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Reversals in Bulk Chirality in a Chiral Nematic Amphiphilic Liquid Crystal Associated with Acylated Proline and Thiaproline

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Chiral detergents derived from the acylation of naturally occuring amino acids have been synthesised. These detergents have been used as chiral dopants with the achiral host potassium laurate (KDD). A correspondence has been found between the molecular stereochemistry in the micelle surface and the resulting bulk chirality. The chiral dopants potassium hexadecanoyl-L-proline (L-KHDP) and potassium hexadecanoyl-L-thiaproline (L-KHDTP) with the host achiral KDD were found to cause inversions in the sense of the twist, abnormal to the general case. These inversions in sense of twist were interpreted as originating from the compensation averaging of the cis-trans molecular conformations, derived from the rotation of the consituents about the C-N peptide bond. NMR evidence is presented to support this assertion.

INTRODUCTION

Inversions or reversals in bulk chirality (sense of twist and sign of optical rotation) in cholesteric liquid crystals were classically usually associated with two or more chiral centres, which compensated against each other.[1] It has been shown in thermotropic chiral liquid crystals one chiral centre cholesterogens can produce inversions in the bulk chirality.[2,3] Reversals in the bulk chirality in chiral amphiphilic liquid crystals have recently been illustrated in several systems.[4] The reversal in the bulk chirality (twist sense) induced by the decyl ester of proline chloride has been attributed, to be derived from the rotamers associated with the ester bond, using ^{13}C NMR.[5]

Cholesteric liquid crystals are obtained, when a chiral centre is introduced into a nematic liquid crystal either as a host or as a dopant. The dissymmetry in the orientational order results in a spontaneously twisted structure. The pitch P is the distance travelled by the director during a 2π rotation of the helix. The director is perpendicular to the helix axis. The twist is the reciprocal of the pitch 1/P. The twisting power is the quotient of twist and concentration. The optical rotation is usually

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measured along the helix axis and is, by convention, opposite in sign to the sense of helix twist. Amphiphilic cholesteric liquid crystals have been prepared using chiral dopants such as brucine[6] and chiral hosts such as the potassium salts of the acylated amino acids e.g. L-KDDA.[7-10] The twists in these systems were determined using the fingerprint texture viewed under a polarising microscope together with laser diffraction measurements.

Bulk chiral properties such as twist and optical rotation are a function of the spatial chirality in the polarisation resulting from the dissymmetry in the electron states associated with the chiral molecule. In isotropic chiral solutions only the chiral molecular interactions are allowed, where the anisotrpic molecular interactions are randomly averaged to zero. These optical rotations are very small. In cholesteric liquid crystals all the intermolecular interactions are non zero averaged in respect to the helix axis. The optical rotation along the helix axis is much larger than in isotropic chiral solutions, sometimes 10,000 times. In micelles the hydrocarbon chain always points towards the centre of the micelle, away from the micelle surface. The averaging of the intermolecular interactions is now in respect to the micelle surface and the helix axis, where there now might be a strong correspondence between the molecular stereochemistry and bulk chirality via spatial chirality.

In amphiphilic cholesteric liquid crystals it has been recently found that naturally occuring α amino acids when acylated and used as chiral dopants the twist senses for all the three cases are the same, while the optical rotation of the precursor amino acids, in isotropic solution are different.[11] If there was a strong correspondence between molecular and bulk chirality in chiral micelle solutions, it might be expected that chiral detergents with the same molecular stereochemistry in the head group would give rise to ACLC's with the same sense of twist. Acylated amino acids fit this profile. In this publication the synthesis and the use as chiral dopants of several acylated amino acids will be assessed, in order to assert any correspondence between the molecular stereochemistry of the headgroup in respect to the chiral micelle surface and the sense of helix twist. Other amino acids with primary nitrogens will be used together with the amino acids L-proline and L-thiaproline which have a secondary nitrogen. The existence of molecular rotamers have been well documented in polypeptide systems, where proline demonstrates different behaviour,[12-16] from the peptides with primary nitrogens

EXPERIMENTAL

The chiral detergents, the potassium salts of naturally occurring acylated amino acids were prepared as previously described. ^{13}C NMR spectra with high S/N were used to check the purity and the structure of the starting materials, the intermediates and the final products. The chiral detergents L-KHDP and L-KHDTP gave rise to ^{13}C NMR spectra of increasing complexity. The proton NMR of the acid derivative of L-KHDTP was also more complex. The NMR spectra of the primary nitrogen chiral detergents gave spectra attributable to one chemical species whereas the for the secondary nitrogen chiral detergents, L-KHDP and L-KHDTP, the spectra were attributable to two isomers.

