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The dependence of mesomorphic behaviour on the extent of hydrogen-bonding in sugar derived polyols

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The thermotropic liquid crystalline properties of a variety of chiral and racemic dodecyloxy substituted polyols derived from carbohydrates were investigated as a function of the number of hydroxyl groups associated with the polyol unit. It was found that all of the materials exhibited smectic A* phases, and that the clearing points increased monotonically with the number of hydroxyl groups. The linear increase was found to be independent of stereochemical structure and the degree of optical purity. A model suggesting that the smectic A* phase has an internal microphase separated structure can be used to account for these observations.

1. Introduction

In classical non-carbohydrate and non-amphiphilic thermotropic liquid crystal systems, it is common to develop property/structure correlations *via* the investigation of the variation in transition temperature(s) as a function of systematic changes in molecular structure [1]. Usually, it is found that the clearing and liquid crystal to liquid crystal transition temperatures are extremely sensitive to small structural changes at the molecular level, and in fact many studies have been made in relation to the effects of substituent size and position on mesomorphic properties [2]. Conversely, similar studies for amphotropic systems with respect to their thermotropic and/or their lyotropic behaviours are relatively scant. However, one such comparison has been completed for the thermotropic properties of the *x*-*O*-dodecyl- α , β -D-glucopyranoses by Miethchen and co-workers [3–4]. Miethchen *et al.* demonstrated the effect on clearing point temperatures as a dodecyl chain is moved sequentially from one position to the next in substituted D-glucopyranose systems, see figure 1.

In order to develop systematic property/structure correlations further for amphotropic systems, we have been concerned recently with a fundamental investi-

gation into the effects of the linking group, positioned between a sugar unit and the aliphatic chain in mono-substituted systems, on the lyotropic and thermotropic properties of acyclic compounds [5]. For this purpose, we chose to make a study of the self-organizing behaviour of alkyl substituted xylitols where the aliphatic chain was attached to the xylitol moiety *via* either an ether, ester or thioether linkage, see general structure I in figure 2. Combining our results on the thermotropic properties of the 1-*O*-alkanoyl-D- or L-xylitols with those already available from Dahlhoff *et al.* [6], we were able to show that the efficiency of the linking group in the formation of thermotropic phases follows the pattern,



whereas, surprisingly, the reverse sequence appears to be the case for lyotropic phases. However, it should be emphasized that the effect of the nature and structural properties of the linking group positioned between the aliphatic chain and the sugar moiety does not markedly affect mesophase formation and stability, unlike the situation normally encountered for linking groups in conventional thermotropic materials.

Following this study we reported the effects on the self-assembling properties caused by the sequential movement of the location of a dodecyl chain in acyclic

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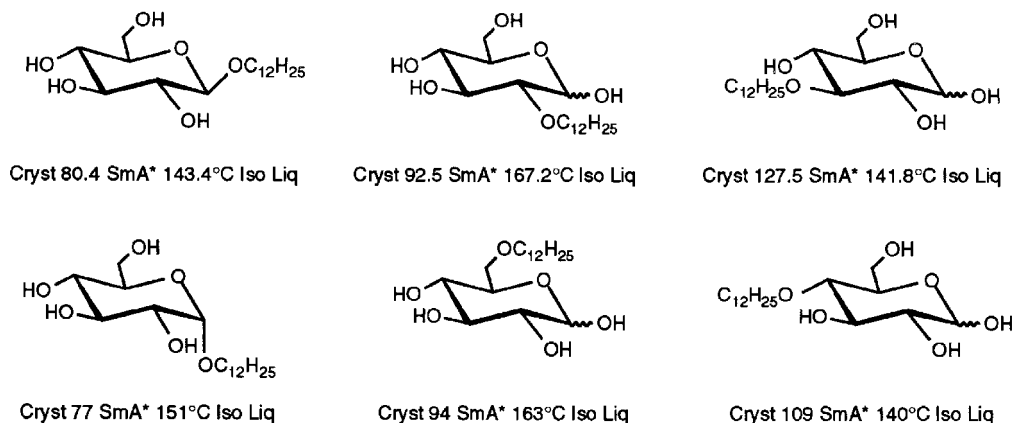


Figure 1. Effect of moving the position of a dodecyl chain in α -*O*-dodecyl- α,β -D-glucopyranoses.

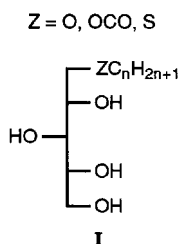
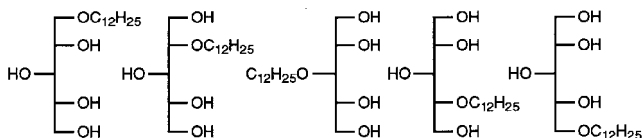


Figure 2.

