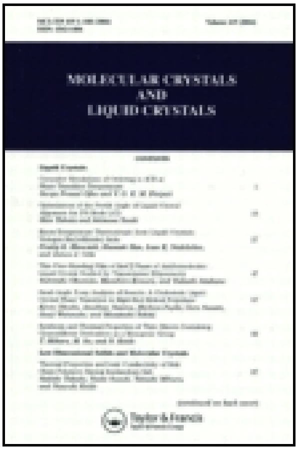

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The Synthesis and Investigation of the Liquid-Crystalline Phase Behaviour of a Series of N,N-bis(1-deoxy-D-mannitol-1-yl)-alkamides

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The Synthesis and Investigation of the Liquid-Crystalline Phase Behaviour of a Series of N,N-bis(1-deoxy-*D*-mannitol-1-yl)-alkamides

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The results of our synthetic efforts and the investigation of the liquid-crystalline phase behaviour of a series of bis-mannosyl-amides are presented. In this investigation the structure of the polar carbohydrate groups was kept constant and the length of the terminal alkyl chain was varied between seven and twelve methylene groups. The results obtained from the DSC measurements, optical polarising microscopy and X-ray diffraction experiments will be reported and a structural model will be discussed.

Keywords: Carbohydrate; Liquid Crystal; Thermotropic; Columnar; Self-Assembly

INTRODUCTION

For liquid-crystalline carbohydrates it is well established that the type of the mesomorphic phases formed and their stability range is dependant on the number of polar groups in the saccharide moiety, the length of the hydrocarbon groups and the overall structure of the molecules. [1-4]

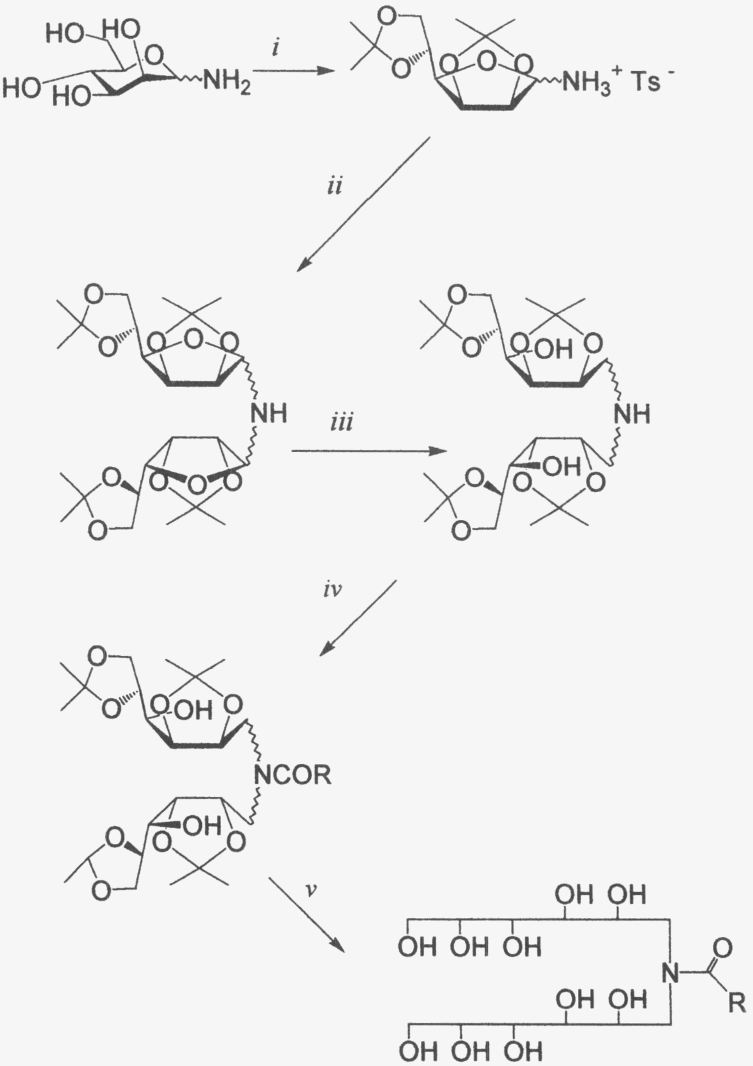


FIGURE 1 synthetic path; *i*): PTSA, 2,2-dimethoxypropane; *ii*): Et3N, reflux, *iii*): reductive cleavage; *iv*): RCOCl, DMAP, pyridine, [R –$(CH_2)_n$-CH_3, n = 8, 9, 11, 13]; *v*): H_2SO_4, EtOH.

In this report we present our investigations into a series of double headed amphiphiles. The synthesis of the materials is a variation of a synthesis which has been reported in detail elsewhere and is thus outlined only briefly [5]. A full and detailed account of the synthesis will be given elsewhere.