Acid L-HDTP ^{1}H NMR spectrum

Isomer 1 C_α(5.029 ppm) and C_β(3.376 ppm); $J_{\alpha\beta} = 4.16$ Hz.; C_γ(4.534 ppm) AB spectrum $\delta_{AB} = 73.01$ Hz, $J_{AB} = 9.57$ Hz; —CH_2CO—N (2.234 ppm):
Isomer 2 C_α(4.939 ppm) and C_β(3.250 ppm); ABX spectrum $\delta_{AB} = 42.07$ Hz, $J_{AB} = 11.76$ Hz, $J_{AX} = 3.65$ Hz, $J_{BX} = 7.15$ Hz; C_γ(4.646 ppm), AB spectrum $\delta_{AB} = 43.66$ Hz, $J_{AB} = 8.28$ Hz; —CH_2CO—N (2.414 ppm):

Unresolved peaks common to isomers 1 and 2

$CH_3CH_2(CH_2)_{12}$ CH_2CO (1.275 ppm); $CH_3CH_2(CH_2)_{12}$ CH_2CO (1.577 ppm); $CH_3CH_2(CH_2)_{12}$ CH_2CO (0.8879 ppm)

Potassium salt L-KHDTP ^{13}C NMR spectrum

Doubled peaks for isomer 1 and 2.
CO_2^- (177.45, 176.72 ppm); > CO—N (173.16, 174 30 ppm); C_α(65.28, 65.44 ppm); C_β(35.53, 34.54 ppm), C_γ(49.81, 49.49 ppm); —CH_2—CO (36.32, 35.72 ppm); CH_2CH_2—CO (25.89, 25.66 ppm);

Other unresolved peaks for isomer 1 and 2

Terminal CH_3 14.443 ppm; other chain CH_2 32.91, 30.66, 30.57, 30.49, 30.33, 23.59 ppm:

Potassium salt L-KHDTP ^{13}C NMR spectrum

Doubled peaks for isomer 1 and 2.
CO_2^- (178.87, 178.06 ppm); > CO—N (173.55, 172.63 ppm); C_α(62.47, 61.96 ppm); C_β(47.60, 46.21 ppm); —CH_2—CO(34.75, 34.37 ppm); CH_2(25.56, 24.85 ppm) and (22.92, 22.65 ppm):

Other unresolved peaks for isomer 1 and 2

Terminal CH_3(14.443 ppm); other chain CH_2(31.91, 29.79, 29.68, 29.37 ppm):

The structure of the micelles in the ACLC's were inferred to be discotic Ch_D using a polarising microscope as previously described.[17,18] When the thin films of ACLC samples are allowed to dry out, a concentration gradient is set up between the chiral nematic phase and the neighbouring dimensionally ordered phase. The planar textures of the middle soap phase and the oily streaks/pseudo-isotropic textures in the lamellar phase indicated in the neighbouring chiral nematic phase cylindrical Ch_C disk Ch_D shaped related micelle structures respectively. Under a polarising microscope thin films of ACLC samples held in "CAMLAB" microslides gave rise to fingerprint textures, which could be used to determine the twist. In parts of the thin film under the polarising microscope Grandjean textures and Cano planes are formed, which could be used to determine the sign of the optical rotation.[19,20] The optical rotation and the sense of

TABLE I

The effects on the magnitude of the twist ($1/P$) when individual chiral dopant ACLC samples are mixed to form new ACLC samples. The host is potassium laurate, at 25°C

