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# On chirality induction in lyotropic nematic liquid crystals

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# On chirality induction in lyotropic nematic liquid crystals

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The induction of lyotropic chiral phases by different, structurally related α-hydroxy carboxylic acids as well as the corresponding potassium salts has revealed a distinct dependence of their helical twisting power upon their molecular structure. Obviously there is an effect of the mean electronic polarizability of the moiety neighbouring the chiral centre of the dopant, similar to that in the case of thermotropic induced chiral phases. A significantly non-linear dependence of the inverse pitch on the concentration has been found and is explained as a micelle size effect. The absolute value of the helical twisting power decreases if instead of a chiral acid, the corresponding potassium salt is used to induce the phase chirality; moreover, the handedness of the twist is inverted. A microscopic model for the evolution of chirality in a micellar phase is proposed.



## 1. Introduction

A lyotropic liquid crystalline state is characterized by a long-range orientational order of anisometric building blocks in a solvent. In the present paper these building blocks are aggregates of amphiphilic molecules in water. In the literature, certain phases have been classified as nematic from the observation of typical textures and/or alignability by magnetic fields, by analogy with thermotropic liquid crystals. (Rather than textures or alignability, the criterion of the nematic state should be a structural one, namely a long-range orientational order associated with the absence of long-range positional order.) The common picture describes a lyotropic nematic phase of surfactant aggregates as rod-like, disk-like or biaxial micelles surrounded by an isotropic solvent, where the respective aggregate axes spontaneously prefer a common direction, the so-called director. The director does not vary in space for an ideal, undistorted nematic phase.

The director field of a nematic phase may, however, become chiral by obtaining a helical superstructure, i.e. the preferred orientation twists spontaneously around a helical axis. This state of matter has been called 'cholesteric' for the historical reason that for thermotropic liquid crystals, the phase chirality was discovered with cholesteryl esters for the first time [1]. Actually, a more appropriate term is 'chiral nematic'.

The chiral superstructure within the long-range orientational order of anisometric micelles is characterized by the pitch $p$ (or its inverse, the twist $p^{-1}$) and the handedness of the twist, right or left (see figure 1).

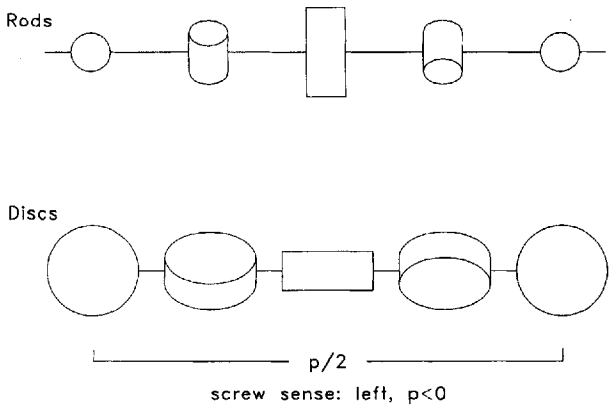


Figure 1. Sketch of the helical arrangement of rod-like and disk-like micelles.

A phase chirality can arise either from the molecular chirality of the aggregated surfactants themselves [2, 3] or can be induced by the solubilization of chiral dopants into an achiral solvent [4] as well as into achiral micelles [5]. We wish to report on the latter case.

Together with its experimental discovery, two models for the origin of lyotropic phase chirality were proposed in 1978 by Radley and Saupe [5]: (1) a sterical interaction model; (2) a chiral dispersion interaction model.

(1) The sterical interaction model assumes that the rod- or disk-like micelles of the appropriate nematic phase are deformed into a chiral shape by the influence of the solubilized chiral guest molecules. Due to the thermal motion in the solvent, the micelles frequently collide with each other and thus chirality information can be transferred sterically

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from one aggregate to its nearest neighbours. A chirally deformed rod could look like a cork screw [4].

(2) An alternative model for the induction of phase chirality in lyotropic systems proposes a pairwise interaction between chiral molecules resident in different micelles. A chiral dispersion interaction can be understood theoretically by means of the multipole expansion of the dispersion interaction energy, if at least a dipole/quadrupole term is present (Goossens theory [6]).

It is one aim of this paper to contribute further to an understanding of the twisting 'mechanism' acting in chiral lyotropic liquid crystals.

