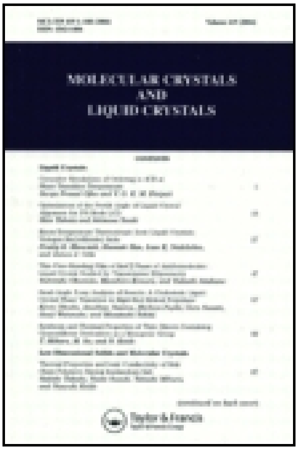

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Chiral Ionbinding in Amphiphilic Cholesteric Liquid Crystals

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Version of record first published: 24 Sep 2006.

To cite this article: Keith Radley & Helene Cattey (1993): Chiral Ionbinding in Amphiphilic Cholesteric Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 226:1, 195-199

To link to this article: http://dx.doi.org/10.1080/10587259308028798

Mol. Cryst. Liq. Cryst., 1993, Vol. 226, pp. 195-199
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Printed in the United States of America

Chiral Ionbinding in Amphiphilic Cholesteric Liquid Crystals

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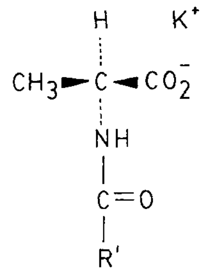
(Received May 28, 1992)

The chirality in three amphiphilic cholesteric liquid crystal samples, prepared from three different detergents each synthesised from a chiral precursor with the S configuration is investigated. Diastereoisomers, resulting from the interaction of the D- and L-alanine enantiomers with the chiral micelle surface have been visualized using NMR. The sign of the optical rotation in each sample is determined using a polarizing microscope. Laser diffraction twist measurements are also made. Inversions in the headgroup and in the alanine enantiomers configuration in respect to chirality are discussed.

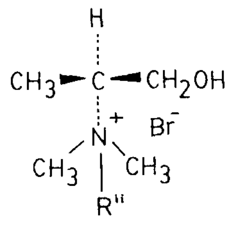
Keywords: Amphiphilic, Cholesteric, Ionbinding, NMR, Laser Diffraction

Cholesteric liquid crystals are formed when a chiral centre is introduced into a nematic liquid crystal. In amphiphilic liquid crystals the formation of nematic liquid crystals involves the occurrence of orientational order derived from inter-micelle interactions. Cholesteric states are nematic states, where a chiral centre creates asymmetry in the orientational order, which facilitates a spontaneously twisted structure. The twist, which is defined as the number of 2π rotations of the micelle axis along the helix axis, is a measurement of the distortion in the symmetry induced in the micelle surface by the chiral centre. The twist in an amphiphilic cholesteric liquid crystal (ACLC) is an indication of the chiral centre density in the chiral micelle surface.[1]

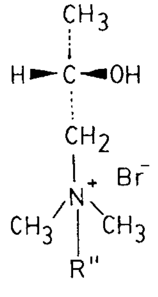
Optical rotation measurements in isotropic chiral systems do not usually give rise to precise information concerning the absolute molecular configurations. Meaningful optical rotation measurements in ACLC samples are usually made on thin films, along the helix axis and can give rise to significant information concerning the absolute molecular configuration as well as that of the chirality of the molecular interactions. In the present study three different ACLC samples have been investigated under a polarizing microscope in order to determine the signs of the optical rotation. Optical rotation and twist (inversed pitch P) have opposite signs.[2] Twists were determined using laser diffraction and the results are presented in the table. The chiral detergents: Potassium dodecanoyl L-alaninate L-KDDA; S-1.2-N Hexadecyl-NN dimethyl-propanol ammonium bromide S-1.2 HDPABr; and S-2.1-N Hexadecyl-NN dimethyl-propanol ammonium bromide S-2.1 HDPABr. The chiral headgroup precursors to these three chiral detergents all had the S configuration.



