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An Inversion of Chirality at a Chiral Micelle Surface

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Two chiral quaternary ammonium bromide detergents *S*-1,2- and *S*-2,1-*N*-hexadecyl-*N*,*N*-dimethyl propanol bromide with the same *S* molecular configuration which are constituent isomers have been synthesised. They were used to prepare Amphiphillic Cholesteric Liquid Crrstal (ACLC) samples where the molecular stereochemistry in respect to the micelle surface was inverted in respect to one another. Concomitant inversions in the sign of the optical rotation were found using the polarising microscope. Laser diffraction was used to determine the twists in these ACLC samples, which were found to be exceptionally small. The small twists were thought to be the result of the hydroxyl group in the chiral amphiphillic head group pushing the chiral centres apart.

Keywords: Amphiphilic liquid crystal, chiral micelle surface, cholesteric liquid crystal.

INTRODUCTION

Optical rotations in an anisotropic chiral solution (a cholesteric liquid crystal) are usually made in a well-defined direction, i.e., along the helix axis, and have been found in some cases to be 10,000 times larger than in isotropic solutions.[1] In isotropic chiral solutions the chirality measured as optical rotation arises from the discriminating interaction energies between two chiral tetrahedral molecules, where chirality is ensured by the different nature (electronegativity, etc.) of the four substituents. In an isotropic environment the asymmetrical part of the interaction field, unlike the symmetrical part, fails to average zero.[2] Optical rotation in a cholesteric liquid crystal (CLC) should never be compared with optical rotation in an isotropic chiral solution.

When a chiral centre is introduced into a nematic liquid crystal as a dopant or as a host a transition to a CLC occurs. The first examples of CLC were cholesteric esters, which were characterised by strong iridescent colours.[3] The formation of thermotropic and amphiphilic nematic liquid crystals is determined by the occurrence of orientational order resulting from inter-molecular and inter-micelle interactions respectively. Cholesteric states are nematic states, where the spontaneously twisted structure is the result of chiral centres creating dissymmetry in the orientational order. In ACLC the dissymmetry of such interactions could produce chiral shaped micelles. These distorted

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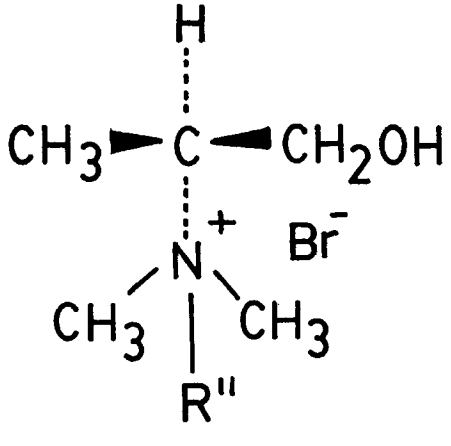
structures are derivatives of the uniaxial shaped N_D and N_C micelles. Brucine was found to be the most efficient twisting dopant for the preparation of ACLC samples where the brucine was thought to be located in the micelle surface.[4] ACLC samples have also been prepared using chiral hosts prepared from both cationic[5,6,7] and from anionic[8,9,10,11] chiral detergents.

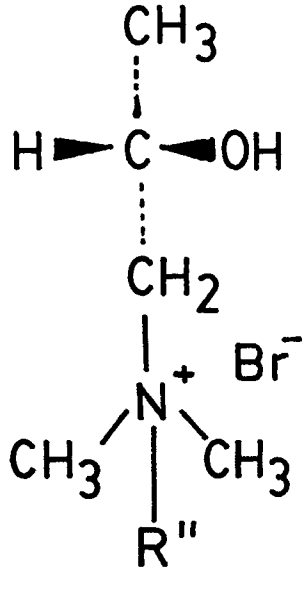
The above results strongly suggest the chirality of the micelle surface plays is important in the formation of chiral micelles in ACLC samples. The twist in an ACLC sample is a measure of the bulk chirality. The optical rotation along the helix axis and the twist are interdependent and have opposite signs[12]. It would seem that in order to investigate the importance of the micelle surface chirality in the formation of an ACLC, the creation of an inversion in the micelle surface molecular stereochemistry and monitoring its effect on the sign of the optical rotation along the helix axis would be a good idea. In the present study an inversion in the micelle surface molecular configuration was created by synthesising *S*-1,2- and *S*-2,1-*N*-hexadecyl-*N*,*N*-dimethyl-propanol ammonium bromide from *S*-2,1- and *S*-1,2-amino-propanol and using these chiral detergents to prepare ACLC samples. The effect of the micelle surface molecular configuration on the chirality was monitored using the sign of the optical rotation and twist measurements in the ACLC sample.