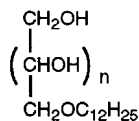
α -*O*-dodecyl-(D or L)-xylitols [7], see figure 3. This work can be compared with results reported on cyclic systems by Prade *et al.* [3].

After studying the effect of linking groups and the position of aliphatic chains in xylitols, we turned our attention to the effects of hydrogen-bonding on transition temperatures. In order to obtain meaningful results we compared the mesomorphic properties of a number of polyols (see figure 4) derived from carbohydrates where one of the materials investigated was a xylitol derivative that was common to our previous studies.



II

Figure 3.



III

Figure 4.

Thus, the following article details the observations that were made on the liquid crystalline behaviour of a variety of dodecyl substituted polyols.

2. Experimental

2.1. Characterization of materials

Phase identifications and phase transition temperatures were determined by thermal polarized light microscopy using a Leitz Laborlux 12 Pol polarizing transmitted light microscope equipped with a Mettler FP82 microfurnace in conjunction with an FP80 Central Processor. Homeotropic sample preparations suitable for phase characterization were prepared by using clean glass microscope slides (washed with water, acetone, water, concentrated nitric acid, water and dry acetone), whereas homogeneous defect textures were obtained by not using specially cleaned slides.

Classification of the mesophases of the products was achieved *via* binary phase diagrams which were constructed by determining the phase transition temperatures of individual binary mixtures of each test material mixed with the standardized compounds octyl β -D-glucopyranoside [8] and 1-*O*-dodecyl-D-xylitol [7, 9]. The binary mixtures were produced by weighing out each individual test material and the known standard material on a microscope slide, and mixing them thoroughly together while in their liquid states. The cooled samples were introduced into the microscope microfurnace and the phase transition temperatures and classification of phase type were performed in the usual manner.

Molecular modelling studies were performed on a Silicon Graphics work station (Indigo XS24, 4000) using the programs Quanta and CHARMM. Within CHARMM, the Adopted Basis Newton Raphson (ABNR) algorithm was used to locate the molecular conformation with the lowest potential energy. The minimization calculations were performed until the root mean square

(rms) force reached $4.184 \text{ kJ mol}^{-1} \text{ \AA}^{-1}$, which is close to the resolution limit. The rms force is a direct measure of the tolerance applied to the energy gradient (i.e., the rate of change of potential energy with step number) during each cycle of minimization. The calculation was terminated in cases where the average energy gradient was less than the specified value. The results of the molecular mechanics calculations were generated using the programs QUANTA V4.0 and CHARMM V22.2. The programs were developed and integrated by Molecular Simulations Inc. The modelling packages assume the molecules to be a collection of hard particles held together by elastic forces, in the gas phase, at absolute zero, in an ideal motionless state; the force fields used are those described in CHARMM V22.2.

2.2. General synthetic procedures

Melting points were determined using an electrothermal apparatus, and are uncorrected. NMR spectra for specimens dissolved in CDCl_3 or $\text{C}_5\text{D}_5\text{N}$ were recorded using a Bruker WB-300 instrument (with Me_4Si as an internal standard). All reactions were monitored by HPLC (Waters 721) using one of the reverse phase columns RP-18 (Merck) or PN 27-196 (Waters) or CPG (Girdel) with columns of either OV 17 or SE 30. Column chromatography was performed over silica gel (60 mesh, Matrex) using gradient elution with hexane/acetone (in each case the ratio of silica gel to product mixture to be purified was 30:1). 1-*O*-Dodecyl-2,3-*O*-isopropylidene-*D,L*-xylitol (**8**), 6-*O*-dodecyl-1,2,3,4-di-*O*-isopropylidene- α -*D*-galactopyranose, and 1-*O*-dodecyl-*D,L*-xylitol (**14**), were synthesized in accordance with methods of the literature [5, 9, 10]. The purities of the compounds were controlled and determined by chromatographic and NMR spectrographic techniques.

The following sections describe the syntheses of various itol amphiphiles [1-*O*-*R*-(*D*)(*L*)-itol] in which each final product carries a dodecyl chain ($n = 12$) linked

to the itol moiety via an oxygen atom. Three general pathways are described, as depicted in schemes 1 to 3.

