Thermotropic Liquid Crystals Based on Oligosaccharides. *n*-Alkyl 1-*O*-β-D-Cellobiosides

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n-Alkyl 1-*O*-β-D-cellobiosides with an alkyl length ranging from 7 to 18 in carbon number *m* were synthesized, and their thermal properties were studied in comparison with those of the already-known monosaccharide homologues, *n*-alkyl 1-*O*-β-D-glucopyranosides. The cellobiosides were found to exhibit a thermotropic mesophase at higher temperatures than the glucopyranosides. Depending on *m* and thermal history, the cellobiosides showed various textures such as homeotropic, transient bâtonnets, polygonal, and fan-shaped textures. Like in the case of the monosaccharide homologues, the difficulty of aligning the samples prohibited a full classification of the mesophase, but the X-ray diffractograms of the unaligned cellobiosides indicated that their mesophase belongs to smectic A(or less possibly, smectic C). The *m* dependence of the lamella thickness was much weaker than (about half) that of the monosaccharide homologues. Possible molecular arrangements of the cellobiosides in the mesophase were presented.

Mono- and oligosaccharides are potential sources of millions of new mesogens.[1] Hitherto, however, only a few have been synthesized, or, if synthesized, recognized as mesogens. A known group of mesogenic carbohydrates have just one *n*-alkyl chain, longer than about six in carbon number, that is linked to the sugar moiety.[1—7] The mesophases of these compounds are commonly characterized by a smectic-type structure in which sugar moieties are supposed to be hydrogen bonded together forming, e.g., head-to-head bilayers.[1,2] Fully acylated cello- and chito-oligosaccharides belong to another group. We have reported that these compounds give discotic columnar phases of varying structure and stability, depending on the number of sugar moieties.[8—11]

In this work, we have synthesized a series of new compounds, *n*-alkyl 1-*O*-β-D-cellobiosides, and studied their thermal and optical properties in comparison with those of the mono-saccharide homologues, *n*-alkyl 1-*O*-β-D-glucopyranosides. Such a study would be important to systematically understand the functionalities of oligosaccharides as mesogens.

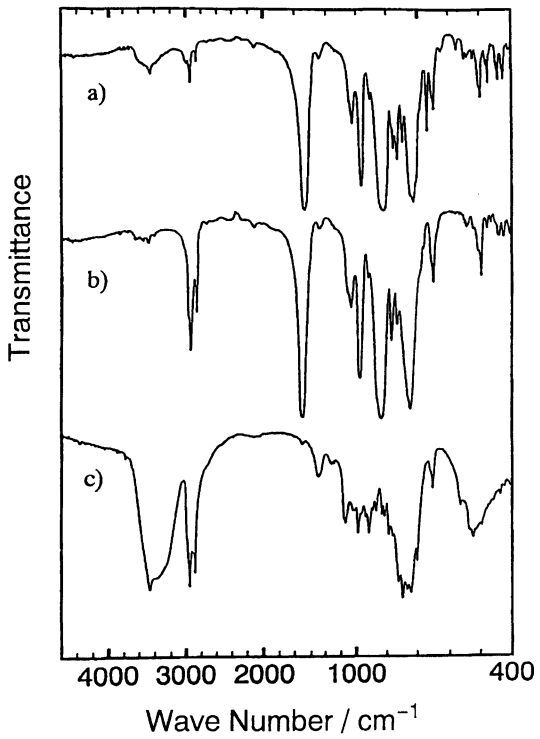


Fig. 1. IR spectra of (a) D-cellobiose octaacetate, (b) heptaacetyl A_{10}CEB, and (c) A_{10}CEB.