Some correlations between the molecular structures of chiral dopants and their twisting efficiency are known from the literature. Vanin, Alcantara *et al.* [7] observed an influence of the hydrophobic/hydrophilic balance of chiral dopants, mainly amino acids. For ionic dopants they suggested an effect of the charge distribution within the micellar surface. In a recent paper these authors showed that the charge and the chemical nature of the amphiphile head groups may affect the dopant orientation in the micelle [8]. Radley and Tracey likewise investigated the behaviour of amino acids in nematic host phases [9] and pointed out that the chiral centre density in the micelle surface is an essential parameter for phase chirality formation. Recently, an extensive study of acylated amino acids in an achiral host phase has revealed a correspondence between the molecular stereochemistry and the resulting bulk chirality [10]. Further structure/property correlations are claimed by Labes *et al.* [11]. According to their report, bulky side chains of a chiral dopant should decrease the helical twisting power (see § 3·2), whereas very hydrophilic side chains should increase it.

There is need of further systematic investigations on structurally very simple chiral dopants to elucidate chirality induction in lyotropic systems, which is more complex than for thermotropics. It is a further aim of our studies to contribute to this point.

In order to keep things as clear as possible we have restricted the major part of our experiments to structurally related dopants with *only one chiral centre* with *R*- or *S*-configuration. We have investigated different α-hydroxy carboxylic acids, as well as three corresponding potassium salts, figure 2 (*a*). Only one substituent at the asymmetric carbon of our dopants was systematically modified; this was chosen to have different sizes, hydrophobicities and polarizabilities. This series of related compounds was available commercially or could be synthesized by standard procedures.

Our α-hydroxy carbon acids are somewhat water-soluble and, moreover, differ in their water solubility.

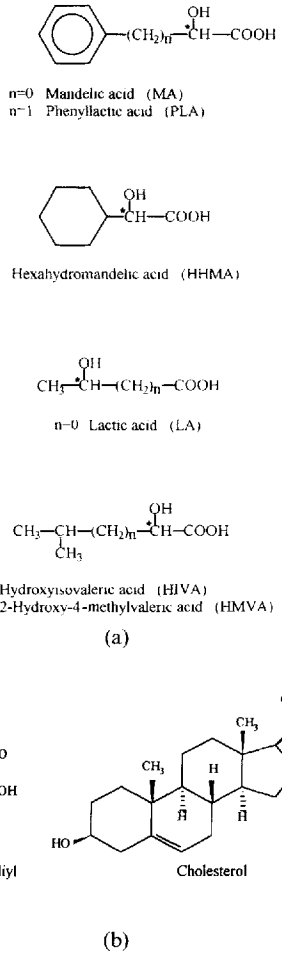


Figure 2. Chiral dopants investigated: (*a*) α-hydroxy carboxylic acids, from MA, HHMA and HIVA the potassium salts were also prepared (KM, KHHM and KHIV); (*b*) the inherent dissymmetric molecule 1,1'-binaphthalene-2,2' diyl hydrogenphosphate, BNDHP, and cholesterol.

Although chiral solvents have also been predicted to induce phase chirality of lyotropic liquid crystals [4], one can assume that any chiral dopant is most effective if it acts directly on the building block constituting the orientational order, that is, is present in, or close to, the micelle. (Therefore one might prefer to use water-insoluble dopants, but then other experimental problems can arise, like the induction of the lamellar phase, see § 3·1). To be sure that we could use all the α-hydroxy carboxylic acids, we determined their partition coefficients $f$ for a water/alkane two phase system ($f$ = concn in alkane/concn in water) [12]. The data for water/octane show that among our dopants only lactic acid (LA) exhibits a value of $f < 1$, that is, prefers to dissolve more in water than in octane. In a micellar solution the partition will be shifted towards solubilization in the micelles due to the amphiphilicity of the dopants; there-

fore the systematic error relating to dopant concentration in the micelles is relatively small. We will further comment on this point in § 3·1 and 3·2.

Besides the carboxylic acids, we were interested in the twisting efficiency of a dopant molecule without any chiral carbon centre, but with an inherent dissymmetry (*R*(–)-1,1′-binaphthalene-2,2′-diyl hydrogenphosphate, BNDHP). Additionally, for comparison and reference to the literature [5], we used cholesterol, figure 2(*b*).

## 2. Experimental

### 2.1. *Nematic host phase*

Our nematic host phase was a mixture of hexadecyldimethylethylammonium bromide CDEAB (28·3 wt %) and water (67·4 wt %); some decanol (4·3 wt %) was added to obtain disk-like micelles [13]. The chiral nematic phases induced from this kind of host phase readily form fingerprint textures which are advantageous for pitch determination [5].

