Molecular Crystals and Liquid Crystals

X-RAY Studies on the Columnar Structures of Discotic Liquid Crystals

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X-RAY STUDIES ON THE COLUMNAR STRUCTURES OF DISCOTIC LIQUID CRYSTALS

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Since the discovery of discotic liquid crystals in 1977 [1] the field has grown rapidly with an estimated 3000 compounds belonging to this category. Generally these compounds have flat or nearly flat cores and surrounded by four to eight long chain substituents. A vast majority of these compounds exhibit the columnar mesophase. This phase is characterized by a structure in which the disc shaped molecules are stacked one on top of the other to form columns, the different columns constituting a two-dimensional lattice. Several variants of the columnar structure have been identified–upright columns, tilted columns, hexagonal lattice, rectangular lattice, etc. The stacking of the discs within the column could be on the one extreme, liquid-like or on the other have a true long range order. Although X-ray measurements on quite a few compounds exhibiting these different structures have been reported, the temperature dependence of the various structural parameters does not seem to have received much attention. We have used an image plate detector to carry out detailed X-ray studies of several compounds exhibiting the columnar phase. Analysis of the X-ray patterns yields, apart from information on the structural symmetry in terms of the planar space groups, quantitative data on (i) the ordering of the chains and the cores of the mesogens, (ii) the core-core correlation length along the column axis and (iii) the intercolumnar spacing. In particular, it is seen that the extent of ordering of the discs within the columns has significant temperature dependence. Data collected as a function of temperature will be presented and questions regarding ordering within the columns addressed, particularly in two compounds, one of which exhibits a columnar to a plastic phase transition and the other, a columnar to a helical phase transition.

INTRODUCTION

Since their discovery [1], considerable progress has been made in eluci-
dating the columnar structures of discotic liquid crystals [2]. It is known
from these studies that the disc-shaped molecules stack one on top of the
other to form columns, the different columns forming a two-dimensional
lattice. Several variants of the columnar structure have been identified:
upright columns, tilted columns, hexagonal lattice, rectangular lattice etc.
The motivation for the present work came from the following two points

1. Unlike other compounds showing the columnar phase, hexahexylthio-
   triphenylene (HHTT for short), which exhibits the rare helical (H)
   phase, has a strongly temperature-dependent intercolumnar spacing in
   its columnar phase [3].
2. Can the intra-columnar arrangement of the discs in the columnar phase
   be simply described as being either long-range ordered or liquid-like? Or
   should one consider the intermediate situations?

To address these points we undertook X-ray studies on a number of dis-
cotic compounds, whose molecular structures and transition temperatures
are shown in Figure 1. Notice that most of the compounds exhibit a single
columnar phase with a two-dimensional hexagonal lattice (referred to as
Col_h phase hereafter), but two compounds also show a second columnar
phase, having a helical superstructure in the case of HHTT and a plastic
phase in the case of a mono-nitro triphenylene derivative (C4MNTP). The
experiments were done using Cu-K$_\alpha$ X-rays from a fine focus sealed-tube
generator in conjunction with double mirror focussing optics. The mirror
optics provides a nearly parallel beam over a long working distance. The
detector was an image plate detector (MAC Science, Japan Model DIP
1030) with an effective resolution of $100 \times 100\ \mu m^2$.

RESULTS AND DISCUSSION

A typical powder diffraction pattern and the extracted one-dimensional
intensity-diffraction angle (I-2θ) profile from the columnar phase of a
discotic compound is given in Figure 2 and shows several characteristic
features of the columnar phase. The spacings of the four low angle ref-
lections are in the ratio of $1:1/\sqrt{3}:1/2:1/\sqrt{7}$ and can be indexed to 10, 11,
20 and 21 reflections of a two-dimensional hexagonal lattice. In the wide-
angle region two broad reflections are seen one of them being relatively
sharp. The very broad one arises due to the interaction between alkyl tails
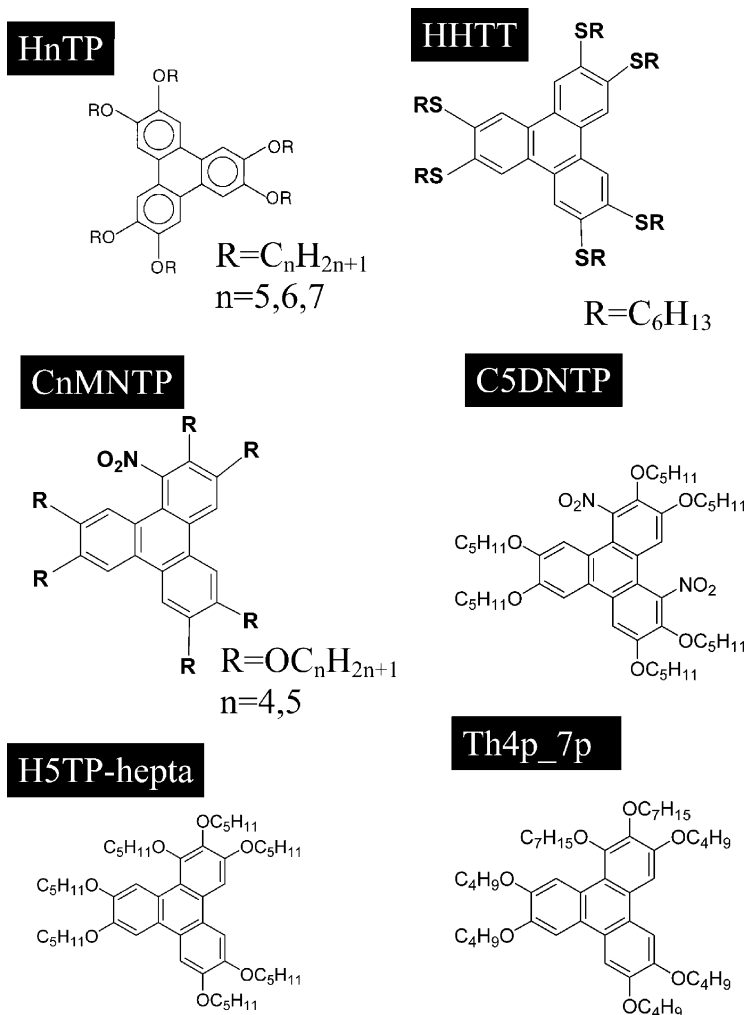in the same column and suggests that the associated order is liquid-like.