Experimental

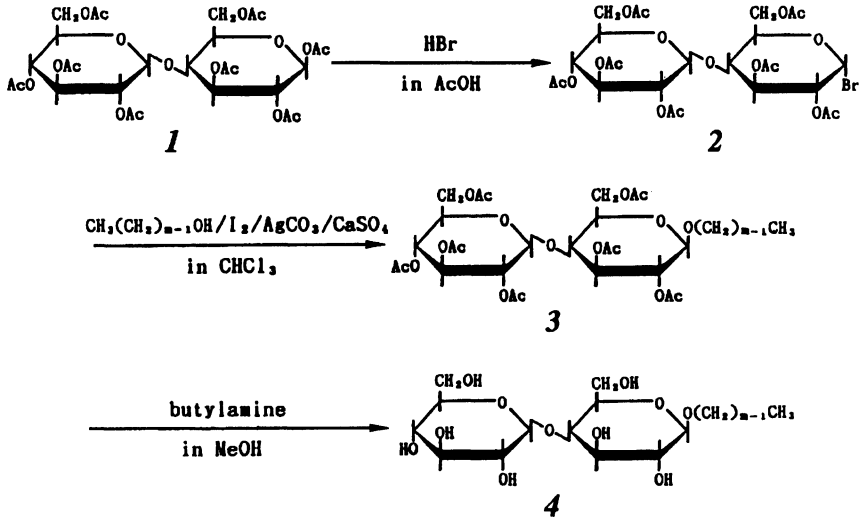
n-Alkyl 1-*O*-β-D-cellobiosides, A_mCEB, with a carbon number *m* from 4 to 18 were synthesized according to the three-step procedure of Wolfrom and Haq (Scheme 1).[12]

In brief, cellobiose octaacetate (**1**) was treated with a 30%-acetic acid solution of HBr ([HBr]/[**1**]=20) for 2 h at the room temperature to obtain heptaacetyl cellobiosyl bromide (**2**), which was purified by repeating the chloro-

Table 1. Phase Transition Temperatures and *d* Spacings of *n*-Alkyl 1-*O*-β-D-Cellobiosides A_mCEBs

m	T_m/°C	T_i/°C[a]	*d*/nm[b]
7	159.7	140[c]	
8	156.1	171.9	
9	151.5	205.0	33.4
10	155.0	226.5	34.7
12	154.0	—	
14	155.2	—	40.4
16	155.4	—	
18	150.1	—	45.4

a) Observed in the heating mode. b) At 170 °C. c) Observed in the cooling mode.



Scheme 1.

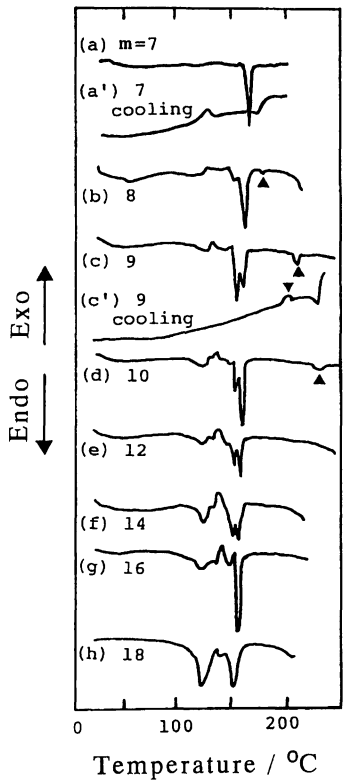


Fig. 2. DSC thermograms of A_mCEB's taken in a heating mode except curves a′ and c′ which were taken in a cooling mode.

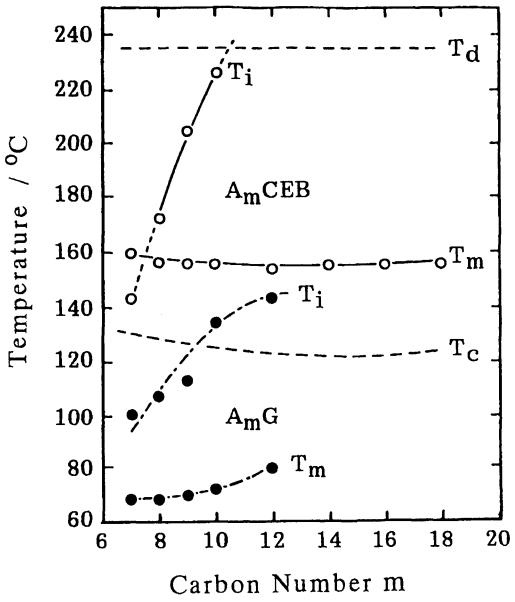


Fig. 3. Transition temperatures of *n*-alkyl 1-*O*-β-D-cellobiosides A_mCEB (open circles) and *n*-alkyl 1-*O*-β-D-glucopyranosides A_mG (filled circles). Curves T_d and T_c represent approximate temperatures of degradation and crystallization, respectively, of A_mCEB. The transiton temperatures T_m and T_i of A_mG are means of literature values.[2,5—7]