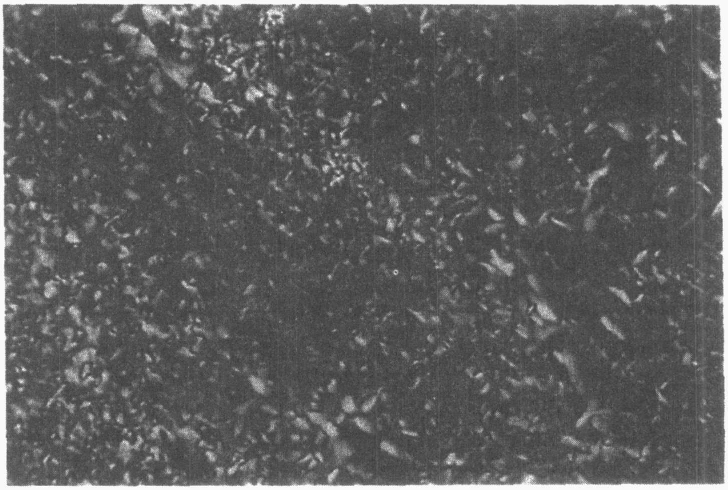
EXPERIMENTAL AND DISCUSSION

The sytnhetic pathway towards the final products, **A**, **B**, **C**, **D** is shown in Figure 1. The compounds were obtained by a synthesis based on the conversion of α, β,-*D* mannopyranosyl-amine into its diisopropyledine derivative, isolated as the toluene sulfonate salt. The free amine was obtained by treatment with triethylamine and the dimerisation to the bis(2,3:5,6-di-*O*-isopropylidene-α,β-*D*-mannofuranosyl)amine was promoted by heating under reflux in methanol in a stream of nitrogen. Reductive cleavage of the furanosyl group followed by acylation with acid chloride mediated by DMAP in pyridine, and subsequent deprotection of the hydroxyl groups under acidic conditions lead to the target materials **A**, **B**, **C**. **D**.

The materials are characterised by the difference in the length of the saturated hydrocarbon groups in the aliphatic chains. The length varies form eight saturated carbons for **A** to nine for **B** to eleven fully saturated carbons for **C**. Compound **D** has the longest hydrocarbon chain containing thirteen carbon atoms.

The materials were investigated by optical polarising microscopy and by DSC and the transition temperatures are listed in Table 1.

Compound **A** has a melting point of 104.1 °C, which is considerably lower than that of the other materials of this series, with those of **B** to **D** found to be in the range of 145.6 °C for **B** to 148.9 °C for **C**. As **A** is the only member of the series with an even number of aliphatic chains, this hints at the possibility at the occurrence of an odd-even effect in the melting register of the materials. At temperatures above the melting point all of the materials exhibit hexagonal columnar phase behaviour, evidenced by the typical defect textures, a typical example is shown in Picture 1 for compound **A** at 110 °C.



PICTURE 1 Photomicrograph, compound A, 110 °C, hexagonal columnar phase

The occurrence of additional liquid-crystalline phases between the melting point and the clearing temperature for all of the materials was monitored by DSC. No further transitions, evidenced by enthalpic peaks could be observed. It was thus concluded that the hexagonal columnar phase is the only thermotropic mesophase present in these sytems. The increase of the aliphatic chain length in these materials results in a marked rise of the isotropisation temperatures.
The clearing temperatures range from 144.3 °C for **A** to 183.0 °C for **D**. The intermediate members of the series **B** and **C** for which clearing points of 157.5 and 183.0 °C could be observed, supporting thus the view that the extension of the aliphatic chain supports the stability of the liquid-crystalline state.

Cpd	n	mp	Transitions (°C)	Enthalpies [ΔH]	
A	8	104.1	Col 144.3	[15.4]	Iso
B	9	145.6	Col 157.5	[1.1]	Iso
C	11	148.9	Col 170.2	[9.5]	Iso
D	13	147.8	Col 183.0	[12.6]	Iso

TABLE 1 Phase transition temperatures (°C) as determined by DSC, transition enthalpy [ΔH] (Jg^{-1}), heating rate (10°C/min, first heating run); Cpd = compound; n = length of alkyl chain, Col = columnar (hex) as determined by optical polarising microscopy.

In order to gain further insight into the arrangement of the molecules in the thermotropic liquid crystal state X-ray diffraction experiments were carried out using station 8.2 at SRS Daresbury.

Powder samples of the materials kept in Lindemann tubes were heated at 2°C/min. It was observed that the materials scattered only very weakly in the liquid–crystalline state and decomposed with increasing temperature. It was not possible to collect reproducible data sets after heating the samples above the isotropisation temperature of the compounds and visual inspection revealed a considerable darkening of the initially colourless powder samples.

The calculated d-spacings associated with the scattering are listed in Table 2. With increasing the alkyl chain length the d-spacing increases from 24.2 Å for **A** to 25.1 Å for **B**, 28.5 Å for **C**, and 32.1 Å for **D**. No discernible variation in the d-spacings in the liquid-crystalline state with temperature was observable. Though only one reflection (ring) was detected, the associated lattice parameters for a hexagonal columnar phase, in line with the observed microscopic textures were calculated and listed in Table 2.

From this data it is possible to calculate in a manner shown for the structurally related carbohydrates [1, 2], that the materials have to assemble in agglomerates. These assemblies consist of species where the aliphatic chains are positioned in the central regions of columns and the carbohydrate head groups are in the average situated at the periphery of these columnar asseblies.

	A	B	C	D
a. (Å)	27.9	29.0	33.0	37.1
d (Å)	24.2	25.1	28.5	32.1

TABLE 2 a = lattice parameter, d = d-spacing

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