FIGURE 1 Molecular structures of the compounds studied.

The relatively sharp peak appears due to the fact that the molecular cores can pack better than the alkyl tails, which are in their molten state and therefore occupy more volume. It should be emphasized that the width of the peak, being inversely proportional to the length over which the cores are correlated, has by no means a unique value in the columnar phase of various materials. The peak can be completely absent for certain materials, but could be quite sharp indicating a large correlation length. This leads to the question mentioned in the Introduction, namely, whether the intracolumnar
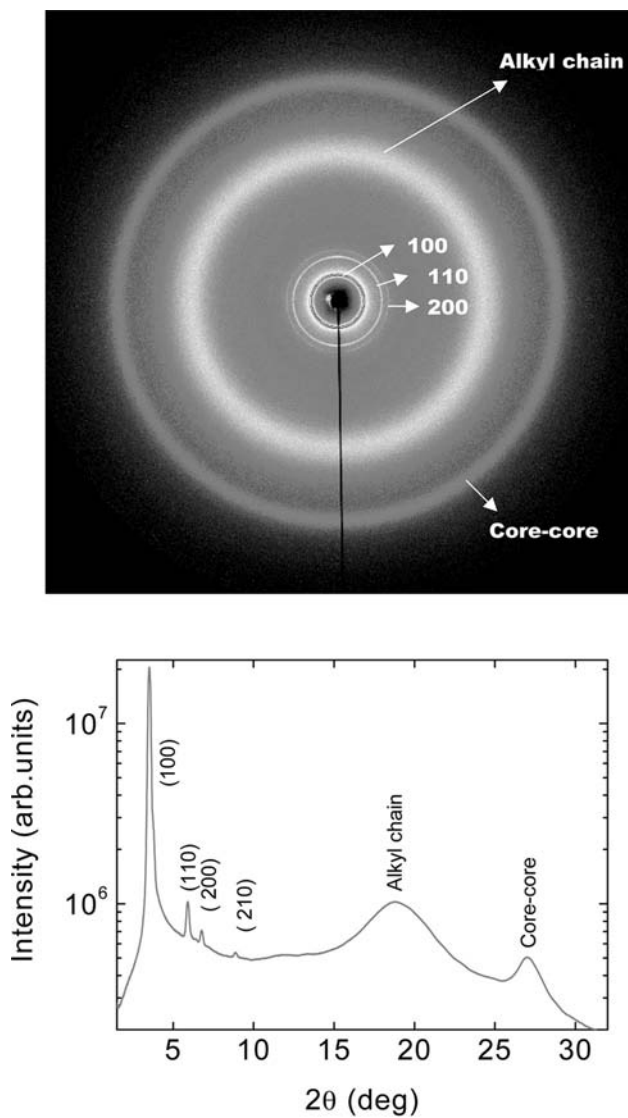
FIGURE 2 Typical Xray powder diffraction pattern (top panel) taken in the columnar phase of a discotic compound. The bottom panel shows the one-dimensional intensity vs. diffraction angle profile extracted from the pattern above.

order can be simply classified to be either liquid-like or three-dimensionally correlated or the intermediate situations should be considered separately. In answer to this question we shall provide experimental results and arguments later.

The 6-fold symmetry of the hexagonal lattice can be directly verified by sending the Xray beam along the column axis. But the actual experiment is not trivial since it is difficult to get a truly monodomain sample, for the following reason. Although by sandwiching the sample between flat substrates and keeping the sample thickness small it is possible to get the column axis oriented normal to the substrate, this is not sufficient to ensure that the local hexagons are also uniformly oriented in the plane. This situation is quite similar to what happens in the case of the orthogonal hexatic phase of rod-like molecules where although the smectic layer normal is uniformly oriented the bond-orientational axis need not be. But by the use of a surface field we have been able to get a high quality
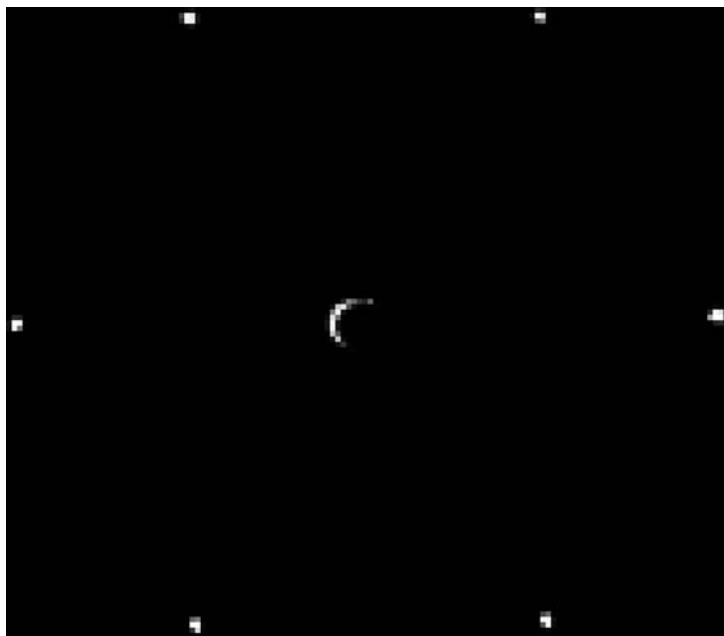

FIGURE 3 Diffraction pattern from a monodomain sample of the Col$_h$ phase obtained by sending the Xray beam along the column axis. The symmetrical distribution of the six spots with equal intensity provides direct evidence of the hexagonal symmetry of the mesophase. (The arc seen in the middle is due to the beamstop.)

"monodomain" sample, the evidence of which is seen in the symmetric 6-spot diffraction photograph (Fig. 3).

