Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 22 Sep 2006.

To cite this article: T. M. H. Do Aido , M. R. Alcantara , O. Felippe Jr. , A. M. G. Pereira & J. A. Vanin (1990): Carbohydrates as Inducers in Cholesteric Lyotropic Mesophases, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 185:1, 61-66

To link to this article: http://dx.doi.org/10.1080/00268949008038489

Mol. Cryst. Liq. Cryst., 1990, Vol. 185, pp. 61–66
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Printed in the United States of America

Carbohydrates as Inducers in Cholesteric Lyotropic Mesophases

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(*Received December 11, 1989; in final form February 9, 1990*)

The use of sugars as chiral dopants for cholesteric lyotropic mesophases preparation is reported. Several aldo-hexoses (*D*-mannose, *D*-glucose and *D*-galactose), a keto-hexose (*L*-sorbose) and a disaccharide (*D*-sucrose) were added to mesophases prepared from potassium laurate (KL). The resulting cholesteric phases correspond to Ch_D systems. Carbohydrates as highly hydrophylic solutes have a very low twisting power. Only at sugar concentrations higher than 2% (molar fraction), detectable pitches can be obtained and directly measured from the polarizing microscope textures. Even in the concentration range where a measurable pitch is not observed, it is possible to characterize the optical activity at the polarizing microscope. These studies show that sugars are able to induce cholesteric lyomesophases however low twisted. The optical activity measurement amplifies the cholesteric characterization towards long pitch systems.

1. INTRODUCTION

Cholesteric mesophases can be prepared by addition of chiral solutes to lyotropic nematic systems. Since the onset of the studies on these cholesteric lyotropic systems several solutes have been used: brucine,[1] other alkaloids,[2] amino acids,[3] cholesterol, tartaric acid,[1,2] etc. Polarizing optical microscopy and circular dichroism have been the main techniques for the investigation of such systems.

In the present work, we report the preparation and characterization of cholesteric lyomesophases induced by sugars. These highly hydrophilic solutes should be located predominantly in the mesophase aqueous portion. The resultant interaction between carbohydrate molecules and lyotropic micelles is responsible for a low twisting power.

2. EXPERIMENTAL

Several carbohydrates were investigated. Aldo-hexoses (*D*-mannose, *D*-glucose and *D*-galactose), a keto-hexose (*L*-sorbose) and a disaccharide (*D*-sucrose) were added in several proportions to a nematic mesophase, N_D, prepared from potassium

laurate (KL) which composition was (in % molar fraction): KL 3.87; KCl 1.92; 1-Decanol 0.86; water 93.35. The cholesteric lyomesophase corresponds to carbohydrate concentration in the range 0.5 to 5.1%. For sugar amounts greater than 2.7% it was necessary to increase the electrolyte molar fraction up to 5.7% in order to preserve the liquid crystalline properties.

All cholesteric mesophases were characterized as Ch_D systems by the textures observed at a Zeiss Universal Polarizing Microscope. Samples were contained in flat capillar cells (Vitrodynamics Inc., N.J.), 0.3 mm in thickness. Textures were photographed at the polarizing microscope after sample orientation by a magnetic field of 1.4 *T* applied in direction normal to or parallel to the flat glass surfaces of the cell (hereafter referred to as "perpendicular orientation" and "parallel orientation," respectively). In the latter case the field was applied perpendicular to the cell long axis. For microscope monochromatic illumination a continuous interference–filter monochromator, Zeiss model 47 43 10, with a passing band of 13 nm, was used.

