fact that here the
skeletal and $CH_2$ deformations of the heptyl chain can
overlap with in-plane aromatic ring vibrations. Neverthe-
less, tire examples discussed above serve to clearly
illustrate the use of DDS in structural studies on
mesogens.

We have measured the integrated absorbance of the
$-C\equiv N$ band in DDS, corrected for the effects of finite
spectral slit width,[5] in a temperature interval close to
the nematic-isotropic transition temperature, $T_c$. These
values, normalized to earlier Raman measurements[6] of the
absolute values of S in 7CB, are shown in Fig. 8.2. The
relative variation of S derived from DDS is seen to be in
quite good agreement with the Raman Data.

The dichroic behaviour of PNT as a guest molecule
was studied by dissolving it in a nematic mixture of
n-octyl cyanobiphenyl (8CB) and n-octyloxy cyanobiphenyl
(8 OCB) in the mole ratio 1.05:1. The concentration of
PNT in the mixture was $\sim$18.4 mole per cent. Figure 8.3
shows the individual spectra of PNT and (8CB + 8 OCB) in
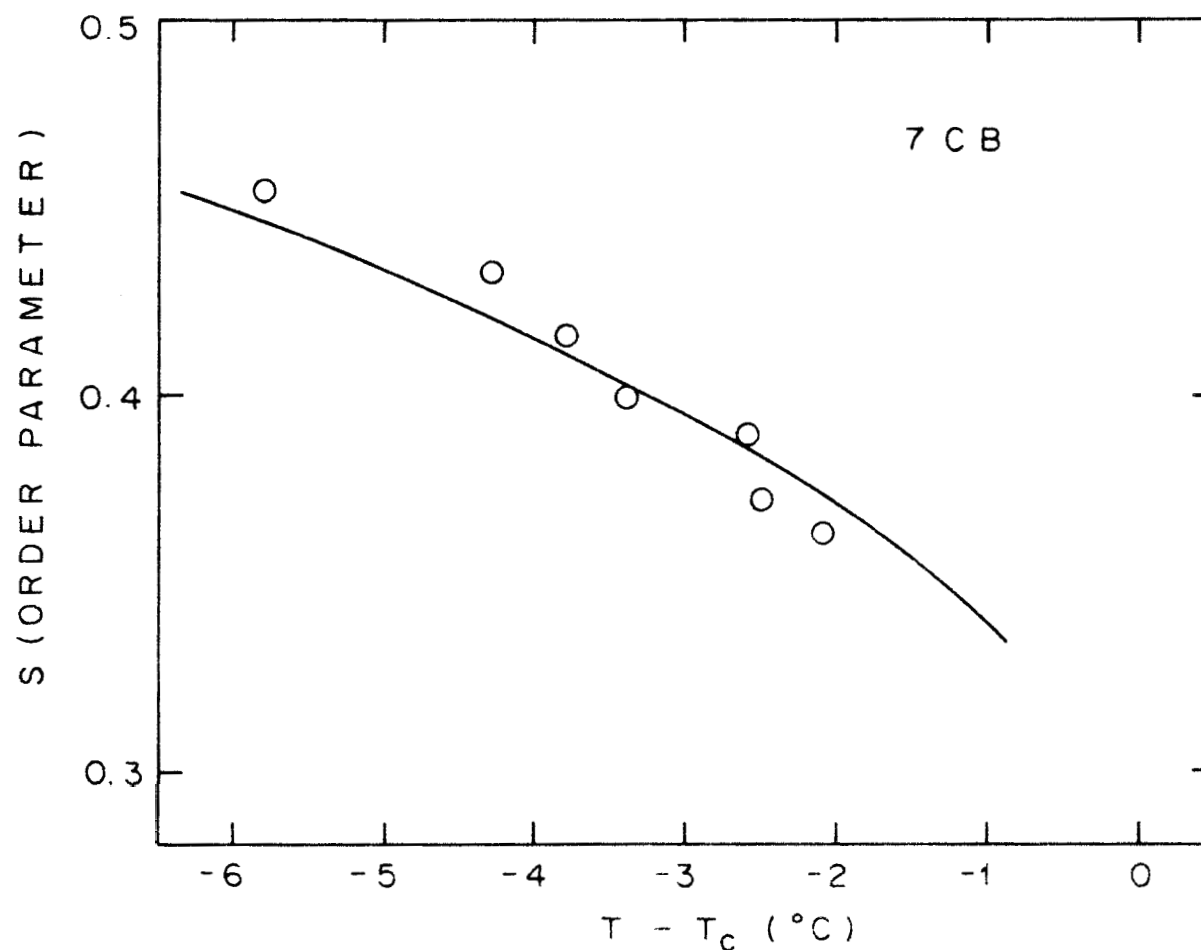the isotropic phase. It is seen that the two spectra

