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Columnar liquid crystals in oligosaccharide derivatives

I. Discotic columnar liquid crystals in cellobiose octadecanoate and cellotriose hendecadecanoate

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Cellobiose octadecanoate and cellotriose hendecadecanoate were synthesized and their mesophase properties were studied. Both ester derivatives show enantiotropic mesophases in the temperature region below 100°C. From the observations of microscopic texture and X-ray pattern, the mesophase was found to be of the hexagonal columnar, in which the column is built up by a periodic stacking of the cellobiose or cellotriose skeleton and packed into a two-dimensional hexagonal lattice. The mesophase is thus similar to the hexagonal ordered columnar (D_{ho}) phase in a class of discotics, indicating that cellobiose and cellotriose moieties can work as discotic mesogens.

1. Introduction

Besides the classical liquid crystals observed in rod-like molecules, thermotropic discotic mesophases consisting of two-dimensional flat aromatic molecules have been extensively studied. So far, two different kinds of discotic phases have been described [1–4]; a nematic (N_D) phase and a columnar (D) phase. In a columnar liquid crystal, four phases, D_{ho}, D_{hd}, D_{rd} and D_t, have been identified on the basis of the structural peculiarities, in which differences are attributed to the regular or irregular stacking of discs along the columns, packed either in hexagonal or rectangular lattices [3, 4].

The molecules forming the discotic liquid crystals are characterized by the presence of the molecular skeleton of a flat, rigid, disc-like mesogenic group connected to the flexible aliphatic chains by an ester or ether linkage. Also, most of the discotic mesogens known so far have a high symmetry, that is, a sixfold, fourfold or threefold symmetry [3, 4] although either the disc-like molecules with a lower symmetry [5–8] or no flat molecules have been found to form a discotic columnar phase [8–10].

More recently, we have synthesized a new type of mesogenic molecule, cello-oligosaccharides with the long alkyl side groups linked by an ester linkage [11]. They have similar structural features to discotic molecules known so far, although a remarkable difference can be seen in that they do not include any aromatic groups and have a low symmetry. Interestingly, we have observed that even in this class of mesogens there can be formed a type of discotic columnar phase in which the

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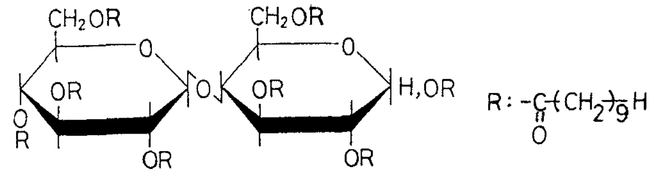
arrangement of the molecules is reminiscent of the situation in discotics. In this paper, we will report the results of the calorimetric, optical microscopic and X-ray investigations of cellobiose octadecanoate and cellotriose hendecadecanoate, and give evidence for their phases being discotic columnar phases.

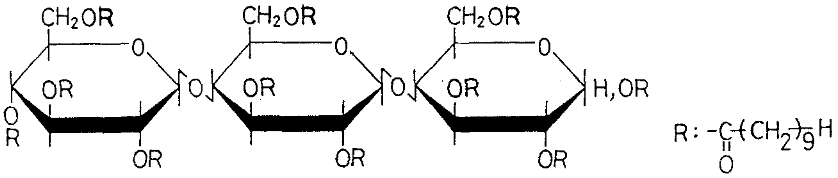
2. Experimental

2.1. *Materials*

Two compounds studied here have the following formulas:



Cel-II-10 (cellobiose octadecanoate).



Cel-III-10 (cellotriose hendecadecanoate).

These were prepared by esterification of cellobiose and cellotriose with decanoic acid as mentioned below. Here, the compounds were denoted by the short notation Cel-N-m, where N is the number of glucose units in the central core and m the carbon numbers of the substituted side group (in this study $m=10$).

The esterification was performed by the following general method. In a typical preparation 4 mmol of cellooligosaccharide was dissolved in a mixture of 40 ml of dioxane and 15 ml of pyridine. The solution was heated to $T=100°\mathrm{C}$ and 10 mmol of decanoyl chloride was added with stirring. After 10 hours of the reaction, the solution was poured into methanol, filtered and washed with fresh methanol and then the residue was dried and recrystallized three times with methanol/tetrahydrofuran. The perfect esterification of hydroxyl groups and the purity of compounds were checked by IR and NMR spectroscopies.