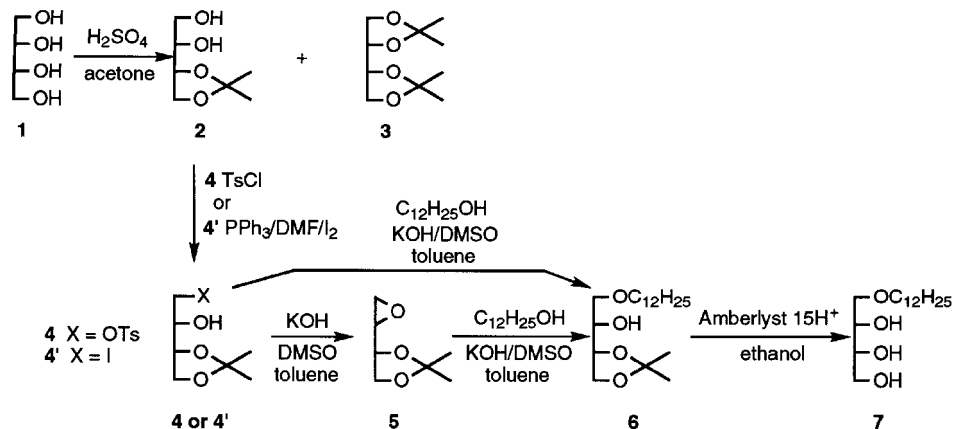
2.2.1. Synthesis of 1-*O*-dodecyl-*D,L*-erythritol 7

2.2.1.1. Preparation of 1,2-*O*-isopropylidene-*D,L*-erythritol (**2**). Method A (selective protection of *meso*-erythritol, **1**). *Meso*-erythritol (**1**) (60 g) was added to a stirred solution of H_2SO_4 (1.3 ml; 0.04M) in acetone (600 ml) at room temperature. After 97% conversion, the solution was filtered, cooled, neutralized with solid NaHCO_3 and the solvent removed under reduced pressure. The desired product was isolated after purification by column chromatography. Yield: 36%, m.p. 40–42°C.

Method B (deprotection of 1,2,3,4-di-*O*-isopropylidene-*D,L*-erythritol, **3**). The diacetal derivative (40 g) was added to a stirred solution of H_2SO_4 (2.1 ml; 0.1M) in ethanol 96°GL (400 ml) at room temperature. After 97% conversion, the solution was cooled and neutralized with solid NaHCO_3 . The mixture was filtered and the solvent removed under reduced pressure. The desired product was isolated after purification by column chromatography. Yield: 40%, m.p. 56–58°C.

2.2.1.2. Preparation of 1,2-*O*-isopropylidene-4-*O*-tosyl-*D,L*-erythritol **4**. To the monoacetal **2** (6 g) dissolved in toluene- $\text{C}_5\text{H}_5\text{N}$ (2:3 v/v, 50 ml), *p*-toluenesulphonyl chloride (7.6 g) dissolved in dry toluene (10 ml) was added at -15°C . After 72 h at 4°C , the mixture was filtered and the filtrate neutralized with saturated aq NH_4Cl . The organic phase was separated, washed with water (twice), dried (Na_2SO_4), and the solvent removed under reduced pressure. The desired product was isolated after purification by column chromatography. Yield: 70% (oil).

2.2.1.3. Preparation of 1-deoxy-1-iodo-3,4-*O*-isopropylidene-*D,L*-erythritol **4'**. To a mixture of the monoacetal **2** (6 g) and triphenylphosphine (19.5 g; 0.5 equiv) in



Scheme 1. Synthesis of 1-*O*-dodecyl-*D,L*-erythritol (**7**).

DMF (60 ml) a solution of iodine (9.4 g) dissolved in DMF (60 ml) was added dropwise at -10°C . After 1 h at -5°C the mixture was neutralized with saturated aq NaHCO_3 and the solvent removed under reduced pressure. The desired product was isolated after purification by column chromatography. Yield: 45% (oil).

2.2.1.4. Preparation of 1,2-epoxy-3,4-O-isopropylidene-D,L-erythritol 5. To a stirred solution of derivative **4** or **4'** (0.02 mol) in toluene- Me_2SO (8:2 v/v, 60 ml) finely powdered potassium hydroxide (2.4 equiv) was added. After 2 h, at room temperature, the solution was neutralized with saturated aq NH_4Cl . The mixture was filtered and the product extracted into toluene. The organic phase was separated, washed with water (twice), dried (Na_2SO_4), and the solvent removed under reduced pressure. The desired product was isolated after purification by column chromatography. Yield: 81% (oil), $n_{\text{D}}^{20} = 1.3741$.

2.2.1.5. Preparation of 1-O-dodecyl-3,4-O-isopropylidene-D,L-erythritol 6. Finely powdered potassium hydroxide (3 equiv) and dodecyl alcohol (4 equiv) were added to a stirred solution of the activated substrate **4**, **4'** or **5** (1 equiv) in toluene- Me_2SO (1:1) maintained at 40°C . After 95% conversion, the mixture was filtered and the filtrate neutralized with solid NH_4Cl . The organic phase was separated, washed with water (twice), dried (Na_2SO_4), and the solvent removed under reduced pressure. The isolated product **6** was not purified, but was used directly in the preparation of compound **7**.

