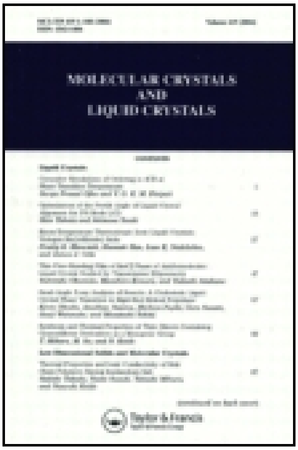

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# A Revised Model for the Molecular Arrangement in the Smectic $A_d$ Phase of Carbohydrate Derived Amphiphiles with One Alkyl Chain†

H. A. Van Doren [a] & L. M. Wingert [a]

[a] Department of Crystallography, University of Pittsburgh, Pittsburgh, PA, 15260, U.S.A.

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# A Revised Model for the Molecular Arrangement in the Smectic $A_d$ Phase of Carbohydrate Derived Amphiphiles with One Alkyl Chain†

H. A. van DOREN[1] and L. M. WINGERT
*Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A.*

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We propose a different molecular arrangement in the bilayers of the smectic $A_d$ phase of mesogenic carbohydrate amphiphiles from that previously postulated. The molecular arrangement proposed in this report is consistent with all experimental data currently available. In this new model, the smectic bilayers are identical (except for the absence of water) to the fluid lamellar ($L_\alpha$) lyotropic phase, i.e., the molecules within the bilayers are arranged tail-to-tail, with the carbohydrate moieties on the outside of the bilayers and partially interdigitized alkyl chains in the core of each layer.

*Keywords: carbohydrates; smectic $A_d$; amphiphiles*

## 1. INTRODUCTION

Over the past decade there has been an increased interest in liquid crystals based on carbohydrates.[2] It has become clear that carbohydrate amphiphiles can provide a source of new liquid crystalline materials. The number which have been reported to display liquid crystalline behaviour has increased from less than 30 in 1986[3] to approximately 1,000 today. The majority of these compounds is formed from a single carbohydrate moiety, with at least two or three free hydroxyl groups and one alkyl chain of sufficient length, usually *n*-hexyl or longer. Thus far, all compounds of this general type form a smectic $A_d$ phase.[2–7] Within a homologous series, the *n*-hexyl or *n*-heptyl derivative are usually monotropic, whereas higher homologues are enantiotropic, with the clearing point reaching a maximum for the *n*-dodecyl or *n*-tridecyl derivatives.[2,6,7]

It is generally accepted[2–18] that the hydrogen-bond forming ability of the carbohydrate moiety is crucial to the formation of mesophases in these amphiphilic derivatives. So far, the model used most often for the molecular arrangement in

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† Dedicated to Professor George A. Jeffrey on the occasion of his 75th birthday.

the layers of the smectic $A_d$ phase consists of a core of (partially overlapping) hydrogen-bonded carbohydrate moieties with exterior hydrocarbon chains[2–7], (MODEL I, see Figure 1a).

Jeffrey[19,20] has recently suggested that the stability of the hydrogen bonds of hydroxyl groups is particularly sensitive to temperature due to their orientational freedom. This observation has led to the proposal of a new model,[20] in which the alkyl chains form the core of the smectic bilayers and the carbohydrate moieties are on the outside (MODEL II, see Figure 1b). In this report we wish to show that this model, which is identical (except for the absence of water) to the model of the fluid lamellar ($L_\alpha$) lyotropic phase, is consistent with the currently available experimental data. MODEL II is also consistent with the thermal behavior of carbohydrate mesogens and the influences of small structural changes in the carbohydrate moiety.