Regarding the first point mentioned in the Introduction, namely, that the intercolumnar spacing has an unusually large variation in the case of HHTT, we show in Figure 4 the temperature dependence of the hexagonal lattice spacing. Notice that there is a strong negative thermal expansion in the Col_h phase. In fact the magnitude of the temperature dependence seen for HHTT is larger than the one generally observed for even the smectic A phase of rod-like molecules. For a quantitative comparison of the thermal expansion, we have determined α, the thermal expansion coefficient for the different substances studied. The values of α shown in Figure 5 are determined from the lattice spacing data over a temperature range of 15–20°C close to the clearing point. In the columnar phase α has a negative sign, a feature attributable to the fact that the alkyl chains stretch and straighten out as the temperature is decreased thereby increasing the lattice spacing. Being very large, the value for HHTT stands out, particularly in comparison with H6TP, the oxygen analogue of HHTT. Further, another unique feature of HHTT is that the spacing between the alkyl chains within the same column hardly shows any temperature dependence. These two features suggest that owing to the presence of the bulky sulphur atom at all the six substitution sites, there is enough degree of freedom for the alkyl chains to have a large spread in the out-of-molecular-core-plane and therefore a reduction in the magnitude of the thermal fluctuations (as the temperature is reduced) results in a strong lateral expansion in the dimension (or diameter) of the columns.
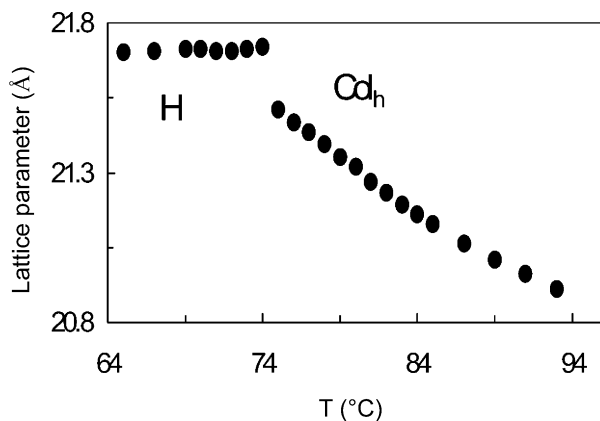

FIGURE 4 Temperature dependence of the intercolumnar lattice spacing in the Col_h and H phases of HHTT. The thermal expansion is large and negative in the Col_h phase, but negligibly small in the H phase.
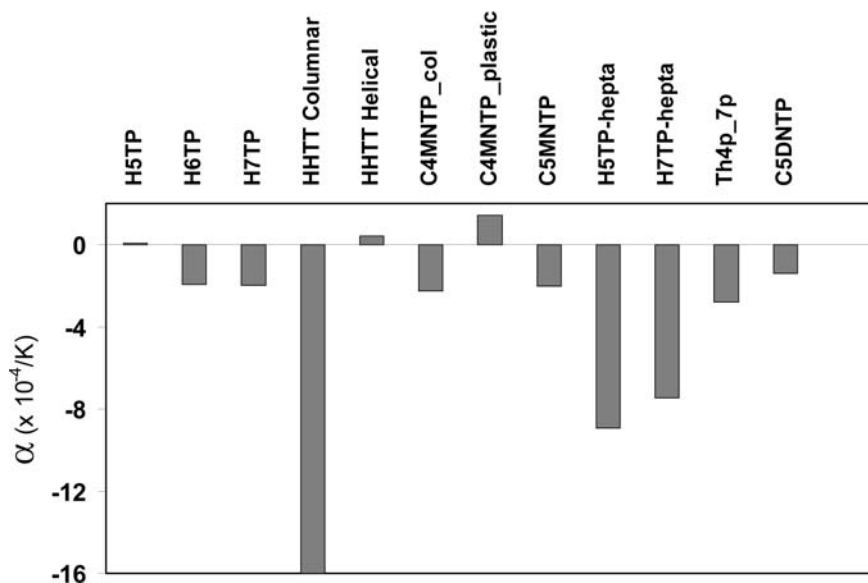
FIGURE 5 Thermal expansion coefficient α for the various compounds studied. Notice particularly the very large obtained value for HHTT.

We have also performed a comparative study of the lattice dimensions when the type and number of substituents to the triphenylene core is varied. The compounds studied and the lattice spacings determined are given in Table I. The first three compounds, which are successive homologues of the same series, showed a monotonic variation of the lattice spacing, as expected. When the oxygen atom of alkoxy chains is replaced with a sulphur atom there is a slight reduction in the value. Such a

TABLE I

Compound	Lattice Parameter (Å)
H5TP	20.1
H6TP	21.1
H7TP	22.4
HHTT	20.9
H5TP-hepta	19.8
C5MNTP	19.8
C5DNTP	19.3
Th4p_7p	19.4

reduction is also seen when the number of chains is increased from 6 to 7 (compare H5TP and H5TP-hepta) or more conspicuously when the number of substituents becomes 8 (compare H5TP, C5MNTP and C5DNTP). However, the value obtained for the mixed tail compound, Th4p_7p, is somewhat surprising. This molecule, whose molecular structure is shown in Figure 1, has 7 peripheral chains, two of which are long having 7 carbon atoms and the others are short with only 4 carbon atoms. Since the longer chains cannot have a preferential azimuthal orientation, one expects the column diameter to be an effective average of that due to the chains with 4 and 7 carbon atoms. But the observed value is substantially smaller. Being 19.4 Å, its value is comparable to that for the hexa substituted compound with all the chains having only 4 carbon atoms. This would mean that the longer chains are folded up. An indirect evidence for such a possibility is seen from the value of the core-core spacing. A value of 3.9 Å for the mixed tail compound being much larger than the typical 3.6 Å for the hexa sub-stituted compounds would mean that the folding of the longer chains prevents the cores approaching each other for a closer packing. Further we also see that the correlation length for the core-core interaction is one of the smallest seen amongst the compounds studied.