2.2.1.6. Preparation of 1-O-dodecyl-D,L-erythritol 7. To a stirred solution of crude **6** in ethanol (125 g l^{-1}), Amberlyst 15H^+ resin (the weight ratio of the resin to substrate was 4:1) was added at 50°C . After 95% of the monoacetalized precursor **6** had disappeared, the mixture was filtered and the solvent removed under reduced pressure. The desired product was isolated after purification by column chromatography. Yield: 91%. ^1H NMR (300 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 0.76 (t, $J = 6.5$ Hz, 3H, $\omega\text{-CH}_3$); 1.12–1.53 (m, CH_2); 3.43 (t, $J_{\alpha,\beta} = 6.5$ Hz, 2H, $\alpha\text{-CH}_2$); 3.84 (dd, $J_{1b,2} = 6.5$ Hz, 1H, H-1b); 3.98 (dd, $J_{1a,2} = 3.3$ Hz, $J_{1a,1b} = 9.8$ Hz, 1H, H-1a); 4.14 (m, 1H, H-4b); 4.17 (m, 1H, H-3); 4.22 (m, 1H, H-4a); 4.26 (m, 1H, H-2); ^{13}C NMR (75 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 14.3

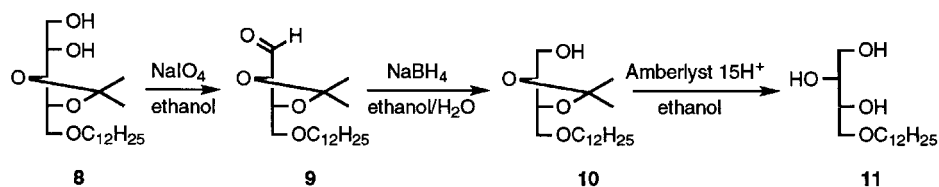
(C ω); 22.9–32.1 (CH_2) $_n$; 65.0 (C-4); 71.7 (C- α); 72.7 (C-2); 73.9 (C-3); 74.2 (C-1). Elemental analysis: found C 66.24, H 11.90; calc. for $\text{C}_{16}\text{H}_{34}\text{O}_4$ C 66.16, H 11.80, O 22.04%.

2.2.2. Synthesis of 1-O-dodecyl-D,L-threitol **11**

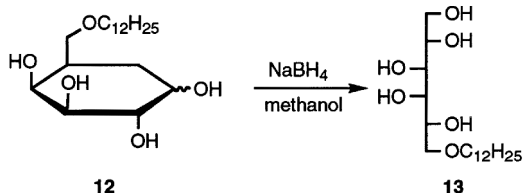
2.2.2.1. Preparation of 4-O-dodecyl-2,3-O-isopropylidene-D,L-threose 9. Sodium periodate (2.79 g) dissolved in water (150 ml) was added at 0°C to a stirred solution of monoacetal **8** (4.7 g) in ethanol (40 ml). After 1 h at room temperature, the mixture was cooled, filtered and the excess solvent removed under diminished pressure. The crude product was then extracted into diethyl ether. The organic phase was separated, washed with water (twice), dried (Na_2SO_4) and the solvent removed under reduced pressure. The aldehyde product (**9**) was characterized by infrared spectroscopy ($\nu_{\text{C=O}} = 1736\text{ cm}^{-1}$), and used in subsequent reactions without further purification.

2.2.2.2. Preparation of 1-O-dodecyl-2,3-O-isopropylidene-D,L-threitol 10. The crude aldehyde **9** (4 g) was dissolved in a mixture of ethanol and water (3:1 v/v, 40 ml) and treated with sodium borohydride (2.77 g; 6 equiv) at room temperature for 30 min. The excess of sodium borohydride was destroyed by treatment with methanol and the solution was concentrated under reduced pressure. The crude product was extracted into dichloromethane, the organic phase was separated, washed with water (twice), dried (Na_2SO_4) and the solvent removed under reduced pressure. The desired product was isolated after purification by column chromatography. Yield: 81% based on **8**; (oil); $n_{\text{D}}^{20} = 1.448$.