2.2. *Methods*

The calorimetric behaviour was investigated by a Perkin–Elmer D.S.C.-II calorimeter at a scanning rate of 10°C/min. The textures of the mesophases were studied using a polarizing microscope (an Olympus BH-2) equipped with a Mettler FP 80 hot stage. Here, the mesophases were set between two untreated cover slips of ordinary glass. X-ray diffraction photographs were taken at different mesophase temperatures by using Ni-filtered Cu Kα radiation. The sample was kept in a glass capillary tube and its temperature was measured and regulated with an accuracy of 0·2°C by a Mettler FP 80 heater.

3. Results and discussion

DSC thermograms of Cel-II-10 and Cel-III-10 are given in figure 1, both samples exhibit two transitions. The lower transition can be attributed to the melting of crystals

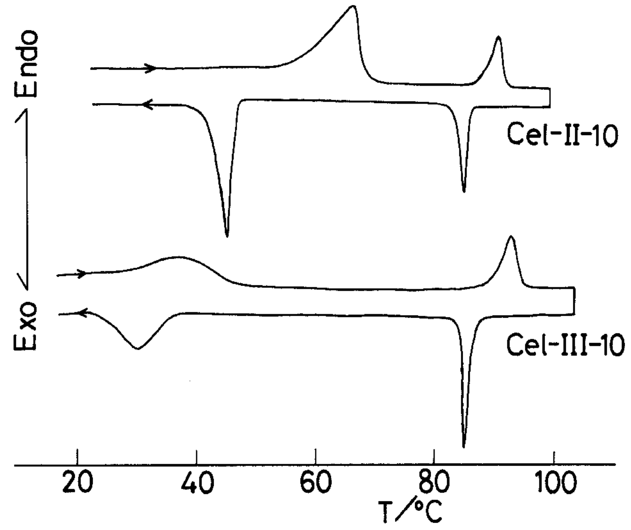


Figure 1. DSC thermograms of (*a*) Cel-II-10 and (*b*) Cel-III-10.

Table 1. Transition temperatures and enthalpy changes (in parentheses) of Cel-II-10 and Cel-III-10.

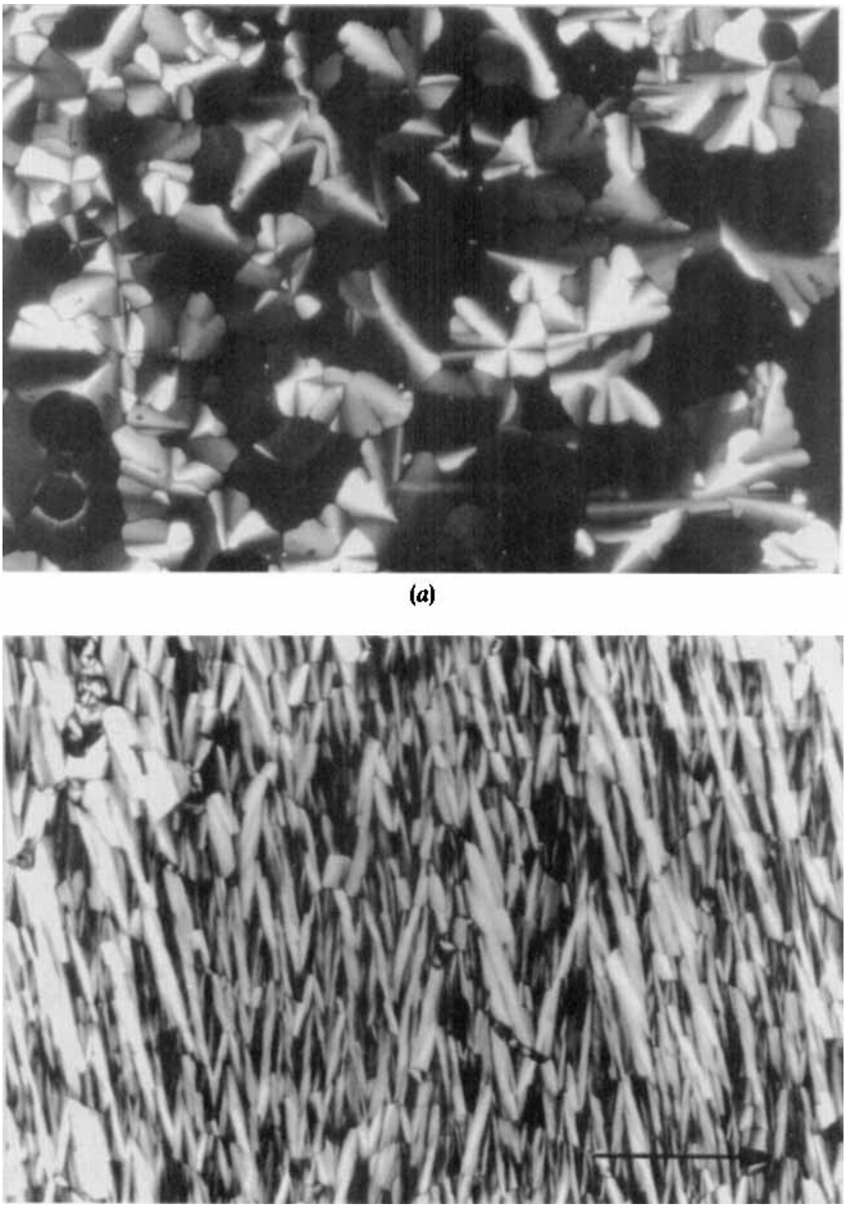
	C ⟶ M	M ⟶ L
Cel-II-10	66°C (7·1 kcal/mol)	90°C (2·2 kcal/mol)
Cel-III-10	38°C (5·3 kcal/mol)	93°C (3·5 kcal/mol)