EXPERIMENTAL

The two chiral quaternary ammonium bromide detergents *S*-1,2-*N*-hexadecyl-*N*,*N*-dimethyl-propanol ammonium bromide (*S*-1,2HDPABr) and *S*-2,1-*N*-hexadecyl-*N*,*N*-dimethyl-propanol ammonium bromide (*S*-2,1HDPABr) were synthesised from the



S-1,2HDPABr



S-2,1HDAABr

TABLE I

Composition of ACLC Samples

Sample	Detergents mg		Decanol mg (%)	H_2O/D_2O mg (%)
	S-1,2HDPABr	*S*-2,1HDPABr		
A	408 (35.5)		40 (3.5)	700[a] (61.0)
B		408 (35.9)	30 (2.6)	700[a] (61.5)
C	360 (45)		40 (5)	400[b] (50)
D		240 (36.1)	25 (3.8)	400[b] (60.1)
E	380 (46.3)		40 (4.9)	400[b] (48.8)
F		410 (49.1)	25 (3.0)	400[b] (47.9)

[a] 5% CsCl; 2.5% TMACl; 0.8% DL-Alanine; 0.2% D_2O.
[b] 5% CsCl; H_2O.

chiral precursors *S*-2,1- and *S*-1,2-amino propanol respectively. These syntheses were achieved first by dimethylation through the Eschweiler–Clark[13] reaction using formaldehyde and formic acid to form the intermediates *S*-1,2 and *S*-2,1-*N*,*N*-dimethyl amino propanols respectively. The intermediates were then alkylated by refluxing with hexadecyl bromide to give the products. The two chiral detergents were recrystallised twice from ethyl acetate and dried under vacuum. Proton decoupled ^{13}C NMR was used to check the structure and purity of starting materials, intermediates and the final products.

ACLC samples were made up by weighing out the ingredients into test tubes, each with a restriction in the middle. The tubes were heat sealed afterwards. The ingredients were mixed by repeated heating and centrifuging of the materials through the restriction in the tube. The compositions of the ACLC sample are based on six standard samples whose compositions are set out in the table. The H_2O and D_2O used in the preparation of the samples was double distilled and the decanol was specially purified by fractional crystallisation. The small additives to H_2O and D_2O are essential for the formation of ACLCs. Some of the samples are prepared with D_2O and others with H_2O because of economics and time. Careful planning can facilitate several separate experiments on each sample. NMR measurements not reported here require D_2O in the samples. Use of H_2O is cheaper and D_2O is not readily available in some third world countries.

Some of the samples were held in micro slides for observation under a polarising microscope. Achiral N_D phase samples give rise to schleiren and pseudo-isotropic textures where as achiral N_C phase samples give rise to schleiren and planar textures but chiral Ch phases with low twists give rise to fingerprint textures, when observed under a polarising microscope. Micelle shapes in these orientationally ordered phase samples can also be indicated by setting up concentration gradients across the sample under a polarising microscope and observing the texture of the adjacent dimensionally ordered phases. The lamellar phases adjacent to N_D and Ch_D phases give rise to oily streaks and pseudo isotropic textures. The middle soap phases adjacent to the N_C and Ch_C phases give rise to fantail and planar textures.[14] Under the right conditions cholesteric phases will give rise to grandjean textures, which can be used to indicate the sign of the optical rotation along the helix axis. Wedges for the observation of Grandjean planes can be created by the introduction of a small amount of an ACLC into the lens like cavity of an undulated microslide (standard biological slide), which is

covered afterwards by a coverslip. The grandjean planes under a polarising microscope should appear as concentric rings, where the movement upon rotating the analyser indicates the sign of the optical rotation. If the analyser is rotated in a clockwise direction the concentric circles observed in the ACLC sample move towards the centre and visa versa for left hand rotation, the rings move away from the centre.