Detergent *A*			Detergent *B*			Calculated		Exp.
	Mol %	$\frac{1}{P_A}$		Mol %	$\frac{1}{P_B}$	$\frac{1/P_A + 1/P_B}{2}$	$\frac{1/P_A - 1/P_B}{2}$	$\frac{1}{P}$
L-DDPG	8.88	215	L-KHDP	4.64	290	236	20	0
L-DDPA	3.61	1570	L-KHDP	8.87	510	1040	530	340
L-DDPA	1.84	720	L-DDPG	10.47	185	456	270	480
L-DDPA	5.31	1990	L-KDDA	6.75	1990	1990	0	1840
L-KDDA	5.54	1770	L-KDDM	6.432	3020	2395	1180	2360
L-KDDM	8.7	4100	L-KDDM	9.35	4360	4240	1130	4080
L-KHDP	6.092	390	L-KDDA	3.49	800	600	200	340
L-KHDTP	13.37	60	L-KHDP	8.98	100	80	20	130
L-KDDMC	5.98	1550	L-DDV	4.15	2000	1775	225	1590
L-DDV	9.76	3350	L-DDNV	2.82	470	1910	1440	2580
L-DDNV	4.14	2000	L-KDDBC	4.22	610	1310	695	1460
L-KDDBC	5.55	570	L-DDL	2.03	580	575	5	620

Mol % = 100 × weight dopant/(weight dopant + weight host)

helix twist by convention have opposite signs. The optical rotation sign was used to infer the sense of helix twist. The sense of helix twist was checked by the mixing of samples with different dopants and then checking for compensation or reinforcing of the twist magnitude see Table I.

The twist (magnitude $> 500\,\text{cm}^{-1}$) of the helix axis of the amphiphilic cholesteric liquid crystal sample was measured using laser diffraction. The wavelength of the laser was 6.328×10^{-5} cm. The temperature of the samples was controlled to within 0.1°C by placing them in a brass block suitably drilled for water flow, sample placement and optical path. The temperature was controlled by circulating water from a thermostatted water bath.

Samples were prepared by weighing out the components into a test tube and after heat sealing were homogeneously mixed by heating and centrifuging as previously described. The ANLC host compositions are presented in Table II. The sample

TABLE II

Compositions of achiral host amphiphilic nematic liquid crystals used in this study. The host detergent is potassium laurate

Detergent Composition	Weight Detergent		Weight Decanol		Weight H_2O		Dissolved Salts
	(mg)	(%)	(mg)	(%)	(mg)	(%)	
j	0.30	32.3	0.03	3.2	0.60	64.5	5% CsCl
k	0.30	31.9	0.04	4.3	0.60	63.8	3% KCl and 2%
l	0.30	31.7	0.045	4.8	0.60	63.5	K_2CO_3
m	0.30	31.6	0.05	5.3	0.60	63.1	
n	0.30	31.2	0.06	6.3	0.60	62.5	

components; decanol was specially purified by fractional crystallisation and the H_2O was double distilled.

RESULTS AND DISCUSSION

Potassium N-dodecanoyl-L-alaninate, -L-serinate, -L-threoninate, (L-KDDA, L-KDDS and L-KDDT.)

Figure I illustrates the use of L-KDDA, L-KDDS, and L-KDDT as chiral dopants, where potassium laurate is the achiral host for amphiphilic cholesteric liquid crystal

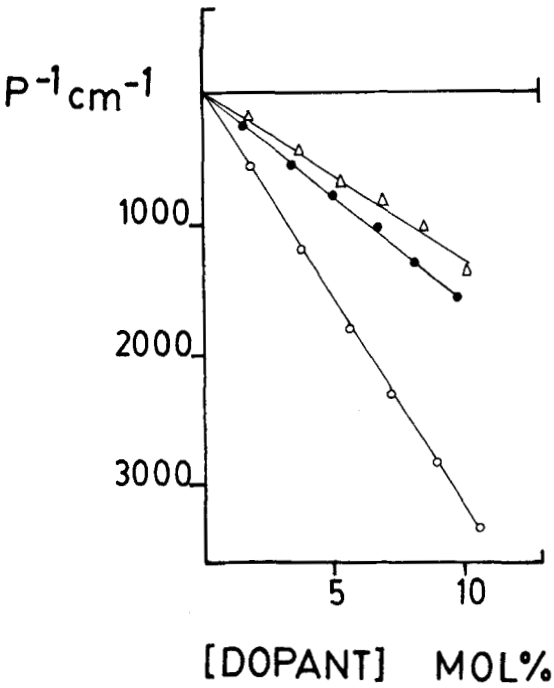
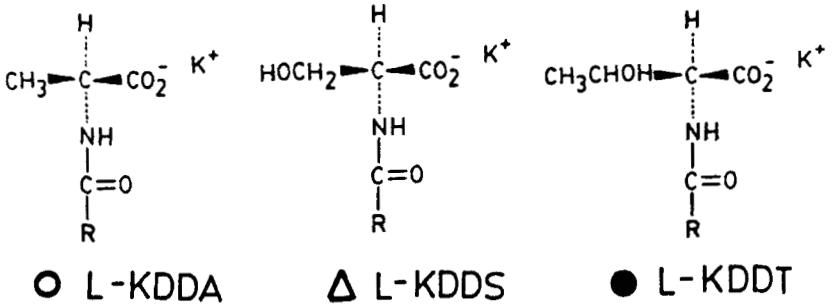