2.2.2.3. Preparation of 1-O-dodecyl-D,L-threitol 11. To a stirred solution of derivative **10** (3 g) in ethanol (25 ml), Amberlyst 15H^+ resin (the ratio of resin to product was 4:1) was added at 50°C . After 95% conversion, the mixture was filtered and the solvent removed from the filtrate under reduced pressure. The desired product was isolated after purification by column chromatography. Yield: 90%; ^1H NMR (300 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 0.87 (t, $J = 6.5$ Hz, 3H, $\omega\text{-CH}_3$); 1.23–1.64 (m, CH_2); 3.52 (t, $J = 6.5$ Hz, 2H, $\alpha\text{-CH}_2$); 3.93 (dd, $J_{1b,2} = 6.5$ Hz, 1H, H-1b); 4.02 (dd, $J_{1a,2} = 5.4$ Hz, $J_{1a,1b} = 9.3$ Hz, 1H, H-1a); 4.24 (dd, 1H, H-4a); 4.29 (dd, 1H, H-4b); 4.36 (m, 1H, H-3); 4.49 (m, 1H, H-2); ^{13}C NMR (75 MHz, $\text{C}_5\text{D}_5\text{N}$)



Scheme 2. Synthesis of 1-O-dodecyl-D,L-threitol (**11**).

Scheme 3. Synthesis of 6-*O*-dodecyl-*D*-galactitol (**13**).

δ : 14.6 (C ω); 23.3–32.5 (CH $_2$) $_n$; 65.9 (C-4); 72.0 (C- α); 71.6 (C-2); 73.6 (C-3); 73.9 (C-1). Elemental analysis: found C 66.17, H 11.80; calc. for C $_{16}$ H $_{34}$ O $_4$ C 66.16, H 11.80, O 22.04%.

2.2.3. Synthesis of 6-*O*-dodecyl-*D*-galactitol **13**

2.2.3.1. *Preparation of 6-O-dodecyl-D-galactopyranose 12.* 6-*O*-*n*-Dodecyl-1,2,3,4-di-*O*-isopropylidene- α -*D*-galactopyranose (5 g) was added at room temperature to a stirred solution of CF $_3$ COOH/H $_2$ O (9:1 v/v, 70 ml). After 15 min, diethyl ether was added and the solution was cooled to -20°C . The desired product was filtered off, washed with diethyl ether (twice) and recrystallized from THF. Yield: 91%; $[\alpha]_D^{20} = 25.4^\circ$ (*c* 1.0, CH $_3$ OH).

2.2.3.2. *Preparation of 6-O-dodecyl-D-galactitol 13.* Compound **12** (2 g) was dissolved in methanol (40 ml) and treated with sodium borohydride (6 equiv) at room temperature for 16 h. The excess of sodium borohydride was destroyed over a period of 5 h at room temperature using formic acid. The solvent was removed under reduced pressure and the crude product recrystallized from methanol. Yield: 96%; $[\alpha]_D^{20} = 14.2^\circ$ (*c* 1.0, C $_5$ H $_5$ N), ^1H NMR (300 MHz, C $_5$ D $_5$ N, 330 K) δ : 0.80 (t, $J = 6.4$ Hz, 3H, ω -CH $_3$); 1.20 (m, CH $_2$); 1.52 (q, $J_{\alpha,\beta} = 6.6$ Hz, 2H, β -CH $_2$); 3.53 (t, 2H, α -CH $_2$); 3.99 (m, 2H, $J_{6a,6b} = 14.7$ Hz, H-6a and H-6b); 4.28 (d, 2H, $J_{1,2} = 5.8$ Hz, H-1a and H-1b); 4.43 (dd, 1H, $J_{2,3} = 1.9$ Hz, H-3); 4.52 (dd, 1H, $J_{3,4} = 8.5$ Hz, H-4); 4.74

(dt, 1H, H-2); 4.81 (dt, 1H, $J_{4,5} = 1.4$ Hz, H-5); ^{13}C NMR (75 MHz, C $_5$ D $_5$ N, 330 K) δ : 14.5 (C ω); 23.2–32.4 (CH $_2$) $_{10}$; 65.7 (C-1); 70.4 (C-5); 72.0 (C α); 72.4 (C-4); 72.6 (C-2 and C-3); 74.4 (C-6). Elemental analysis: found C 61.70, H 11.02; calc. for C $_{18}$ H $_{38}$ O $_6$ C 61.68, H 10.92, O 27.40%.

3. Results

3.1. Transition temperatures

The phases exhibited by the final products, **7** and **11** (*D,L* mixtures), and **13** and **14** (*D*-configuration), were investigated and classified by thermal optical microscopy and miscibility studies; the resulting transition temperatures and melting points are shown together in the table. In addition to the materials shown in the table, compound **15**, 1-*O*-dodecylpropanetriol and compound **16**, 1-*O*-dodecyl-*D*-mannitol, which have been previously reported to exhibit liquid crystalline properties, are included for comparison [12, 13]. The classification of the mesophase (SmX) exhibited by compound **15** is undefined in the literature report; however, as it was not identified as a smectic A phase it might be expected to be more ordered phase (i.e. smectic B or a tilted analogue). Nevertheless, its classification is unimportant to the analysis that follows.