From the diffuse scattering profiles in the wide-angle region, Levelut [4] distinguished the intracolumnar order of the molecular cores from the more liquid-like order of the alkyl tails. The presence of the two diffuse peaks can be attributed to the competition between molecular stacking at two different nearest neighbour distances: a more favoured tail-tail packing distance and a shorter core-core approach distance. Of course, a disordered intracolumnar order helps in the coexistence of two different mean distances. Experimentally, the mean distances are given by the angular positions of the diffuse peaks, whereas the width of the peaks gives information about the correlation length or the domain size over which the correlation persists. Figure 6 shows the temperature depen-dence of the spacing between the alkyl tails for three different com-pounds. Notice that the variation is significant and nonlinear with temperature. Since the alkyl chains are in a molten state they take a random conformation and owing to thermal fluctuations fluctuate signi-ficantly about a mean position. An activation energy barrier generally governs the thermal fluctuations. Consequently an attempt has been made to describe the temperature variation of the alkyl chain spacing with an exponential function and the solid lines in Figure 6 show that the data is well described by such a function.

In order to determine the magnitude of the correlation length for the stacking of the cores, we have used two different expressions. The first one is the Scherrer's equation [5] for line broadening due to small crystallite size, according to which the correlation length is given by
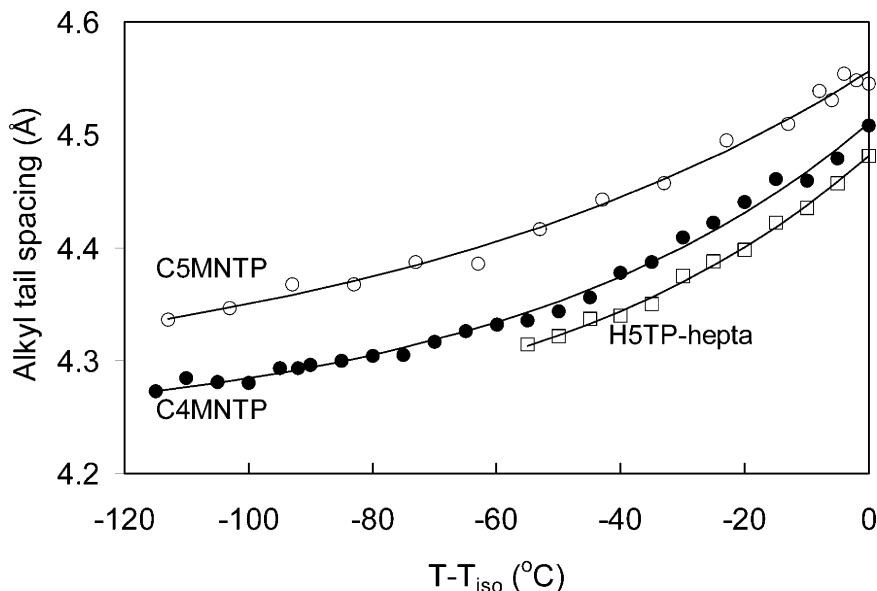
FIGURE 6 Thermal variation of the spacing between the alkyl chains in the same column for three compounds. The solid line represents a fit to an exponential function.

$$\xi_S = \frac{0.89\lambda}{\beta \cos \theta} \tag{1}$$

Here β is the full width at half maximum with λ and θ having the usual meanings. The coefficient 0.89 is a correction factor that depends on the shape of the domains. For fairly regular shapes it usually varies between 0.8 and 1.0. Following the derivation by Bragg [6] we have taken the value to be 0.89. Alternatively, we must consider the fact that the broadness of the peaks indicates short-range order and therefore the appropriate function to describe the profiles would be a sum of two Lorentzians, with q_j as the peak wave vector and k_j the half width.

$$I(q) = I_o + \sum_j \frac{I_j k_j^2}{(q - q_j)^2 + k_j^2} \quad \text{and}$$

$$\xi_L = \frac{1}{k_j} \tag{2}$$

With these definitions, we consider the example of C5MNTP to compare the values obtained at a particular temperature. ξ_s, the correlation length value calculated using the Scherrer's expression reaches a value

as high as 300 Å or nearly 79 nearest neighbours, which seems to be quite a large number to refer to the associated order to be liquid-like. But using the Lorentzian expression we get 54 Å or only about 14 nearest neighbours. For the tail-tail interaction similar calculations yield $\xi_s \sim 40$ Å or nearly 10 neighbours and $\xi_L \sim 6.5$ Å, i.e., about 1 to 2 neighbours. Since we know that the tail-tail interaction remains liquid-like, the ξ_L values make more sense. As a further check we did measurements on a pure long chain alkane liquid, viz., Octadecane. The ξ_s and ξ_L values obtained correspond to ~ 6 and 1 near neighbour distance respectively. Clearly the ξ value given by the Lorentzian profile analysis is more realistic.

The profiles corresponding to the wide-angle peak due to core-core interaction, obtained for C5MNTP at five different temperatures in the Col phase show (Fig. 7) that, even on a qualitative level there is a significant temperature dependence of the ξ_L. A detailed diagram showing the thermal variation of ξ_L is given in Figure 8; the behaviour seen is not specific to this compound, but is generally true. Also notice that the variation is smooth without any abrupt changes suggesting growth of short-range order in the system. Therefore we feel that the
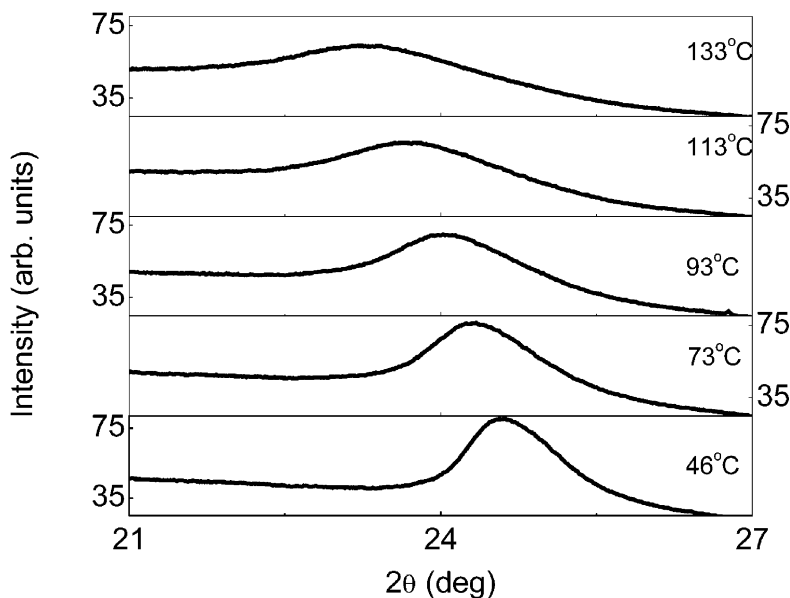

