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THE USE OF THE DECYL ESTERS OF AMINO ACID HYDROCHLORIDES AS CHIRAL DOPANTS IN THE FORMATION OF AMPHIPHILIC CHOLESTERIC LIQUID CRYSTALS

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Abstract The decyl ester hydrochlorides of the amino acids serine, alanine, leucine, methionine and methyl cysteine are accessed as chiral dopants in amphiphilic cholesteric liquid crystal formation. The sense and magnitude of the induced helical twist is found to be dependent on the achiral host detergent, which were various alkyl-methyl ammonium bromide salts. The results are interpreted in terms of the trans and cis rotamers associated with the ester linkage. ^{13}C-NMR is used to measure the rotamer populations. Each rotamer makes an opposite but an unequal contribution to the total twist. The results for the serine ester did not fit this interpretation completely.

INTRODUCTION

Micellar nematics are orientationally ordered lyotropic liquid crystals formed by solvating or heating dimensionally ordered liquid crystals. Dimensionally ordered lamella and middle soap phases are associated with cylindrical and disk shaped micelles respectively.[1] It was found that when chiral dopants were added to micellar cholesteric states were formed.[2] The chiral center in cholesteric liquid crystal facilitates a spontaneously twist helical structures characterized as a repeat distance called the pitch. The twist is the inverse of the pitch. The twisting power is the differential of the twist inrespect to the concentration extrapolated to the origin. In the present study the ACHIRAL HOST DETERGENTS will be alkyl methyl ammonium bromides mixed with decanol and water:-$C_{14}H_{29}(CH_3)_3N^+Br^-$ (TDTMABr); $C_{12}H_{25}(CH_3)_2NH^+Br^-$ (DoDMABr); $C_{12}H_{25}(CH_3)NH_2^+Br^-$ (DoMABr) and $C_{10}H_{21}NH_3^+Br^-$ (DMABr).

Amino acids can be used as convenient sources of chiral centres in the synthesis of chiral dopants, ie. as precursors to esters and amide chiral detergent derivatives. It has been shown recently in the case of acylated (amide potassium salts) amino acids, that there is a strong relationship between the molecular stereochemistry and bulk chirality in amphiphilic cholesteric liquid crystals.[3] The acylated amino acids derived from primary nitrogens in all cases gave rise to cholesteric states with the same sense of helical twist. In two cases proline and thiaproline, derived from secondary nitrogens, with the host detergent potassium laurate the sense of the helical twist was reversed. This reversal in the sense of the helical twist was explained in terms of trans and cis rotamers in which each rotamer makes an opposite in sense and not necessarily equal in magnitude contribution, to the total twist. This explaination was backed up by ^{13}C NMR, which facilitates the measurement of the rotamer populations.

Trans-cis rotamerisation is a well known phenomenon in peptide chemistry. Barriers of rotation in amides have been extensively studied using NMR since the 1960's[4].

The decyl ester hydrochloride of alanine has been used previously as a chiral host, which resulted in smaller twists than in the corresponding amides[5]. The decyl ester hydrochloride of proline has been used as a chiral dopant, where a concentration dependent reversal in twist sense was observed[6]. This phenomenon was explained in terms of trans-cis rotamers, where the rotamer populations were determined by ^{13}C NMR.

There is a less extensive literature for the ester rotamers than the amide rotamers. Rotamerisation in methyl formate has been studied both theoretical and experimentally[7,8]. Ester rotamers are thought to play a role as an inhibitor in the hydrolysis of β lactam esters(penicillic)[9].

Inversions in chirality have been observed in chiral thermotropic systems such as the phenyl esters[10].

EXPERIMENTAL

The chiral detergents were synthesized as previously described by passing HCl through the amino-acid refluxing in decanol[5]. The amino-acids chiral precursors were:- SERINE, ALANINE, LEUCINE, METHYL-CYSTEINE and METHIONINE.

The magnitudes of the helical twists was determined using laser diffraction through Bragg's law and using a polarizing microscope through observing fingerprint textures.