**FIGURE 8.2:** Variation of S in the nematic phase of **7CB** as a function of the relative temperature, $T-T_c$; $T_c$ represents the nematic–isotropic transition temperature. Solid line shows the mean variation of the absolute values of S obtained **from** Raman data (Ref. 6). Open circles denote the values **determined** in this study after being **normalized** to the absolute variation of S near the middle of the temperature range of interest.

FIGURE 8.3

(a) Absorption spectrum of the nematic
    mixture (8CB + 8 OCB) in its isotropic
    phase; T ~ 69°C.

(b) Absorption spectrum of liquid PNT at
    60°C.

(8CB + 8 OCB)-ISOTROPIC PHASE

(a)

p-NITROTOLUENE-LIQUID PHASE

(b)

FREQUENCY (CM⁻¹)
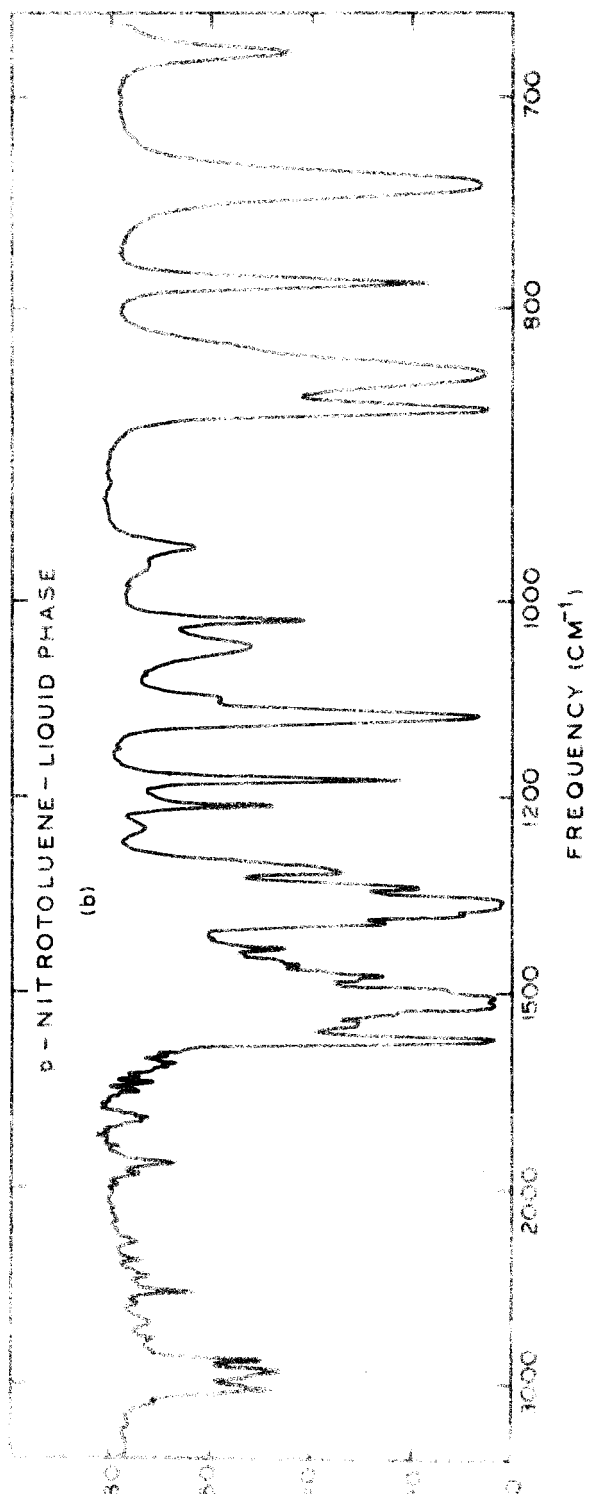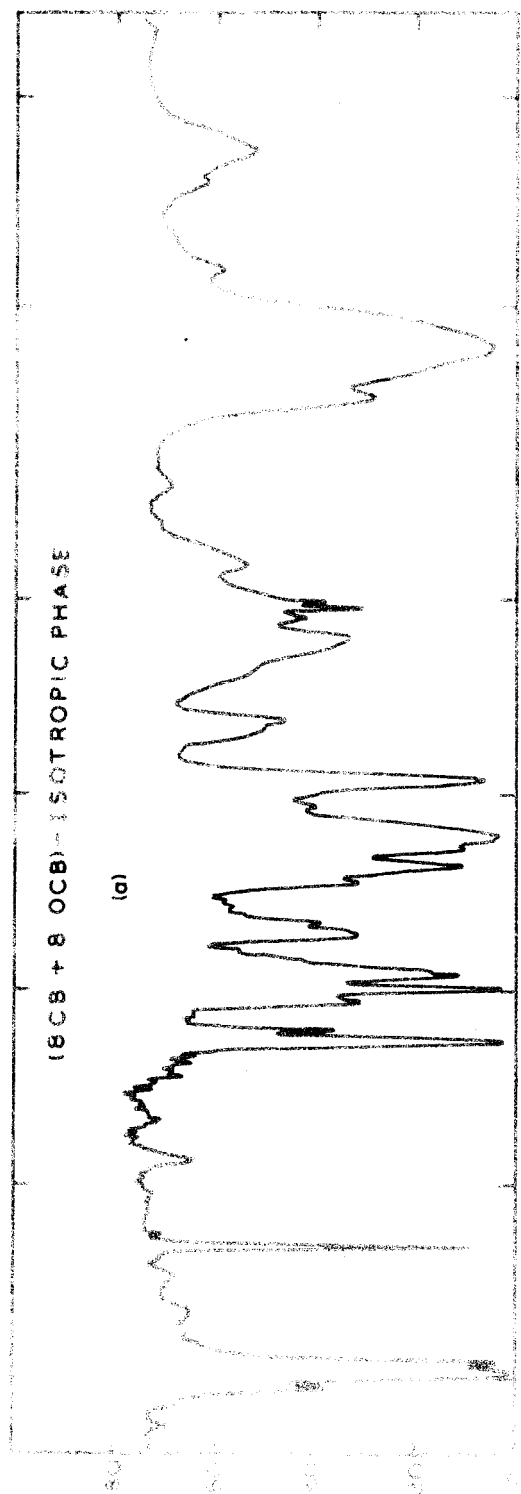
overlap rather strongly, especially in the range 900–1700 cm$^{-1}$. As will be seen below, the differential technique allows almost complete compensation for host absorption bands. The sample of PNT dissolved in the nematic mixture was kept in the sample beam while that of the pure nematic mixture was in the reference beam. The nominal thickness of both samples was $\sim 6$ μ. First, both samples were heated to the isotropic phase and the thickness of the reference sample was slightly adjusted until exact compensation of tho host absorption bands was attained. This could be conveniently monitored through the disappearance of the $-C \equiv N$ band in the spectrum. Under these conditions, the compensated 'isotropic' spectrum of randomly oriented PNT molecules could be recorded. Next, both samples were cooled t o the nematic phase where they were homoeotropically oriented. The reference sample, however, was maintained at a suitably higher temperature in order t o match the lower value of S in the sample containing PNT. low the compensated spectrum of 'homoeotropically' aligned PNT molecules could be recorded. Due to the relatively low concentration of PNT in the nematic mixture, only the very intense solute bands were clearly observed in these spectra. Figure 8.4 shows illustrative results for the three most intense bands, together with their dichroic difference at the peak. Note the almost perfect compensation of host absorption bands