FIGURE 7 Core-core correlation peak taken at different temperatures in the Col$_h$ phase of C5MNTP. The correlation length, being inversely proportional to the width of the peak shows a significant increase with decrease in temperature.
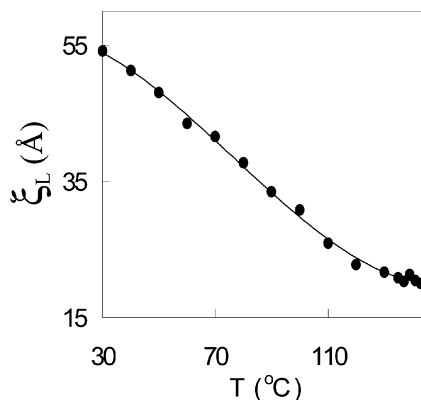
FIGURE 8 Growth of the core-core correlation with temperature in the Col_h phase of C5MNTP; notice that the growth is smooth without any abrupt jumps. The value at the lowest temperature ($\sim 110°C$ away from the Col_h–Iso transition) corresponds to ~ 14 near-neighbour correlations, supporting our argument that the core-core correlation is still liquid-like.

intracolumnar order should still be considered to be liquid-like. This situation is somewhat similar to the development of smectic-like short-range order in the nematic phase. As long as the smectic correlation is short-ranged or in other words, as long as it is not limited by the resolution of the set up, the phase is referred to as nematic. In a similar fashion, as the core-core interaction is short-ranged we should refer to the Col phase as columnar phase with liquid-like intracolumnar order or disordered columnar phase.

We have also considered two cases where the correlation length for the core-core interaction reaches the instrumental resolution of the set up. The first case is that of HHTT which shows the columnar to helical (H) phase transition. The Xray pattern and the I-2θ profile obtained in the H phase are shown in Figure 9 and clearly indicate the 3D positional order of the H phase. Concomitant with the jump seen for the lattice spacing (see Fig. 4), the core-core spacing as well as the associated correlation length abruptly increase at the transition, the latter parameter increasing from $\sim 20\,\text{Å}$ to $\sim 300\,\text{Å}$ (see Fig. 10). Although a pretransitional increase is seen as the temperature approaches the transition from the Col to the H phase the clear jump points to the fact that the transition is first order, as is evidenced by calorimetric measurements. The transition from the H phase, having a strong coupling between the columns with the conformational degree of freedom for the chains fully frozen out, to the Col phase with very weak coupling between the columns provides, perhaps, one of the best examples of one-dimensional melting.
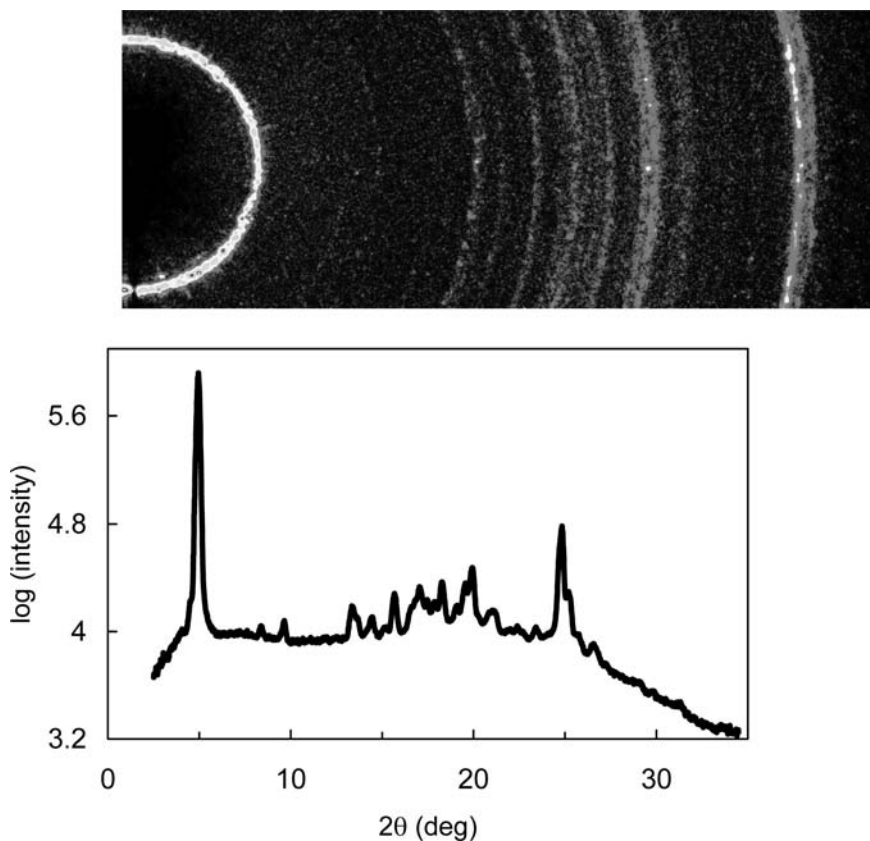
FIGURE 9 Xray pattern and I-2θ profile obtained in the H phase of HHTT. The large number of reflections and the very sharp peaks present in the wide-angle region are diagnostic of a three-dimensionally correlated structure.

