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Recently, the first monosaccharide derivatives containing a fully intact monosaccharide and two vicinal OH-groups which display thermotropic chiral mesophases were synthesized. These liquid crystals have a rigid core, with a *trans*-decalin-like skeleton incorporating the D-glucopyranose ring, substituted with an alkoxylated polarizable aromatic group, *e.g.* a phenyl 4-octyloxybenzoate, on one side and an alkoxyphenyl group at the anomeric centre. On the basis of the focal-conic fan-like texture displayed and the existence of a blue phase in the UV, we expected the cholesteric helix to have a very short pitch. The compounds possessed an exceptionally high helical twisting power. Extrapolation of these data to dopant concentrations of 100 % also indicates a very short pitch (30 - 90 nm).

Keywords: monosaccharide, liquid crystals, cholesteric phase, blue phase, helical twisting power.

INTRODUCTION

Carbohydrates can be used as the source of chirality in low-molecular-weight liquid crystals provided that their hydrophilic character is sufficiently reduced. This can be achieved by masking or eliminating the hydroxyl groups: mesogens containing a 'mutilated' monosaccharide and displaying various chiral liquid crystalline phases have been reported.[1,2] The current approach provides a

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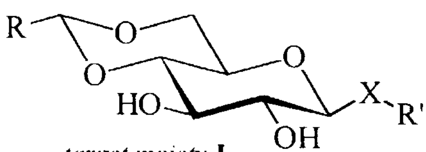
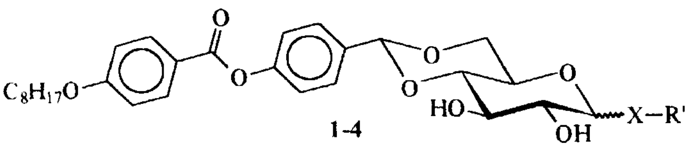


target moiety **I**

carbohydrate-derived building block for the preparation of liquid crystals containing an intact monosaccharide moiety.[3] A D-glucopyranose ring is embedded in a rigid *trans*-decalin-like skeleton. During the assembly of this moiety, a range of substituents R and X-R' can be introduced in equatorial positions. First, X-R' is introduced at the anomeric carbon, (the configuration is determined by the reaction conditions[4,5]) followed by the condensation of the 4- and 6-hydroxyl groups of the resulting D-glucopyranoside with an aldehyde R-CHO. In order to induce liquid-crystalline behavior, **I** needs to be extended with a polarizable aromatic moiety. When an aromatic Schiff base is coupled to **I**, smectogens are obtained.[3] Recently, a phenyl benzoate ester moiety[6] was introduced as the substituent R; these derivatives of **I** display a cholesteric mesophase[7], the phase-transition temperatures are given in Table 1. These are the first compounds with a fully intact monosaccharide moiety which display chiral thermotropic mesophases. Compounds **1** and **2**, having an alkoxyphenyl substituent at the anomeric centre in a ß-configuration, display enantiotropic cholesteric phases. The ß-S-alkyl derivative **3** has a monotropic cholesteric phase, in contrast, the α-anomer **4** is not liquid-crystalline. The cholesteric phases of **1-3** have a focal-conic fan-like texture. When a sample of **2** is cooled from the isotropic phase, the cholesteric phase is preceded by a blue phase in the UV. These observations indicate that the compounds may not only have a

Table 1. Phase-transition temperatures of compounds 1-4.