## 2. HISTORY OF RESEARCH ON CARBOHYDRATE MESOGENS

Fischer and Helfrich[21] reported on the anomalous melting behaviour of several long-chain alkyl glucopyranosides in 1911. In 1938 this 'double melting point' was interpreted[22] in terms of mesophase formation. The first paper[8] to propose a model for the molecular arrangement in the liquid crystalline phase of a carbohydrate amphiphile appeared in 1982. It was based on the crystal structure of *n*-heptyl 1-thio-α-D-mannopyranoside (Cr 64 S 152 I) in which the sugar-moieties are hydrogen-bonded head-to-head and the all-trans alkyl chains are intercalated. The layer spacing in the mesophase of approximately 21 Å corresponds closely to the separation between the terminal carbon atoms in the alkyl chains of two molecules in the head-to-head position. This observation led to the proposal for the following two-step model for the thermal behavior of carbohydrate mesogens. (1) At the crystal-to-liquid crystal transition, the hydrocarbon chains melt, but the hydrogen bonding in the carbohydrate moieties persists, providing the core for the liquid crystalline phase. The 'liquid' alkyl chains are no longer intercalated. (2) At the liquid crystal-to-isotropic transition the hydrogen-bonded structure breaks down and true melting of the compound takes place.

An investigation by Goodby[4] of the mesophase textures and powder X-ray diffraction patterns of several monoalkylated monosaccharides supported this model. The mesophase was tentatively classified as smectic $A_d$ (Figures 2 and 3 show some typical textures). Attempts to characterize the mesophase by miscibility experiments failed, presumably because of the incompatibility of the hydrogen-bonded structures in carbohydrate mesogens with the aromatic smectogens that were used.

As more carbohydrate derivatives were reported to exhibit liquid crystalline behavior,[5,23–27] it appeared that the mesophases were bilayers regardless of whether the sugar moiety was cyclic or acyclic.[5] The only exceptions were several fully acylated inositol derivatives reported by Praefcke *et al.*,[28,29] which are believed to form discotic mesophases.

In 1985 Marcus and Finn[13] reported a successful miscibility study, which showed that the smectic mesophase of *n*-decyl β-D-glucopyranoside was thermodynamically

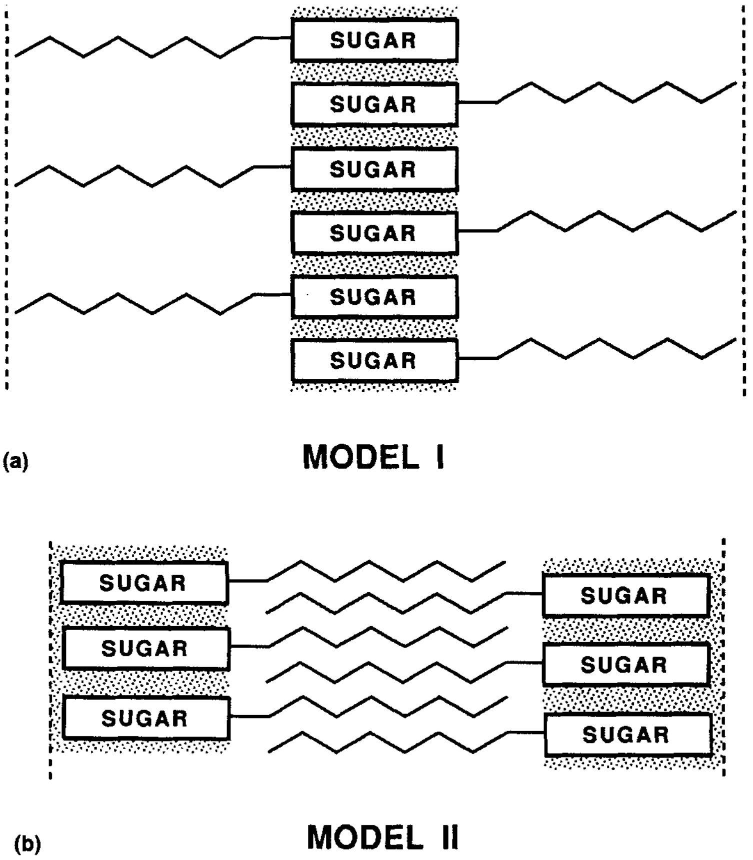

FIGURE 1 Schematic drawings of the two proposed molecular arrangements in the bilayers of the smectic $A_d$ phase of carbohydrate amphiphiles with one alkyl chain. Shading denotes regions of dynamic hydrogen bonding; a, MODEL I with (partially) overlapping carbohydrate moieties in the core and exterior alkyl chains; b, MODEL II with (partially) overlapping alkyl chains in the core and exterior carbohydrate moieties (compare with the fluid lamellar $L_\alpha$ phase).

identical to the fluid lamellar $L_\alpha$ phase of Aerosol OT (sodium bis-2-ethylhexylsulfosuccinate).

