Liquid Crystals

Columnar liquid crystals in oligosaccharide derivatives. II. Two types of discotic columnar liquid-crystalline phase of cellobiose alkanoates

A. Takada[a]; T. Fukuda[a]; T. Miyamoto[a]; Y. Yakoh[b]; J. Watanabe[b]

[a] Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan [b] Department of Polymer Chemistry, Tokyo Institute of Technology, Tokyo, Japan

PLEASE SCROLL DOWN FOR ARTICLE

Columnar liquid crystals in oligosaccharide derivatives

II. Two types of discotic columnar liquid-crystalline phase of cellobiose alkanoates

by A. TAKADA, T. FUKUDA and T. MIYAMOTO

Institute for Chemical Research, Kyoto University,
Uji, Kyoto 611, Japan

Y. YAKOH and J. WATANABE*

Department of Polymer Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan

A series of cellobiose octaalkanoates, Cel-II-n (n is the carbon number of the alkyl chain), with $n = 7$–14 were prepared and their mesogenic properties examined by differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction. All of these compounds form enantiotropic discotic columnar phases, in which the columns are built up by a regular stacking of the cellobiose moieties and are packed in a two dimensional lattice. Homologues with $n = 9$–14 form the D_{ho} phase only whilst the compound with $n = 7$ forms the D_{ro} phase. The $n = 8$ compound forms the D_{ho} phase at higher temperatures and the D_{ro} phase at lower temperatures. Structural parameters obtained from X-ray diffraction studies are presented for both phases.

1. Introduction

Since the discovery of the first discotic liquid crystals, there has been an increasing number of studies involving the synthesis, mesophase properties and structures of discogenic compounds [1, 2]. From these studies, it appears that the typical discogenic molecule has a flat, rigid, disc-like core connected to a number of flexible aliphatic side chains by ester or ether linkages. Most of the discotic mesogens encountered so far, have high rotational symmetry, i.e. six-fold, four-fold or three-fold symmetry, although some disc-like molecules with lower symmetry and some non-flat molecules have also been found to form discotic columnar phases.

Recently, we have investigated a series of polysaccharide and oligosaccharide based liquid crystals [3, 4], and found that cellobiose octadecanoate and cellotriose hendecadecanoate can also form hexagonal ordered columnar (D_{ho}) phases. In addition, similar columnar phases have been reported for acylated chitooligosaccharides [5], peracylated glucosides [6, 7] and cellobiosides [8], and other types of modified carbohydrates [9, 10]. These materials behave quite differently from the discotic materials based on aromatic cores and can therefore be classified as a distinct subgroup of discotic compounds.

In this study, to gain a better understanding of the discotic mesophase properties exhibited by these new materials, we have prepared a series of cellobiose octaalkanoates with alkyl side chains of various lengths and have examined the effect of the chain length on the mesogenic properties.

* Author for correspondence.

A. Takada *et al.*

2. Experimental

2.1. *Materials*

The compounds studied here have the following general formula:
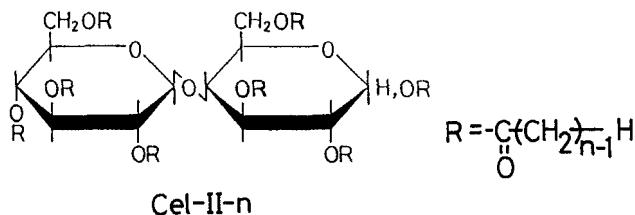
Cel-II-n

They were prepared by esterification of cellobiose with the corresponding alkanoic acid chloride as described below. The compounds are denoted by the abbreviated notation Cel-II-n, where II is the number of glucose units in the centre of the mesogen and n the number of carbon atoms in each substituent side chain.