form-extraction/water-washing procedures. Bromide **2** was then dissolved in chloroform and reacted with an *n*-alcohol ([alcohol]/[**2**]=70) for 60 h at 40 °C under a nitrogen atmosphere and in the presence of I_2, Ag_2CO_3, and $CaSO_4$. The precipitate, heptaacetyl alkyl cellobioside (**3**), was washed several times in an excess of *n*-hexane, and dissolved in chloroform, followed by washing with 10%-aqueous Na_2SO_4 and pure water and precipitating into methanol. Compound **3** was deacetylated by treatment with a refluxing methanol solution of butylamine for 6 h. A white crystalline compound, A_mCEB, was recovered, washed several times with chloroform and dried.

Complete alkylation and deacetylation were confirmed by both IR and elemental analyses (cf. Fig. 1).

The thermal properties of the cellobiosides were studied on a differential scanning calorimeter (Rigaku Denki Model DSC-8230, Japan) at a heating/cooling rate of 10 °C min^{-1}. Photomicroscopic observation was made with a Nikon Model Optiphoto-Pol, Japan, along with the use of a Mettler hot stage Model FP-82 equipped with a temperature controller Model FP-80. Thermal data are summarized in Table 1.

X-Ray diffraction photographs were taken by use of Ni-

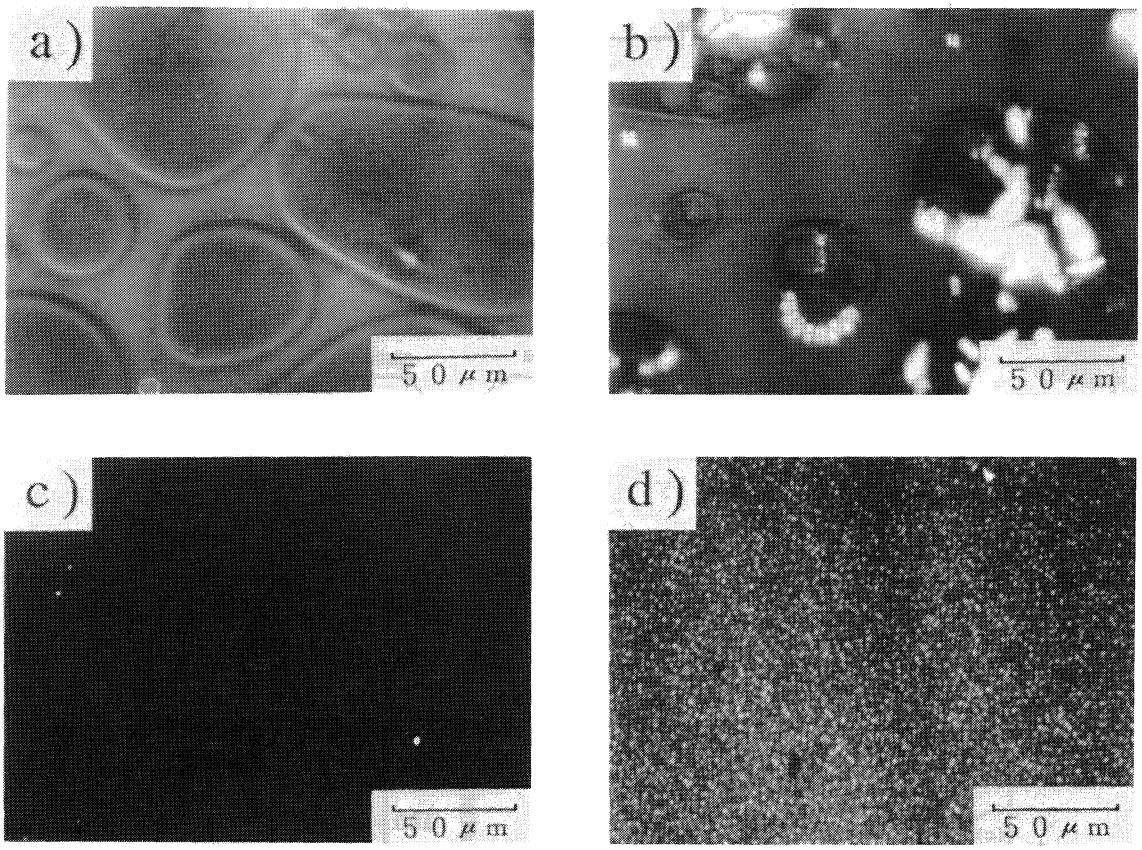


Fig. 4. Photomicrographs of A_8CEB:(a) homeotropic/isotropic coexisting phase (171 °C); (b) transient bâtonnets (168.5 °C) (c) homeotropic phase (135 °C); (d) polygonal texture (150 °C) resulted from the homeotropic phase (c) after application of a temperature jump.

filtered Cu $K\alpha$ radiation. The sample was held in a glass capillary tube installed in a Mettler FP-80 temperature regulator.