FIGURE I Laser diffraction determined twist measurements plotted as a function of chiral dopant concentration Mol. %. Temperatures as Table III. Mol % = 100 × weight dopant/(weight dopant + weight host).



formation. These results are taken from reference 11. The data in each case was RMS fitted for a straight line. The twisting powers, the gradient of the straight line, were calculated to be $-31{,}300 \pm 400\,cm^{-1}$ for L-KDDA; $-12{,}600 \pm 1{,}000\,cm^{-1}$ for L-KDDS; and $-15{,}000 \pm 1{,}300\,cm^{-1}$ for L-KDDT. It is noted the sense of the helix twist was negative for all three cases when used as chiral dopants, where the sign of optical rotation in isotropic solution for each of the amino acid precursors was different. There is no relationship between the sense of helix twist derived from the chiral detergents in anisotropic solutions and the optical rotation for the precursor amino acids in isotropic solutions, even though the amino acids and the derivatives have the same molecular stereochemistry. It is well known that there is no relationship between the optical rotation and molecular stereochemistry in isotropic solutions, but the results would seem to imply that there is some relationship between the sense of helix twist and molecular stereochemistry at the chiral micelle surface. This will become more apparent when further results are discussed, (see Table III).

Potassium N-dodecanoyl-L-methionate, -L-methyl cysteinate and -L-benzyl cysteinate, (L-KDDM, L-KDDMC, and L-KDDBC)

When L-KDDM was used as a chiral dopant with potassium laurate as the achiral host the resulting twisting power was found to be $-45{,}900 \pm 1000\,cm^{-1}$ (see Figure II). This number was exceptionally high and its sign was negative as with the first three cases. Attempts to use L-KDDM as a chiral host failed. When this chiral detergent L-KDDM is used as a chiral dopant the hydrophobic $CH_3SH_2CH_2$-chain in the methionine headgroup easily tucks into the micelle interior and produces an idealised headgroup

TABLE III

The average twisting power with various chiral dopants and achiral hosts. Determinations at 25°C unless otherwise stated

Precursor	Detergent	Twisting Power[c]	Sign of OR in precursor	R-S Notation
L-Alanine	L-KDDA	$-31{,}300 \pm 400$[b,j]	+	S
	L-DDA	$-8{,}600$[b,·]		S
L-Valine	L-DDV	$-15{,}100$[b,·]	+	S
L-Serine	L-KDDS	$-12{,}600 \pm 1{,}000$[b,j]	−	S
L-Methyl Cysteine	L-KDDMC	$-24{,}700 \pm 1{,}200$[m]	−	R
L-Benzyl Cysteine	L-KDDBC	$-26{,}900 \pm 800$[m]	−	R
L-Methionine	L-KDDM	$-45{,}900 \pm 1{,}000$[m]	+	S
L-Phenyl Alaninate	L-DDPA	$-39{,}800 \pm 3{,}200$[a,k]	−	S
L-Threonine	L-KDDT	$-15{,}000 \pm 1{,}300$[b,j]	+	S
L-Norvaline	L-DDNV	$-22{,}000$[b,·]	−	S
L-Leucine	L-DDL	$-28{,}600$[b,·]	−	S
L-Phenyl Glycine	L-DDPG	$-2{,}400 \pm 350$[m]	+	S
L-Proline	L-KHDP	$3{,}600 \pm 1{,}000$[n]	−	S
L-Thiaproline	L-KHDTP	$1{,}400 \pm 170$[n]	−	R

Note: [a]denotes 20°C and [b]denotes 30°C

[j,k,l,m,n]denote composition with chiral host as in Table II.

