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Trans and Cis Rotamerization in Amphiphilic Cholesteric Liquid Crystals Where the Chiral Dopant is The Hydrochloride of Decyl-L-Proline

Keith Radley [a] & Neil McLay [a]
[a] Department of Chemical and Biological Sciences, The University of Huddersfield, Queensgate, Huddersfield, HD1 3DH, UK
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Trans and Cis Rotamerization in Amphiphilic Cholesteric Liquid Crystals Where the Chiral Dopant is The Hydrochloride of Decyl-L-Proline

KEITH RADLEY and NEIL McLAY

Department of Chemical and Biological Sciences, The University of Huddersfield, Queensgate, Huddersfield, HD1 3DH, UK

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Data from a previous study, where a reversal in the sense of the helical twist in an amphiphilic cholesteric liquid crystal (ACLC) is induced by the chiral dopant the hydrochloride of decyl-L-proline, is taken and its interpretation extended. The interpretation involves trans and cis conformers resulting from hindered rotation. The ^{13}C NMR data is used to determine the rotamer populations, which facilitates the calculation of the twisting powers for the individual rotamers. The twisting powers of the trans and cis rotamers are found to be $3900 \pm 900\ cm^{-1}$ and $-650 \pm 150\ cm^{-1}$ respectively.

Recently it has been shown, when the hydrochloride of decyl-L-proline (L-DEPCI) was doped into an amphiphilic nematic liquid crystal (ANLC), where the achiral host detergent was tetradecyltrimethylammonium bromide (TDTMABr), the sense of the induced twist was reversed with ever increasing amounts of the chiral dopant.[1] The results are illustrated in Figure 1, where it was observed that the twist increased initially with the dopant concentration, then the twist fell towards zero at 12% of chiral dopant, and then with an ever increasing dopant concentration the sense of the helical twist was finally reversed. Initially the sense of the helix twist was positive and finally the sense of the helix twist was negative. It was suggested this reversal in the sense of helix is due to the trans and cis conformations resulting from hindered rotation about the ester amino acid link. Each rotamer might make an opposite, but not necessarily equal contribution to the total twist. ^{13}C NMR data was presented to support this assertion.

Trans and cis conformations, associated with hindered rotation about the amide link in polypeptides[2,3,4], have for a great many years been extremely interesting to biological chemists. Hindered rotation in simple amides was extensively investigated with ^{1}H NMR in the 1960's, where rotation barrier energy in a large number of cases was determined.[5] It was later found in polypeptide systems, with primary

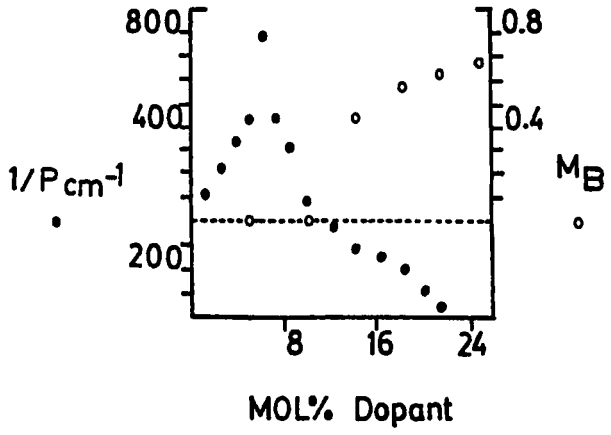

FIGURE 1 Twist ($1/Pcm^{-1}$) measurement at 25°C as a function of the mol% of the chiral dopant L-DEPCI (●). Also plotted is M_B (○) determined through ^{13}C NMR. Data was taken from reference 1.

nitrogens such as alanine, the trans rotamer was preferred, while with secondary nitrogens such as proline the cis rotamer was preferred. It has been found in amphiphilic cholesteric liquid crystals that the reversals in the sense of the helical twists, when the chiral dopants were salts of acylated proline and thiaproline, could be conveniently explained in terms of trans and cis rotamerization.[6,7]

The trans and cis rotamerization associated with the ester link has been investigated both experimentally and theoretically[8,9] in the model methyl formate system, but by no means as extensively as the rotamers associated with peptides. It is thought the rotamerization of the ester group is responsible for the inhibition of β-lactam antibiotics.[10] Inversion in twist sense have been found in both thermotropic[11,12] and amphiphilic[13] liquid crystal systems, where the explanation could involve ester group rotamerization.

The simplest way to process the data is to assume a linear relationship between the total twisting power T_T and the individual twist powers T_A and T_B of the rotamers A and B, such that:

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

where M_B is the mol fraction of the rotamer B in respect to the total amount of chiral dopant. The twisting power T_T is the quotient of the twist and the mole fraction of the chiral dopant in respect to the total detergent concentration. T_T was plotted as function of M_B derived from the ^{13}C NMR data, which is illustrated in figure II. When the data in Figure 2 was rms fitted to a linear regression, the twisting powers of the rotamers T_A and T_B were found to be -650 ± 150 cm^{-1} and 3950 ± 900 cm^{-1} respectively.

The T_A could be assigned to the cis rotamer, which dominates when small amounts of the chiral dopant are present and T_B might then be assigned to the trans rotamer, which dominates when large amounts of the chiral dopant are present. The

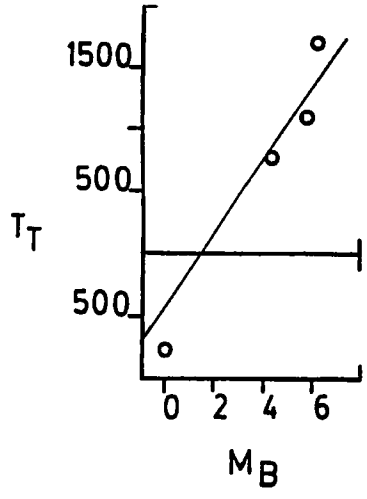

FIGURE 2 Plot of the total twisting power T_T against mol fraction of rotamer B $M_B \times 10$ at 25°C.Data is taken from Figure I.

senses of the helical twisting powers of the two rotamers were found to have opposite signs and the magnitudes were unequal. This confirms the assertion that trans and cis rotamers are responsible for the reversal in the sense of the helical twist observed in the ACLC, when the chiral dopant L-DEPCI is doped into the achiral host ANLC based on TDTMABr.

The fit to a linear regression of the data showed quite a large error although this does not detract from the confirmation of the original assertion. The fitting did not include data where small amounts of chiral dopant below about 8% were present. In this region there is a large swing in the magnitude of the helical twist, when the M_B rapidly approaches zero see Figure 1. At these mole fractions the ^{13}C NMR was not sensitive enough to measure the population of both rotamers. In this region of lower concentration the twisting powers of the rotamers must be dependent upon the chiral dopant concentration unlike in the high concentration region, where it was assumed to be independent of the chiral dopant concentration.

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