The esterification was performed by the following general method. In a typical preparation 4 mmol of cellobiose was dispersed in a mixture of 40 ml of dioxane and 15 ml of pyridine. The solution was heated to 100°C and 100 mmol of alkanoyl chloride was added, with constant stirring. After 10 h, the solution was poured into methanol, filtered and washed with fresh methanol. The solid material was then dried and recrystallized three times from methanol/tetrahydrofuran. The complete esterification of the hydroxy groups and the purity of the compounds were confirmed by IR and NMR spectroscopy.

2.2. *Methods*

The calorimetric behaviour was investigated with a Perkin–Elmer DSC-II calorimeter at a scanning rate of $10°C \, min^{-1}$. The optical textures were studied with an Olympus BH-2 polarizing microscope equipped with a Mettler FP 80 hot stage (the samples being held between two untreated cover slips of ordinary glass). X-ray diffraction photographs were taken at different mesophase temperatures using Ni-filtered Cu-K_α radiation. The sample was held in a glass capillary tube and its temperature was measured and regulated by a Mettler FP 80 heater.

3. Results and discussion

3.1. *Phase behaviour*

Figure 1 indicates the DSC thermograms for Cel-II-n where n ranges from 7 to 14 and the corresponding thermodynamic data are listed in table 1. All of the materials exhibit two or three transitions. The mesophases can be observed in the temperature range below 120°C and their temperature ranges become narrower as n is increased. This behaviour results from both a rise in the melting temperature (T_m) of the crystalline phase and a fall in the isotropization temperature (T_i) of the mesophase as n is increased. All of the materials, with the exception of Cel-II-8, exhibit one mesophase. Cel-II-n with $n = 9$ to 14 form a hexagonal ordered columnar phase (D_{ho}) as previously reported for Cel-II-10, whilst Cel-II-7 forms another type of columnar phase that we provisionally call D_x the structural characteristics of which will be presented later. The intermediate Cel-II-8 specimen appears to form two mesophases, the D_{ho} phase at higher temperatures and the D_x phase at lower temperatures. The order in which these mesophases appear suggests that the D_x phase is more highly ordered than the D_{ho}
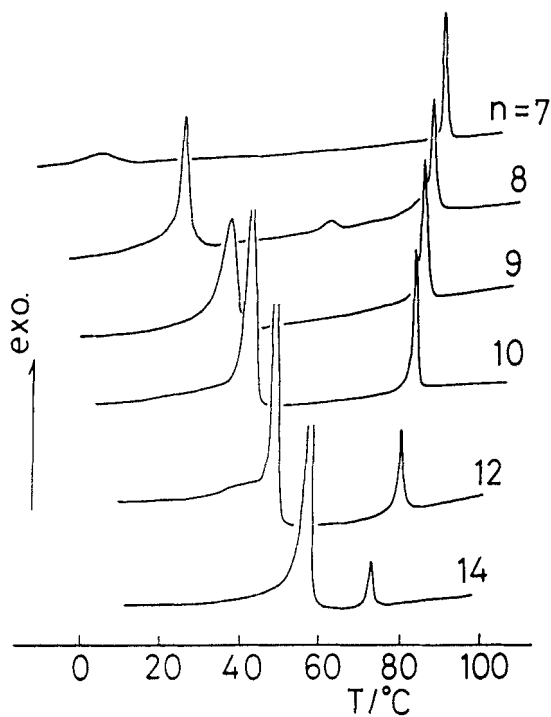
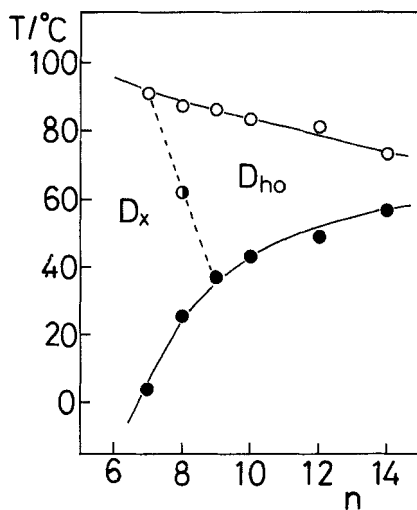Figure 1.   The DSC cooling curves of Cel-II-*n*.