In the table C stands for the crystalline phase, M for the mesophase and L for the liquid phase.

to a mesophase and the higher one to the isotropization of the mesophase. On the basis of the heating data, the mesophase temperature region is estimated to be from 66 to 90°C for Cel-II-10 and from 38 to 93°C for Cel-III-10. The isotropization enthalpy, ΔH_i, is 2·2 and 3·5 kcal/mol for Cel-II-10 and Cel-III-10, respectively. These data are summarized in table 1.

In the microscopic observation, the mesophases of both specimens display mosaic or fan-shaped textures as shown in figure 2. Although these textures are compatible with the classical smectic liquid crystals [12], the peculiar chemical structure of the present material ensures that a columnar phase is formed and not a smectic layered phase.

Very slow cooling from the isotropic melt allows detailed observation of the columnar character of mesophase. Initially, the anisotropic mesophase appears as circular germs. The germs grow in size on further cooling and have the six vertices of the hexagon resulting in the six branches as flowers; a typical example is shown in figure 3. Each branch forms new branches and the germs finally coalesce to the fan-shaped or mosaic texture as shown in figure 2 (*a*). Such a flower-like shape of the nucleation germs



(*a*)

(*b*)

Figure 2. Optical microscopic textures in the mosophase of Cel-II-10; (*a*) the untreated mesophase and (*b*) the oriented mesophase prepared by shearing (the arrow indicates the shearing direction).

indicates the hexagonal symmetry of the mesophase responsible for the hexagonal columnar phase [13].

More detailed information of mesophase structure can be given by the X-ray diffraction pattern. The mesophases of both specimens display a similar powdered X-ray pattern, which is divided into two zones; the small angle contains two or three sharp diffraction rings while a sharp ring and a broad band are seen at large angles. The

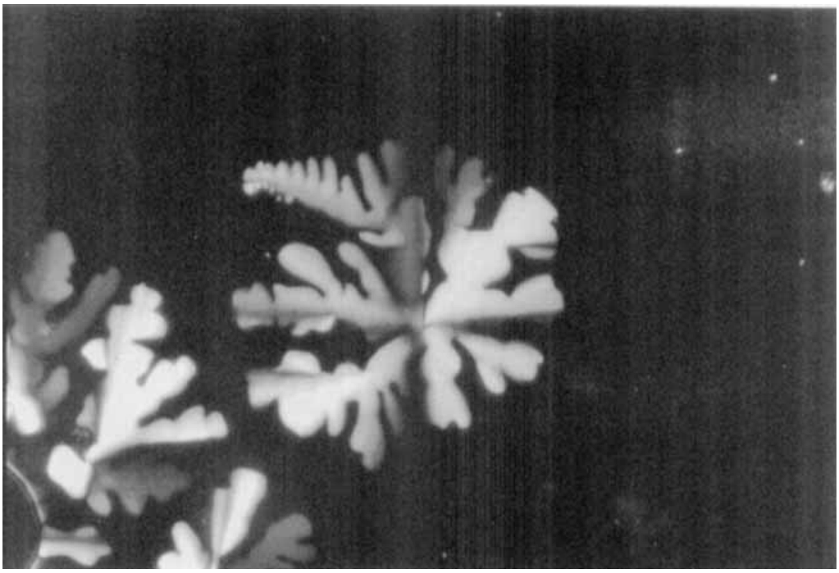


Figure 3. Optical microscopic texture of the anisotropic nucleation germs with a flower-like shape appearing on slow cooling from liquid.

Table 2. X-ray data.