Results and Discussion

General Phase Behavior. The phase behavior of A_mCEBs were studied by differential scanning calorimetry (DSC) and photomicroscopic observation. The DSC thermograms are presented in Fig. 2. In a heating mode, each compound gave a large endothermic peak in a 150—160 °C range, which was assigned to the melting temperature T_m. Compounds with $8 \leq m \leq 10$ gave another small peak at a higher temperature, which, by microscopic observation, was confirmed to correspond to the mesomorphic to isotropic transition temperature T_i. No T_i peak was observed for $m \geq 12$. They are mesomorphic from T_m up to the degradation temperature T_d of about 235 °C. In a cooling mode, an exothermic peak was observed for $7 \leq m \leq 10$ at a temperature close to the T_i observed in the heating mode. Thus these compounds are enantiotropic. The T_i of A_7CEB was observable only in the cooling mode, because $T_i < T_m$ for this compound. Like in the case of *n*-alkyl 1-*O*-β-D-glucopyranosides (A_mGs),[2] the DSC thermograms taken in the cooling mode gave no clear indication of crystallization. However, microscopic observations of A_mCEBs with $7 \leq m \leq 10$ confirmed that they crystallize in a 120—130 °C range. The crystallization of other compounds ($m \geq 12$) could not be confirmed microscopically, either, due to similarities of the solid and mesophase textures (see below). Presumably, we can assume that the crystallization temperature T_c is nearly independent of m, as T_m is.

Figure 3 compares the phase behavior of A_mCEB with that of A_mG. Both T_m and T_i of the cellobiosides are much higher than those of the mono-saccharide equivalents.

Mesomorphic Textures. As already noted, A_mCEBs with $7 \leq m \leq 10$ can be brought to an isotropic state by raising the temperature, while those with $m > 10$ cannot. This makes the optical textures of the former group of compounds appear very different from those of the latter group.

A_8CEB, for example, is an isotropic liquid at temperatures above 172 °C. When gradually cooled down from the isotropic state, it gives a homeotropic (or pseudo-homeotropic) phase. Figure 4a shows a homeotropic phase in droplets (the relatively brighter areas in the fig-

