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J. W. Goodby^a; M. A. Marcus^a; E. Chin^a; P. L. Finn^a; B. Pfannemuller^b

^a AT & T Bell Laboratories, New Jersey, USA ^b Hermann-Staudinger-Haus, Institute of Macromolecular Chemistry, University of Freiburg, Germany

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The thermotropic liquid-crystalline properties of some straight chain carbohydrate amphiphiles

by J. W. GOODBY, M. A. MARCUS, E. CHIN, P. L. FINN

AT & T Bell Laboratories, Murray Hill, New Jersey, 07974, U.S.A.

and B. PFANNEMÜLLER

Institute of Macromolecular Chemistry, Hermann-Staudinger-Haus, University of Freiburg, Stefan-Meier-Strasse 31, D-7800 Freiburg, F.R. Germany

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A variety of homologous 1-deoxy-1-(*N*-methylalkamido)-D-glucitols were prepared and their liquid crystal phases characterized. In this study the thermotropic liquid-crystalline properties of these materials are investigated. The mesophases formed are shown to be of the smectic A class with an interdigitated bilayer ordering of the constituent molecules. This ordering is thought to be stabilized by hydrogen-bonding between neighbouring carbohydrate moieties. The properties of these materials are compared with those of other closely related acyclic carbohydrates.

1. Introduction

Alkylated carbohydrates have been shown to be extremely useful materials in the extraction of certain proteins from membrane structures [1-3]. These detergents are also known to exhibit both lyotropic [4] and thermotropic [5] liquid-crystalline behaviour due to their dichotomous, hydrophilic-hydrophobic, molecular structures. For example, *n*-dodecyl maltoside is a very potent detergent, and is known to exhibit a thermotropic smectic A phase which is also miscible with water resulting in the formation of lamellar lyotropic mesophases [6, 7].

The thermotropic mesophases formed by acyclic and cyclic carbohydrates are novel in that they are not miscible with any known mesophases of conventional liquid crystals. However, physical studies indicate that the mesophases formed are of the smectic A type [8]. The smectic A class is known to be further subdivided into a variety of subgroups depending on the layer ordering, i.e., dependent on whether the molecules are packed in bilayers (A_2), monolayers (A_1), or interdigitated bilayers (A_d). For systems such as the *n*-alkyl-1-O- β -D-glucopyranosides X-ray diffraction studies have shown that the lamellar spacing is between one and two times the molecular length of the constituent molecules, thus indicating that the mesophase has an interdigitated structure. In contrast, it is interesting to note that many cyclic carbohydrates have crystal structures that are essentially composed of bilayers, whereas acyclic systems can have either bilayer or monolayer crystal structures. Furthermore, in some cases the straight chain carbohydrates can have crystal structures where the constituent molecules have a head to tail packing arrangement [9]. This indicates that the structures of the solid phases of these compounds are not necessarily related to the molecular ordering in the mesophase.

Recently, we examined the liquid-crystalline properties of some straight chain *N*-*n*-alkyl-gluconamides [10] and found that they also exhibited smectic A phases

that were miscible with the pyranosides. This lead us to conclude that these phases also have interdigitated bilayer structures. However, recent X-ray diffraction studies by Baeyens-Volant and David on the same materials suggested that this might not be the case, and that in fact the straight chain carbohydrates may have monolayer (A1) structures [10, 11].

In this present study we have examined the morphology of some closely related 1-deoxy-1-(*N*-methylalkanamido)-*D*-glucitols, series A (sometimes called the *N*-*n*-alkanoyl-*N*-methyl-glucamides, MEGA-*n*), *N*-(2-(alkanamido)ethyl)-*D*-glucanamides, series B, and *N*-(2-(*N*-methylalkanamido)ethyl)-*D*-glucanamides, series C. In the following sections results obtained for these materials are compared with those found for the *N*-*n*-alkyl-gluconamides. The major finding from these investigations is that these straight chain carbohydrates generally have interdigitated smectic A structures as previously predicted.

2. Experimental

The materials were prepared by methods described previously [2, 12]. The thermotropic properties of these straight chain carbohydrates were investigated by thermal optical microscopy using a Zeiss Universal polarized-light microscope in conjunction with a Mettler FP52 microfurnace and an FP5 control unit, and by differential scanning calorimetry using a Perkin-Elmer DSC-4-TADS system. Miscibility phase diagrams, in order to determine phase classifications, were generated by thermal optical microscopic studies on individually weighed binary mixtures.