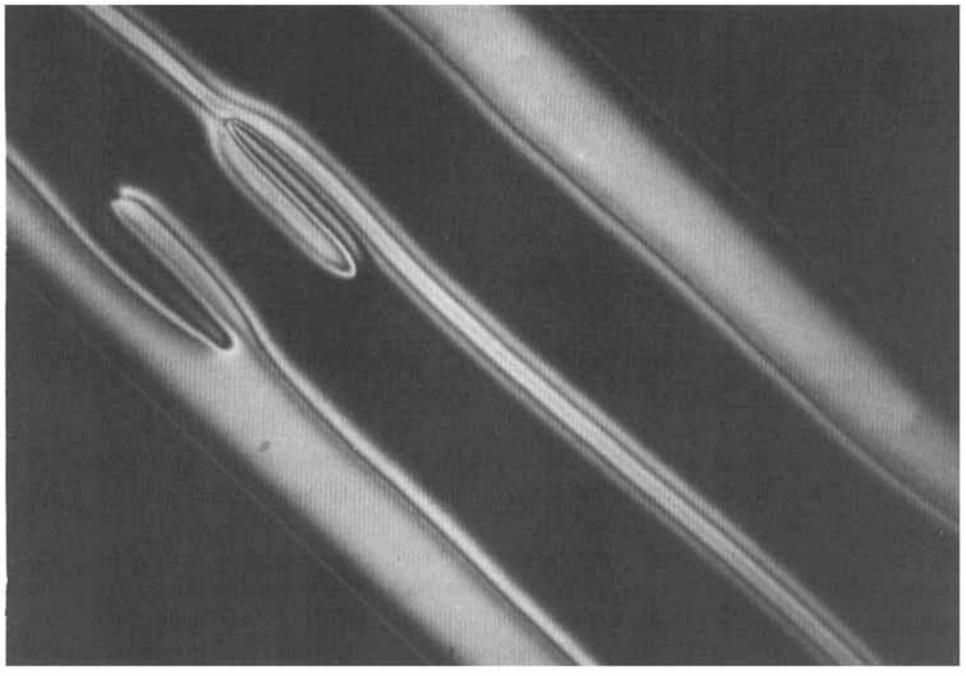
3. RESULTS AND DISCUSSIONS

Chiral hydrophobic solutes are usually added to lyotropic nematic systems in the concentration range of 0.1 to 1 (% molar fraction). These amounts are enough to produce a cholesteric mesophase with a detectable pitch length extending from 50 to 150 μm.[1,4] In the present work it was verified that for highly hydrophilic solutes, like sugars, these concentrations lead to systems which in parallel orientation exhibit, at the polarizing microscope, a pseudo-isotropic texture instead of the typical chevron or fingerprint pattern. For the high limit of this range, orientational defects shaped as bright lines or regions can be seen (Figure 1).

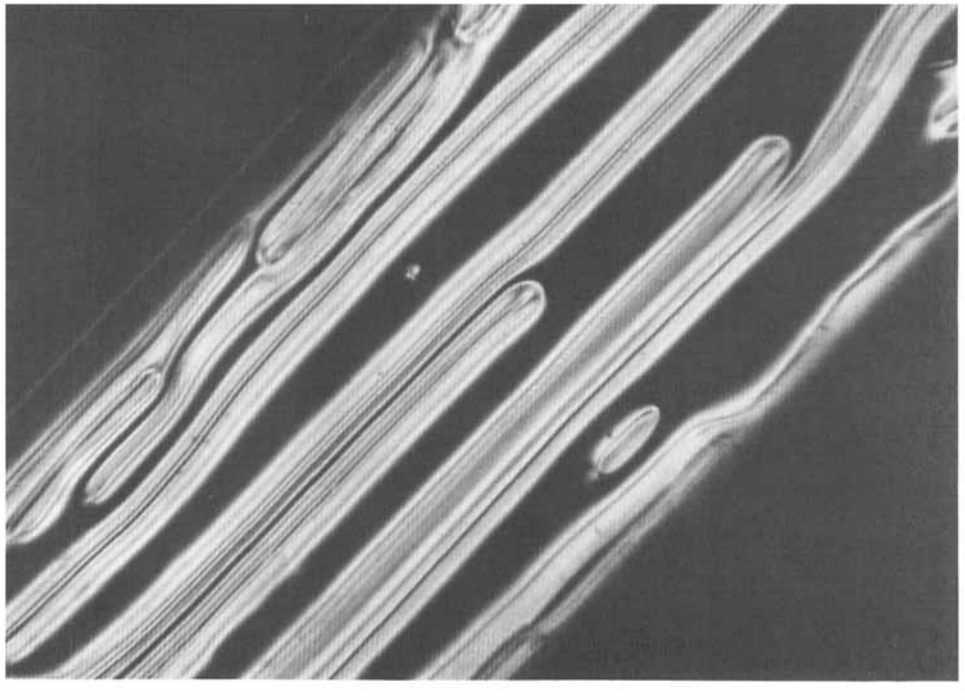
Samples with increased sugar amounts were prepared in order to investigate the cholesteric behavior dependence on inducer concentration.