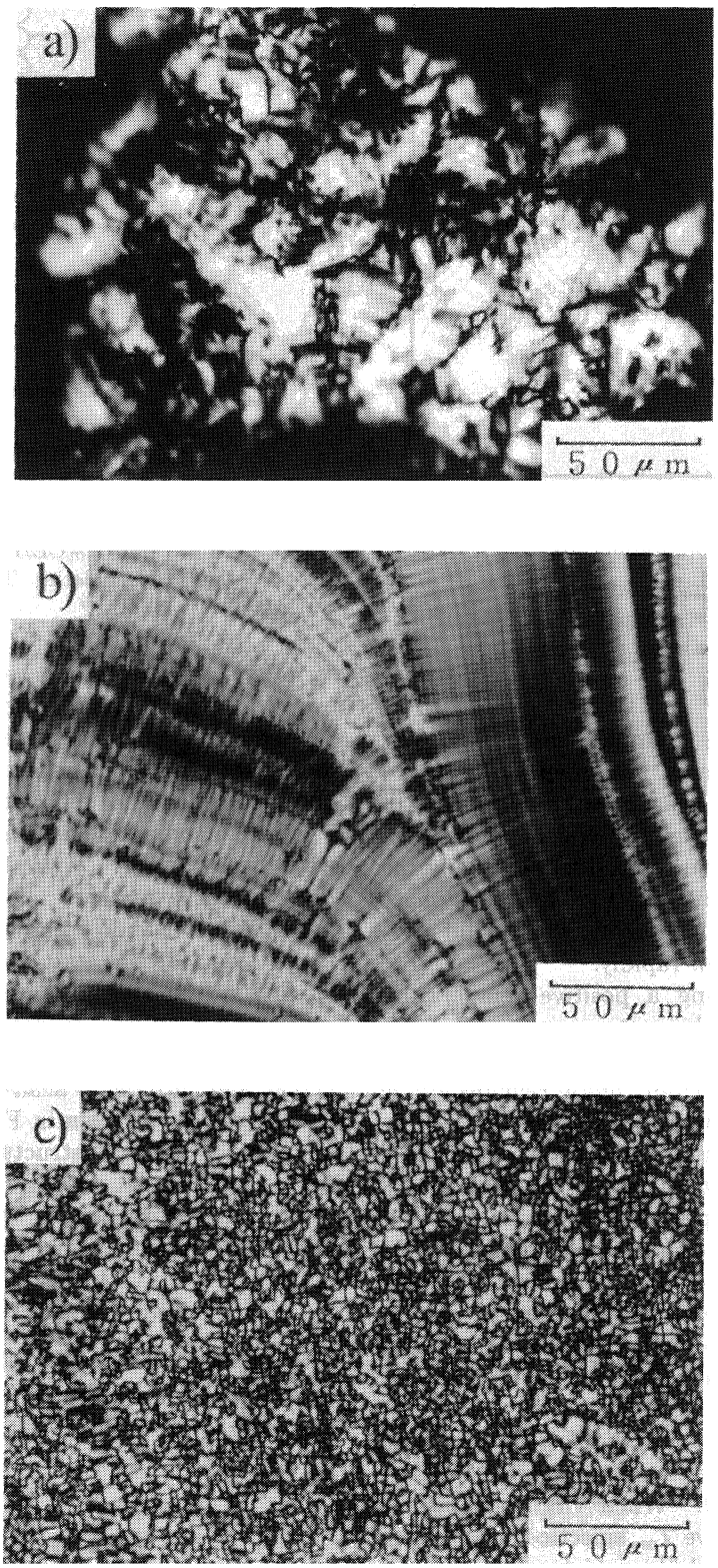


Fig. 5. Photomicrographs of (a) A_{14}CEB (160.1 °C) and (b) A_{10}CEB (198.5 °C). Texture (c) was obtained by shearing A_{14}CEB at 205 °C.

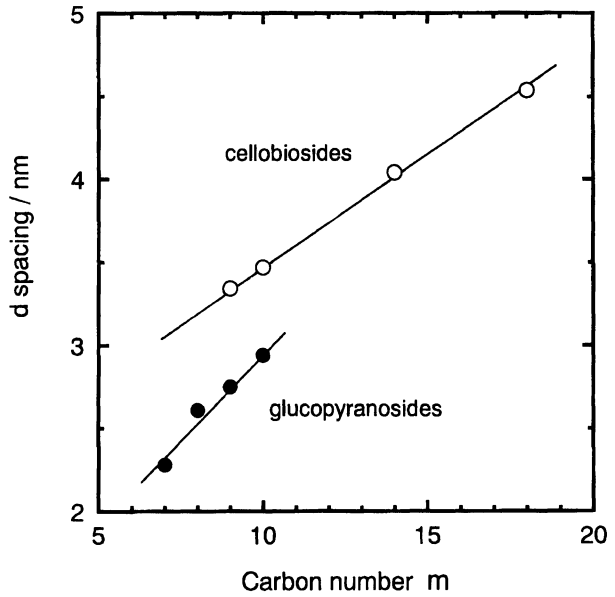


Fig. 6. The obsered d spacings plotted against the carbon number m of the alkyl groups in A_mCEB (open circles) and A_mG (filled circles).

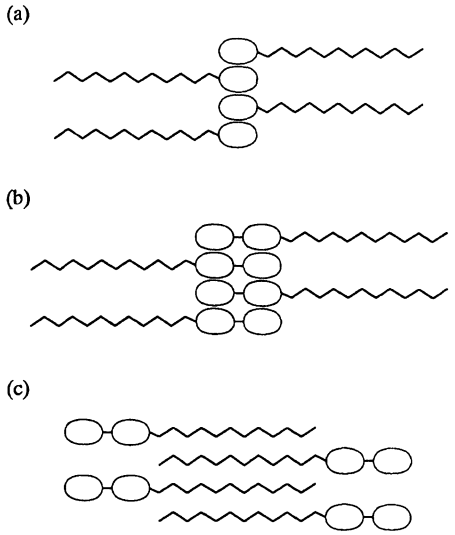


Fig. 7. Molecular arrangements in the smectic phases of A_mG (a) and A_mCEB (b and c). The ovals denotes the sugar moieties. The structure (a) was suggested by Goodby.[2]

