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Helical Twisting Power of Amino Acids in a Nematic Lyophase

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The nematic lyophase of disodium cromoglycate dissolved in water can be made chiral by adding a wide variety of amino acids whose ability to induce helicity is systematically studied. Long, bulky side chains lead to small helical twisting power (HTP), whereas increased hydrophilicity of side chains leads to larger HTP. Some dipeptides have dramatically large HTP's. These factors can be understood in terms of a geometric and steric model.

INTRODUCTION

In a series of recent papers[1-4] on the properties of the lyophases of disodium cromoglycate in water, it has been pointed out that the nematic phase can function as a solvent for a large number of water soluble chiral compounds thus producing chiral nematic or cholesteric lyophases. In particular, many amino acids and dipeptides are quite soluble, and short pitch chiral systems can be prepared showing characteristic optical transmission and reflection in the visible region of the spectrum.

It was the purpose of this investigation to measure the "helical twisting power" (HTP) of a large variety of amino acids to look for structural correlations. In the limit of low concentration of a chiral solute in a thermotropic nematic phase, it is well known that the pitch of the induced cholesteric phase is inversely proportional to concentration, the proportionality constant being called the "HTP" of the solute. In addition to these measurements, some investigation of the dependence of pitch on temperature and ionic strength are reported.

EXPERIMENTAL

DSCG was kindly furnished by Fisons Ltd. as a crystalline solid. It contains some tightly bound water, estimated at from 5 to 6 molecules in the relative humidity range 30–70%. This compound is indexed as 4H-1-benzopyran-2-carboxylic acid, 5,5′-[(2-hydroxy-1,3-propanediyl)bis(oxy)]-bis(4-oxo)-disodium salt, Registry No. 15826-37-6. Amino acids and dipeptides were obtained from Aldrich, Sigma, or Alfa Chemical Companies and used without further purification.

DSCG, water, and/or optically active additives were mixed in rubber septum-capped polyethylene vials. For optical microscopy studies between crossed polarizers on Nikon or Zeiss microscopes, these solutions were introduced by syringe into rectangular capillaries varying in thickness from 20–300 μm and widths 4–20 times their thickness which were obtained from Vitro Dynamics, Inc., New Jersey. The ends of the capillaries were sealed with a rapid setting epoxy resin, which also served to affix the capillaries to a conventional microscope slide. Magnetic field alignment was achieved by placing the capillaries on a microscope slide in a 6-inch electromagnet for a

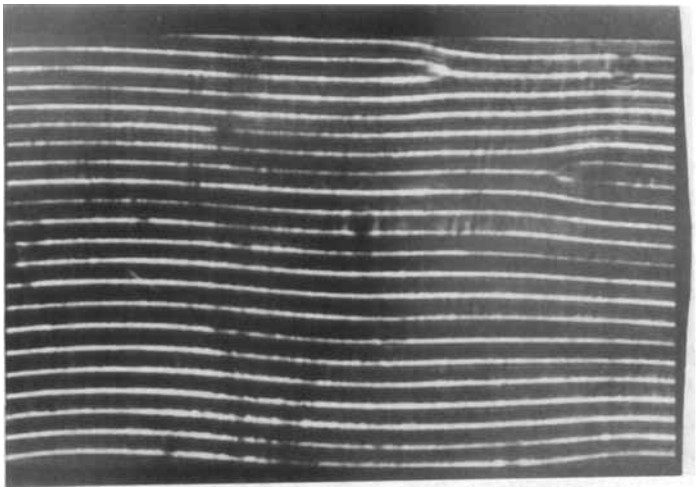


FIGURE 1 Fingerprint texture of the induced cholesteric phase of 10.3 wt% DSCG/3.3 wt % *l*-alanine/2.4% Na-*d*-mandelate/H_2O. Sample pitch is 21 μm after being aligned in a 60 kG magnetic field perpendicular to the fingerprint lines at 21 °C.

prescribed period of time in either *X* (length) or *Y* (width) direction with respect to the field.

As has been reported earlier,[1] the cylindrical aggregates of DSCG/H_2O have a negative diamagnetic anisotropy. A helical array of such cylinders therefore has its magnetic axis coincident with its helix axis. By placing samples in a magnetic field in the sample plane, the helix axis therefore aligns parallel to the glass walls of the capillary producing the fingerprint texture of the cholesteric phase (Figure 1). In this texture the helix pitch is the distance between two such "fingers", i.e. a rotation of the optic axis (causing extinction) of 360°.