It could be observed that for systems containing less than 2% molar fraction of sugar the cholesteric character was verified by their unequivocal optical activity, in spite of a lack of a detectable pitch. The rotatory power was measured at polarizing microscope on previously perpendicular oriented samples observed under monochromatic illumination (580 nm). Two methods can be employed. In the first, extinction zones are observed for wedge shaped samples, as reported by Berthault *et al.*[5] An easy way to get the sample in the proper geometry was developed by us,[6] through the use of a culture cell microslide, which cavity provides the necessary continuous variable thickness. The second method is applied for samples in flat capillary cells. In this case, the polarizing microscope is used as a polarimeter being the rotatory power measured directly from the analyzer rotation angle.[7–9] In all cases, the optical activity remained without significant changes, at least for the time interval (few minutes) in which the measurements are done.

The dependence of the rotation angle (ϕ) upon the carbohydrate concentration expressed as percent molar fraction (x) is illustrated in Figure 2. It is observed that the cholesteric mesophase rotatory power increases with increasing amounts of the inducer in a linear relationship. This behavior was obtained for almost all inducers



(a)



(b)

FIGURE 1 *Typical textures obtained for parallel oriented cholesteric lyomesophases induced by sugars* (crossed polarizers; capillar width 3 mm; magnification ×5). a) L-Sorbose; b) D-Galactose.

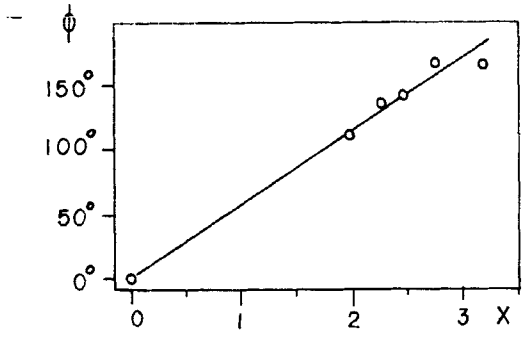


FIGURE 2 Plot of rotation angle (ϕ) vs. chiral dopant % molar fraction, x. Data refer to cholesteric mesophases prepared with sucrose as inducer.

studied. These results confirm the rotation angle measurement as an optical activity parameter and therefore a convenient technique for cholesteric characterization of large pitch systems.

The use of rotation angle (ϕ) as an optical activity measurement is limited since its value refers to the angle of the light beam polarization plane emerging at the sample surface. For high optical activity (typically 5000 to 10000°/cm), the polarization plane rotates more than 360°, even for a thin sample. In such cases, the ϕ vs. x plot could not fit a linear relation and the ϕ value could differ from the effective rotation value by an integral number of half turns.