[c]extrapolated to zero concentration.

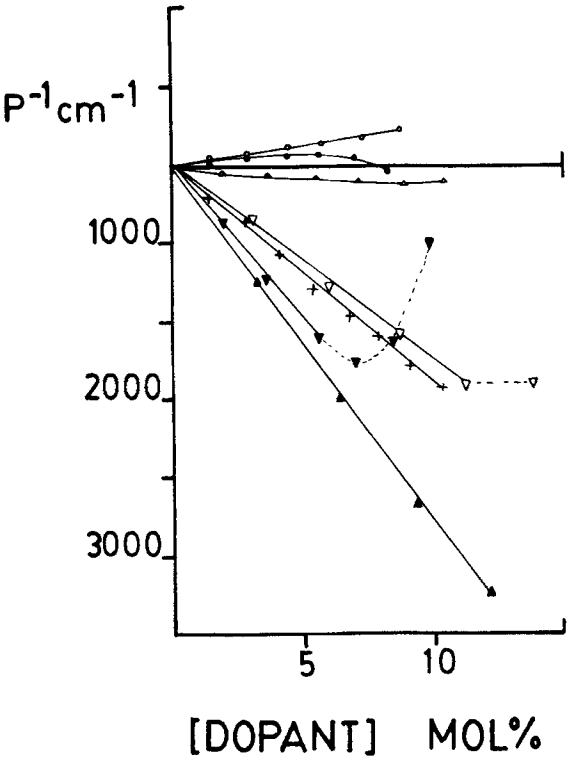
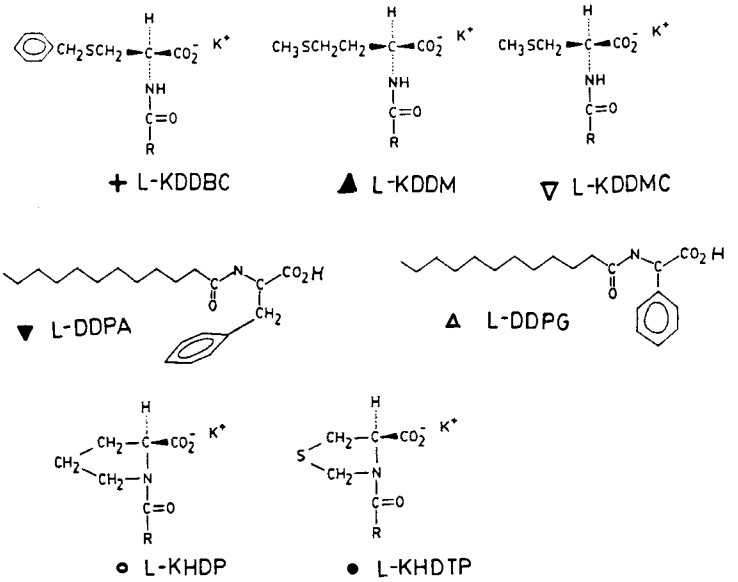


FIGURE II Laser diffraction determined twist measurements plotted as a function of chiral dopant concentration Mol. %. Temperatures as Table III. Mol % = 100 × weight dopant/(weight dopant + weight host).



orientation. When this chiral detergent is used as a chiral host, the $CH_3SH_2CH_2$- chain increases the size of the headgroup and the bulky headgroup does not favour ACLC formation. The twisting powers for L-KDDMC and L-KDDBC as chiral dopant were found to be smaller in both cases $-24{,}700 \pm 1{,}200\,cm^{-1}$ and $-26{,}900 \pm 800\,cm^{-1}$. In this group all three twist senses were negative as with the first group, but the sign of the optical rotation for the isotropic solution of the precursor amino acids were negative for L-benzylcysteine and the L-methylcysteine, but positive for L-methionine. The data was RMS fitted to a straight line (Figure II).