Samples were thermostated in the magnet on a temperature controlled brass stage which could be transferred to the optical microscope. Some samples were also transferred to a Mettler FP-5/52 heating stage for temperature dependence studies.

RESULTS AND DISCUSSION

HTP is the slope of the plot of $1/p$ vs C where p is the optically measured pitch and C is the concentration (in mole % in Table I). The linearity of such plots has already been presented in a previous paper for the cases of *l*-alanine and *l*-proline dissolved in DSCG/H_2O.[1] Plots of $1/p$ vs C were in fact quite linear up to the solubility limits of the amino acids given in Table I.

In interpreting such data, it is necessary to understand how added solute can affect the pitch of the system by simply perturbing its ionic strength, hydrogen bonding, or total number density. Figure 2 indeed indicates that even added inactive amino acid can cause perturbations of the pitch of an induced cholesteric, presumably by simply affecting hydrogen bonding or number density. Table II indicates that added salt can effect both the pitch and the transition temperature of an induced cholesteric system. The effect on transition temperatures has already been reported for nematic DSCG/H_2O.[1] However, since HTP's were determined at quite low concentrations of chiral additives, little or no departure from linearity can be attributed to temperature or ionic strength variations.

The temperature effect on the HTP of the induced cholesteric phase of DSCG/H_2O is shown in Figure 3. The value of HTP does not change when the temperature is changed from 13° to 20 °C. This is to be expected from the information in the literature[5] concerning the variation of the pitch of the cholesteric helix with temperature in a one component cholesteric system when considering a temperature region

TABLE I

HTP of Amino Acids and Dipeptides in 15 wt % DSCG/H_2O

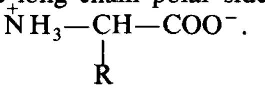
Chiral Dopant	Molecular Weight	Sign of Specific Rotation of Amino Acid	Helical Sense	HTP $(10^5$ nm mol%$)^{-1}$	Wt %[a] at 20 °C
l-alanine	89.09	+	R	3.0	12
l-proline	115.13	−	R	2.4	16
l-Arginine · HCl	210.66	+	L	31.3	7.4
l-Asparagine	132.13	−	L	4.8	6.7
l-cysteine	121.16	+	R	1.2	19
l-cystine	240.30	−	R	< 0.1	0.01
l-histidine	155.16	−	R	7.4	6
l-isoleucine	131.17	+	R	< 0.1	3
l-leucine	131.18	−	R	< 0.1	2
l-lysine · HCl	182.65	+	L	0.8	20
l-methionine	149.21	−	L	< 0.1	3
l-phenylalanine	165.19	−	R	< 0.1	2.7
l-serine	105.10	−	R	2.8	4
l-Threonine	119.12	+	L	< 0.1	11.2
l-Tryptophan	204.23	+	R	< 0.1	1
l-valine	117.13	+	R	1.6	9
cis-4-hydroxy-*l*-proline	131.13	−	L	11.7	26
cis-4-hydroxy-*d*-proline	131.13	+	R	11.6	26
trans-4-hydroxy-*l*-proline	131.13	−	R	11.6	26
l-azetidine carboxylic acid	101.10	−	R	5.0	18
carbobenzyloxyl-*d*-proline	249.27	−	R	< 0.1	1
l-alanyl-*l*-alanine	160.17	+	R	12.9	10
l-alanyl-glycine	146.2	+	L	2.3	10
l-alanyl-glutamic acid	218.2	−	L	1.9	14
l-alanyl-*l*-serine	176.2	+	R	2.4	10.2
l-alanyl-*l*-histidine	226.2	+	R	3.6	10.2
l-alanyl-*l*-lysine	253.7	−	R	25.2	10
l-lysyl-*l*-lysine · 2HCl	347.3	+	R	116.6	2.4

[a] Solubility limit where $1/p \propto$ HTP · C.

sufficiently far away from the transition temperature to a smectic or an isotropic phase.