The second case we consider is that of C4MNTP exhibiting the columnar to plastic phase transition. The discovery of the plastic phase was first reported by Prof. Wendorff's group [7]. The diffraction patterns obtained from the columnar and plastic phases of C4MNTP are shown in Figure 11. Notice particularly the wide-angle core-core reflection which is diffuse in the columnar phase, but in the plastic phase becomes very sharp, although split into two. The I-2θ profile from the Col phase (also shown in Fig. 11) is as expected, with the low angle reflections that can be indexed to a two-dimensional hexagonal lattice. In contrast the profile for the plastic phase has reflections having mixed indices, as was indeed seen by Glusen et al. [7]. Further, it is the presence of the diffuse peak
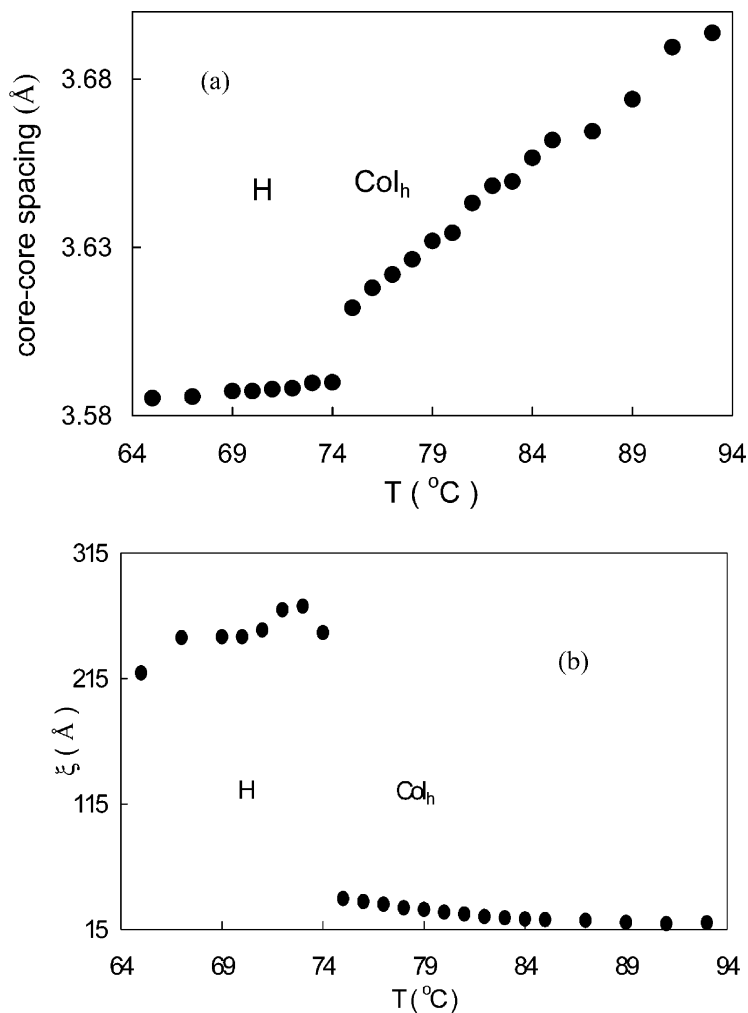
FIGURE 10 Temperature dependence of the (a) core-core spacing and (b) associated correlation length in the Col_h and H phases of HHTT. The jumps in the value seen at the transition are expected for a first order transition.

due to the alkyl chains that differentiates this phase from a truly crystalline phase. These features point to the fact that the plastic phase has a 3-dimensional positional order with the absence of any sliding motion of one column with respect to its neighbour, a feature characteristic of the Col phase. But the presence of the diffuse peak due to the alkyl chains points to the presence of a rotational degree of freedom for the discs to
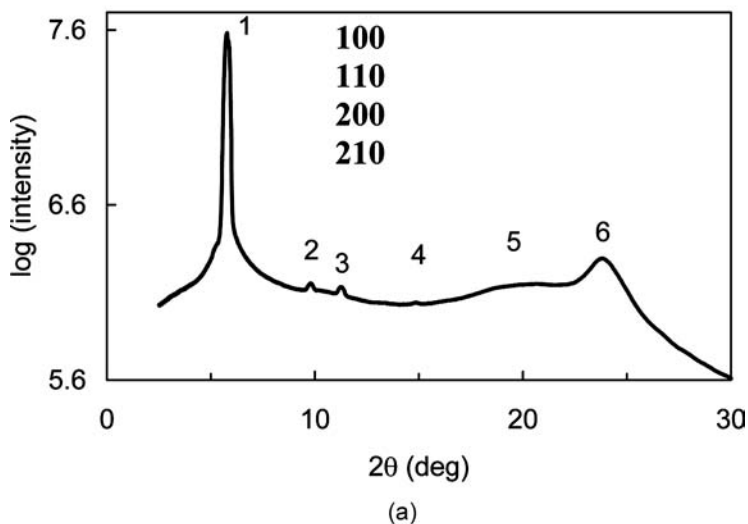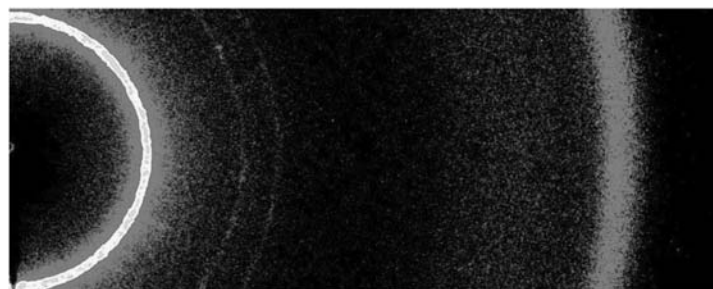
Columnar phase

FIGURE 11 Xray pattern and I-2θ profile obtained in the (a) Col$_h$ and (b) plastic phases of C4MNTP. While the Col$_h$ phase exhibits a pattern typical of a hexagonal columnar phase with a short-range core-core correlation, the plastic phase has additional reflections, which can be associated with a 3-dimensionally correlated structure.

rotate about the column axis. Our dielectric experiments, presented below, support this scenario.