Baeyens-Volant *et al.*[16] proposed that the N-*n*-alkyl-D-gluconamides have a monolayer smectic phase, based upon the observed d-spacings and the fact that these compounds form monolayers in the crystalline state. On the other hand, Pfannemüller *et al.*[5] reported complete miscibility of these compounds with the smectic $A_d$ phase of alkyl β-D-glucopyranosides. The observed layer spacing for the mesophase of N-*n*-undecyl-D-gluconamide is also indicative of a smectic $A_d$ phase.[20]

Van Doren *et al.*[17] concluded that the two-step melting point model described above could neither explain the observed thermal behavior within homologous series nor account for the large differences in thermal behavior between molecules that differ only slightly in the carbohydrate moiety. Using MODEL I, the experimental data were very adequately explained by assuming that the crystal structure is completely broken down at the melting point and that new aggregates are formed

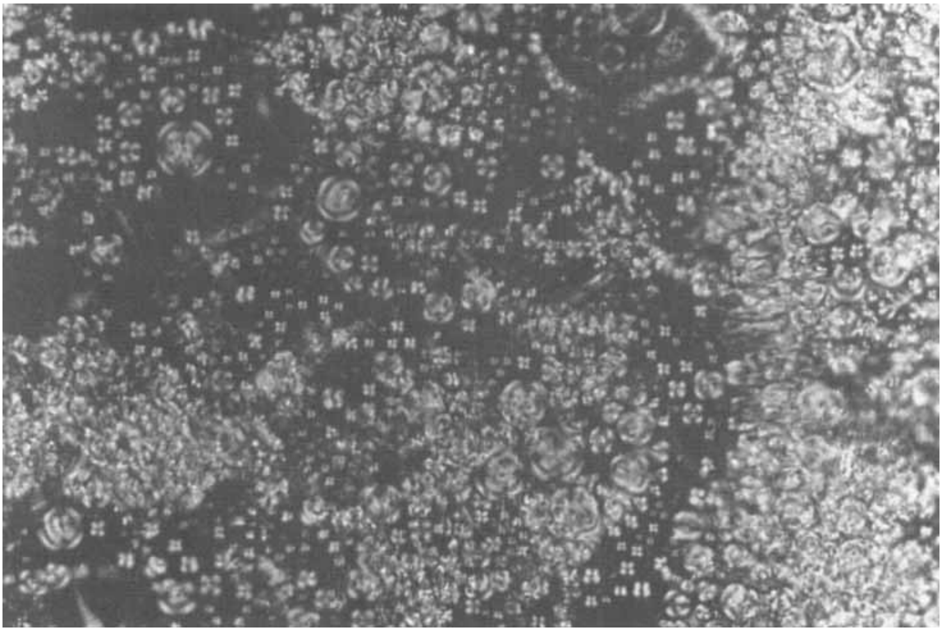

FIGURE 2 The texture of the smectic $A_d$ phase of *n*-heptyl 1-thio-α-D-glucopyranoside obtained upon heating a crystalline sample above the melting point (110°C, crossed polarizers). See Color Plate I.

that are held together by dynamic hydrogen bonding. In order to obtain a smectic $A_d$ phase, these aggregates would have to be rod-like 'dimers', as in the 4-alkoxybenzoic acids[30] and the 2-(4′-alkylcyclohexyl)-1,3-propanediols.[31]

Praefcke *et al.*[32] reported that the aldose dialkyl dithioacetals,[17,33–35] which have a peg-like structure, form a hexagonal columnar mesophase ($D_{hd}$). For these compounds, disc-like aggregates are proposed, consisting of 4 or 5 molecules, with the hydrogen-bonded sugar moieties in the middle and the alkyl chains filling the periphery (compare with the inverted hexagonal, $H_{II}$, lyotropic phase).

In both types of aggregates, some of the hydroxyl groups serve to hold together the rods or disks. The remaining hydroxyl (or other polar) groups provide the lateral attractions necessary to form the smectic layers or columnar packing respectively. The observed differences in clearing points with variations in the carbohydrate moiety and constant alkyl chain lengths can be explained in terms of the effect of these variations on the strength of the lateral cohesions.