Cel-II-10			Cel-III-10		
$d_{obs.}$/Å	Index†	$d_{calc.}$/Å†	$d_{obs.}$/Å	Index†	$d_{calc.}$/Å†
20·8	100	20·8	24·5	100	24·5
12·1	110	12·0	14·0	110	14·1
10·4	200	10·4			
5·4	Meridional		5·4	Meridional	

† Based on the two-dimensional hexagonal lattice of $a = 24·0$ Å and 28·2 Å for Cel-II-10 and Cel-III-10, respectively.

spacings of reflections are listed in table 2. In the oriented X-ray patterns taken for the aligned samples, which are prepared by shearing, all of the reflections at small angles lie on an equatorial line perpendicular to the shearing direction (for example, see figure 4). In addition, their lattice spacings are in the ratios 1, $1/\sqrt{3}$ and 1/2 although the spacing of the corresponding reflection is relatively larger for Cel-III-10 than for Cel-II-10 as found in table 2. These observations dictate hexagonal columnar mesophases in which the columns, with their long axes oriented parallel to the shearing direction, are packed into a two-dimensional hexagonal lattice. The packing structure of columns is illustrated in figure 5. On the other hand, a sharp reflection at a large angle appears on a meridional line (see figure 4) and hence comes from the periodicity along the column axis. Its intensity is fairly weaker for Cel-III-10 than for Cel-II-10, but the same spacing of 5·4 Å is observed for both specimens. The outer broad band at around 4·5 Å relating to the alkyl chains remains nearly isotropic, reflecting a high degree of orientational disorder of the alkyl chains.

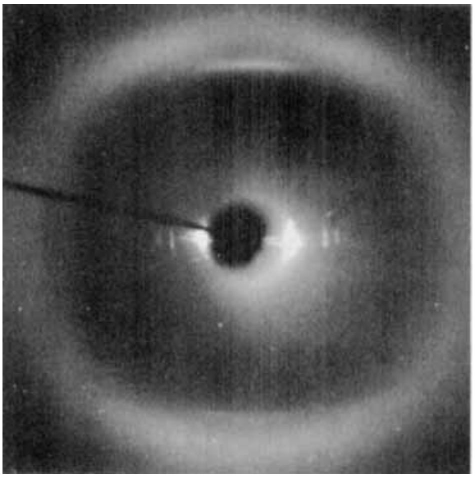


Figure 4. Oriented X-ray pattern of Cel-II-10 mesophase taken at 80°C. The oriented mesophase was prepared by shearing. The shearing direction is in a vertical direction.

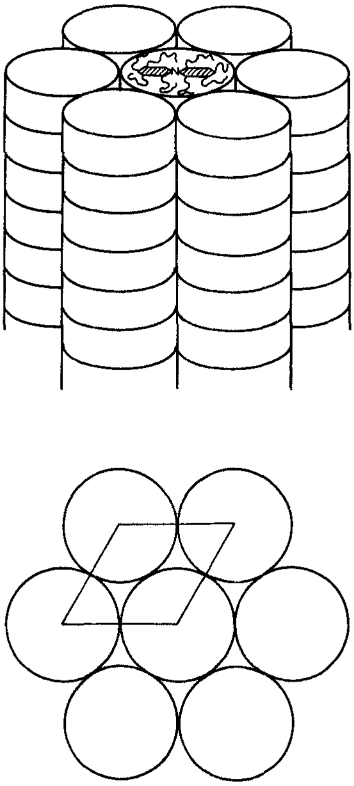


Figure 5. Schematic representation of two-dimensional hexagonal packing of columns. Here, each column is built up by the regular stacking of cellobiose or cellotriose moiety.

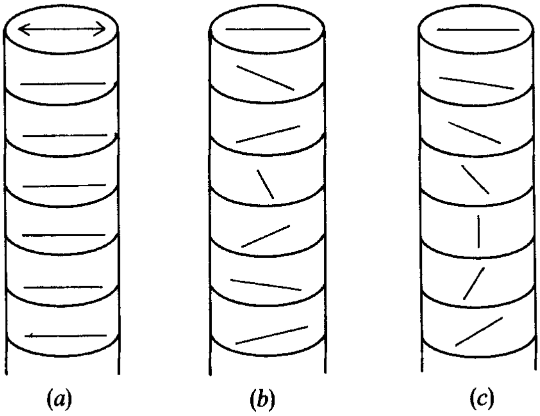


Figure 6. Possible stacking structures of cellobiose or cellotriose moiety within a column, which are different with respect to the arrangement of twofold axis (indicated by the arrow).