Structural investigations were made by X-ray diffraction using two different techniques. For the comparative material, *N*-*n*-octadecyl-gluconamide, X-ray diffraction studies were carried out using a Rigaku 100 rotating anode unit employing position-sensitive detectors and a doubly bent quartz crystal monochromator. This compound was investigated by loading the material into a quartz capillary tube and controlling the temperature of the specimen to better than 0.1°C. For 1-deoxy-1-(*N*-methyldecanamido)-*D*-glucitol (MEGA-10) X-ray measurements were made using a pinhole camera with photographic detection. The camera was calibrated using *n*-decanoic acid as a standard. The X-ray source was a monolithic channel-cut crystal on Beamline X-15A at NSLS operating at 1.54 Å. The samples were held in quartz capillaries, with temperature control to better than 2°C. The exposure times ranged from 5 to 20 min.

3. Results

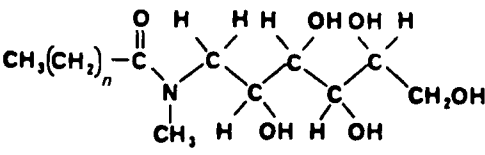
3.1. Mesophase characterization

All of the materials involved in this study were investigated firstly by thermal optical microscopy. The transition temperatures obtained for the three series (A, B, and C) are given in tables 1 to 3 respectively. From these tables it can be seen that series B, the *N*-(2-(alkanamido)ethyl)-*D*-glucanamides, and series C, the *N*-(2-(*N*-methylalkanamido)ethyl)-*D*-glucanamides, do not appear to exhibit any normal liquid-crystalline behaviour. However, for the 1-deoxy-1-(*N*-methylalkanamido)-*D*-glucitols series A, the later members from *n*-nonamido onwards exhibit smectic mesophases.

For series A, the transition temperatures were also confirmed by differential scanning calorimetry. The enthalpies of transition were determined and are reported in table 1. The melting transitions from the crystal generally gave enthalpies in the range of 20 to 40 cal/g, whereas for the clearing point transitions the values were in the range of 0.5 to 1 cal/g. These results are typical of liquid-crystalline behaviour

Table 1.

Series A
1-deoxy-1-(*N*-methylalkanamido)-*D*-glucitols



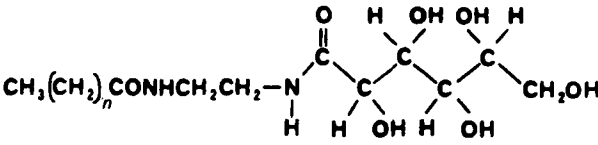
<i>n</i>	m.p.	A-Iso	Rec. †	
4	70.94 (21.33)	—	< 25	MEGA-6
5	86.65 (31.88)	—	< 25	MEGA-7
6	78.07 (26.74)	—	< 25	MEGA-8
7	89.86 (29.37)	60.86 (0.64)	< 25	MEGA-9
8	91.08 (32.12)	88.38 (0.71)	< 25	MEGA-10
9	92.35 (28.89)	113.07 (0.82)	< 25	MEGA-11
10	94.28 (37.85)	125.32 (0.77)	< 25	MEGA-12

† All of the temperature and enthalpy values were determined by differential scanning calorimetry, except for the recrystallization processes which were not detectable down to room temperature by D.S.C. at cooling rates of 2 degrees/min.

() Enthalpy values are in cal/g, temperatures are in degrees centigrade.

Table 2.

Series B
N-(2-(alkanamido)ethyl)-*D*-glucanamides



<i>n</i>	m.p.	Rec.	Cl-C2	C2-C3	or Iso	C3-C4	or Iso	C4-C5	C5-Iso
4	184	169	151.5		165		—	—	—
6	183.3	175.5	166.7 (0.68)	(8.9)	181	(33.26)	183	—	—
8	168.7	148.1	80.1 (2.18)		99.2 (1.2)		163 (3.6)	181.6 (29.3)	184.2

()—Enthalpy values in cal/g determined by D.S.C. Values between the columns represent the total enthalpy for the two columns on either side. In these cases the individual peaks could not be resolved.

The melting point and the recrystallization temperatures were determined by thermal optical microscopy. The other temperatures were determined by D.S.C.