TABLE I

Measured pitch length for several sugar concentrations.

inducer	concentration (% molar fraction)	pitch length (μm)
D-Glucose	2.77	390
	2.98	340
	3.45	290
	3.89	210
	4.10	190
D-Galactose	3.39	340
	3.43	330
	4.10	280
	4.58	250
	5.04	230
D-Mannose	2.29	60
	2.40	80
	2.59	60
	2.58	50
D-Sucrose	1.95	380
	2.13	340
	2.45	230
	2.53	210
	5.12	190

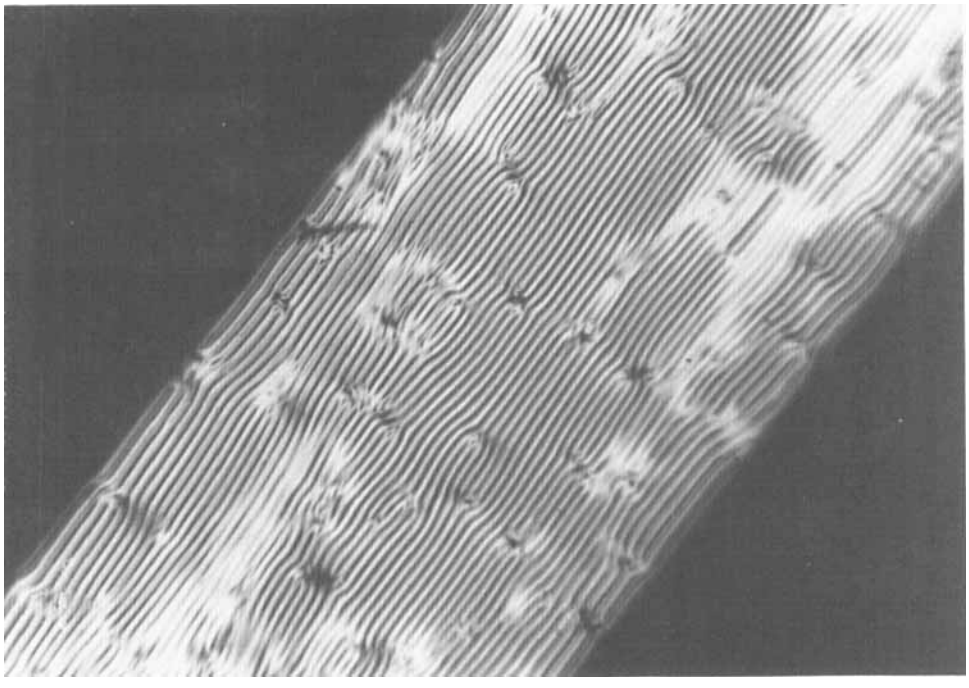


FIGURE 3 Typical fingerprint texture for a cholesteric lyotropic mesophase. The photomicrography was obtained for a system using *D*-Mannose as inducer (crossed polarizers; capillar width 3 mm; magnification ×5).

For inducer concentrations higher than 2% molar fraction, the typical fingerprint texture was observed allowing the direct pitch measurement (Figure 3). The increase of the sugar concentration leads to a cholesteric twist increase and consequently to a pitch length reduction. The results are shown in Table I. It should be emphasized that the twisting power depends on the sugar nature too.

Sugars are highly hydrophilic solutes and therefore have a weak interaction with the micelles, specially at low concentrations. Consequently, these low twisting power inducers probably are not able to distort the lyotropic micelles. For these cholesteric mesophases the dispersion forces anisotropy[10] should play an important role in creating the asymmetric interaction between micelles to generate the macroscopic twist.

The literature points out the helical pitch as the fundamental cholesteric character, so that it was assumed previously that sugars do not induce cholestericity.[2] In the present work it was noted that even in the concentration ranges where the pitch was too large to be determined from fingerprint textures we could verify the existence of an inherent twist by the optical activity measure on perpendicularly oriented films. The systems here reported are really cholesteric however low twisted. Additionally, the optical activity measurement amplifies the cholesteric characterization towards long pitch systems.

Acknowledgments

We are indebted to the financial support from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPq) and Financiadora de Estudos e Projetos (FINEP/PADCT).

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