Figure 12 shows the ε'' versus frequency profile in the Col and Plastic phases and also in the transition region for the compound C4MNTP.
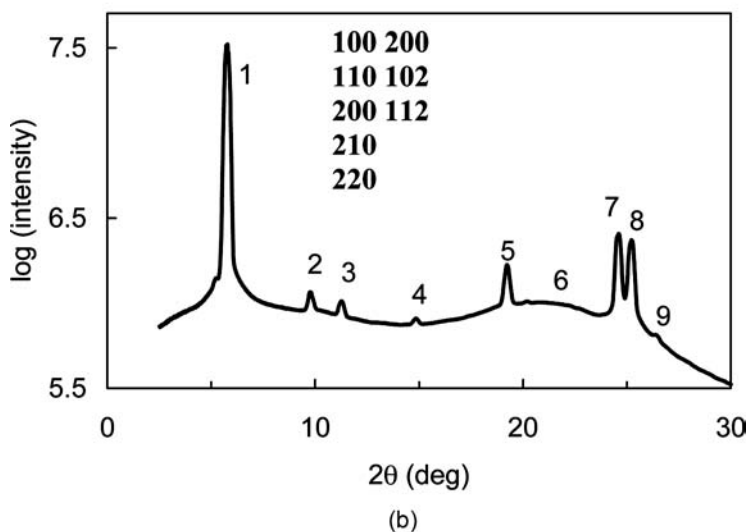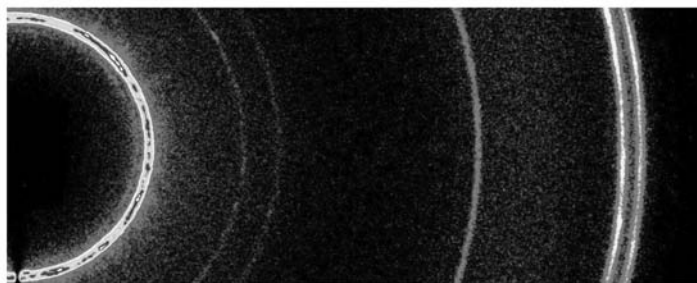
Columnar plastic phase

FIGURE 11. (*Continued*).

While only one peak is seen in each of the two phases, coexistence of two peaks is observed in the transition region. This is to be expected for the following reason. As evidenced by calorimetric measurements the Col-plastic phase transition is strongly first order associated with a two-phase coexistence. Also, as we shall see later, the dielectric relaxation frequency changes significantly across the transition, enabling one to observe the coexistence of peaks due to both the phases in the
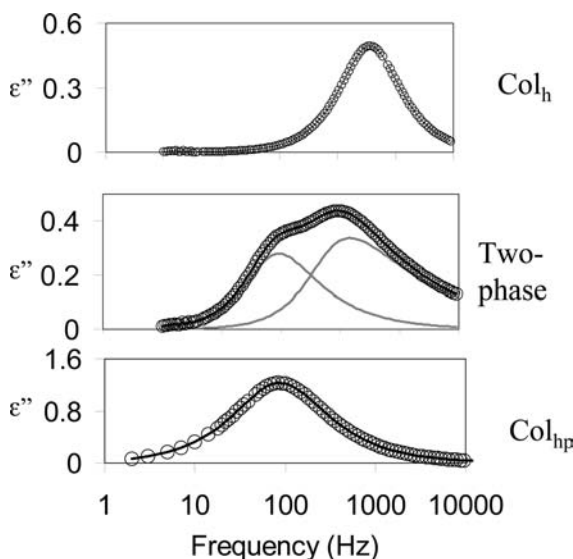
FIGURE 12 Representative plots of ε'' versus frequency in (a) the Col_h phase and (c) the plastic Col_{hp} phase of C4MNTP. The profile in panel (b) shows the coexistence of peaks due to both the phases in the transition region indicating the transition to be first order. The solid lines through the experimental data (O) are fits to single HN functions in the panels (a) and (c) and a sum of the two HN functions in the coexistence region with the individual HN functions shown as grey coloured lines in panel (b).

transition region. Thermal variation of the relaxation parameters $\Delta\varepsilon$ (dielectric strength) and f_R (relaxation frequency) obtained by fitting the ε'' vs. frequency data to a Havriliik-Negami function, are shown in Figure 13. It is observed that the transition is accompanied by an upward jump in the magnitude of $\Delta\varepsilon$ and a concomitant downward jump in f_R – additional features characteristic of a first order transition. The fact that the dielectric relaxation is still observed in the plastic phase indicates that the rotational degree of freedom for the discs to rotate about the column axis is still retained, although the whole process is slowed down.

The temperature dependence of the lattice parameter for the compound C4MNTP is shown in Figure 14 and exhibits a smooth variation without any abrupt jump across the Col-plastic transition. Up to a certain temperature in the Col phase the thermal expansion is negative as is common for the Col phase, but changes sign at a temperature close to the transition to the plastic phase. A possible reason for this behaviour is that at high temperatures in the Col phase the stretching of the alkyl chains with
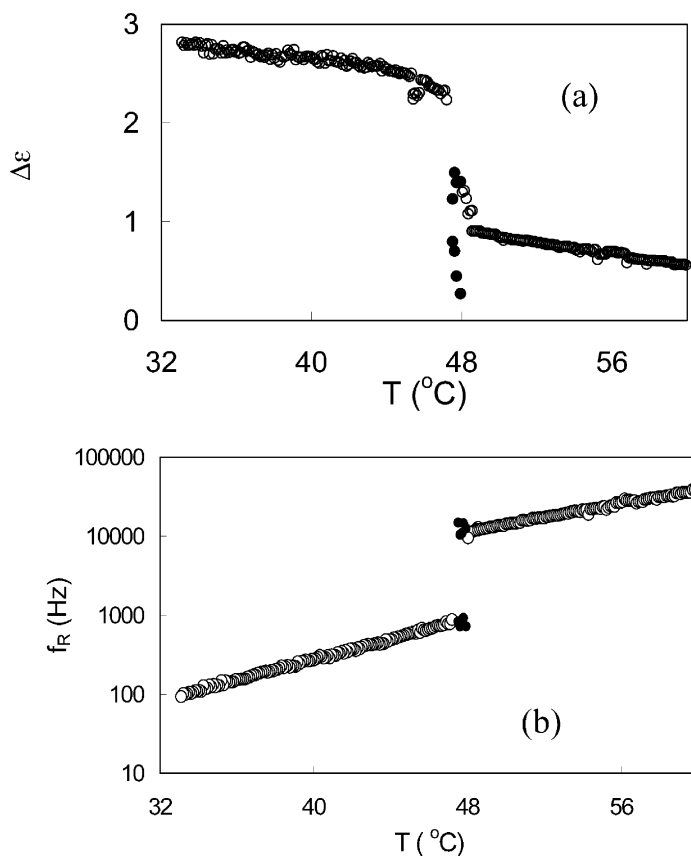
FIGURE 13 Variation of the dielectric strength $\Delta\varepsilon$ and the relaxation frequency f_R across the Col$_h$ phase to the plastic Col$_{hp}$ phase transition in C4MNTP. The open and solid circles represent the data in the two phases and the transition region respectively.