Hexadecyldimethylethylammonium bromide was purchased from Merck (>98%) and decanol from Jannsen Chimica (99%). Both were used without further purification. The required amounts of each component (surfactant, cosurfactant and bidistilled water) were weighed into a flask. In order to homogenize the mixture it was stirred for 48 h at about 40°C in a water bath. Each newly prepared nematic mixture was tested for constant composition by determination of its clearing temperature; for this purpose it was filled into microslides (Camlab, England), sealed to prevent evaporation and warmed in a heating stage (accuracy: 0·1°C). The clearing temperature of our nematic host phase ranged from 31·3°C to 31·5°C.

### 2.2. *Chiral dopants*

BNDHP (for structures/abbreviations see figures 2(*a*) and 2(*b*)) and all the α-hydroxy carboxylic acids, except MA (Aldrich Chemical Co.), were products of Fluka Chemicals Ltd. (*ee*>97%). Cholesterol was purchased from Sigma Chemical Co. (>99%). All of these dopants were used without further purification. From MA, HHMA and HIVA, the respective potassium salts (KM, KHHM, KHIV) were prepared by reaction with potassium hydroxide in ethanol at room temperature. The crude products were recrystallized twice from ethyl acetate/ethanol. By way of example, the purity of potassium mandelate and especially the preservation of the absolute configuration of its chiral centre were checked by measuring the specific optical rotation. The obtained $[\alpha]_D^{20}$ value reproduced the literature value within −3% [14].

### 2.3. *Chiral nematic phases*

Homogeneous chiral nematic phases were obtained by weighing the required amounts of dopant and host phase into 4 ml sample vials (Neolab) and rotating the vials slowly for 48 h at about 40°C.

To achieve fingerprint textures, the chiral nematic samples were sealed in microslides of 0·4 mm layer thickness and annealed in a heating stage until an equilibrium texture was observed. The formation of fingerprints of constant width may take several hours, sometimes even some days. The duration of the alignment process decreases with increasing dopant concentration (decreasing pitch) and increasing temperature.

In order to obtain the best possible comparability within the series of the different α-hydroxy carboxylic acids, the pitch measurements versus the dopant concentration were usually performed at the constant difference of 3°C below the clearing temperature. For comparison with the literature data, cholesterol and BNDHP were examined at a constant temperature of 25°C. The pitches of the chiral nematic samples were determined using the distance between a pair of stripes of the fingerprint texture by use of an eyepiece micrometer (Leitz RZD-DO). Each measurement was carried out ten times and averaged. The measuring error was estimated to be less than 5%.

The handedness of the twist was determined from the optical rotation using the results of de Vries theory [15, 5].

## 3. Results and discussion

### 3.1. *Concentration dependence of the clearing temperature*

The addition of a further component to a host phase of course affects the thermodynamic stability of its lyotropic liquid crystalline state. Therefore we started our studies with a check of the influence of the dopants on the chiral nematic to isotropic phase transition. The dopant concentration, $x$, was defined as the molar fraction of aggregated material.

As illustrated by figure 3(*a*), the clearing temperature $T_C$ of the induced phases decreases with increasing dopant concentration for the relatively small and hydrophilic dopants MA, PLA, HIVA, LA. The same holds for the salts KM, KHIV, KHHM at elevated concentrations. In contrast, $T_C$ shifts upwards for the small, but more hydrophobic dopant HHMA, as well as for the two large hydrophobic dopants cholesterol and BNDHP, figure 3(*b*).

In the case of HHMA, at higher dopant concentration (8 and 10%), a two-phase region (isotropic/bâtonnets) occurs between the chiral nematic and isotropic phases, figure 3(*b*). Also the samples with 4 and 6% HHMA became biphasic with increasing temperature, the biphase consisting of chiral nematic droplets (fingerprint) surrounded by a schlieren texture. Finally for the sample with 2% HHMA, a pure nematic-like schlieren texture