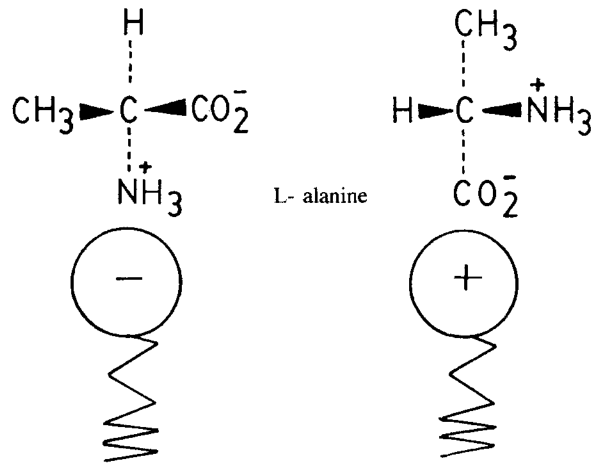
L-KDDA



S-1.2HDPABr



S-2.1HDPABr



L- alanine

FIGURE 1

During the synthesis of these three chiral detergents no chemical reaction was undertaken, which would undermine the transformation of the S configuration from the starting material via the intermediate to the final product. (The reader is here strongly advised to carefully inspect the diagrams of the chiral molecule in respect to configuration) (Figure 1). The micelle structure in all these ACLC samples was inferred as disk shaped, through observing the lamellar textures in the neighbouring dimensionally ordered phase when concentration gradients were set up under the polarizing microscope.[3]

The twists in the S-1.2 HDPABr ACLC sample and in the S-2.1 HDPABr ACLC sample have opposite signs (Table I). This reversal in the sign of the twist results from the apparent inversion of the headgroup configuration with respect to the chiral micelle surface. The hydrocarbon chain in each chiral detergent is linked to the headgroup via the quaternary ammonium nitrogen. In the two headgroups the nitrogen and hydroxyl positions are interchanged, which effectively inverts the

TABLE I

Signed parameters resulting from polar microscopy and NMR. Studies in three amphiphilic cholesteric liquid crystal samples at 303 K.

	Polar Microscopy		NMR	Composition wt %		
Detergent in ACLC sample	Optical Rotation	twist $\frac{1}{p}$ cm^{-1}	$\Delta=\delta_L-\delta_D$	Detergent	Decanol	D_2O
L-KDDA	+ ve	-4994	-56.0 [a]	29.5	6.04	64.4[c]
S-1.2 HDPABr	- ve	+ 670	-59.0 [b]	35.5	3.48	61.0[d]
S-2.1 HDPABr	+ ve	- 360	+69.0 [b]	35.9	2.63	61.5[d]

[a] 400 MHz Brucker Spectrometer, Hz.

[b] 270 MHz Brucker Spectrometer, Hz.

[c] D_2O 6% CsCl; 4% NaOH; 5% Na_2CO_3; 0.8% DL-alanine; 0.2% L-alanine

[d] D_2O 5% CsCl; 2.5% TMACl; 0.8% DL-alanine; 0.2% L-alanine.

configuration in respect to the hydrocarbon chain, but does not invert the absolute S configuration of the two chiral headgroups. The sign of the twists in the L-KDDA and the S-1.2 HDPABr ACLC were observed to be opposite, but the absolute S configuration with respect to the micelle surface would appear to be the same. This inversion in the chirality could be due to the location of the chiral centre in respect to the micelle surface. In the L-KDDA ACLC sample micelle, the chiral centre is inside the micelle between the charge and the hydrocarbon chain, while in the S-1.2 HDPABr ACLC sample micelle the chiral centre is outside the micelle surface, where the charge is between the link and the chiral centre.