Another explanation was suggested by Thiem *et al.*[18] The stability of the mesophase is discussed in terms of the required volume of a rotating molecule in the mesophase. In monosaccharide derivatives with a cyclic sugar moiety, this volume is influenced by the geometry of the hydroxyl groups. The higher the required volume, the lower the clearing point. It would seem to be much more complicated to explain the differences in clearing points for acyclic compounds along these lines. The authors also used the increased polarity and hydrogen-bond forming ability of the carboxyl group to explain the significantly higher clearing points of the glu-

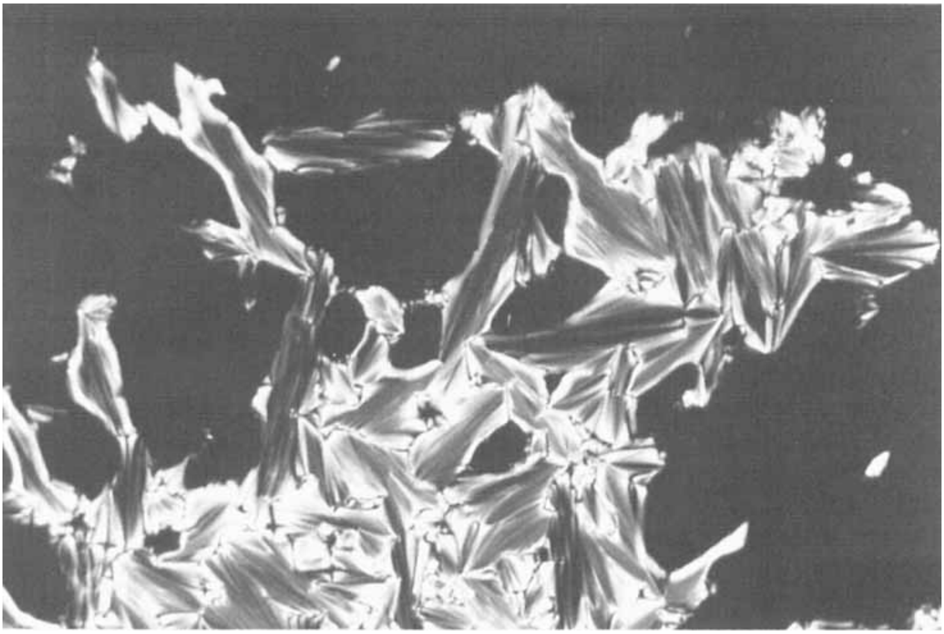

FIGURE 3 The focal-conic fan-like texture and pseudoisotropic regions of the smectic $A_d$ phase of *n*-heptyl 1-thio-α-D-glucopyranoside obtained upon slow cooling of the isotropic liquid (133°C, crossed polarizers). See Color Plate II.

curonic acid glycosides as compared to the corresponding glucose derivatives. The latter explanation is closely related to that of van Doren *et al.*[2,17]

The fact that mesogenic mono-alkylated carbohydrate derivatives form a smectic $A_d$ phase seems to be generally accepted. Some doubts have been expressed with regard to the molecular arrangement within the mesophase[6,36], but MODEL I was not really challenged prior to the proposition of MODEL II by Jeffrey.[19]

## 3. DISCUSSION

The reader may ask: "What is the difference between these two models other than an arbitrary distinction caused by the drawing of lines to define layers?" Indeed, when we consider a stack of bilayers, alternating polar and apolar regions will be found for both models. However, in MODEL I the polar carbohydrate moieties are interdigitized, indicating that the shear between layers would be in the apolar regions. In MODEL II the alkyl chains are interdigitized and the shear between layers would occur in the polar regions, with the dynamic hydrogen bonding between the sugar moieties causing fluidity, similar to the function of water in the fluid lamellar phase.

How do the experimental data that have been reported in the past decade allow us to discriminate between MODELS I and II?