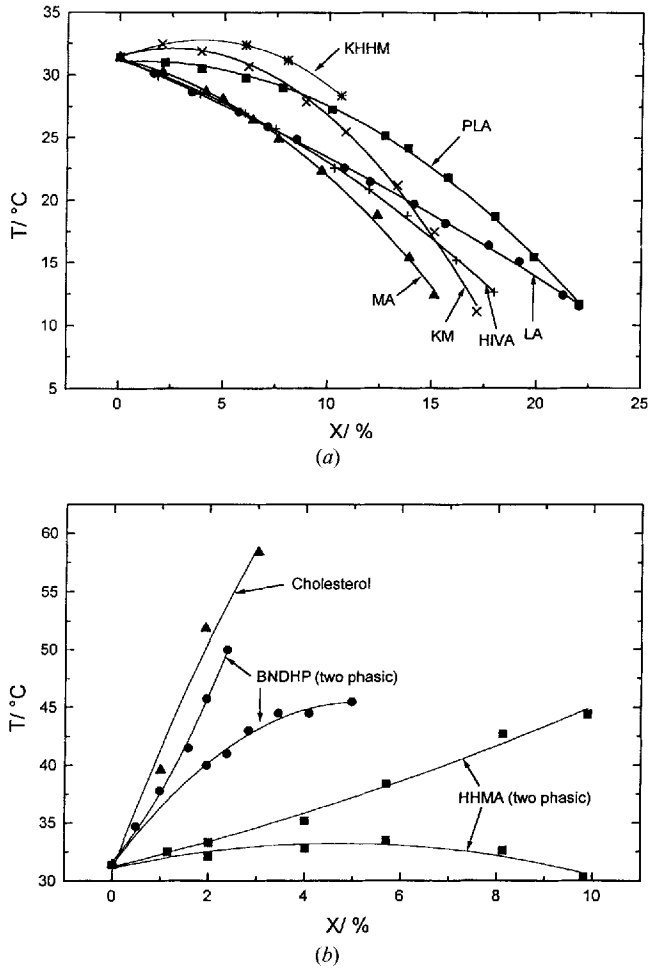


Figure 3. Clearing temperatures, $T_c$ vs. dopant concentration, $x$: (*a*) for the hydrophilic dopants; (*b*) for the hydrophobic and bulky dopants.

instead of the standard fingerprints was observed just below the clearing point. For this dopant, obviously a continuous helix unwinding occurs on approaching the clearing temperature. The temperature dependency of the twist of our systems is currently being investigated in more detail and results will be published elsewhere. For the BNDHP-samples with more than 2% dopant, likewise a biphasic region was observed (isotropic/bâtonnets). The concentration, $x$, of the dopants shown in figure 3(*b*) could be increased only up to 5–10%, because further doping led to the loss of the chiral nematic state; a lamellar phase appeared instead, induced by the dopant (see also [5, 18]).

The influence of the dopant solubilization on the clearing temperature is explained in terms of micelle size variation enforced by the guest molecules. The small and more hydrophilic dopants will prefer locations in the outer, polar shell of the aggregates, whereas the more hydrophobic HHMA, cholesterol and BNDHP will solubilize in the inner, less polar region of the aggregates. The solubilization of dopants in the outer shell of the micelles leads to a stronger curvature of the aggregate surface; smaller aggregates with a reduced anisometry will consequently be formed, which results in the observed clearing temperature reduction (Onsager theory of the nematic state of hard rods or disks [16]).

In the introduction, we mentioned the water solubility of some of our α-hydroxy carboxylic acids. We must assume that there is a distribution of these dopants between water and micelles which is unknown and varies within our series. But, the observed clearing temperature depression is quite similar for all our hydrophilic guest molecules, see figure 3(*a*). To a first approximation we assume that equal numbers of different dopant molecules solubilized in the host micelles lead to equal clearing temperatures. This assumption allows for the comparison of the solubilization degrees of our dopants. We estimate that there is a variation of less than 50% in the partition coefficient; the application of an appropriate factor between 1 and 1·5 to the concentration scale would reduce all clearing temperature curves roughly to one. If we would take into account the different dopant sizes, the concentration scaling factor would reduce further towards 1 (see, e.g. the sequence MA, HIVA, LA, figure 3(a)). Thus we conclude that although the proportion of any dopant present in the micelles is not known exactly, it does not differ too much within the series of the small carboxylic acids; finally we conclude that we can well compare their twisting properties on a relative scale.

### 3.2. *Concentration dependence of the twist*

It is known that for induced chiral nematic phases the twist (i.e. the inverse pitch) is a function of the chiral dopant concentration, $x$. At sufficient dilution (i.e. $x \rightarrow 0$), the absolute value of $p^{-1}$ increases linearly with $x$. Then the helical twisting power (HTP), which can be defined as the slope of the twist versus dopant concentration $(\partial p^{-1}/\partial x)$, is constant over some concentration range [17].