Figure 2.   Variation of transition temperatures with *n* (the carbon number of the side chain group). Here the data are based on the DSC cooling curves.

Table 1. Phase transitions for Cel-II-*n*; C=crystal; I=isotropic liquid; ( )=transition enthalpies (ΔH).

	C	D_x	D_{ho}	I
Cel-II-7	● 4°C (12·1 kJ mol^{-1})	●	91°C (13·8 kJ mol^{-1})	●
Cel-II-8	● 25°C (17·6 kJ mol^{-1})	● 62°C (0·4 kJ mol^{-1})	● 87°C (12·1 kJ mol^{-1})	●
Cel-II-9	● 37°C (15·5 kJ mol^{-1})		● 86°C (11·3 kJ mol^{-1})	●
Cel-II-10	● 43°C (29·7 kJ mol^{-1})		● 83°C (9·2 kJ mol^{-1})	●
Cel-II-12	● 49°C (59·4 kJ mol^{-1})		● 81°C (7·1 kJ mol^{-1})	●
Cel-II-14	● 56°C (83·6 kJ mol^{-1})		● 73°C (5·9 kJ mol^{-1})	●

phase although this difference in the structural order is small as judged from the small transition enthalpy of approximately $0.4 \, \text{kJ mol}^{-1}$. Figure 2 shows the way in which transition temperatures and mesophase type vary with *n*. It is apparent that the compounds with the longer alkyl side chains tend to form the D_{ho} phase while those with the shorter alkyl side chains form the D_x phase. The structural characteristics for both phases are described in the next section.

3.2. D_{ho} Phase

In a previous paper [4], the mesophase of Cel-II-10 was identified as a D_{ho} phase from its characteristic optical textures and X-ray diffraction pattern. Similar observations, indicating that the mesophases of Cel-II-8, Cel-II-9 and Cel-II-12 are also D_{ho}, are briefly described in the following. In samples cooled from the isotropic melt, the D_{ho} phase initially appears as circular nuclei which grow into hexagonal flower-like units (see figure 3 (*a*)). These then coalesce to give a fan or mosaic texture. The hexagonal symmetry of the D_{ho} mesophase is responsible for the appearance of these textures. The X-ray diffraction pattern of the oriented D_{ho} phase usually contains three sharp equatorial reflections in the small angle region, and a sharp meridional reflection and broad ring in the wide angle region. As recorded in table 2, the equatorial reflections (indexed as *hk*0) correspond to spacings in the ratio, 1, $1/\sqrt{3}$ and 1/2, indicating that the columns are packed in a two dimensional hexagonal lattice. The sharp meridional reflection indexed as 001 indicates that there is a regular lateral packing of cellobiose moieties along the column. The broad ring in the wide angle region can be attributed to the disordered alkyl side chains. The structure of the D_{ho} phase can be depicted as shown in figure 4 of [4].