The twist of the helix was determined using laser diffraction, where the wavelength of laser light was 6.328×10^{-5} cm. The temperature of the samples was controlled to within 0.1°C by placing the sample in a brass block suitably drilled for water flow, sample placement and optical path. The temperature was controlled by circulating water from a thermostatted bath. The laser beam was shone along an axis perpendicular to the axis of the cylindrical tube. If the tube was a NMR tube, used for temperature measurements, where the sample has been aligned in the magnetic field of a Bruker 270 MHz NMR spectrometer, for positive diamagnetic anisotropy the diffraction pattern appeared as parallel lines perpendicular to the axis of the tube. If a test tube was used to contain the ACLC sample the laser patterns appeared as concentric rings. If the twists are large, the cylindrical lens cross-section of the tube distorts the diffraction pattern and the rings become ellipses. Laser diffraction is a very good method for determining twists above 1,000 cm^{-1} although useful measurements can be made down to 500 cm^{-1}. Below 500 cm^{-1} twists are better determined by counting the stripes in the finger print polarising microscope texture observed after the sample has been aligned in a magnetic field. The two methods can only be properly compared in the range where twists are between 500 cm^{-1} to 1,000 cm^{-1} where neither method is at its best. When the twist is 1,000 cm^{-1} plus, the fingerprint texture is unresolved and the texture appears planar. At constant temperature both methods give identical data within the limits of each method. The accuracy of the twist measurements using either method was estimated to be 10%.

RESULTS AND DISCUSSION

When selected samples of the ACLC systems used in the present study were viewed under a polarising microscope, fingerprint textures were observed. When some of the same samples were allowed to dry out, concentration gradients were set-up. At the lower water side of the cholesteric phase, oily streak and pseudo isotropic textures were observed, which inferred disk shaped micelles in the corresponding ACLC samples. Two samples A and B were introduced into NMR tubes and spun in the magnetic field of a Brucker 270 MHz NMR spectrometer, where the spinning axis of the NMR tube corresponds to the magnetic field axis. When a laser beam was shone through the NMR tubes, where the laser beam was perpendicular to the spinning axis of the tubes, diffraction patterns of parallel lines perpendicular to the spinning axis of the NMR tube appeared. The above observation shows the helix axis of the ACLC sample is aligned parallel to the magnetic field. Those observations are indicative of positive diamagnetic anisotropy in the chiral plase and negative diamagnetic anisotropy in the corresponding achiral phase. If the chiral phase sample had possessed negative diamagnetic anisotropy the helix of the ACLC sample placed in a magnetic field would have unwound. In the absence of aromatic ions and fluorocarbon chains in the ACLC

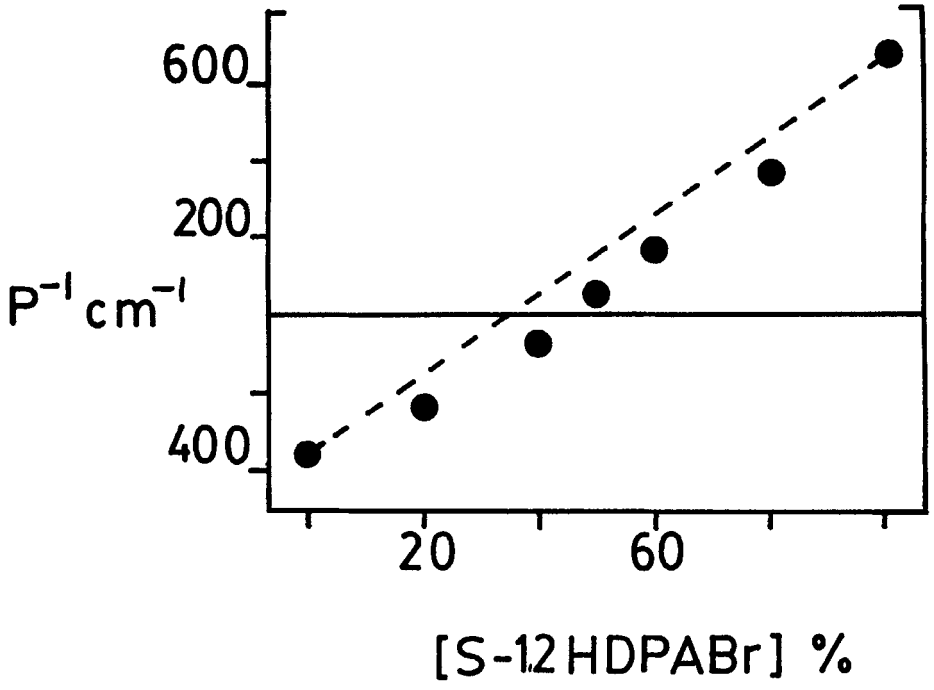


FIGURE 1 The magnitude of the twist ($1/p$) induced a mixed cationic detergent system where the detergent were *S*-1,2 HDPABr (Sample A 100%) and *S*-2,1HDPABr (Sample B 100%). Laser diffraction measurements of twist were made at 303°K.

sample, the positive diamagnetism in the chiral phase and the negative diamagnetism in the achiral nematic phase corresponds to the disk shaped micelles, which is consistent with the observed polarising microscope textures.