In our study we have always found deviations from linearity (figure 4). Anyway, even more than in the thermotropic case, no linearity may be expected within extended concentration ranges, because lyotropic systems behave like non-ideal mixtures due to possible aggregate size variations. But a common feature of our systems can be recognized from figure 4(*a*): the HTP of the small and rather hydrophilic chiral guests increases with increasing dopant concentration. The opposite is true for the more hydrophobic dopants HHMA, cholesterol and BNDHP, see figure 4(*a*,*b*). For the two bulky chiral solutes cholesterol and BNDHP, the twist

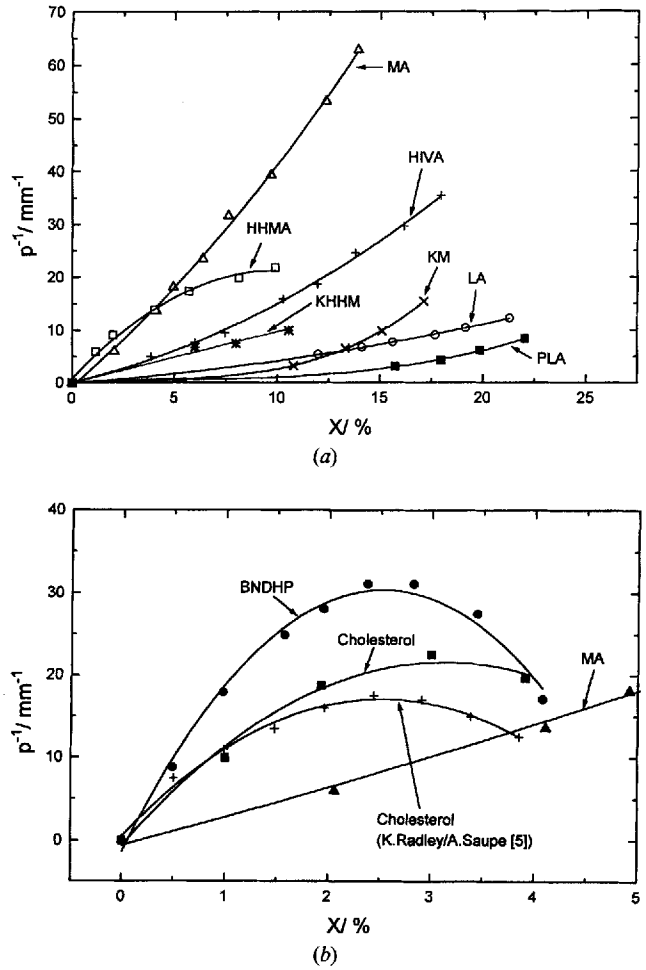


Figure 4. Twist, $p^{-1}$ vs. dopant concentration, $x$: (*a*) for the hydrophilic dopants; (*b*) for the hydrophobic and bulky dopants.

even passes through a maximum; that is, the HTP changes its sign above a certain dopant concentration.

Corresponding to the clearing temperature variation, the positive and the negative deviation from linearity of the twist versus concentration can be understood by the micelle size variation. An over-proportional increase of the twist in the case of the rather hydrophilic dopants is obviously due to a decrease of the micelle size. When more and smaller micelles are formed, the micelle number density increases, and consequently the mean micelle distance is reduced. This can be rationalized by the following arguments: generally, the twist of a chiral liquid crystal can be assumed to depend on the square of the number density $\rho$ of the chiral building blocks (in our case number density of chiral micelles $\rho_m$), because the interaction is pairwise. Further, it must be affected linearly by the chirality $\Delta$ of the micelles:

$$p^{-1} \propto \rho_m^2 \Delta$$

For lyotropic induced chiral nematics the chirality parameter $\Delta$ will increase with the number density of the chiral dopant molecules $\rho_d$; for sufficiently small micelles, $\Delta$ will increase also with the volume $v_m$ of the micelle.

$$\Delta \propto \rho_d v_m \propto x v_m$$

$$\Rightarrow p^{-1} \propto \rho_m^2 x v_m$$

At constant surfactant concentration we conclude:

$$\rho_m \propto v_m^{-1}$$

$$\Rightarrow p^{-1} \propto \frac{x}{v_m}$$

This result gives a qualitative explanation of our experimental observation.

The opposite case of decreasing HTP with increasing dopant concentration is due to the respective decrease of the micelle number density. It has been interpreted already in the 1970s by Radley and Saupe [5] and more recently by Acimis and Kuball [18] as a pretransitional effect caused by the approach to the lamellar phase. Hydrophobic dopants like cholesterol and BNDHP obviously increase the micelle size (as can be deduced from the clearing temperature increase), and the pitch is increased.

For all our data it was possible to achieve a good fit of the twist curves by polynomials of order 2. The first derivative of the fit polynomials provides the HTP values listed in table 1 for some of our dopants (infinite dilution).