The sense of the helical twist is by convention opposite to the sign of the optical rotation.

$$\Theta = -2\pi P d(\Delta n/\lambda)^2$$

The sign of the optical rotation could be determined in two ways.

(a) By mixing samples containing different chiral dopants and then checking the magnitude of the resulting helical twist for compensation or reinforcement.

(b) By optical microscopy through the observation of Grandjean textures and Cano wedges.

^{13}C NMR was taken with long acquisition times in order to obtain quantitative spectra for cis and trans rotamer population determination.

RESULTS and DISCUSSION

When the achiral host was tetradecyl-trimethyl ammonium bromide $C_{14}H_{29}(CH_3)_3N^+Br^-$ TDTMABr\ decanol\ water(CsCl), all the twisting powers produced by the chiral dopants were positive except the serine ester case. Whereas when the achiral host was decyl ammonium bromide $C_{10}H_{21}NH_3^+Br^-$ DABr\water\(NH_4Cl), all the twisting powers were negative including the serine ester case. It was attempted to acquire more results before any reasonable explanation might be put forward. The two more of the less well known alkyl methyl ammonium bromide detergent were investigated. When the host was dodecyl-dimethyl ammonium bromide $C_{12}H_{25}(CH_3)_2NH^+Br^-$ DoMABr\decanol\water (KCl) the twisting powers were negative in all cases except the serine ester case. Investigation with the host dodecyl methyl ammonium bromide $C_{12}H_{25}(CH_3)NH_2^+Br^-$ DoDMABr could not be made as the detergent at this time was unavailable.

TABLE :-Twisting powers cm^{-1} determined for various achiral hosts and chiral dopants

	DABr	DoDMABr	TMABr
DESCl	-3,200	+750	-2,100
DEMCl	-13,500	-1,950	+1,650
DEACl	-10,600	-850	+600
DEMCCl	-15,700	-1,000	+380
DEAL	-21,100	-5,000	+4,400

The data for the case of the decyl ester alanine hydrochloride DEACl, illustrated by plotting the twist as a function of dopant concentration (see figure I) was processed using microsoft origin, where the twisting power in each case was the slope of the line extrapolated through the origin, where the error was about 10%.

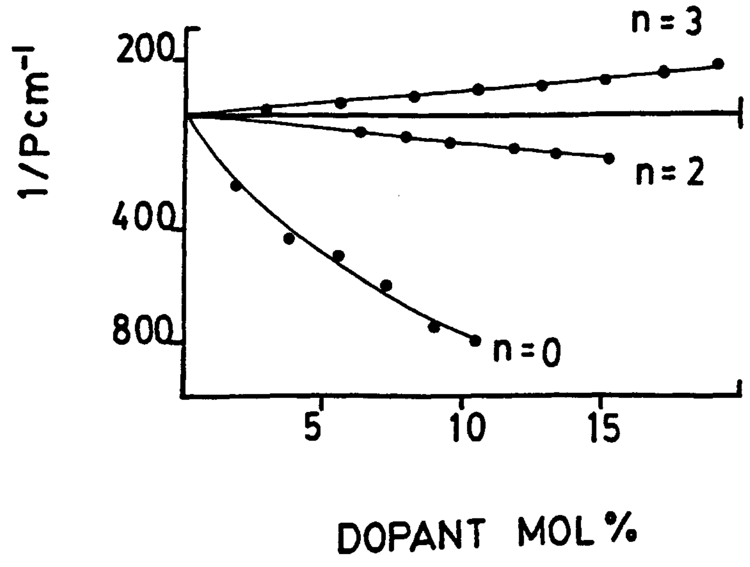

FIGURE I :-**The twist data derived from the chiral dopant DEACI (alanine) plotted as a function of dopant mol% for three alkyl methyl ammonium bromide host detergents, where n denotes the number of methyl groups in the ammonium headgroup @ 25 °C.**