Generally the polarising microscope textures in the ACLC samples consisted of areas of fingerprint textures inter disposed with areas of planar texture, where grandjean planes were extremely difficult to observe. In these planar textures the helix axis is perpendicular to the film surface, where the colour order observed during the rotation of the polarising microscope analyser is an indication of the sign of the optical rotation along the helix axis. The twist, which is defined as the number of 2π rotations of the micelle director along the helix axis is a measure of the distortion in the asymmetry induced in the interaction of the chiral headgroups in the micelle surface by the chiral centres. Optical rotation and twist have opposite signs, therefore the sign of the twist measured by laser diffraction could be inferred from the sign of the optical rotation. The twist in an ACLC sample is an indication of the chiral centre density in the chiral micelle surface. The twists in the *S*-1,2-HDPABr ACLC sample A and in the *S*-2,1 HDPABr have opposite signs positive and negative respectively. The inversion in the sense of the twist in these two ACLC samples in best illustrated in Figure 1. The measured twist composition line only slightly deviates from the theoretical line that would be produced if the chemical and inter cholesterogen molecular interactions (described by Labes and Bak[15,16]) were absent. In a recent mixed chiral anionic

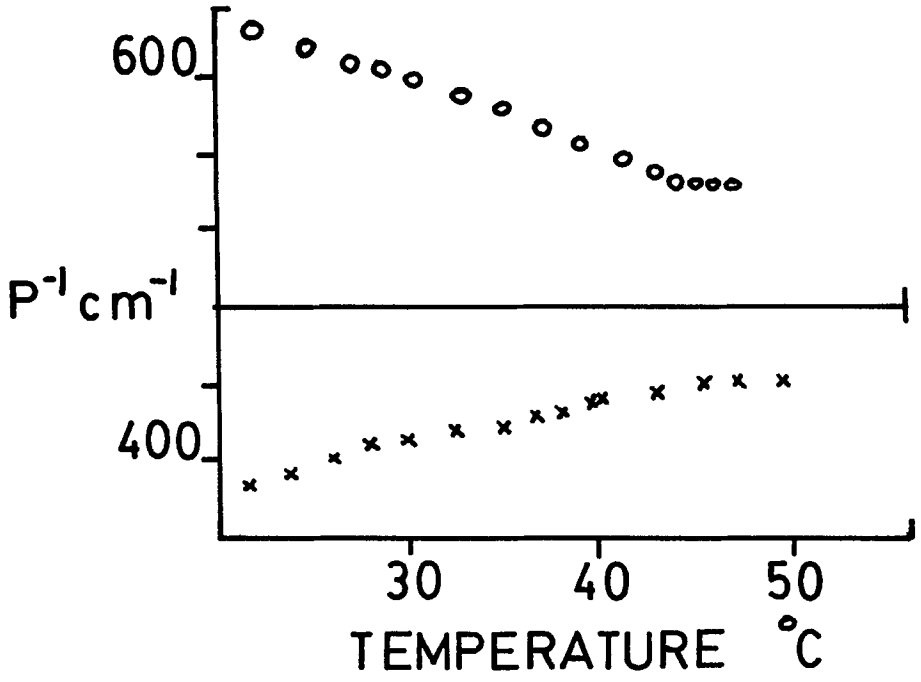


FIGURE 2 The effects of temperature on the laser diffraction twist measurements in samples $E(O)$ and $F(X)$.

detergent study with *L*-KDDA and *L*-KDDS involving both racemised and chiral detergents, it was possible to separate out both the chemical and the intercholesterogen interaction, there the latter was found to be zero! In the present study the racemised detergents were not readily available so similar conclusions could not readily be drawn.

Temperature dependence twist measurements were made using laser diffraction in two ACLC samples C and D, where the sample C contained the chiral detergent *S*-1,2 HDPABr and the other sample D contained the detergent *S*-2,1 HDPABr. The senses of the twist in the ACLC samples C and D were found to be opposites through optical rotation sign determination, positive and negative respectively. In both samples C and D the twist (results presented in Figure 2) decreased in magnitude with increasing temperature by a factor of about one half although near possible phase transitions they became temperature independent. In thermotropic CLC two mechanisms have been proposed to explain the twist's temperature dependence. Both mechanisms involve variations in the molar volume resulting from variation in the thermal motion, where each of these processes have opposite effects in the twist. The first process varies the intermolecular distance along the helix axis and the second involves the variation of the average displacement angle of one of the molecules (of micelles) with respect to the adjacent chiral molecule. These processes are opposites and if both were as equally important they would effectively cancel each other out as in the case of the *L*-KDDT study[10] as well as in the present study near the phase transitions. In most