### Powder X-ray Diffraction

The original evidence for the formation of a smectic $A_d$ phase in carbohydrate mesogens was obtained from powder X-ray diffraction patterns. Molecules appear to be somewhat shorter than their calculated lengths due to thermal motion and deviation from the all-trans configuration of the molecules, as well as imperfect orientation perpendicular to the layers. Usually d-spacings are found which correspond to 1.3 to 1.6 times the calculated molecular lengths. The data for single compounds could fit either MODEL I or II. However, differences should arise when we use either MODEL I or II to predict the increase in d-spacings within a homologous series. For MODEL I, one would expect an average increase of up to 2.5 Å (due to a $—CH_2—$ being added on both sides of a smectic layer) in going to the next higher homologue (see Figure 4a). For MODEL II the average increase would be no more than 1.25 Å, assuming that the distance between the terminal methyl group of each molecule to the polar moiety of the opposing molecule(s) remains the same (see Figure 4b). The d-spacings reported by Goodby[4] for four *n*-alkyl-β-D-glucopyranosides would seem to favor MODEL I. Powder patterns obtained from homologous series of *n*-alkyl 1-thio-α-D-glucopyranosides[7] and 1-(alkylamino)-1-deoxy-D-glucitols[2] show an average increase of 1.2–1.4 Å per methylene unit, which is very close to the expected value for MODEL II. In order for MODEL I to accomodate these data, one would have to assume a more severe tilting of the molecules within the layers than is likely in smectic A phases.[37]

### Studies Comparing Smectic $A_d$ and Lamellar Lyotropic ($L_\alpha$) Phases

The fact that the smectic $A_d$ phase of decyl β-D-glucopyranoside was found to be fully miscible with the fluid lamellar phase of Aerosol OT (in water)[13] strongly favors MODEL II. In the same paper, Marcus and Finn report that the mesophase of decyl β-D-glucopyranoside does not change upon addition of up to 20 wt% of water. Similar behavior was found for dodecylmaltoside,[38] which can incorporate up to 42 wt% of water before a transition to the hexagonal lyotropic ($H_I$) phase occurs. This behavior, as well as the observed gradual increase in the d-spacings with increasing water percentages, is readily explained in MODEL II. As the headgroups become more hydrated, their volume increases and they are pushed further apart. At the same time, the volume of the alkyl chains does not increase. In order to maintain the same total volume of the apolar region, it has to become thinner, thus partly offsetting the total expected increase in d-spacings due to the addition of water.

### Phase Dependent Water Penetration

We have recently discovered that the lyotropic behavior in contact preparations of carbohydrate amphiphiles and water is dependent upon the phase of the anhydrous amphiphile.[39] For example, when water is added to crystals of heptyl 1-thio-α-D-glucopyranoside[40] at room temperature, neither dissolution nor water penetration into the crystals is observed. The sample must be heated to 46°C in order to dissolve (no lyotropic mesophase formation occurs at this temperature). On the other hand, when we add water to the same compound in the super-cooled smectic $A_d$ phase,