1-4

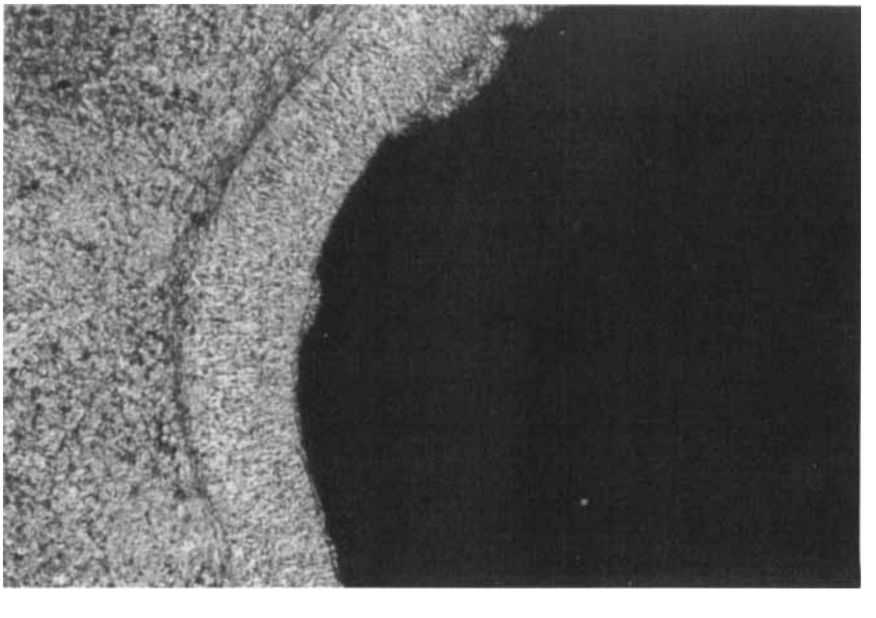
1	ß-O-C_6H_4-O-hexyl	K	78	K	88	Ch	117	I
2	ß-O-C_6H_4-O-dodecyl	K	82	K	112	Ch	130	I
3	ß S-decyl	K	70	K	132	(Ch	120)	I
4	α S-octyl	K			126			I

cholesteric phase with a short helical pitch,[8] but they may also be powerful chiral dopants.[9,10] Here, we present the first results of measurements of the helical twisting power of chiral dopants based on moiety **I**.

RESULTS AND DISCUSSION

Miscibility studies were performed to obtain information about the compatibility of compounds **1-4** with commercially available liquid crystals, and to obtain indirect proof of the nature of the mesophase. The cholesteric phase of **1** was miscible with the nematic phase of 4-cyano-4'octylbiphenyl. Upon cooling, a blue phase and a TGB phase were formed in the contact region, see Figure 1. A contact preparation of **1** with 4'-hexyloxyphenyl 4-decyloxybenzoate (HOPDOB) showed several chiral mesophases: a blue phase, cholesteric and smectic C* phases were formed. These results show that these carbohydrate containing liquid crystals are compatible with nematogens and can induce various chiral mesophases.

Figure 1. Contact preparation of 1 (left) and 4-cyano-4'-octylbiphenyl (right). Isotropic, Blue Phase, TGB, induced cholesteric phase, 49.1°C.



Determination of the helical twisting power

The helical pitch of the induced cholesteric phase of mixtures of **1-4** with the nematic host E7 were measured as a function of the concentration. Samples containing 6-22 % of chiral dopant showed selective reflection of visible light; the cholesteric pitches of oriented samples were measured using a UV/Vis spectrophotometer.[11] The pitch of the cholesteric helix decreased slightly upon increase of the temperature. The shortening of the pitch became more pronounced in a temperature range 10° below the clearing point (*c.p.*) (see Figure 2).

The helical twisting power, HTP= (pitch × c)$^{-1}$, was calculated using the molar ratio of the chiral dopant and E7 for the concentration *c*, to allow comparison of the data with literature values of other carbohydrate-derived chiral dopants.[9] The HTP's of **1-4** are exceptionally high (see Table 2). Cholesteryl derivatives are known to possess a strong helical twisting power, HTP values of 12 μm^{-1} for cholesteryl laureate and 10 μm^{-1} for cholesteryl cetyloxybenzoate were reported.[9] Only the carbohydrate derivative 2,5-di-(*p*-hexyloxybenzoyl)-dianhydro-D-glucitol was shown to have a comparable HTP value (62 μm^{-1}).[9]

Within the concentration ranges studied, the inverse reflection wavelength ($1/\lambda$), measured approximately 10° below *c.p.*, changed linearly with the concentration (Figure 3). Linear extrapolations to 100% gave values of 30 - 90 nm for

Figure 2. Temperature dependence of the cholesteric helix of 1 in E7.