ACLC samples the first mechanism seems to dominate. In micelles the second mechanism operates at two levels. At a lower level it applies to the interaction of chiral centres leading to chiral micelles (as with thermotropics) and at a higher level the mechanism involves the interaction between adjacent micelles. Recently temperature dependant inversions in the chirality have been observed in one chiral centre thermotropic systems. No such inversions were observed in the present studies.[17]

Four ACLC samples were prepared by adding 20 mg quantities of *S*-1,2 HDPABr to samples *E* and 10 samples were prepared by adding 20 mg quantities of *S*-2,1 HDPABr to sample *F*. Laser diffraction twist composition measurements were made on sample set *E* and sample set *F* at 303°K and 298°K respectively. The magnitude of the twist in sample sets *E* and *F* increased from 550 to 630 cm^{-1} and increased from 280 to 600 cm^{-1} respectively with increasing detergent. The sign of the twists in sample set E was positive and opposite in sign to the twists in sample set *F* which was negative. The increase in twist with increasing detergent concentration is similar to findings in previous studies with *L*-KDDA,[8,9] *L*-KDDS,[11] *L*-KDDT[10] and *S*-HMPMBr.[7] Increasing detergent concentration will induce a change in the headgroup orientation with a concurrent increase in the twist of the ACLC. The increase of the twist with increasing amounts of detergents, results from changes in the orientation of the headgroup, where the twist is a measure of the distortion induced in the micelle surface by the chiral centres. Also increasing the detergent composition decreases the area per headgroup and increases the interaction between the micelles and hence larger micelle size. On the other hand these results could be looked upon as the presence of decanol in the micelle, which dilutes the amphiphile headgroup, pushing the chiral centres apart lowering the twist. Studies with ACLC samples prepared with mixed chiral and racemised detergents show that the twist is directly proportional to the chiral detergent concentration excess under compatible chemical situations.[9,10] Twist in an ACLC sample is therefore a consequence of the chiral centre density in the micelle surface.

In the present study exceptionally low magnitudes of twists were recorded for these ACLC samples prepared with the chiral detergents derived from the amino alcohols compared to those derived from the amino acids. Those amino alcohols would appear at first sight to be closely related to the amino acids. *S*-2,1 amino propanol could easily be produced by the simple reduction of *L*-alanine. The small magnitudes of twists could be due to the location of the chiral centre in respect to the micelle surface. In the acylated amino acid ACLC sample micelles, the chiral centre is inside the micelle, between the charge and the hydrocarbon chain, at the micelle surface, while in the amino alcohol quaternary ammonium sample micelles the chiral centre is outside the micelle surface, where the charge is between the link and the chiral centre. It has already been discussed that the presence of the hydroxyl group on the decanol dilutes the amphiphile headgroup pushing the chiral centres apart lowering the twist. The hydroxyl group on the amino propanol quaternary ammonium group could have a similar effect.

CONCLUSIONS

The thrust of the present study was to investigate the effect of the molecular configuration of the amphiphile headgroup in a chiral micelle surface on the chirality (optical

rotation, twist) in an ACLC sample. To this end an inversion in the molecular configuration in the chiral amphiphile headgroup in respect to the micelle surface was created. *S*-1,2 and *S*-2,1HDPABr two chiral quaternary ammonium bromide detergents with the same absolute configuration *S*, which are constituent isomers were synthesised. The precursors each had the same absolute molecular configuration, which was retained throughout the synthetic steps and the ACLC sample preparation, but the hydrocarbon chains were connected at opposite sides of the chiral headgroup, hence the molecular configurations in each case in respect to the chiral micelle surface was inverted with respect to one another. Although the *R*–*S* classification system is systematic, it is arbitrary and in isotropic chiral solution the *R*–*S* system does not predict the sign of the optical rotation. Experimentally determined inversion in the signs of optical rotation and the inferred inversion of the signs of the twists in ACLC samples were found to be concomitant with the inversion in the molecular stereochemistry of the amphiphile headgroup in respect to the micelle surface under equal conditions in the present study where constituent isomers were involved. In a recent complementary study *L*-alanine, *L*-threonine and *L*-serine which all have the same absolute molecular configuration S were acylated and their potassium salts used to prepared ACLC samples. In isotropic chiral solution *L*-threonine and *L*-serine have the same sign of optical rotation, negative, whereas *L*-alanine has the opposite sign, positive. The sign of the optical rotation along the helix axis in the resulting ACLC samples was in each case positive.[18] These results would seem to be consistent with the present study where the molecular stereochemistry corresponds with the chirality at the chiral micelle surface.

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