The clearing points are plotted as a function of the number of hydroxyl groups in the molecular structures of each compound in figure 5. This figure demonstrates quite clearly, over the number of materials studied, that there is a roughly linear dependence of the clearing point on the number of hydroxyl groups present in the material. This result is irrespective of material source and the method of preparation (provided that the materials are of sufficient purity); for example remarkable agreement is obtained for the clearing points of compounds **7** and **11**, and compounds **13** and **16**.

However, as the number of free hydroxyl groups is

Table. Transition temperatures ($^\circ\text{C}$) for compounds **7**, **11**, and **13** to **16**.

Compound 15	Compound 11	Compound 7	Compound 14	Compound 13	Compound 16
				—OH	—OC $_{12}$ H $_{25}$
			—OH	—OH	HO—
—OH	—OH	—OH	—OH	HO—	HO—
—OH	OH—	—OH	HO—	HO—	—OH
	—OH	—OH	—OH	—OH	—OH
—OC $_{12}$ H $_{25}$	—OC $_{12}$ H $_{25}$	—OC $_{12}$ H $_{25}$	—OC $_{12}$ H $_{25}$	—OC $_{12}$ H $_{25}$	—OH
SmX 32 Iso Liq m.p. 48	SmA 71.0 Iso Liq m.p. 58.2	SmA 73.9 Iso Liq m.p. 68.5	SmA* 114.7 Iso Liq m.p. 49.5	SmA* 168.7 Iso Liq m.p. 142	SmA* 167 Iso Liq m.p. 111.2

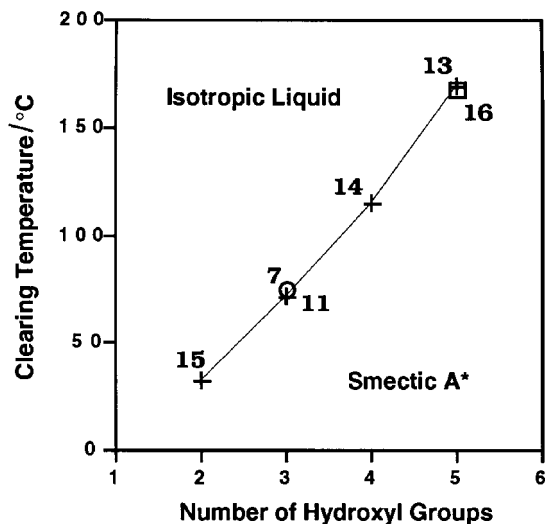


Figure 5. Variation of clearing temperatures ($^{\circ}\text{C}$) as a function of the number of free hydroxyl groups.

increased, it is expected that the steepness in the rise of the clearing points will slow down and eventually level off. In addition, comparison between the erythritol and threitol derivatives, **7** and **11**, shows that the nature of the stereochemistry at the 3-position does not markedly affect the clearing temperatures. Similarly the differences in the stereochemical structures of compounds **13** and **16** do not apparently affect the mesophase behaviour greatly in terms of the clearing point or phase type. Nevertheless, the small difference detected in the clearing points between compounds **13** and **16** appears to be real, as similar differences have been found in other related systems [14]. Conversely, the melting points of the materials in these two comparisons are markedly different, emphasizing that the crystal structures of the comparative materials are not the same and are possibly dependent on their stereochemical structures.

3.2. Phase characterization

Classification of the mesophases formed by the final products was achieved in two ways: firstly from observations of the defect textures exhibited by the mesophases on cooling from the isotropic liquid, and secondly through miscibility studies with the standard materials octyl β -D-glucopyranoside and 1-O-dodecyl-D-xylitol.

On clean glass substrates all of the materials formed mainly homeotropic textures, but some patches of focal-conic and oily streak defects were observed. On untreated glass substrates, focal-conic defects characterized by their elliptical and hyperbolic lines of optical discontinuity were observed. The presence of focal-conic defects and homeotropic alignment in variously treated specimens is diagnostic for the presence of a smectic A* phase [15]. In addition, as the molecules are chiral the

specimens were examined for any indication of the formation of a helical macrostructure, e.g. banding in the focal-conic domains, rotation of plane polarized light and selective reflection of light, but none of these effects were found. Thus the materials do not exhibit the twisted form of the smectic A* phase—the twist grain boundary phase. Thus these observations classify the phase as being smectic A* in type.

Miscibility studies with *n*-octyl β -D-glucopyranoside and 1-O-dodecyl-D-xylitol, which are standardized carbohydrates that exhibit smectic A* phases [8, 9], confirmed the above classifications of the liquid crystal phases of the materials synthesized.