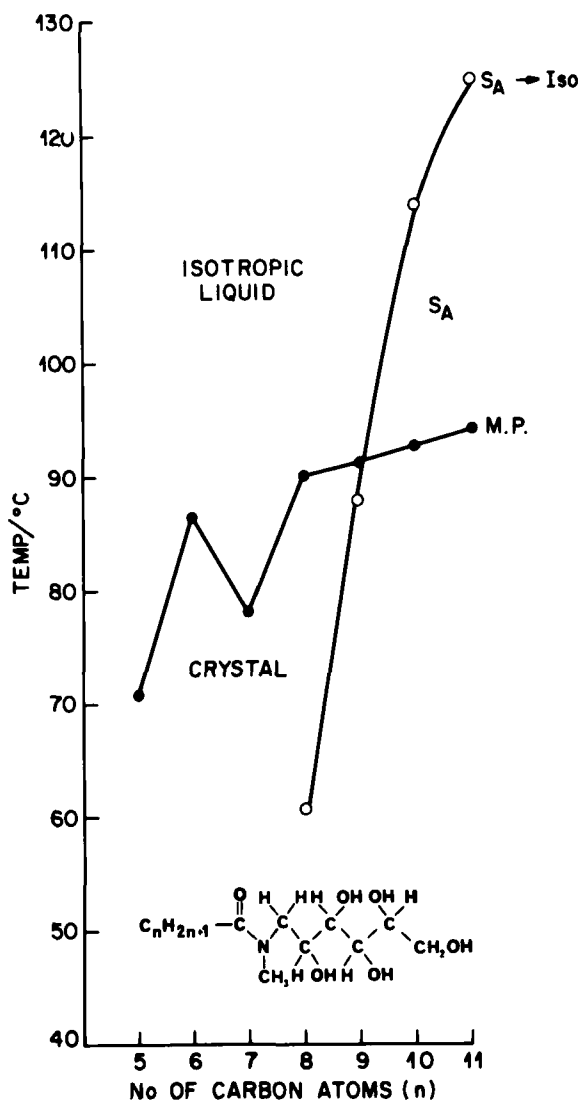


Figure 1. The transition temperatures (degrees centigrade) plotted as a function of the number of carbon atoms in the terminal *n*-alkanoyl chain of the 1-deoxy-1-(*N*-methyl-alkanamido)-*D*-glucitols. Key: ●, crystal to isotropic liquid or mesophase on heating; ○, mesophase to isotropic liquid.

its internal surfaces coated with rubbed poly-butylene terephthalate, the bâtonnets coalesce and adhere to the surface to produce a focal-conic texture, as shown in figure 3. In untreated cells as the bâtonnets adhere to the surface they reorient and reorganize to form a homeotropic texture. Both of these textures are consistent with the formation of a smectic A phase [13]. Miscibility studies with the standard material *n*-dodecanoyl-1-*O*- β -*D*-glucopyranoside [8] shows that the 1-deoxy-1-(*N*-methyl-alkanamido)-*D*-glucitols possess the same phase type, previously classified as smectic A, as shown in figure 4. Contact studies with other carbohydrate liquid crystals confirm this observation.