Dodecanoyl-L-phenylalaninic acid, and Dodecanoyl-L-phenylglycinic acid. (L-DDPA and L-DDPG)

When L-DDPA and L-DDPG were used as chiral dopants, where potassium laurate was the achiral host, the sense of helix twist in each case was negative, although the sign of the optical rotation for each the precursor amino acids in isotropic solution was different. The magnitude of the twist associated with the chiral dopant L-DDPA rose to over $2{,}000\,cm^{-1}$ but eventually fell off with the destruction of the cholesteric phase. The twists associated with the chiral dopant L-DDPG were very small compared to those associated with the chiral dopant L-DDPA i.e. less than $250\,cm^{-1}$. The associated twisting powers were calculated to be $-39{,}500 \pm 3{,}000\,cm^{-1}$ and $-2{,}450 \pm 350\,cm^{-1}$ respectively. The difference in the magnitude of the twist for these two chiral dopants would be due to differences in the headgroup orientation at the chiral micelle surface. The L-phenyl alanine and L-phenyl glycine molecular structures differ only by a CH_2 group. In the L-DDPA case, with the extra CH_2 group, the hydrophobic phenyl group will easily tuck into the interior of the micelle, facilitating easy ACLC formation. In the case of L-DDPG, minus the CH_2 group, the hydrophobic phenyl group is less likely to find a suitable orientation, where the plane of the phenyl group is parallel to the detergent hydrocarbon chains. The hydrophobic phenyl group in this case will more than likely be forced to sit in the hydrophobic micelle surface, destabilising the micelle surface and hence giving rise to small twists. (Figure II). When a dopant in a micellar system has a well defined hydrophobic and hydrophilic segment it would be expected the hydrophobic and hydrophilic parts of the micelle and dopant would lay side by side. The situation would be more complex as in some biological systems where the hydrophobic and hydrophilic boundary is not well defined. For example aromatic rings might find themselves situated in the surface of a biological membrane.

Acids N-Dodecanoyl-L-Alaninic acid, L-Valinic, L-Leucinic and L-Norvalinic, (L-DDA, L-DDV, L-DDL and L-DDNV)

When L-DDA, L-DDV, L-DDL and L-DDNV were used as chiral dopants the resulting data illustrated in Figure III showed large deviations from a straight line. Calculating twisting powers would be meaningless. The twisting power calculated from the first data point is included in Table III. The achiral host sample with no chiral dopant will have a high pH, but the addition of the acid will lower the pH depending on the pK of the acid. An equilibrium will be set up between the ionic detergent and the neutral acid species. Each of these species will have an individual twist, where the

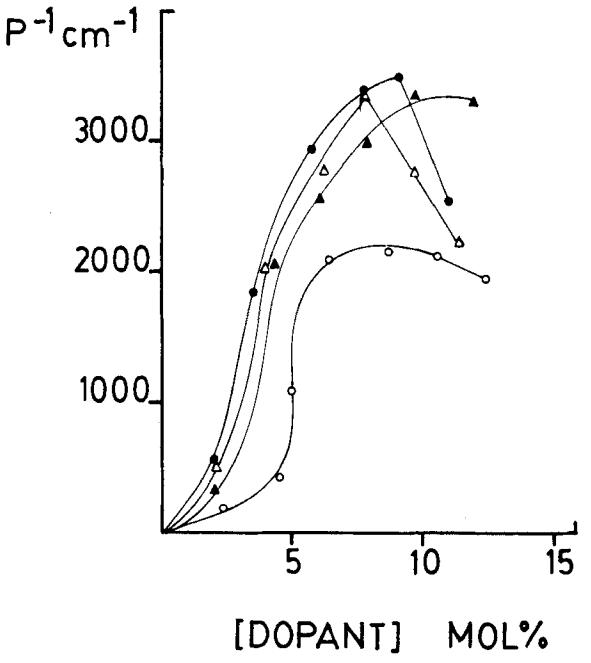
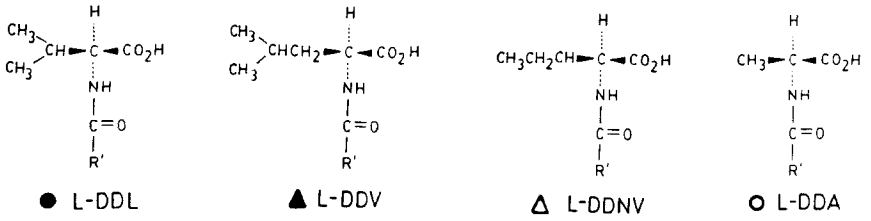


FIGURE III Laser diffraction determined twist measurements plotted as a function of chiral dopant concentration Mol. %. Temperatures as Table III. Mol % = 100 × weight dopant/(weight dopant + weight host).