ure)which coexists with an isotropic phase (the darker areas). Transient bâtonnets are often observed to emerge from the isotropic phase near the periphery of the homeotropic droplets (Fig. 4b), which quickly turn to stabler homeotropic orientations, and eventually the whole area becomes homeotropic (Fig. 4c). This phase remains stable down to about 120 °C, where solid crystallites are observed to grow rapidly.

Interestingly, on applying a positive temperature jump of, say, 15 °C to the homeotropic phase, it turns to a polygonal texture, which stays stable (Fig. 4d). On the other hand, the homeotropic phase remains stable against negative temperature jumps. This reminds us of the similar phenomenon observed for a polypeptide derivative, in which a negative (but not positive, in this case) temperature jump applied to its cholesteric planar phase induced a planar-to-polygonal change.[13] The cholesteric pitch of this polymer increases with decreasing temperature, which means that the planar orientations of the polypeptide molecules become destabilized by such a temperature change that gives rise to an increase of the twisting angle of the helix.[13]

For the latter group of cellobiosides ($m \geq 10$), homeotropic orientations were not realized, for they could not be isotropicized. When virgin samples of this group were heated above T_m, smectic-type textures were obtained (Figs. 5a and 5b), which, on applying a shear, turned to a polygonal texture (Fig. 5c). Pitch-band-like lines were often observable in the fan-shaped textures (Figs. 5a and 5b).

Mesophase Structure. Like the glucopyranosides,[2,5] the cellobiosides were found to be difficult to align, and it was not possible to accomplish a full description of their mesophase by X-ray analysis. However, the X-ray diffractograms of the unaligned samples showed a single diffuse ring of scattering, which is commonly associated with a smectic A or C phase.[2] The observed spacings of reflection, d, are given in Table 1.

Figure 6 compares the d spacings of the cellobiosides with those of the glucopyranosides.[2,5] The slope of the d vs. m curve for the cellobioside is about 0.13 nm per unit increase of m, about half that for the glucopyranoside. As the strongest candidate in the classification of the glucopyranoside phase, Goodby[2] suggested the smectic A modification (Ad) which involves overlapping carbohydrate groups hydrogen-bonded together and forming a head-to-head bilayer structure, as schematically shown in Fig. 7a. For an exact overlap between the chair-structured carbohydrate moieties (about 0.52 nm long[14]) and an all-trans conformation of the alkyl moieties, the lamellar spacing L_a for this molecular arrangement would be roughly given by

$$L_a = 0.52 + 0.25(m + 1) \text{ (nm)}, \quad (1)$$

which reasonably agrees with the observed d spacings.[2] If we assume a similar structure for the cellobiosides (Fig. 7b), the lamellar spacing would be expected to vary as

$$L_b = 2 \times 0.52 + 0.25(m + 1) \text{ (nm)}, \quad (2)$$

which is at variance with the observations for $m > 10$. In order for such a molecular arrangement to be compatible with the experiments, there has to be a tilt of the molecular axis, i.e., a C phase, and the tilt angle has to vary with alkyl length. Alternatively, one could assume the A phase of interdigitated structure shown in Fig. 7c. For an exact overlap of the alkyl moieties, the

approximate lamellar spacing for this structure would be

$$L_c = 4 \times 0.52 + 0.25(m + 1)/2 \quad \text{(nm)}. \tag{3}$$

Equation 3 closely reproduces the experimental results for all m. Moreover, this structure appears favorable with regard to the packing density, too.

As in the case of the glucopyranosides,[2] a smectic C structuring cannot be totally ruled out for the cellobioside phase, too. If this structure should be true, the possibility of a chiral smectic C would be high. The texture studies noted above are in some favor of the chiral structure. However, attempts to prove or disprove the chiral C structure by, e.g., the application of a direct current to the cellobioside phases were unsuccessful, providing no clear answer. At present, we believe that the liquid crystal phase exhibited by *n*-alkyl 1-*O*-*β*-D-cellobiosides is classifed as a smectic A, since the available experimental data can be interpreted in terms of this structure by introducing the least assumptions.

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