One is left with attempting to extract a structural pattern from the data in Table I. The following observations are clear:

(a) Only five *l*-amino acids cause a left-handed twist of the helicoidal array. All have long chain polar side groups (—R($\geq C_3$)—) in the basic structure



$$\overset{+}{N}H_3-\underset{\substack{|\\ R}}{CH}-COO^-.$$

TABLE II

KCl Effect on the Pitch of 13 wt % DSCG/12 wt % *l*-alanine/H_2O

KCl Concentration mole liter^{-1}	Pitch (μ) at 20 °C	$T_{Ch \to I}$ (°K)
0	6	314.3
1×10^{-1}	12	306.1
1×10^{-2}	25	305.0
1×10^{-3}	30	301.5
1×10^{-4}	35	300.5
1×10^{-5}	30	301.7

(b) Measured HTP's of amino acids are all within one order of magnitude of each other, *l*-Arginine · HCl being the highest HTP. Many other amino acids have very small HTP's—they include some of the bulkiest hydrophobic side groups.

(c) Dipeptides have about one order of magnitude higher HTP, *l*-lysl-*l*-lysine · HCl being spectacular. Both helicoidal senses occur.

According to Kimura *et al.*,[6] the cholesteric helicity $q(= 2\pi/p)$ involves both polar and steric effects of optically active additives. The steric effect is proportional to the deflection angle between the principal axis of a pair of molecules closely in contact. The sign and size of the steric effect depend upon the geometry of the additives. According to Goossens,[7] the polar effect is closely related to the optical activity of the additives, but the relation is actually not so simple. Those

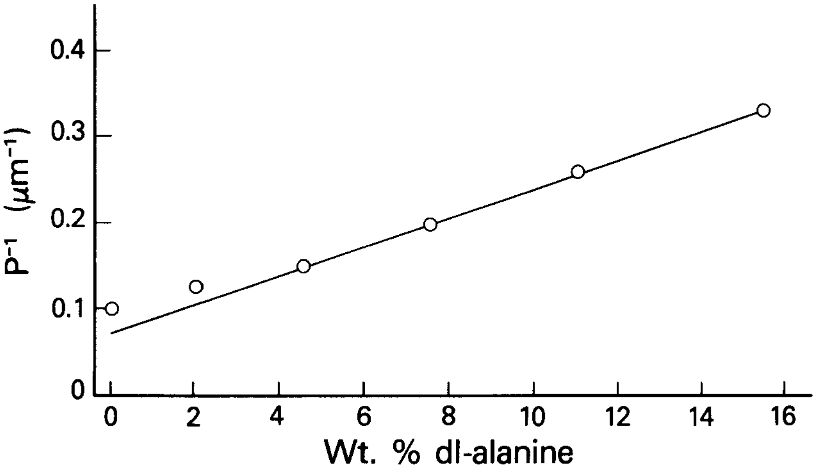


FIGURE 2 Non-chiral dopant effect on the pitch of 14 wt % DSCG/19.66 wt % *t*-4-hydroxy-*l*-proline.