From the variation of the diffraction spacings with *n*, we can explore in more detail the structure of the D_{ho} phase. From table 2 it is evident that the spacings of the equatorial *hk*0 reflections increase with an increase in the side chain length while the spacing of the meridional 001 reflection remains constant at 5·4 Å. Over the range of side chain lengths examined, the calculated density remains relatively constant at a value of about $0.97 \, \text{g ml}^{-1}$. This indicates that the structure of the central core of the column is the same for all homologues and that the diameter of the column increases as the side chains become longer. In figure 4 the area of the unit cell of the two dimensional
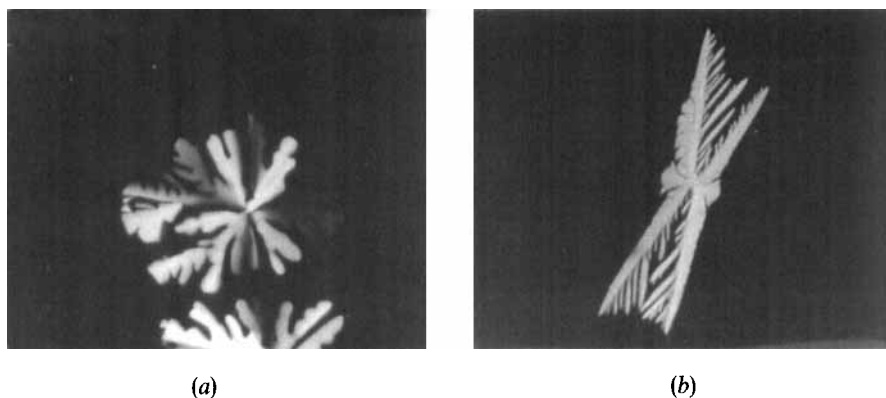
Figure 3. Optical textures of the nuclei of the columnar phases appearing on slow cooling from the isotropic liquid. (a) The D_{ho} phase of Cel-II-12 and (b) the D_x phase of Cel-II-7.
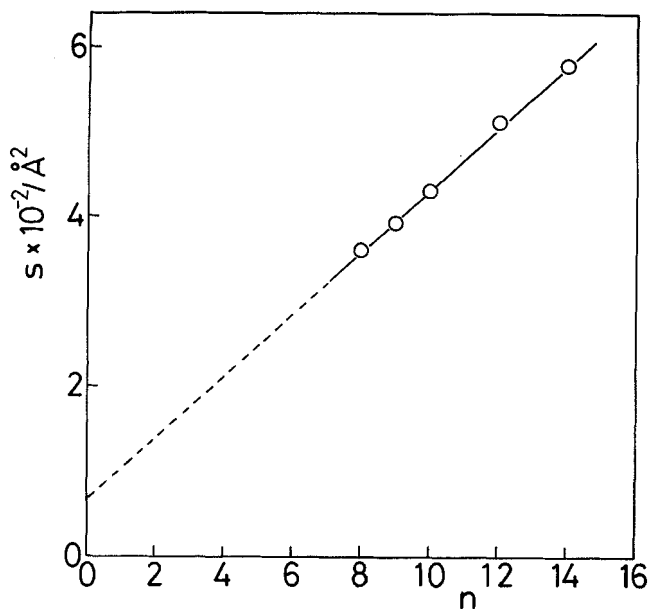

Figure 4. Variation of the area of the two dimensional hexagonal lattice in the D_{ho} phase with n (the carbon number of the side chain group).

Table 2. X-ray data for the D_{ho} phases.

Cel-II-8 $d_{obs.}/Å$	Cel-II-9 $d_{obs.}/Å$	Cel-II-10 $d_{obs.}/Å$	Cel-II-12 $d_{obs.}/Å$	Cel-II-14 $d_{obs.}/Å$
19·1 (100)†	19·9 (100)	20·8 (100)	22·6 (100)	24·0 (100)
11·0 (110)	11·6 (110)	12·4 (110)	13·1 (110)	
9·54 (200)	9·92 (200)	10·4 (200)		
5·41 (001)	5·40 (001)	5·40 (001)	5·41 (001)	
4·5 dif.‡	4·5 dif.	4·5 dif.	4·5 dif.	4·5 dif.

† Indices are based on a hexagonal lattice.
‡ dif. Indicates a diffuse reflection.

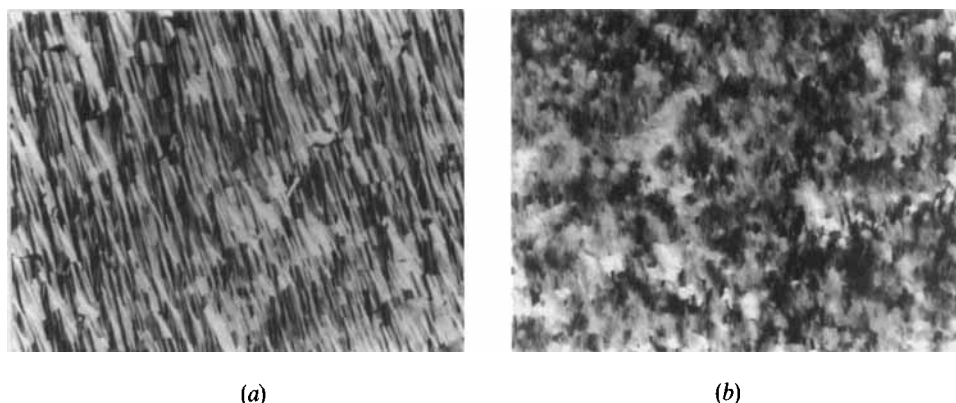(a)   (b)