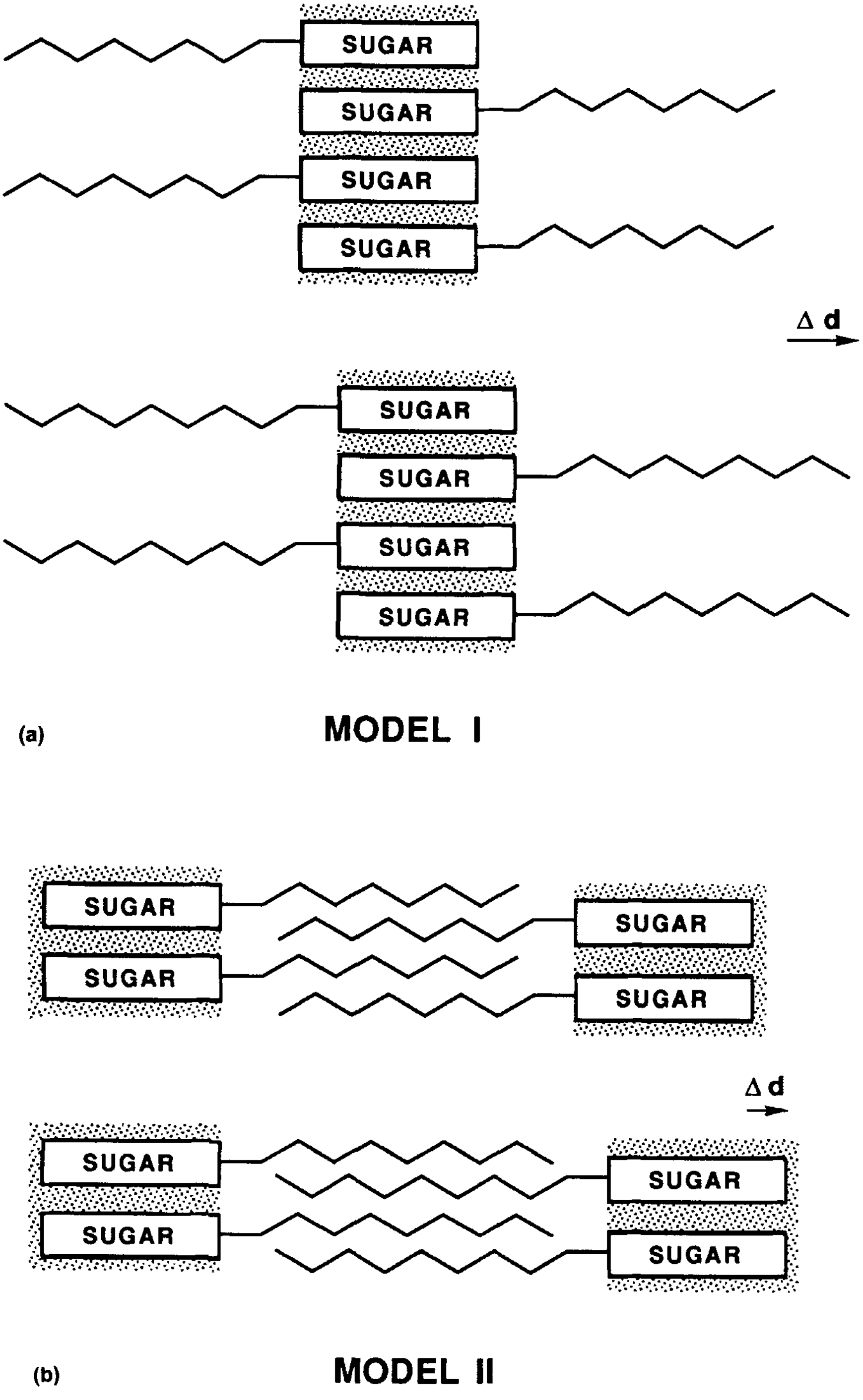

FIGURE 4 A schematic drawing of the expected increase in d-spacing as a result of adding one —$CH_2$— group to the alkyl chain (a) for MODEL I, (b) for MODEL II.