decreasing temperature results in an increase in the lattice parameter. As the temperature is lowered the chains become very stiff and with further lowering of the temperature the chains in the neighbouring columns interdigitate thereby decreasing the intercolumnar diameter. Owing to the fact that the tail-tail correlation peak remains diffuse even in the plastic phase, the corresponding spacing varies smoothly across the transition (Fig. 15). In contrast, the spacing as well as the correlation length asso-ciated with the stacking of the molecular cores shows an abrupt jump at the transition (Fig. 16).
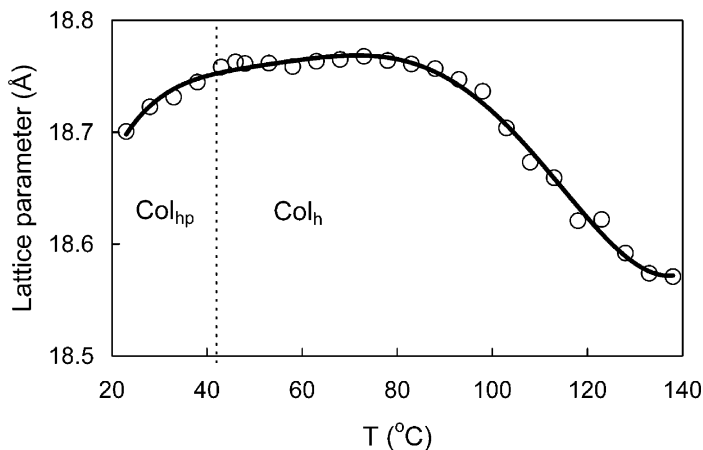
FIGURE 14 Plot showing a smooth variation of the lattice spacing across the Col_h–Col_{hp} phase transition in C4MNTP suggesting that the two-dimensional hexagonal lattice remains essentially the same in the two phases.

In summary, we have shown that the columnar phase typically shows a negative thermal expansion, although the magnitude observed for HHTT is large. We have argued that a more realistic value of the correlation length for the stacking of the molecular cores within a column is obtained by the Lorentzian profile description.
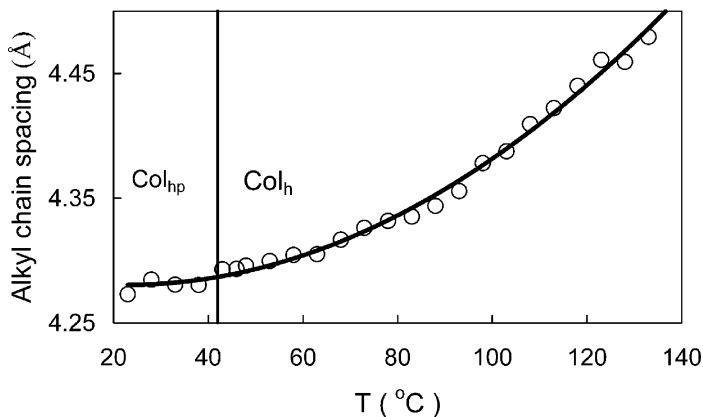

FIGURE 15 Temperature variation of the alkyl chain spacing across the Col_h–Col_{hp} phase transition in C4MNTP indicating that the tail-tail correlation is still liquid-like in the plastic phase.
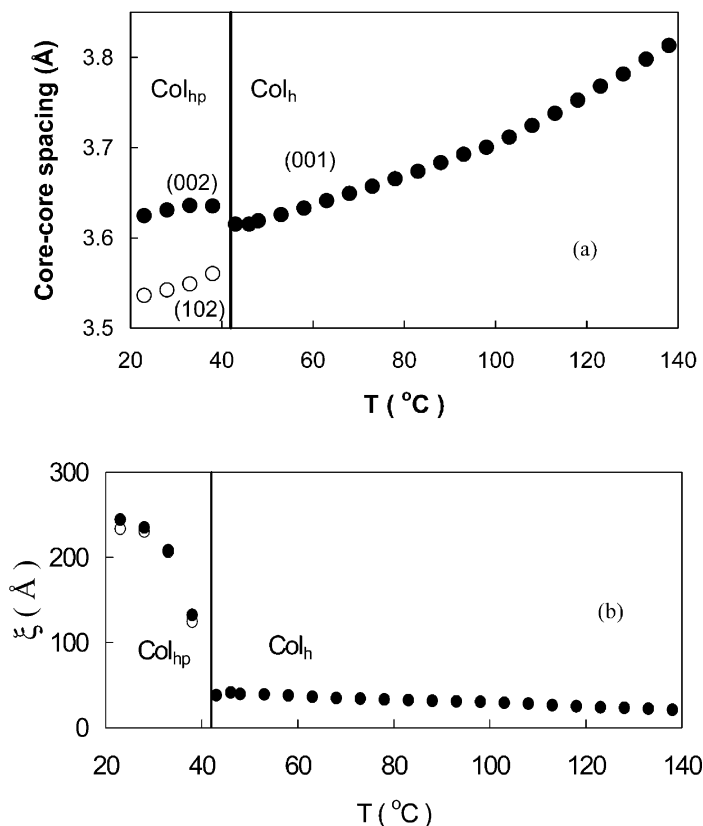
FIGURE 16 Temperature dependence of the (a) core-core spacing and (b) associated correlation length across the Col_h–Col_{hp} phase transition in C4MNTP.

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