Figure 5.   Optical textures of the oriented mesophases of Cel-II-8. (a) The D_{ho} phase at 70°C and (b) the D_x phase at 50°C.

lattice, i.e. the cross-sectional area per column, $S = (2/\sqrt{3})d^2_{100}$, is plotted against n. The value of S increases proportionally with n. An average increment of S per unit of n is 42·3 Å^2 giving a volume per one methylene unit of 28·6 Å^3. This corresponds to a density of 0·81 g ml^{-1}, which is reasonable for diordered alkyl chains. The extrapolation of S to $n = 1$ gives a value of 68·0 Å^2 from which a density of 1·31 g ml^{-1} can be calculated for the central core composed of the cellobiose moiety and the ester groups. This figure might be larger than the true value, since it is obtained under the assumption that the entire side chain has the same density of 0·81 g ml^{-1}, but it does indicate that the cellobiose moieties are densely packed in the central core of the column.

3.3. D_x Phase

This phase is also fluid but appreciably more viscous than the D_{ho} phase. On cooling the isotropic melt of Cel-II-7, the D_x phase initially appears as butterfly-like nuclei (see figure 3(b)), which grow and coalesce to give an ill-defined texture. The textures of the D_x phase are remarkably different from those of the D_{ho} phase. The difference in optical texture of the D_{ho} and D_x phases can also be easily recognized for the Cel-II-8 specimen which exhibits both types of phase. The textures of the D_{ho} and D_x phases are compared in figure 5, which were observed at the same position in the sample but at different temperatures. It is apparent that the fan texture of the D_{ho} phase (see figure 5(a)) is transformed to the broken fan texture (see figure 5(b)) at the transition to the D_x phase. This texture change is completely reversible on cooling and heating, and is very similar to that observed for the transition from the classical smectic A to smectic C phase [11].

The X-ray pattern of this phase exhibits several reflections in the small angle region and one reflection in the large angle region. As in the D_{ho} phase, the former reflections can be attributed to the lateral packing of the columns and the latter to the periodic stacking of cellobiose moieties along the column. The diffraction pattern also shows a broad reflection at 4·5 Å, indicating that the side chains are still in the disordered state. The spacings of these reflections are listed in table 3. We can see that the spacing corresponding to the repeat length along the column has a constant value of 5·38 Å while the spacings of the reflections attributable to the lateral packing of the columns are larger for Cel-II-8 than for Cel-II-7.

Table 3. X-ray data for the D_x phases.

Cel-II-7			Cel-II-8		
$d_{obs.}/\text{Å}$	$hk0\dagger$	$d_{calc.}/\text{Å}\dagger$	$d_{obs.}/\text{Å}$	$hk0\dagger$	$d_{calc.}/\text{Å}\dagger$
18·0	110	18·5	19·0	110	19·4
15·3	200	15·0	16·1	200	16·4
12·0	020	11·8	12·4	020	12·2
5·38	001		5·38	001	
4·5	dif.		4·5	dif.	

† The calculated spacings and indices are based on a two dimensional rectangular lattice (see text).