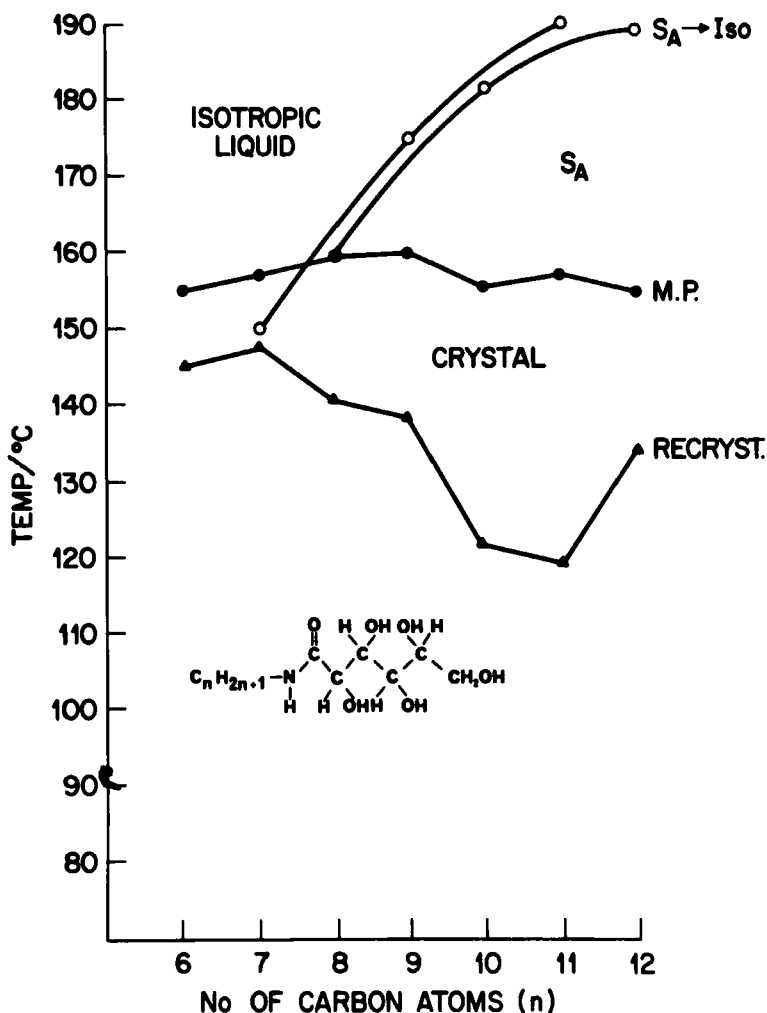


Figure 2. The transition temperatures (degrees centigrade) plotted as a function of the number of carbon atoms in the terminal *n*-alkyl chain of the *N*-*n*-alkyl-gluconamides. Key: ●, crystal to isotropic liquid or mesophase on heating; ○, mesophase to isotropic liquid; ▲, isotropic liquid or mesophase to crystal on cooling.

Series B, the *N*-(2-(alkanamido)ethyl)-D-gluconamides, was also examined in a similar way to series A. Microscopic observations indicate that the materials studied simply melt from the crystal to the isotropic liquid. On cooling, the isotropic liquid generally supercools a few degrees before recrystallization occurs. However, differential scanning calorimetry shows that this process for each homologue is not as simple as that deduced from microscopic investigations. For example, the *n*-hexanamido member melts *via* several crystal forms that occur within 30°C of the melting point. Similarly, the *n*-octanamido member also melts *via* a number of crystal-crystal changes. Lastly, the *n*-decanamido homologue is the only material studied for this series that shows potential for the production of liquid crystal phases. On heating, at least four crystal-crystal phase transitions are observed, with five peaks occurring in the thermogram. The fourth peak has the largest enthalpy, thus suggesting that it is

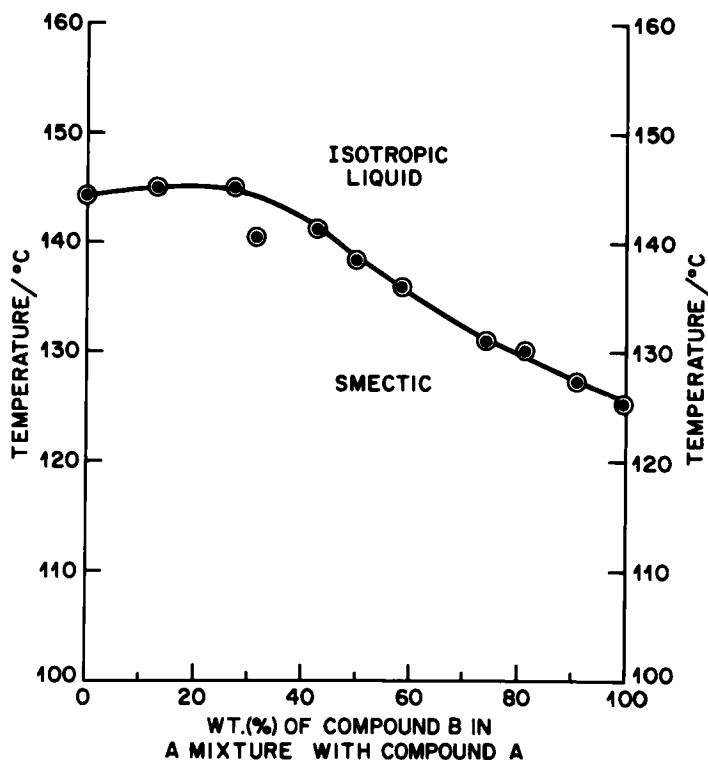


Figure 4. Miscibility phase diagram for binary mixtures (wt.%) between *n*-dodecyl-1- β -D-glucopyranoside (A) and 1-deoxy-1-(*N*-methyldodecanamido)-D-glucitol (MEGA-12) (B).

the true melting point, see figure 5. Therefore, this would indicate that the fifth peak is associated with a liquid crystal to isotropic liquid phase transition. However, this transition is not reversible on cooling, which is contrary to what is expected for a liquid crystal phase change [13]. Moreover, optical microscopy does not produce any evidence to support such a phase transition being present. Therefore, the fifth peak in the D.S.C. thermogram may be due to other factors associated with the complex melting process of this material.