Obviously the twisting efficiency decreases within the sequence HHMA, MA, HIVA, LA. It is emphasized here that the HTP-values differ by much more than a factor of 1·5, which had been estimated as the maximum uncertainty in dopant concentration (see §3·1). This makes it certain that the HTP values determined, despite the different water solubility of the dopants, reflect the correct ranking with respect to their twisting efficiency.

From thermotropic induced chiral nematic liquid crystals, it is known that among the physico-chemical parameters responsible for the twisting efficiency of a dopant, the mean electronic polarizability of the molecular moiety directly adjacent to the chiral centre plays an

Table 1. Helix handedness induced by some of the acids and their corresponding potassium salts.

| Dopant | HTP (x→0)/mm$^{-1}$ | Mean electronic polarizability/10$^{-30}$m$^3$ | |
|---|---|---|---|
| *R*(−)-HHMA | −410 | Cyclohexane | 136·6 |
| *R*(−)-MA | −330 | Benzene | 127·7 |
| *S*(+)-HIVA | +90 | Liq. Propane | 79·0 |
| *S*(+)-LA | +25 | Liq. Methane | 35·2 |

essential role [19]. This has been explained by the Goossens theory [6] with the assumption of a dispersion type chiral interaction. Indeed, the same correlation is confirmed for our lyotropic chiral nematic systems through the above listed data which hints at similar physical origins of the chirality transfer.

In view of the fact that toluene possesses a larger mean electronic polarizability than benzene, a surprisingly low twist and HTP-value is obtained for PLA, see figure 4(a). Apparently only the electronic polarizability of the group directly adjacent to the chiral carbon, i.e. the polarizability of the methylene group, has a strong effect. The polarizability of the methylene group is further decreased through the neighbouring electron-withdrawing phenyl group, and thus the resulting twisting efficiency is similar to that of LA.

As previously mentioned, the addition of HHMA to our nematic host phase enhances the clearing temperature. Therefore we can compare this dopant to that of the other hydroxy carboxylic acids only at low dopant concentrations. Anyway, cyclohexane possesses a slightly increased mean electronic polarizability with respect to benzene and thus fits perfectly into the sequence of HTP($x \rightarrow 0$) and polarizability.

A surprising result has been obtained for the three potassium salts investigated. For these dopants one might have expected twist and HTP-values comparable to those of the corresponding acids. But they are found to be much smaller, at low dopant concentrations even too small to be determined from fingerprint textures with sufficient accuracy. To explain this unexpected behaviour, one has to take into account the grossly different dissociation behaviour of the carboxylic acids compared to their salts. The investigated acids are very weak acids; their p$K$ values amount to about +4 in water. They are solubilized in water, as well as in the micelles, almost exclusively as neutral molecules. In the apolar micellar interior, the carboxylic acids are expected to dimerize.

The opposite holds for the corresponding salts. They have to be regarded as nearly completely dissociated. Therefore the solubilization locations accessible for acid and salt are quite different. Whereas the neutral acid molecules could be solubilized in the polar, as well as in the hydrophobic inner part of a micelle, the ionic moieties of the chiral salts will occupy the positions of counterions in our host system; there they compete with the bromide counterions of the surfactant. In solutions of the cationic surfactant hexadecyltrimethylammonium bromide, binding degrees of about 80% (for organic counterions) have been determined [12]. The partition bromide/chiral counterion is not known, but the dependence of the clearing temperature on the dopant concentration, see figure 3(*a*), reveals that the hydrophobic moieties of the salt anions are solubilized quantitatively in the micelles as well.

The HTP-values of the α-hydroxy carboxylic acids are small compared to those of the two bulky dopants cholesterol (HTP = 1390 mm$^{-1}$ and BNDHP (HTP = 2510 mm$^{-1}$) and those of other known chiral molecules (e.g. brucine sulphate, HTP = 3200 mm$^{-1}$ [5]). The helical twisting power is influenced by the orientational order parameter of the chiral dopant in the nematic matrix [6]. We must expect a relatively low orientational order of our carboxylic acids with their small form anisotropy, compared to cholesterol and BNDHP.

From the comparison of cholesterol and BNDHP we see that the phase chirality is by no means exclusively linked to the presence of chiral carbon atoms. BNDHP does not possess any chiral carbon centre, but exhibits a rather strong twisting power. This is in agreement with the presumption that the twisting efficiency of a molecule depends on the polarizability and/or the sterical chirality of special moieties of a molecule. In the case of BNDHP, the whole inherent dissymetric structure possesses a fairly high polarizability. Inherent dissymetric molecules have also been found to be very effective in the induction of thermotropic chiral nematic phases [20].