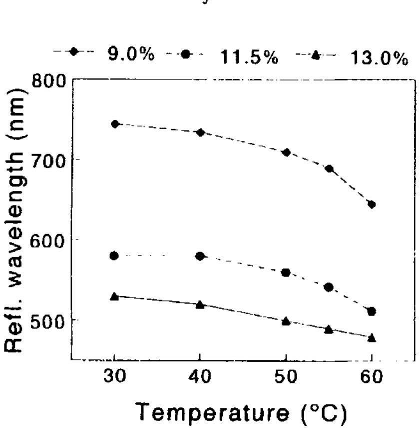
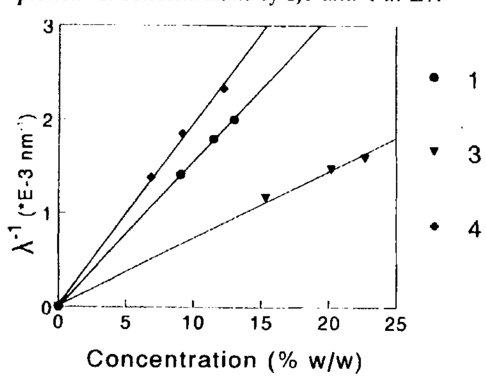


Figure 3. Concentration dependence of the selective reflection of the cholesteric phase. The reciprocal reflection wavelength (1/λ) is plotted vs. concentration of 1,3 and 4 in E7.



the pitch of the cholesteric helix in the pure materials **1-4**. These values provide an additional indication of the very short helical pitch of the pure compounds.

Table 2. Helical twisting power, HTP, of compounds 1-4.

compound	HTP (μm^{-1})
1	55
2	57
3	23
4	64

The compatibility with the nematic host is facilitated by the long alkyl chains and the aromatic substituents on **I**. The length of the alkoxy chain does not influence the HTP, compare compounds **1** and **2**. The effects of the nature of the anomeric substituent and its configuration are more pronounced. The helical twisting power of the ß-S-decyl derivative **3** is comparitivily moderate but still higher than that of the cholesteryl derivatives.[9] The difference with the α-anomer **4**, which is not liquid-crystalline itself, is striking. The axial orientation of the substituent on **I** modifies the molecular shape of the dopant in such a way that it magnifies the helical twisting power. The chiral induction of the carbohydrate-derived moiety **I** is powerful; fine-tuning can be achieved by a proper choice of the substituents R and X-R'.

CONCLUSIONS

The D-glucopyranose-containing moiety **I** is an excellent building block for the preparation of chiral liquid crystals; the cholesteric phases of **1-3** have a very short helical pitch. The *trans*-decalin like moiety induces a strong helical twist which can be regulated by a proper choice of classical mesogenic elements as substituents R and X-R'. Surprisingly, the non-mesogenic compound **4**, bearing an α-S-octyl substituent at the anomeric centre, is the most powerful chiral dopant. We are currently investigating the influence of small modifications on derivatives of **I**, such as the type of linkage between the mesogenic and carbohydrate moiety and the length of the alkoxy chains, on the liquid-crystalline properties and helical twisting power.

EXPERIMENTAL

The carbohydrate derivatives were prepared as described in ref. 4,5,7. The nematic host E7, $T_{S\text{-}N}$ < -40 °C, $T_{N\text{-}I}$= 60 °C, $\bar{n}$= 1.5609, was purchased from Merck. The selective reflection of the cholesteric phase was measured with a UV-Vis spectrometer (Unicam PU8755). The samples were introduced in polyimide-coated and rubbed glass cells spacered at 6 μm. A depolarizer, a polarization filter, a quarter-wave plate, a thermostatted sample holder containing the sample and a second depolarizer were placed in the optical path, respectively. The measurements were performed at: 55°C (**1**); 50° (**2**); 60° (**3**); 45° (**4**). For thermomicroscopy the hot stage, a Mettler FP 800 system, was mounted on a Nikon polarization microscope.

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