The last series, the *N*-2-(*N*-methylalkanamido)ethyl)-D-glucanamides (C), exhibit behaviour that is the reverse of series (B). For the members of this series that were studied the D.S.C. thermograms appeared relatively simple, with large enthalpies occurring at the melting point, thus indicating a single crystal to isotropic liquid phase transition. Microscopic studies, on the other hand, suggest that a more complex phenomenon is taking place for all of the homologues reported. The melting points appeared to be spread out over a relatively wide temperature range, with the possibility that an isotropic plastic phase may be generated during this process. These results are reflected in table 3, where the temperature ranges for the melting processes are given. However, it should be noted that no normal liquid-crystalline behavior was detected. The D.S.C. suggests that the lack of reversibility indicates that these plastic phases actually may be artifacts of the melting process itself. Yet is it not inconceivable that these phases are present because these compounds tend to decompose at such elevated temperatures, and this in turn would lead to abnormalities in the cooling cycles made by differential scanning calorimetry.

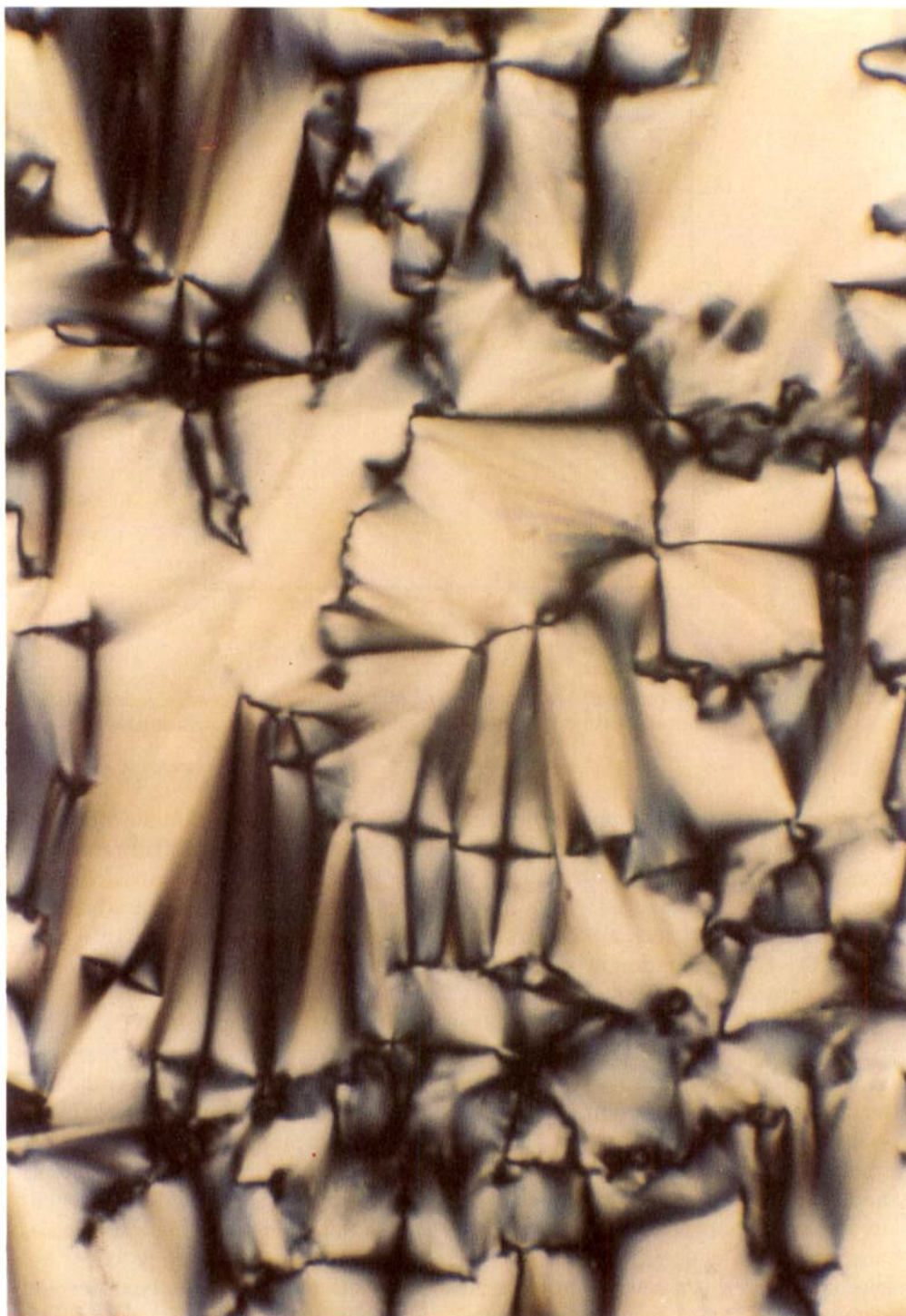


Figure 3. The focal-conic fan texture of the smectic A phase of 1-deoxy-1-(*N*-methylundecanamido)-*D*-glucitol (MEGA-11).