Small entities such as D- and L-alanine, when dissolved in an amphiphilic nematic liquid crystal, give rise to high resolution proton NMR spectra derived from the dipolar coupling constants, which are the result of orientation and molecular structure.[4–6] The D- and L-alanine enantiomers have been visualized in the proton spectra, due to differences in the degrees of orientation. This spectra was not chemically shifted. The differences in the degrees of orientation in the D- and L-alanine enantiomers is due to the chirality in the interactions between the D and L enantiomers and the asymmetrical orientational order field. The proton NMR spectra would have been chemically shifted due to diastereoisomers, if the interaction between the D- and L-alanine enantiomers and the chiral micelle surface were significant. In the present study the proton NMR spectra of the —CH_3 group of the D- and L-alanine enantiomers were chemical shifted Δ in all three ACLC samples. Δ for both the S-1.2 HDPABr and the S-2.1 HDPABr ACLC samples were observed to have opposite signs, which is to be expected if the twists have opposite signs (Figure 2). The alanine entity is an amino acid, which with suitable

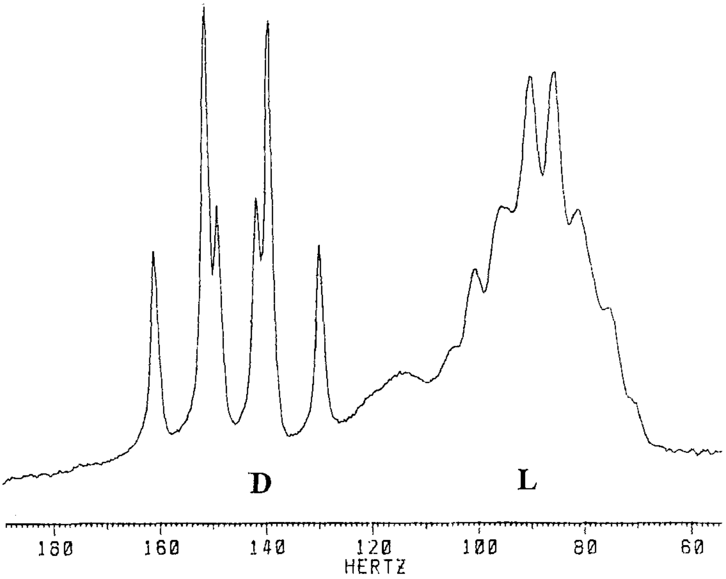


FIGURE 2 Brucker 270 MHz proton NMR spectrum of the D- and L-alanine —CH$_3$ group in a S-2.1 HDPABr ACLC sample at 303 K.

pH control, could be a zwitterion. In these chiral cationic detergent ACLC samples the —CO$_2^-$ groups of the D- and L-alanine enantiomers interact significantly with the chiral micelle surface via the quaternary nitrogen to produce chemically shifted NMR spectra resulting from diastereoisomers. When the ion and the amphiphile in the chiral micelle surface possess the same charge, the interactions appear to be much weaker than in the opposite charged ion and amphiphile case. In the L-KDDA and the S-2.1 HDPABr ACLC samples of the Δ of the chemical shifts have opposite signs, but the sign of the twist in each sample is the same. It has already been noted the alanine can form a zwitterion and the alanine and the cationic detergent interacts via the —CO$_2^-$ group in the alanine and the quaternary nitrogen in the detergent. In the case of the anionic detergent and the alanine, the interaction would be via the alanine —NH$_3^+$ group and the —CO$_2^-$ group in the detergent. This situation would effectively invert the chirality of the chiral zwitterion-amphiphile interaction so inverting the sign of Δ in the chemically shifted diastereoisomers. In this paper due to restricted space only the Δ for the chemical shifts for the —CH$_3$ group have been presented. It is worth noting, in respect to reverse chirality, the Δ for the —CH group at the opposite side of the alanine entity has an opposite sign to the Δ for the —CH$_3$ group in all three samples.

In this preliminary investigation, NMR, polar microscopy and laser diffraction studies are presented illustrating the effects of headgroup configuration and ion-binding on the chirality in ACLC samples.

Acknowledgment

Thanks to Professor M. I. Page in the Department of Chemical and Physical Sciences at the University of Huddersfield for facilitating a self-supporting visiting Research Fellowship beginning in January 1991. The authors would like to thank the University for providing a small research grant to buy chemicals.

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