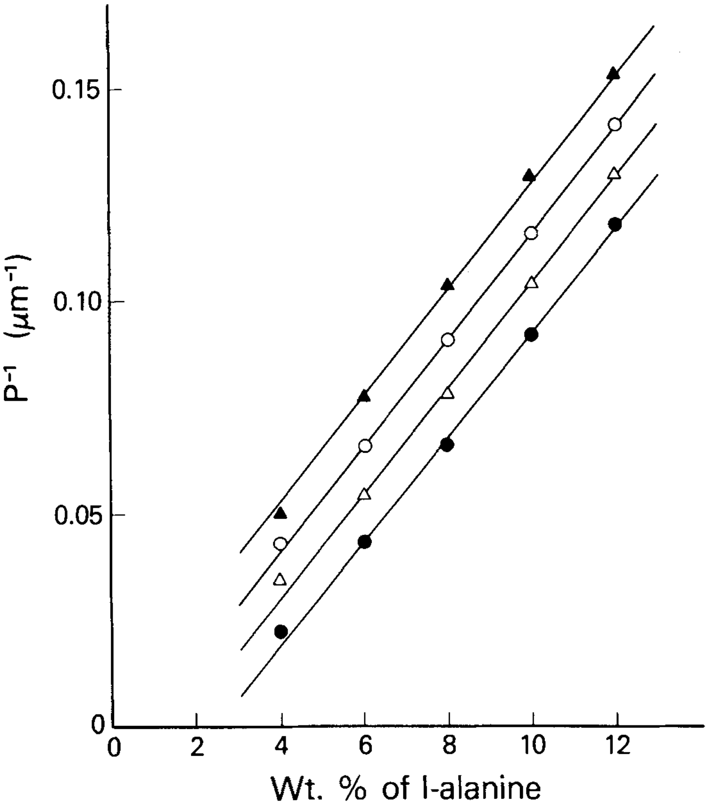


FIGURE 3 Temperature effect on HTP of 12 wt % *l*-alanine + *d*,*l*-alanine/15% DSCG/H_2O. ▲: 13 °C; ○: 15 °C; △: 17 °C; ●: 20 °C.

components of the optical tensor which are related to the coupling constant do not contribute to the optical rotation in isotropic solution, but only to the rotation of a light beam traveling perpendicular to the long axis of the molecule.[8]

The following relationships between side chain structure of the amino acid and HTP can be deduced (see Table I-A).

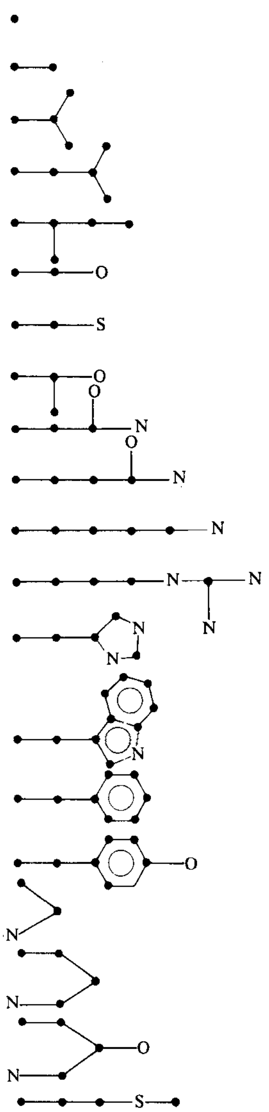
(a) When the side chain becomes longer or bulkier, HTP becomes smaller;

(b) When the chain has a strong hydrophilic group or groups, HTP is increased.

These facts can be related to the anticipated change in intermolecular or interaggregate distance along the helix axis and the concomitant increase in the displacement angle between adjacent molecules in the

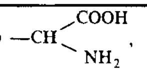
TABLE I-A

HTP and Structural Features of the Amino Acid Side Chain[a]



	$HTP(10^5 \text{ nm mol\%})^{-1}$
Glycine	
Alanine	3.0
Valine	1.6
Leucine	< 0.1
Isoleucine	< 0.1
Serine	2.8
Cysteine	1.2
Threonine	< 0.1
Asparagine	4.8
Glutamine	< 0.1
Lysine	0.8
Arginine	31.3
Histidine	7.4
Tryptophan	< 0.1
Phenylalanine	< 0.1
Tyrosine	< 0.1
Azetidinecarboxylic Acid[b]	5.0
Proline[b]	2.4
Hydroxyproline[b]	11.7
Methionine	< 0.1

[a] In the representations of the side chains attached to



$$-CH\begin{smallmatrix}COOH\\NH_2\end{smallmatrix},$$

the following symbols are used:

N: $>NH$ or $-NH_2$; O: $-OH$ or $=O$; S: $-SH$ or $-S-$.

[b] In these representations, the side chains return to the amino acid nitrogen.

helical stack. Long or bulky side chains have a large steric hindrance due to their large rotational and vibrational non-harmonicity. Therefore, the intermolecular or interaggregate distance will increase and the pitch becomes large (small HTP). Hydrophilic groups will hydrogen bond with water or DSCG molecules to induce a short intermolecular or interaggregate distance and the pitch becomes small (large HTP).

On the other hand, when the nematic phase of an induced cholesteric contains hydrophobic aggregates or molecules, HTP is expected to increase with increasing hydrophobic character of optically active additives. This situation would be consistent with a report by Gottarelli *et al.*,[9] on chirality in thermotropic aromatic nematics, who found that the value of the HTP greatly increased by increasing the size of the aromatic moiety, and by increasing the bulk of pendant alkyl groups, when the aromatic moiety is the same.

Acknowledgment

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