(a)   (b)
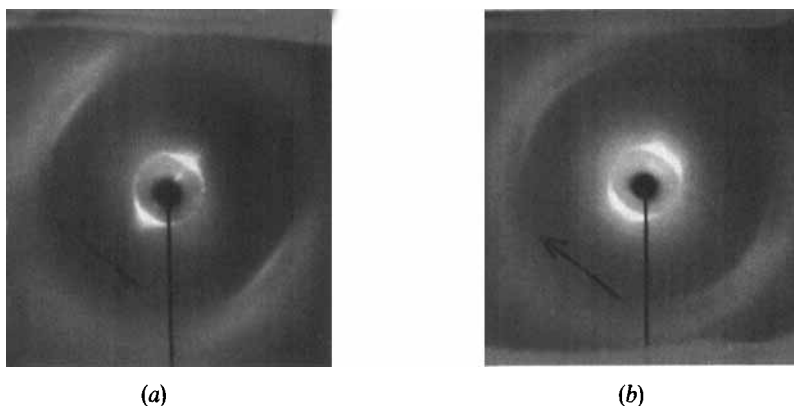
Figure 6.   Oriented X-ray patterns of the mesophases formed by Cel-II-8. (a) The D_{ho} phase at 70°C and (b) the D_x phase at 50°C. The arrow indicates the initial orientation of the column axes in the D_{ho} phase.

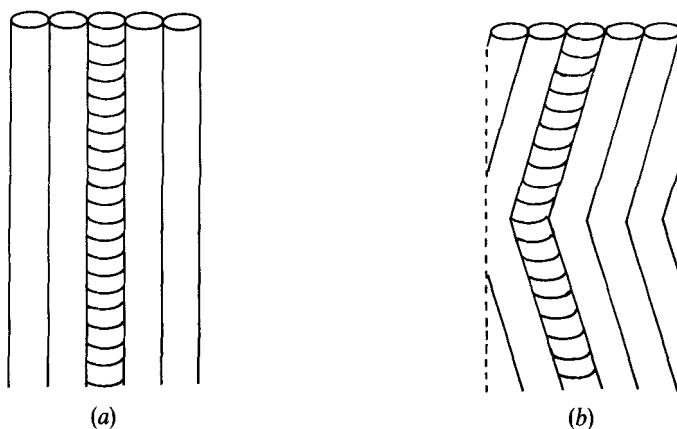(a)   (b)

Figure 7.   Structure change inferred from the X-ray patterns of figure 6. (a) Indicates the initial orientation of the columns in the D_{ho} phase and (b) the tilted orientation of the columns in the D_x phase which may be attained through the undulation of the columns.
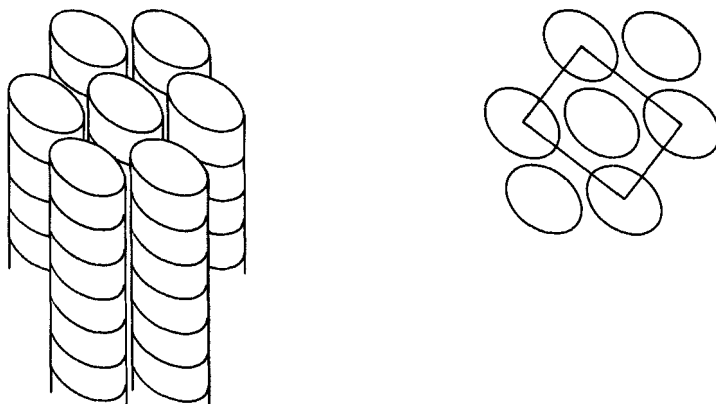
Figure 8. Schematic representation of the two dimensional rectangular packing of the columns in the $D_x(D_{ro})$ phase. The columns are built up by a regularly tilted stacking of the cellobiose moieties and their packing is illustrated with a symmetry of C2/m as a most probable model.