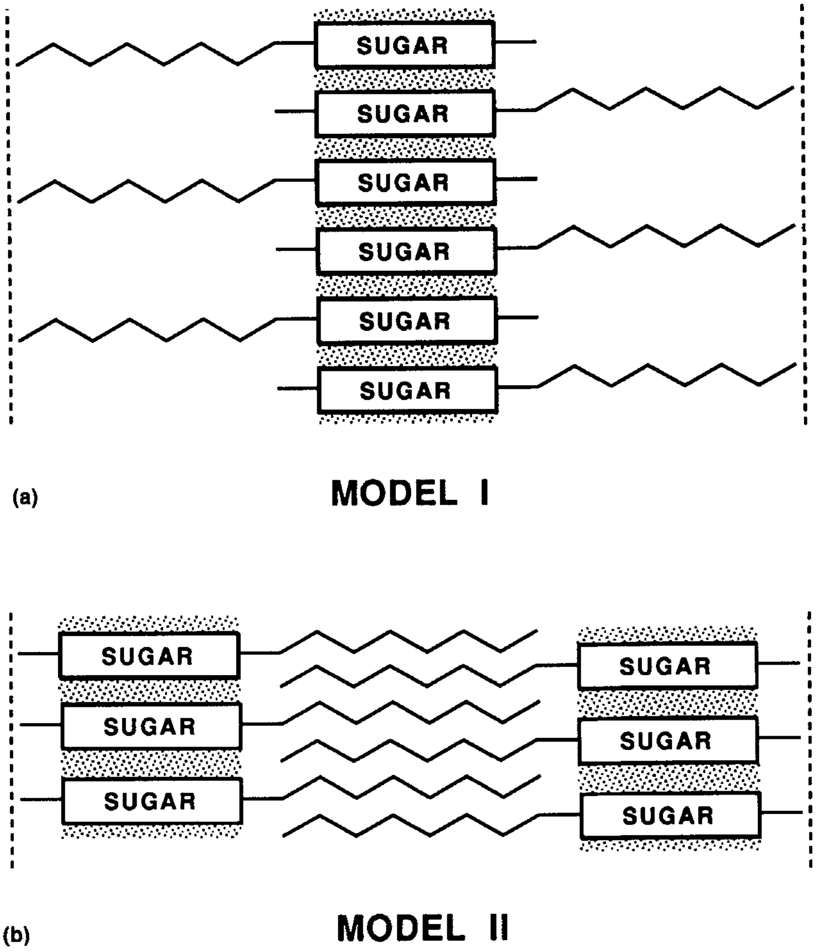

FIGURE 5 A schematic drawing of the expected effect of a terminal methyl group on the dynamic hydrogen bonding in the smectic $A_d$ phase of derivatives of 6-deoxy sugars (a) for MODEL I, (b) for MODEL II.

penetration occurs readily at room temperature and the formation of cubic and hexagonal lyophases is observed. The greater accessibility of the smectic phase is much better understood if the polar groups are on the outside of the bimolecular layers (MODEL II).

### Behavior of Derivatives of 6-Deoxy Monosaccharides

In L-rhamnose (6-deoxy-L-mannose) and L-fucose (6-deoxy-L-galactose), the hydroxyl group on C-6 is absent, thus introducing a small apolar region. In the 1-(alkylamino)-1-deoxy-alditols,[41] the clearing points are lowered dramatically when the sugar moiety is L-rhamnitol or L-fucitol, compared to derivatives of the fully hydroxylated sugars with the same alkyl chain. MODEL I offers no immediate explanation for this phenomenon (see Figure 5a), but from MODEL II it is clear

TABLE I

The clearing points of five *n*-dodecyl derivatives of acyclic carbohydrates

| Compound | clearing point (°C) | reference |
|---|---|---|
| 1-(*n*-dodecylmethylamino)-1-deoxy-D-glucitol | 100 | 2 |
| 1-(*n*-dodecylamino)-1,2-dideoxy-D-glucitol | 123 | 2 |
| 1-(*n*-dodecanoylmethylamino)-1-deoxy-D-glucitol | 125 | 6 |
| 1-(*n*-dodecylamino)-1-deoxy-D-glucitol | 173 | 2 |
| N-(*n*-dodecyl)-D-gluconamide | 189 | 5 |

that the interlayer attractions will be severely disrupted by the introduction of terminal non-polar groups in the carbohydrate moiety (see Figure 5b). The same effect has been described previously for the $D_{hd}$ forming aldose dialkyl dithioacetals.[17,32,34,35] Praefcke *et al.*[32] suggested that the formation of the disk-like aggregates, necessary for obtaining a columnar mesophase, is inhibited by the terminal non-polar groups in the sugar moieties of the L-fucose and L-rhamnose S,S-acetals.

When the implications obtained from the experimental data presented above are combined, sufficient evidence arises to warrant a revision of the original model for the molecular arrangement of the smectic $A_d$ phase of carbohydrate amphiphiles. The actual arrangement is now considered to be the one proposed in MODEL II. As in MODEL I, the formation of this molecular arrangement in the smectic bilayers requires the hydrogen-bonded network in the solid state to break down at the melting point.[17] The explanation of van Doren *et al.*[2] for the influence of small structural changes in the carbohydrate moiety on transition temperatures needs to be modified. As before, the polar groups that are closest to the alkyl chains provide the specific lateral cohesion necessary for the formation of the smectic layers. Instead of forming rod-like ‘dimers’ (in MODEL I), the hydroxyl groups furthest removed from the alkyl chains are at the interfaces between layers (in MODEL II) and provide the attractive forces necessary for the stacking of the layers. Table I shows the clearing points of five *n*-dodecyl derivatives of acyclic carbohydrates with the only variations being close to the alkyl chain. The stronger the hydrogen-bonding ability of the polar groups, the higher the clearing point should be. The observed order in the clearing points is in excellent agreement with the above explanation.

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