Although cholesterol and BNDHP possess a considerable twisting efficiency, we could not achieve short pitches in the range of visible light wavelength; this is prevented by the induction of the lamellar phase through the solubilization of these dopants.

### 3.3. *Twist sense*

It is well known that the use of opposite enantiomers of any chiral dopant induces opposite twists, but it cannot be predicted *ab initio* which enantiomer induces a certain handedness. From the comparison of structurally similar, but not homologous dopants, Radley *et al.* [21, 22] concluded that the so-called 'absolute' configuration of a chiral centre does not uniquely determine the twist sense of an induced helix. The corresponding *R,S*-nomenclature characterizes a chiral carbon atom, for example, by means of a ranking of its substituents; the ranking criterion is essentially the atomic number [23] which is, however, obviously not essential for the handedness of an induced twist in a liquid crystal.

Our experiments, too, reveal no simple correlation of the handedness of the chiral nematic helix with any obvious chirality property of the dopant. Remarkably, the two homologous dopants *R*(–)-MA and *S*(–)-PLA induce the same handedness, although their chiral carbons possess opposite absolute configurations. MA and PLA differ only by one methylene group in the length of the chain between the chiral centre and the phenyl moiety, and this might point to an odd/even effect;

similar results have been established for the twist sense of thermotropic systems with respect to the aliphatic spacer length between a chiral centre and the stiff core moiety of a chiral molecule [24]. This aspect is actually under investigation. We suppose that the intramolecular orientation of the stiff phenyl ring with respect to the chiral centre is important, because it affects the intermolecular orientation of the chiral centre with respect to the micelle surface; solubilized molecules with ring moieties prefer orientations of their ring planes parallel to the axes of the hydrocarbon chains of the host micelle [25].

A further unexpected result is that all of the salts investigated induce the opposite twist sense with respect to the corresponding acids, although they possess identical chiral centres (see table 2). In order to be sure of the correctness of this observation, contact preparations of acid- and salt-doped nematic phases were investigated in addition to the measurement of the optical rotation. In an intermediate sample region we observed a homeotropic texture between widened fingerprints, which is evidence of twist compensation, i.e. opposite twist senses of the chiral nematics in contact.

The twist reversal ongoing from an acid to a salt could be due to the dimerization of the acid molecules; the salt ions are monomeric. As a matter of fact the aggregation of two or more chiral particles can form helices of any handedness. This can be rationalized by a geometric consideration as follows. As a model, consider a rectangular plane frame of wires; twist the short sides of the frame against each other with some handedness. Then the long sides of the frame will twist too, but with opposite handedness. Two identically twisted frames can be aggregated to form a helix. The resulting handedness of the helix will depend on the orientation of the aggregated frames with respect to the helix axis. Regarding our system, the handedness of an induced chiral nematic phase could change with the orientation (i.e. with the effective chirality) of the dopant within the nematic phase; we speculate that this might occur with the elongated dimeric acid molecules and the small monomeric salt anions, respectively.

Table 2. Helical twisting powers HTP of the dopants investigated and corresponding mean electronic polarizabilities. The sign of the HTP refers to the handedness of the helix.

| Dopant | Helical Twist Sense |
|---|---|
| *R* (–)-HHMA | – |
| *R* (–)-KHHM | + |
| *R* (–)-MA | – |
| *R* (–)-KM | + |
| *S* (+)-HIVA | + |
| *S* (+)-KHIV | – |

## 4. Model for a chiral nematic phase of disk-like micelles

The idea of our model originates from some observed analogies between lyotropic and thermotropic induced chiral nematic phases (see § 3·2 and 3·3). To illustrate the point, we take a closer look at a micelle as a microscopic object, consisting of about some hundred monomers; in a simplified sketch of a disk-like micelle (disregarding its rim), the long axes of these monomers possess a preferred orientation which is normal to the disk plane. This state of the aggregated monomers resembles a local orientational order. (The local orientational order within a micelle has to be distinguished strictly from the long-range orientational order of the micelles giving rise to the liquid crystalline state.) However, accepting this point of view, it seems straightforward that a chiral guest molecule within an orientationally ordered environment will act similarly as in thermotropic liquid crystals; the chiral dopant induces a twist of the preferred orientation of its neighbouring achiral molecules. In a micelle, the twisting action could be performed even more easily than in a thermotropic nematic, because the micelle has confined dimensions and is surrounded by an isotropic liquid. Therefore the chirality can develop without frustration into two dimensions, from the centre of a micelle towards its rim. Explicitly, our model proposes an average non-zero tilt of the surfactant long axis with respect to the normal of the disk; the tilt angle increases towards the rim of the disk. A sketch of this intramicellar chirality model is given in figure 5 [26].