X-ray data also allow the evaluation of the mesophase density and so give an insight into the molecular packing along a column. In a simple hexagonal phase of the present system, the column cross sectional area S can be given by $S=a^2(\sqrt{3}/2)$ where a is the lattice parameter of the two-dimensional hexagonal lattice as given in table 2. Since the periodicity along the column is 5·4 Å, the unit volume can be evaluated by the equation $5{\cdot}4S$. If we assume here that each molecule is included in this unit volume, the specific gravities are calculated as 0·97 and 0·98 g/ml for Cel-II-10 and Cel-III-10 mesophases, respectively. These values are in good agreement with those observed (around 1·0 g/ml) and also very plausible since they are similar to those of the columnar liquid crystals which are observed nearly independently on the compounds [1]. We, thus reach the simple model of column as illustrated in figure 5 where the column is built up by the periodic stack of the cellobiose or cellotriose moiety, as in the discotic column composed of the disc-like molecules. Such a column is also found to be satisfactorily constructed in the space filling model.

Overall, the structural features of the present mesophase are reminiscent of the situation in discotics and it can be concluded that the type of mesophase is classified into the hexagonal ordered columnar (D_{ho}) phase in a class of discotic phases [3]. This conclusion seems to be particularly interesting since the following two points can be extracted.

(1) Non-aromatic groups are necessary for the mesogenic groups of discotics.
(2) Discotic columnar phases with hexagonal symmetry can be formed even if the central core of the mesogen has a fairly anisotropic shape with a low symmetry (twofold symmetry).

One would not have any doubt about the first point; in practice, few kinds of non-aromatic discogenic molecules, such as soaps [14] and sugar [15], have been already discovered. The second point, however, may hardly be accepted at a glance but some plausible models can be illustrated by assuming three types of columns which are the same in that they are constructed by the lateral stacking of molecules but different with respect to the arrangement of their twofold axes. These columns are schematically represented in figures 6 (*a*), (*b*), (*c*). First, one supposes the column with a regular side-by-side stack of molecules, that is, a regular orientation of two-fold axes as in figure

6 (*a*). In this case, the resultant column has a biaxial nature and is not cylindrical. Hence, their packing with the hexagonal network may be promised only by the free rotation of columns around their long axes. Secondly, the column has a cylindrical shape responsible for the hexagonal phase. Such a column can be constructed by the stack of molecules with the random orientation of twofold axes (figure 6(*b*)). Thirdly, in a particular case of the present chiral system, the column is quasi-cylindrical with the helical twist of twofold axes (figure 6(*c*)). Further examination is needed to clarify the details of the molecular arrangement within a column.

References

[1] Chandrasekhar, S., 1981, *Molec. Crystals liq. Crystals*, **63**, 171.

[2] Destrade, C., Tinh, N. H., Gasparoux, H., Malthête, J., and Levelut, A. M., 1981, *Molec. Crystals liq. Crystals*, **71**, 111.

[3] Destrade, C., Foucher, P., Gasparoux, H., Tinh, N. H., Levelut, A. M., and Malthête, J., 1984, *Molec. Crystals liq. Crystals*, **106**, 121.

[4] Chandrasekhar, S., and Ranganath, G. S., 1990, *Rep. Prog. Phys.*, **53**, 57.

[5] Tinh, N. H., Gasparoux, H., and Destrade, C., 1981, *Molec. Crystals liq. Crystals*, **68**, 101.

[6] Billard, J., Dubois, J. C., Vaucher, C., and Levelut, A. M., 1981, *Molec. Crystals liq. Crystals*, **66**, 115.

[7] Carfagna, C., Iannelli, P., Roviello, A., and Sirigu, A., 1987, *Liq. Crystals*, **2**, 611.

[8] Malthête, J., Collet, A., and Levelut, A. M., 1989, *Liq. Crystals*, **5**, 123.

[9] Levelut, A. M., Malthête, J., and Collet, A., 1986, *J. Phys., Paris*, **47**, 3571.

[10] Zimmermann, H., Poupko, R., Luz, Z., and Billard, J., 1988, *Liq. Crystals*, **3**, 759.

[11] Itoh, I., Takada, A., Miyamoto, T., and Watanabe, J. (private communication).

[12] Gray, G. W., and Goodby, J. W. G., 1984, *Smectic Liquid Crystals* (Leonard Hill).

[13] Bouligand, Y., 1980, *J. Phys., Paris*, **41**, 1307.

[14] Abied, H., Guillon, D., Skoulios, A., Weber, P., Giroud-Godquin, A. M., and Marchon, J. C., 1987, *Liq. Crystals*, **2**, 269.

[15] Kohne, B., and Praefcke, K., 1984, *Angew. Chem.*, **96**, 70.