3.3. Molecular simulations

In order to examine the nature (rigidity/flexibility/shape) of the molecular structures of the compounds, each individual material was geometrically optimized in molecular simulation studies. The minimized structures for all of the materials are shown together for comparison in figures 6 and 7. In addition simulations of the four final products were carried out at various temperatures within the smectic A* phase. CHARMM dynamics were achieved constraining only bonds attached to hydrogen atoms and using the parameter specified geometry. The molecular dynamics calculations were carried out in three stages: heating, equilibrating at a fixed temperature and simulation of the motion of the molecule at the following temperatures in the gas phase for each of the four compounds prepared in this study:

compound **7**, 333 K, compound **11**, 333 K,

compound **13**, 383 K, and compound **14**, 433 K.

The first two stages are necessary to prepare the models for the third simulation stage where CHARMM dynamics were performed for a simulated time of 6.4 ps, thereby generating 640 conformations. Average coordinates of these conformations produced time-average structures of the four polyols which were respectively found to be very similar to the conformations with the lowest potential energy.

If figures 6 and 7 are examined, it can be seen that the four polyols have very similar minimized structures in the gas phase at absolute zero. The aliphatic chain for all four materials generally adopts an all *trans*-conformation, whereas some differences occur in the polar head groups. As the number of hydroxyl groups is increased intramolecular hydrogen-bonding rather than intermolecular hydrogen-bonding becomes feasible. For compound **13**, the flexible head group appears to bend back on itself and hydrogen bonds are formed from one end of the sugar moiety to the other, thereby producing a quasi-ring structure. Such intra-

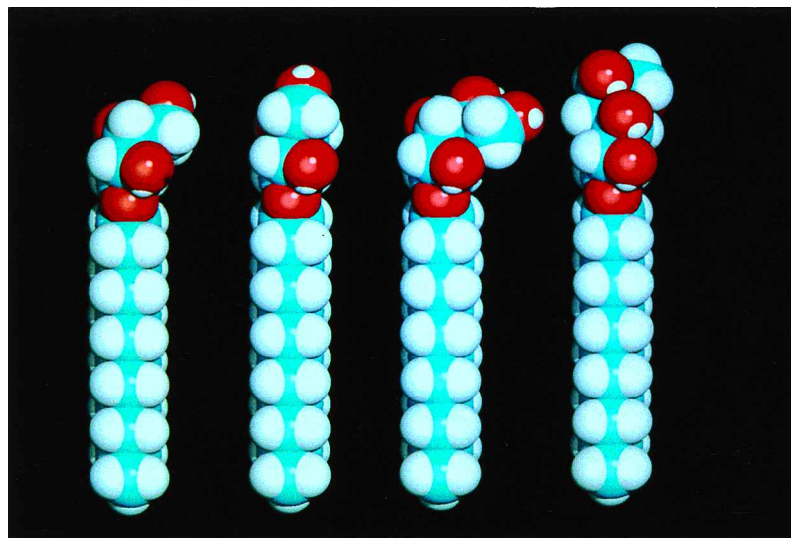


Figure 6. A space filling representation of the molecular structures of compounds **11**, **7**, **14**, and **13**. Each individual compound was geometrically optimized in molecular simulation studies using QUANTA/CHARMm.

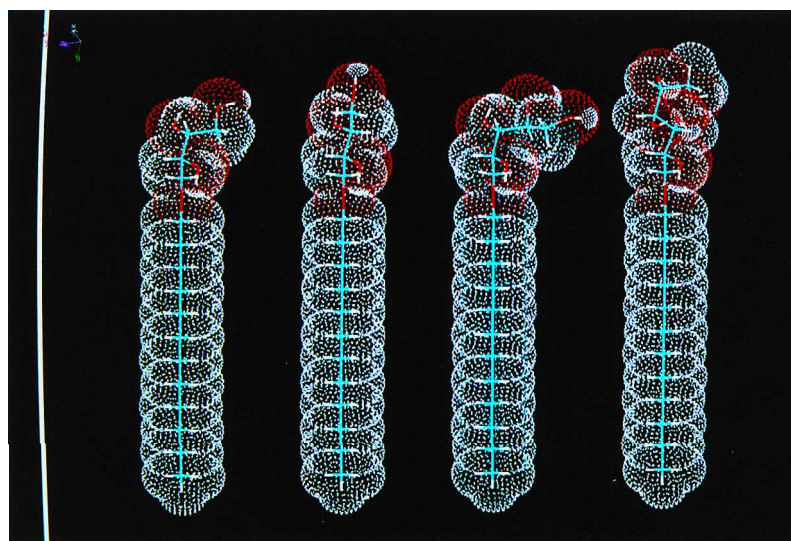


Figure 7. A surface charge representation of the molecular structures of compounds **11**, **7**, **14** and **13**. Each individual compound was geometrically optimized in molecular simulation studies using QUANTA/CHARMm. The structure shows that as the number of CH₂OH groups is increased, the skeleton bends back on itself to create a more linear structure with the aid of intra-molecular hydrogen bonding.

molecular hydrogen-bonding, however, does not appear to affect the clearing temperature. The ineffectual nature of intramolecular hydrogen-bonding on the clearing point may be due to the fact that the molecules are in dynamic motion and as a consequence all of the hydrogen-bonding interactions are time dependent, so that the overall interactions (inter- and intra-molecular hydrogen-bonding) are averaged out.