It is likely that the two dimensional lattice in this phase has lower symmetry than that in the D_{ho} phase since the spacings of the reflections are not related in simple ratios. The small number of reflections observed does not enable an unequivocal determination of the lattice structure but at the present time, a centred rectangular lattice with two columns per unit appears to be the most plausible model. This has $a = 30.0$ Å, $b = 23.6$ Å for Cel-II-7 and $a = 32.0$ Å and $b = 24.4$ Å for Cel-II-8. The calculated spacings based on this type of lattice are listed in table 3 and are in good agreement with the observed values. Further support for this lattice can be obtained from the reasonable densities of 1.08 g ml^{-1} and 1.07 g ml^{-1} calculated for Cel-II-7 and Cel-II-8, respectively, which are somewhat greater than that of the D_{ho} phase.

The appearance of a rectangular (or distorted hexagonal) lattice dictates that each column must be deformed from the cylindrical shape. This probably results from a tilting of the cellobiose moieties in the central core of the column [1]. Supporting evidence for this tilting comes from the X-ray patterns of oriented specimens of the Cel-II-8. These were prepared by shearing the D_{ho} phase [4] and allowing it to cool to the D_x phase. As shown in figure 6 there is a remarkable change in the diffraction pattern which occurs reversibly at the transition temperature. The equatorial reflections for the D_{ho} phase, split above and below the equatorial line upon transition to the D_x phase and at the same time the meridional reflection also splits from the meridional line. The splitting angle of 40° for both reflections is almost the same. Such a change in the diffraction pattern can be understood in terms of an undulation of the columnar rods and a successive tilting of the columns with respect to the initial orientation axis (see figure 7) as has been generally observed for the smectic A to smectic C transition [12]. This structural change can therefore be related to a tilted association of the mesogenic moieties along the column axis and can be interpreted as resulting from the tilting of the columns with respect to the initial orientation axis of the cellobiose moieties as illustrated in figure 7. The tilt angle should be about 20°, since it is equal to half of the splitting angle of the reflections. Overall, the structure of the D_x phase can be illustrated as in figure 8. According to Destrade's terminology [1], this phase is consistent with a rectangular ordered columnar (D_{ro}) phase.

References

[1] DESTRADE, C., FOUCHER, P., GASPAROUX, H., TINH, N. H., LEVELUT, A. M., and MALTHETE, J., 1984, *Molec. Crystals liq. Crystals*, **106**, 121.

[2] CHANDRASEKHAR, S., and RANGANATH, G. S., 1990, *Rep. Prog. Phys.*, **53**, 57.

[3] YAMAGISHI, T., FUFUDA, T., MIYAMOTO, T., YAKOH, Y., TAKASHINA, Y., and WATANABE, J., 1991, *Liq. Crystals*, **10**, 467.

[4] ITOH, T., FUKUDA, T., MIYAMOTO, T., YAKOH, Y., and WATANABE, J., 1991, *Liq. Crystals*, **9**, 221.

[5] SUGIURA, M., MINODA, M., FUKUDA, T., MIYAMOTO, T., and WATANABE, J., *Liq. Crystals* (to be published).

[6] ZIMMERMANN, R. G., JAMESON, G. B., WEISS, R. G., and DEMAILLY, G., 1985, *Molec. Crystals liq. Crystals Lett.*, **1**, 183.

[7] VILL, V., and THIEM, J., 1991, *Molec. Crystals liq. Crystals*, **9**, 451.

[8] TAKADA, A., MA, Y. D., FUKUDA, T., and MIYAMOTO, T., 1990, *Bull. Inst. chem. Res. Kyoto Univ.*, **68**, 21.

[9] KOHNE, B., and PRAFECKE, K., 1984, *Angew. Chem.*, **96**, 70.

[10] MORRIS, N. L., ZIMMERMANN, R. G., JAMESON, G. B., DALZIEL, A. W., REUSS, P. M., and WEIS, R. G., 1988, *J. Am. chem. Soc.*, **110**, 2177.

[11] GRAY, G. W., and GOODBY, J. W. G., 1984, *Smectic Liquid Crystals* (Leonard Hill).

[12] RIEKER, T. P., CLARK, N. A., SMITH, G. S., PARMER, D. S., SHIROTA, E. B., and SAFINYA, C. R., 1987, *Phys. Rev. Lett.*, **59**, 2658.