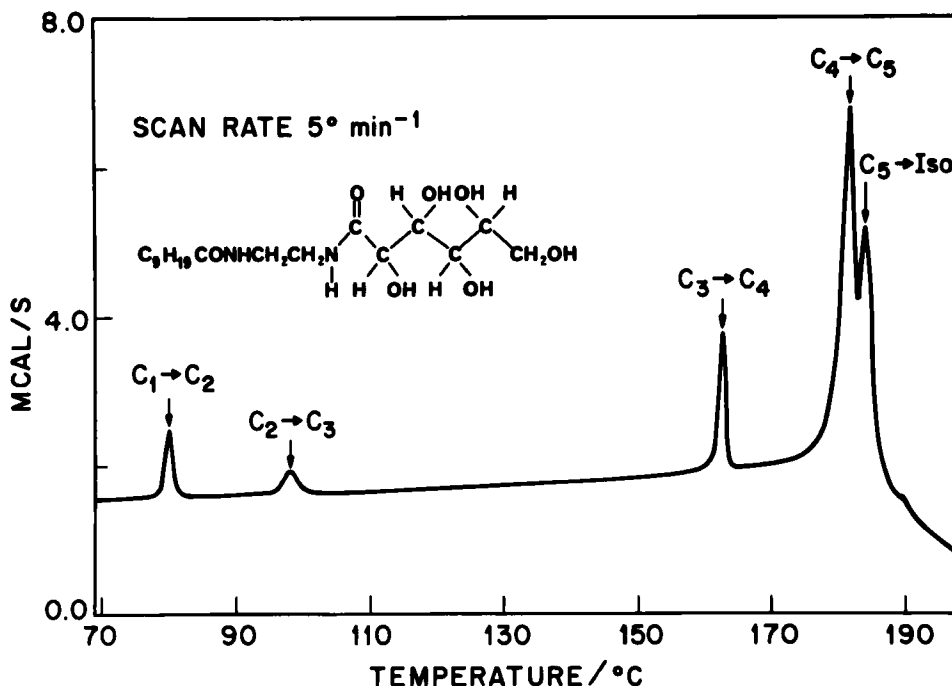


Figure 5. Differential scanning thermogram for *N*-(2-(decanamido)ethyl)-D-glucitol. The heating rate is 5 degrees/min.

3.2. Structural studies

X-ray diffraction studies were carried out on one member of series A, 1-deoxy-1-(*N*-methyldecanamido)-D-glucitol (MEGA-10), and on *N*-*n*-octadecyl-gluconamide (GA-18) for comparative purposes. For both materials the lamellar spacing was measured as a function of temperature while the material was in its liquid-crystalline phase. The results obtained for the lamellar spacing (d) for both materials at specific temperatures are given in table 4. It can be seen that the lamellar spacing is in excess of the fully extended molecular length (l). The approximate molecular length of each molecule in its all *trans* conformation was calculated with the aid of Dreiding models. The ratio d/l was then determined for both materials, the result being that the lamellar spacing was found to be less than two times, but greater than a single molecular length. Thus, the phase probably has an interdigitated bilayer structuring where the molecules overlap with each other.

The variation of the lamellar spacing with respect to temperature is shown in figure 6 for *N*-*n*-octadecyl-gluconamide (GA-18). As the temperature is raised

Table 4. Lamellar Spacing in Ångströms.