## FIGURE 8.4

Compensated absorption spectra of PNT dissolved in the nematic mixture (8CB + 8 OCB).

(a)   Isotropic orientation of the molecules: reference sample at 69°C; sample with PNT at 44°C.

(b)   Homoeotropic orientation of the molecules: reference sample at 54°C; sample with PNT at 30°C.

(c)   Dichroic difference D, at the peak.

p - NITROTOLUENE
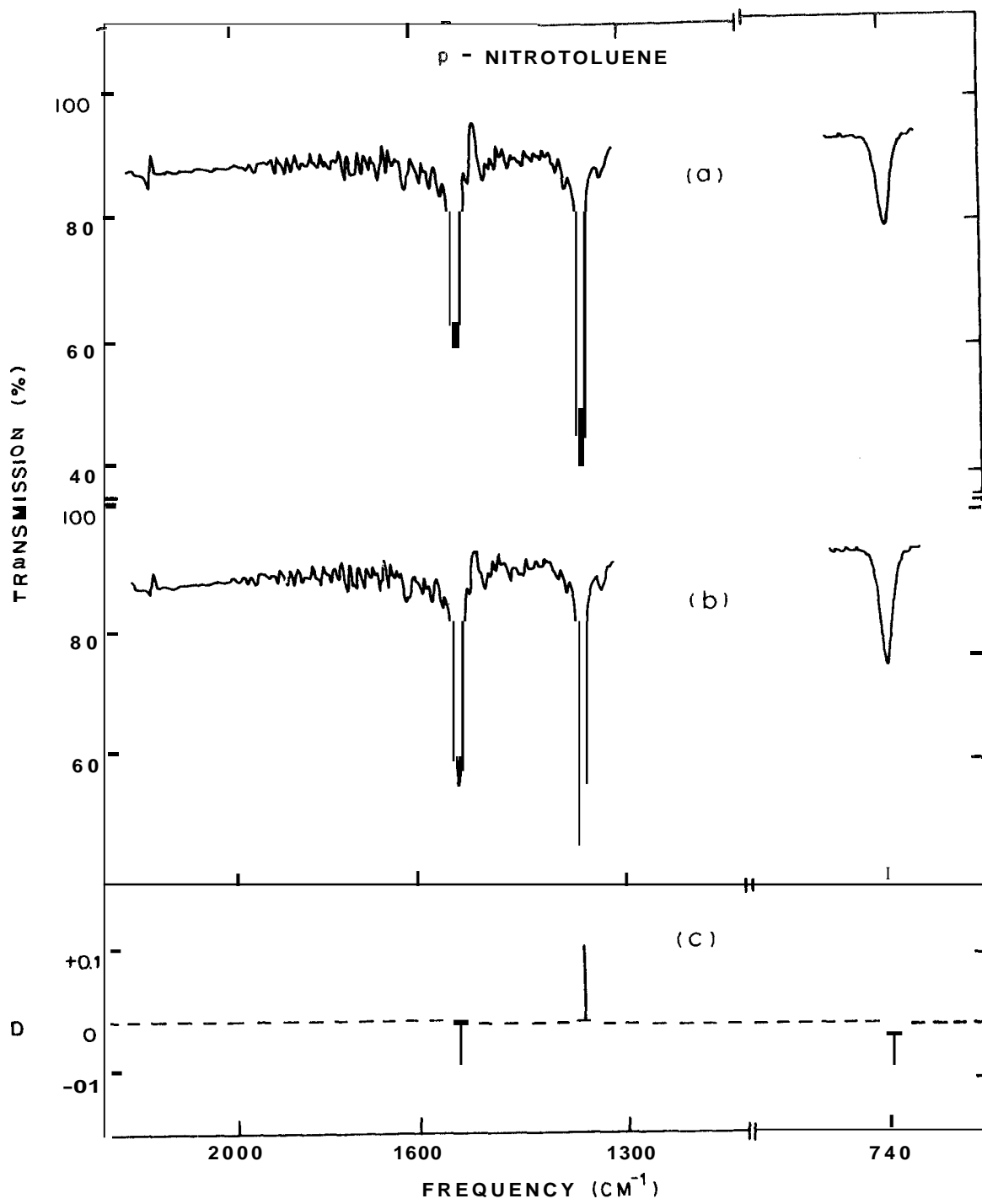
as revealed from the absence of the $-C\equiv N$ band in these spectra. The very weak signal at the position of the $-C\equiv N$ band, which resembles the derivative of a normal lineshape, seems to indicate that at the concentrations of PNT used here there is still some interaction between guest and host molecules. Due to this the $-C\equiv N$ band could have been shifted to a slightly higher frequency in the sample containing PNT, thereby causing the weak, anomalous signal. We assign[7] the bands at 1515 and 1348 $cm^{-1}$ to the asymmetric and symmetric stretching modes, respectively, of the $NO_2$ group in PNT. Their transition moments ehoufd hence be perpendicular and parallel, respectively, to the long axis of the molecular. As expected, the asymmetric mode does exhibit a negative dichroic difference whereas the symmetric mode shows the opposite behaviour. The rode at 738 $cm^{-1}$ can be assigned to an out-of-plane C-H bending mode of the phenyl ring in PNT; this assignment is also supported by its negative dichroic difference.

## 8.5   Conclusions

DDS is seen to be an attractive method for the study of host and guest molecules in liquid crystals. The potential use of the technique is quite general and it is applicable to any system which can be uniaxially oriented. In addition to the nematic phase, this method can therefore

be used to investigate the smectic A and smectic B
liquid crystals as well.

# References

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