If the *inter*micellar interaction is sensitive to the orientation of the surfactant long axes on the rim of the micelles (e.g. via the charge distribution), a macroscopic twist of the liquid crystalline phase will arise as a consequence of the local, *intra*micellar twist induced by the solubilized chiral dopants.

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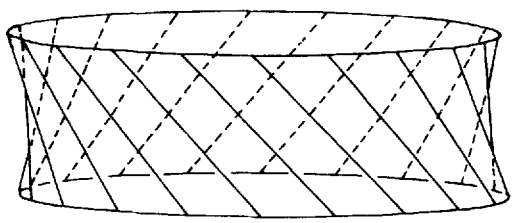

Figure 5. Sketch of a disk-like micelle with preferred tilted orientation of the surfactant molecules.

## References


[1] REINITZER, F., 1888, *Monatsh. Chemie*, **9,** 421.
[2] ACIMIS, M., and REEVES, L., 1980, *Can. J. Chem.*, **58,** 1533.
[3] RADLEY, K., and LILLY, G., 1993, *Mol. Cryst. liq. Cryst.*, **231,** 183.
[4] OSIPOV, M., 1988, *Nuovo Cimento*, **10,** 1249.
[5] RADLEY, K., and SAUPE, A., 1978, *Mol. Phys.*, **3,** 1405.
[6] GOOSSENS, W., 1970, *Mol. Cryst. liq. Cryst.*, **12,** 237.
[7] HENRIQUES DO AIDO, T., ALCANTARA, M., FELIPPE, O., GALVAO, PEREIRA, A., and VANIN, J., 1991, *Mol. Cryst. liq. Cryst.*, **195,** 45.
[8] ALCANTARA, M., and VANIN, J., 1995, *Liq. Cryst.*, **18,** 207.
[9] RADLEY, K., and TRACEY, A., 1984, *Can. J. Chem.*, **63,** 95.
[10] RADLEY, K., and LILLY, G., 1995, *Mol. Cryst. Liq. Cryst.*, **268,** 107.
[11] LEE, H., and LABES, M., 1984, *Mol. Cryst. Liq. Cryst.*, **108,** 125.
[12] REKKER, R., 1977, *The Hydrophobic Fragmental Constant*, (Amsterdam, Oxford, New York: Elsevier) p. 25.
[13] HERTEL, G., and HOFFMANN, H., 1988, *Prog. Colloid Polym. Sci.*, **76,** 123.
[14] *Beilstein E III*, **10,** 445.
[15] DE VRIES, H., 1951, *Acta Cryst.*, **4,** 219.
[16] ONSAGER, L., 1949, *Ann. N.Y. Acad. Sci.*, **78,** 627.
[17] TRACEY, A., and RADLEY, K., 1985, *Mol. Cryst. liq. Cryst.*, **122,** 77.
[18] ACIMIS, M., DORR, E., and KUBALL, H., 1995, *Liq. Cryst.*, **17,** 299.
[19] FINKELMANN, H., and STEGEMEYER, H., 1974, *Ber. Bunsenges. phys. Chem.*, **78,** 870.
[20] GOTTARELLI, G., HIBERT, M., SAMORI, B., SOLLADIE, G., SPADA, G., and ZIMMERMANN, R., 1983, *J. Am. chem. Soc.*, **105,** 7318.
[21] RADLEY, K., and CATTEY, H., 1993, *Mol. Cryst. liq. Cryst.*, **226,** 195.
[22] RADLEY, K., and CATTEY, H., 1994, *Mol. Cryst. liq. Cryst.*, **250,** 167.
[23] CAHN, R., INGOLD, C., and PRELOG, V., 1966, *Angew. Chem.*, **78,** 413.
[24] GRAY, G. W., and MCDONNELL, D. G., 1977, *Mol. Cryst. liq. Cryst. Lett.*, **34,** 211.
[25] KHETRAPAL, C., KUNWAR, A., TRACEY, A., and DIEHL, P., 1975, *Nuclear Magnetic Resonance Studies in Lyotropic Liquid Crystals*, (Berlin, Heidelberg: Springer) p. 56.
[26] VAN DER MEER B., 1979, PhD thesis, Groningen, The Netherlands, p. 28.