Compd.	l	d	T	d/l	$l(c)$	$l(co)$	$l(ao)$
GA-18	32-33	40.5	152	1.24	10	54	42
MEGA-10	23-23.5	31.57	85	1.35	12	34	35

$l(c)$ is the approximate length of the carbohydrate moiety. $l(co)$ is the molecular pair length when the carbohydrate moieties overlap. $l(ao)$ is the molecular pair length when the aliphatic chains overlap. T is the temperature.

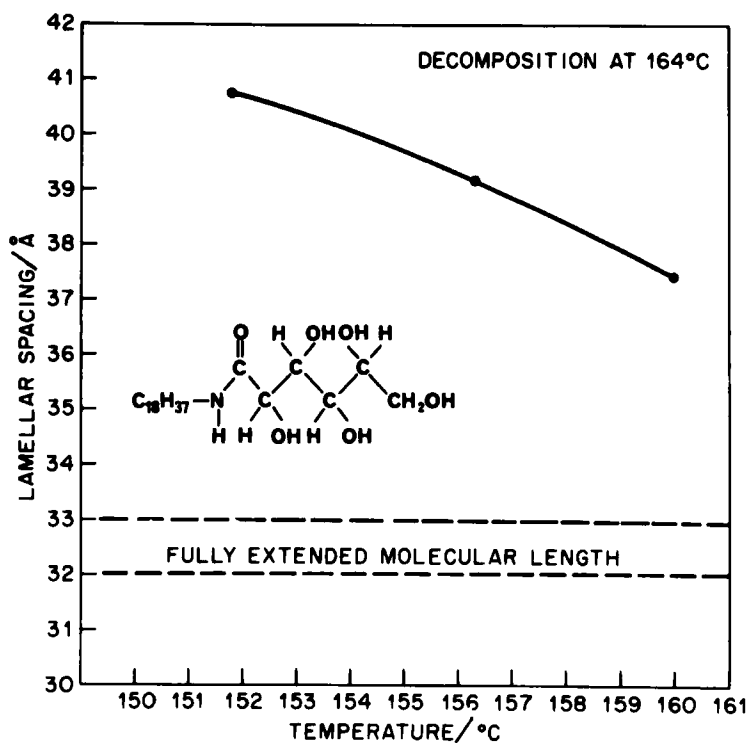


Figure 6. The lamellar spacing (Angstrom) determined as a function of temperature for *N-n*-octadecyl-gluconamide.

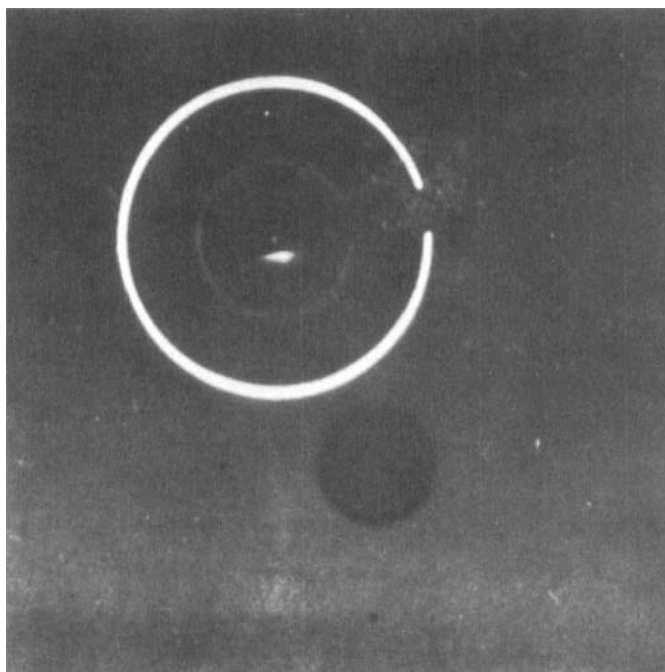


Figure 7. The X-ray diffraction pattern for 1-deoxy-1-(*N*-methyldecanamido)-*D*-glucitol (MEGA-10) taken at 80 degrees.



Figure 8. Heating into the isotropic liquid at 95 degrees for 1-deoxy-1-(*N*-methyldecanamido)-*D*-glucitol (MEGA-10) produces an X-ray diffraction pattern that shows some residual ordering of the molecules.

towards the clearing point the lamellar spacing appears to shorten. This may be due to the increased mobility of the molecules and also to the decomposition of the material which was usually found to occur above 160°C. Extrapolation of the data to lower temperatures suggests that the lamellar spacing would tend to increase, possibly reaching values of 42 to 43 Å before recrystallization occurs, i.e. $d/l = 1.3$.