4. Discussion

It appears from the data collected that the clearing transition temperatures of acyclic polyols are primarily dependent on the number of hydroxyl moieties in the molecule which are free to hydrogen bond internally or externally. However, there appears to be no appreciable effect on the clearing temperature of variations in stereochemical structure or sugar type for a system with a

given number of hydroxyl groups. Variations do however occur for pyranose and furanose systems, primarily because of the uncertainty of the availability of all of the hydroxyl groups to form hydrogen bonds [16].

The linear relationship between hydroxyl group number and clearing point evokes a rather simple model [17] of the mesophase structure in order to explain the observations. Simply put, the mesophase could be envisaged as an internally micro-segregated structure composed of layers of sugar groups sandwiched between aliphatic lamellae. There is no local ordering of the molecules, and in such a dynamically oscillating system every orientation of the head group of an individual molecule will be presented to its nearest neighbours. This would result in no substantive effect of stereochemical structure. Thus as the number of hydroxyl groups is increased, the layer spacing of the lamellae

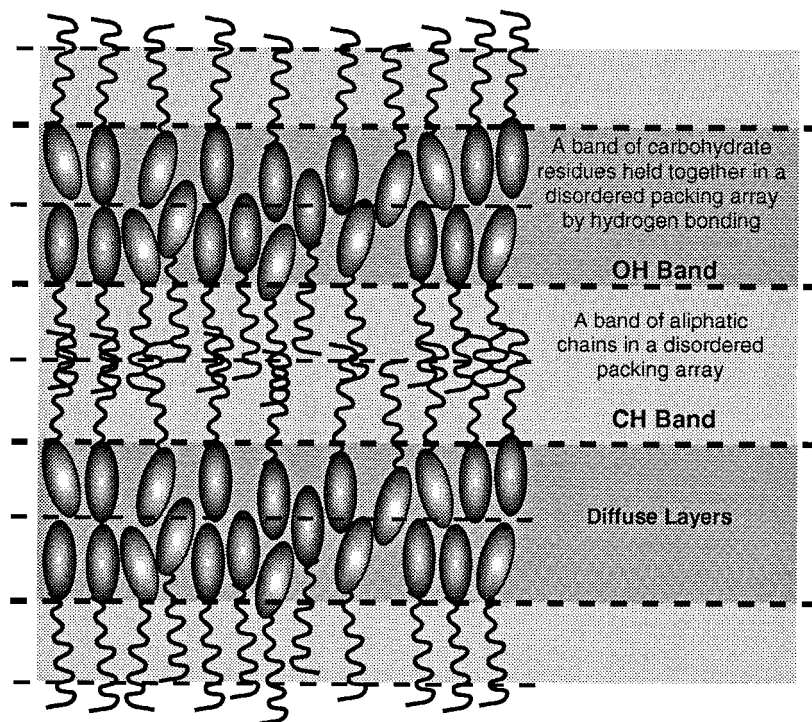


Figure 8. Proposed microphase separated structure of the smectic A* phase of acyclic polyols.

containing the sugar head groups simply gets larger in a stepwise fashion, and concomitantly the average interactions between the molecules also increase incrementally. This suggests that the head groups are arranged in a bilayer structure (which X-ray diffraction shows is preferred over the monolayer structure)—see figure 8. Structures with interdigitated head groups might be expected to be less likely to occur as the overlap of the head groups would have to change in a particular way as the polyol series is ascended in order to maintain a linear increase in clearing point.

5. Summary

Overall, there appears to be no strongly delineated bilayer structure as often portrayed for smectic A* phases of glycolipids, e.g. bilayers with interdigitated head groups or interdigitated aliphatic chains. Rather the mesophase appears to be held together by the strong interactions of the hydroxyl groups, while the aliphatic chains almost act as a solvent between the layers of the head groups, i.e. *the system is internally and completely microphase separated*. In comparison with conventional thermotropic systems, glycolipids have structures where their internal competing parts (i.e. the polar head group and the aliphatic chain) are more dissimilar than the competing parts found in classical thermotropic materials. Thus in order to affect or change mesophase formation in glycolipids, greater changes to the structures of the competing parts are necessary.

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