overall twist, through the influence of the micelle structure, will be the sum of these individual twists. The cholesteric phase is an intermediate phase between the isotropic and the lamellar phase. The ionic detergent species destabilises the cholesteric phase towards the isotropic phase with increasing twist, while the neutral acid species destabilises the cholesteric phase towards the lamellar phase with decreasing twist. Despite the complex twist concentration dependence, the sense of twist was determinted to be negative as with the previous three groups of chiral detergents. It has been the author's long experience with these multi-component systems which form amphiphilic cholesteric liquid crystals that an increase in the ionic detergent concentration generates an isotropic phase. This is contrary to the sequence of phase changes in most binary systems, where increasing ionic detergent leads to a lamellar mesophase.

Potassium hexadecanoyl-L-prolinate and -L-thiaprolinate, (L-KHDP and L-KHDTP)

When L-KHDP and L-KHDTP were used as chiral dopants with potassium laurate as the achiral host the resulting twists were small with a positive twist sense (see figure II). The twisting powers were calculated to be $+ 3{,}400 \pm 1{,}000\,cm^{-1}$ and $1{,}400 \pm 200\,cm^{-1}$ respectively. The small magnitude of the twist could be due to the proline/thiaproline ring restricting the chiral centre from reaching the optimum molecular orientation in the chiral micelle surface for the formation of ACLC's. The C_{16} hydrocarbon chain in the chiral dopants L-KHDP and L-KHDTP is rather long compared to the C_{12} chain of the laurate. It might be expected a shorter chain dopant whose chain length is compatible to the hosts would be needed for efficient ACLC formation. On the other hand L-KHDP has been used as a chiral host in a mixed detergent system, where the twists were found to be small.[21] The abnormal sense of twist for the chiral dopant L-KHDP and L-KHDTP are more than likely the result of variations in the orientation of the chiral dopant headgroup in the micelle surface as well as changes in molecular sterecochemistry associated with the proline and thiaproline ring at the micelle surface.

These reversals in the twists sense involving the chiral dopants L-KHDP and L-KHDTP could originate from the irregular molecular orientation of the chiral headgroup ring in the micelle surface. The molecular orientation controls the spatial dissymmetry of the electronic states in the chiral micelle surface. The reversal in the twist sense would originate from a continuous change between two molecular orientations of opposite spatial dissymmetry. The ring structure of proline and thiaproline are bulky in respect to chiral micelle formation. The charged part of the chiral micelle is not part of the ring, although the hydrocarbon chain is attached to the ring through the secondary nitrogen via an amide link. Molecular orientation changes due to the bulky headgroup could effect the twist considerably, but only in rare cases might it affect the sense of the helix twist. The only way molecular orientation could reverse the sense of the helical twist in a chiral micelle would be for the molecular stereochemistry of the chiral headgroup to be reversed in respect to the micelle surface. This could only be the case if the hydrophobic hydrocarbon chain pointed away from the chiral micelle surface out into the aqueous region. The situation is difficult to imagine. The direction of the macro helix twist will run in a direction generally parallel to the flat surface of the micelle. A tensor with a least five independent parameters must be used to adequately describe bulk chiralty. A vector is not adequate because it only has a maximum of three independent parameters.

A more rational explanation for the origin of the twist sense reversals induced by the chiral dopants L-KHDP and L-KHDTP would involve molecular conformations. The molecular conformations could result from the restricted rotation of the constituents about the C-N peptide link. There is an extensive literature base concerning the cis-trans rotamers associated with the C-N peptide link in biologically important polypeptides reporting NMR and X ray data. It has been found in polypeptides, where the C-N link involves a primary nitrogen such as alanine, that the trans rotamer is nearly always present. In peptides where the C-N link involves a secondary nitrogen, such as proline, the cis rotamer is preferred. The two rotamers might make opposite