If the basic assumption concerning the generation of the twist in an ACLC is that the total bulk twist is equal to the sum of the individual micro-twists, the following equation could be derived for the total twisting power T_T.

$$T_T = T_A + M_B (T_B - T_A)$$

where T_A and T_B are the individual twisting powers of rotamer A and B respectively and M_B is the fraction of rotamer B. It was assumed within experimental error that the magnitudes of T_A and T_B are independent of the achiral host and there is no inter doping chiral interactions. The populations of the trans and cis rotamers were calculated from the ^{13}C NMR data, hence M_B could be calculated. The twisting power data was plotted as a function of M_B, and was then fitted to a linear progression based on the above equation, where T_A and T_B were determined to be respectively. -23,100 ±2000 and 244,000 ±20,000 cm^{-1}. It is assumed that the magnitudes of T_A and T_B 's were host independent within experimental error. (See Figure II)

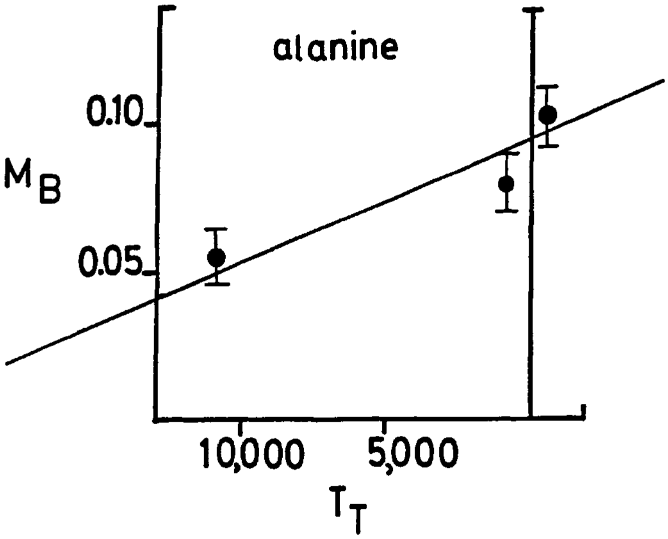

FIGURE II :- **The twisting powers for DEACl (alanine) derived for data shown in figure I are plotted as a function of M_B the mole fraction of isomer B calculated from ^{13}C NMR derived rotamer rotios @ 25 °C.**

The other chiral dopants DELCL (leucine), DEMCl (methionine), and DEMCCl (methyl cystiene) demonstrated the same general trends in the twisting power, ie host trimethyl - positive, host dimethyl - negative and host nomethyl - negative. For the chiral dopant DEMCCl no second rotamer was detected in the ^{13}C NMR spectra, and for the chiral dopants DELCl and DEMCl the rotamer ratio's were found to be .20 ±.04 and .21 ±.02 respectively, constant within experimental error. The rotamer ratios in these cases will be less important in determining the twisting power, but the nature of the head group now is much more important. T_A and T_B will now be a function of the host headgroup. The above three chiral dopants all have elongated sidechains in the chiral detergent headgroups, which will disrupt the chiral micelle surface.

With the chiral dopant DESCl (serine) there was no trend in the twisting powers the various host detergents, although the rotamer ratios are host dependent in a similar way to DEACl cases. Serine has an OH group in the side chain which will react strongly with the chiral micelle surface where T_A and T_B might be reversed. Although the molecular stereo chemistry of the chiral headgroup in all cases is similar the dissymmetry of the molecular polarization and hence the molecular chirality and bulk chirality in this case DESCl is more than likely reversed, as was observed with two of the hosts.

CONCLUSIONS

^{13}C NMR reveals that the decyl esters of four of the five amino acids investigated occurr as two rotamers. In the case of serine and alanine the rotamer ratio was host detergent dependent, but host detergent independent in the case of leucine and methionine. These two rotamers each make an opposite in sense and unequal in magnitude contribution to the total twisting power. These contributions in all cases except alanine appear to be host detergent dependent. There also may be evidence to suggest that the basic assumption that there is no inte-detergent interactions is not valid.

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