Powder diffraction studies of 1-deoxy-1-(*N*-methyldecanamido)-*D*-glucitol (MEGA-10) show a sharp ring of scattering commonly associated with the smectic A phase, see figure 7. If this material is heated into the isotropic phase some residual scattering still remains as shown in figure 8. This indicates the possible presence of cybotactic groups of the smectic A phase in the isotropic liquid at temperatures just above the clearing point. This is probably due to the strong hydrogen-bonding between the carbohydrate moieties which holds remnants of the smectic A phase structure together even in the amorphous liquid.

Both of these materials are predicted to have a d/l ratio in the region of 1.3, and therefore they have comparable mesophase structures. Typically for other interdigitated systems, such as the 4-alkyl-4'-cyano-biphenyls, this value is approximately 1.4. Thus, these carbohydrates approximately fit the model for an interdigitated system.

4. Discussion

Structural studies show that the straight chain carbohydrates investigated have interdigitated smectic A_d structures. In this structure it is possible that the aliphatic chains or the carbohydrate moieties might overlap with one another. Closer inspection of the X-ray data shows that for 1-deoxy-1-(*N*-methyldecanamido)-*D*-glucitol

(MEGA-10) either is possible. Table 4 gives the approximate length for the carbohydrate moiety in its all *trans* conformation. This allows us to estimate the length of a molecular pair assuming that either the carbohydrate or the aliphatic moieties are overlapping. For this compound the values are approximately the same, and both are slightly longer than the measured spacing. These values are reasonable however, because in the smectic phase the chains are assumed to be relatively liquid-like and therefore appear shorter than their all *trans* conformational length. For the *N*-*n*-octadecyl-gluconamide (GA-18), the carbohydrate overlapping model produces a molecular pair length that is approximately 10 Å longer than the measured bilayer spacing, whereas an aliphatic chain overlapping model produces a molecular pair length that is commensurate with the bilayer spacing. However, this does not mean that the aliphatic chain overlapping model is the correct interpretation of these results. In many studies of liquid crystal mesophases the aliphatic chains have been shown to undergo many conformational changes at a rapid rate. Conformational bending shortens the effective molecular length considerably with respect to the all *trans* conformation. Commonly, reductions of 4 to 6 Å in length are experienced for materials that have a single *n*-octadecyl aliphatic chain. Therefore in a bilayer structure such as the one under discussion, a reduction of 8 to 12 Å with respect to the all *trans* conformation is possible. In the aliphatic chain overlapping model this would mean that the *n*-octadecyl chains would have to be in their all *trans* formats to give the desired bilayer spacing, a highly unlikely proposition for such a fluid mesophase.

It is also possible, however, that these overlapping portions of the molecules may not be directly keyed with one another and may be off-set slightly, thereby bringing some uncertainty to the model. However, it should be expected that as the hydrogen-bonding interactions are the strongest of the local intermolecular interactions that they will be dominant. This would produce a bilayer with the carbohydrate moieties in the centre and the aliphatic chains on the outside. This is the reverse of the situation in the lyotropic phases where the polar carbohydrate groups are on the outside of the bilayer where they interact with the solvent, and the non-polar aliphatic chains are interacting with one another in the internal part of the bilayer.

In series B and C, the introduction of a strongly polar group separated by an ethylene spacer group from the strongly interacting core (in this case the carbohydrate moiety) suppresses liquid-crystalline behaviour, as is often observed for many other liquid-crystalline systems. The amide linkage of the ethylenediamine residue that is removed from the carbohydrate core by an ethylene spacer strongly interacts with similar groups in neighboring molecules and can depress liquid crystal formation. However, this is not necessarily the case for lyotropic systems where the bilayer is turned inside-out and this polar group can interact directly with a solvent such as water. Therefore these materials would be expected to show lyotropic, but not necessarily thermotropic behaviour. The lyotropic properties of these materials have been well documented previously [12]. Clearly, this demonstrates how competing intermolecular interactions can stabilize or destabilize certain mesomorphic tendencies whether they are thermotropic or lyotropic.

Finally, we note that in a personal communication to us, Professor Jeffrey indicated that he has also investigated the crystal and mesophase structures of some of these materials and finds that the mesophases have bilayer structures, thus confirming our observations. However, the transition temperatures that he reports are somewhat different to ours. This we believe may be due to differences in sample origin.

We would like to thank W. Welte for his contributions to this work, and Professor Jeffrey for many useful discussions.

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