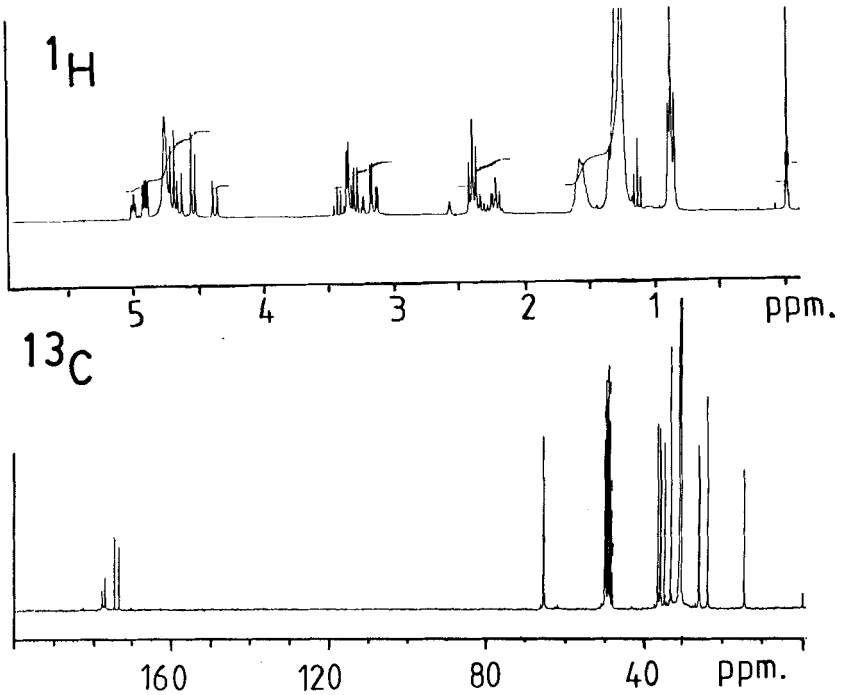
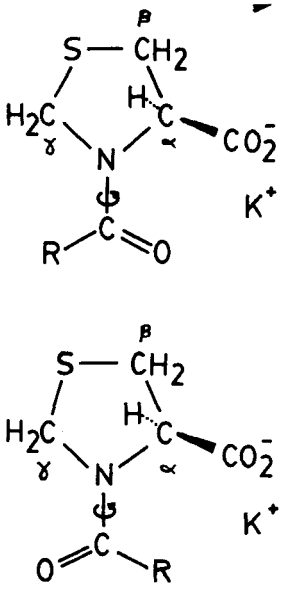


FIGURE IV (a) The ^{1}H NMR spectra of L-HDTP dissolved in CD_3OD (5%). (b) The ^{13}C NMR proton decoupled spectra of L-KHDTP dissolved in CD_3OD (5%) Spectra taken on a Bruker 270 MHz NMR spectrometer at 23°C.



contributions (not necessarily equal) to the total twist. Similar arguments could be made with the thiaproline derivative, although no similar extensive literature exists. The assertion that the reversal of twist sense for the chiral dopants L-KHDP and L-KHDTP is due to molecular rotamers is supported by the ^{13}C NMR spectra in both cases and the ^{1}H NMR spectrum in the case of L-KHDTP. In each case the NMR spectra demonstrates the existence of two isomeric forms of the chiral detergent. The ^{1}H for L-HDTP and ^{13}C NMR for L-KHDTP and L-KHDP are illustrated in Figure IV. A complete analysis of these NMR spectra is presented in the experimental section. The fact that the different isomers are observed certainly does not confirm they are responsible for the observed reversal in the sense of the twist. No doubt they contribute to the observed twist and it is postulated that this represents the source of the observed behaviour, but there is no absolute confirmation here.

CONCLUSION

It is concluded in the present study that there is a strong correspondence between the molecular stereochemistry and the twist sense, through the spatial dissymmetry of cholesteric liquid crystals and the chiral micelle surface. It would appear that acylated naturally occuring α-amino acids with simple side chains and primary nitrogens all have the same sense of helix twist, when acting as chiral dopants with the achiral host potassium laurate. The sign of the optical rotation of the amino acid precursors in isotropic solutions are not always the same. This may not be the general rule as it was seen with proline and thiaproline. α-amino acids with hydrophilic side chains such as aspartic acid and glutamic acid together with other chiral or achiral hosts could produce opposite results.

The reverse behaviour of the acylated proline and thiaproline was explained in terms of the molecular conformers created by the rotation of the constituents about the C-N link. In this way chiral micelles mimic the behaviour of enzymes, where some cases involving proline derivatives exhibit different behaviour in respect to molecular rotamers about the C-N link. This assertion is supported using NMR. This is by no means confirmation.

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