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Quantified chirality, molecular similarity, and helical twisting power in lyotropic chiral nematic guest/host systems

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Lyotropic liquid crystals can exhibit phase chirality. The mechanism behind the transfer of chirality between a chiral dopant and a liquid crystalline host phase is still under discussion. Our own recent results and proposals are the following. Lyotropic phase chirality can exist even at very low concentrations of chiral dopants, with less than 1 chiral dopant per 50 micelles. There is evidence for an intramicellar double twist which could be due to the induction of chiral conformations in the achiral surfactant chains. The chirality of arbitrary molecules can be quantified by means of the 'Hausdorff distance'. Increasing chirality of a dopant does not necessarily imply increasing helical twisting power, and molecular similarity between chiral guest and achiral host is essential for effective chirality transfer.

'*Παντα ρει*'. *Everything flows.*

We propose a supplement to these famous words of Heraklit: 'Almost everything is chiral'.

1. Introduction

An arbitrary object is termed chiral if it cannot be superimposed upon its mirror image. In the past a considerable amount of research has been published on chiral liquid crystals, mostly on thermotropics (cholesteric, blue, and a variety of smectic phases) [1]. Lyotropic liquid crystals can also exhibit phase chirality. There exists a lot of data about the magnitude and sense of the twist in several micellar chiral nematic systems made up from chiral surfactants or from achiral surfactants doped with some chiral additive [2].

Figure 1 shows the result of a typical experiment: the twist (which is the inverse pitch p^{-1}) is plotted versus the concentration x of the chiral dopant in an achiral host phase. Often, a linear relation is found at sufficiently low dopant contents. Nevertheless, the example shown is uncommon, as the twist of the sample is clearly non-zero even at only 1 chiral molecule per 50 micelles.

So far, the 'mechanism' behind the development of phase chirality in lyotropic solutions has not been fully explained. The discussion of structural models has not yet moved far beyond the first report on 'cholesteric' lyotropic phases by Radley and Saupe in 1978 [3]. They proposed two possible ways of transfer of chiral information between micelles: (i) a chiral sterical interaction between micelles of chiral shape, and (ii) a chiral dispersion force acting directly between chiral molecules located in neighbouring micelles. In the face of the example of figure 1, mechanism (ii) is more than doubtful. In any case, the proposed mechanisms need extensive elaboration and specification.

Recently we have published a more detailed model of intramicellar chirality based on the assumption of a local twist of the preferred orientation of the surfactant molecules within disc-like micelles, resulting in a double twist cylinder [4] (see figure 2).

2. Definition of a chirality measure

To a certain extent, experimentally determined helical twisting powers [$\mathrm{HTP} \equiv (\partial p^{-1}/\partial x)_{x\to 0}$] depend on the host phase, but in the first instance they are properties of the dopants themselves. Some chiral guest molecules twist a host phase effectively, whereas others do not. The question arises as to whether this experimental fact is due to a 'difference in chirality' between the dopants. Therefore we looked for correlations between the helical twisting power of a dopant and its chirality. In order to check this point, a parameter needs to be defined which

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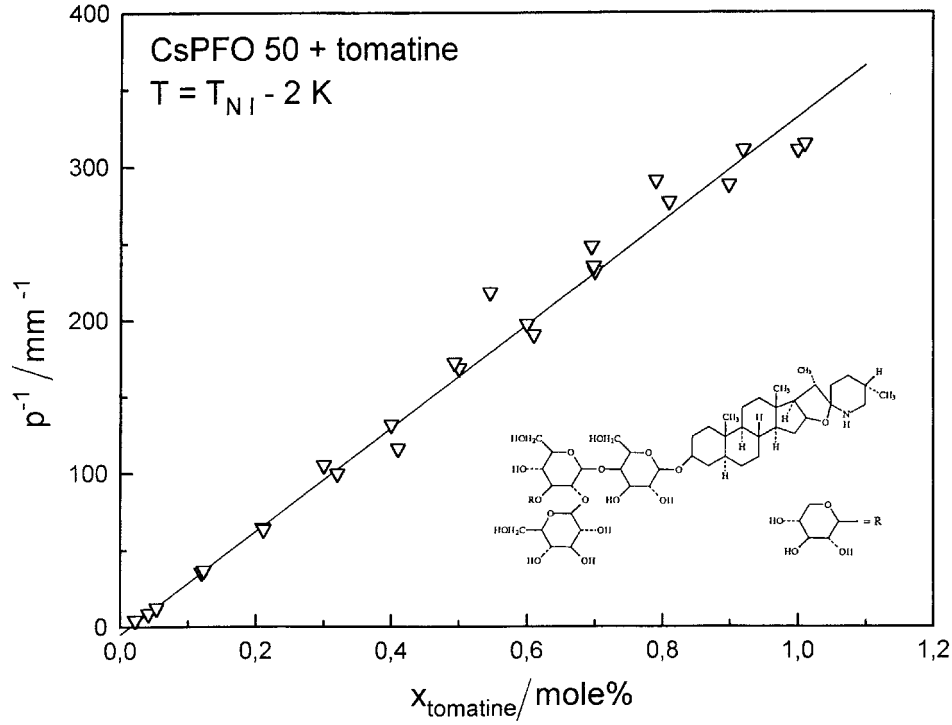

Figure 1. Twist versus dopant concentration ($x \equiv$ mole fraction of aggregated matter; CsPFO 50 ≡ host phase 50 wt % cesium pentadecafluoro-octanoate/50 wt % water).

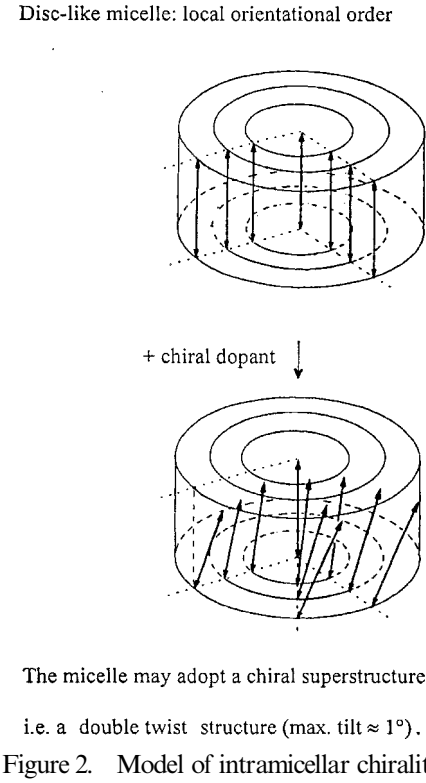

Figure 2. Model of intramicellar chirality.

quantifies molecular chirality. Chirality characterizes a certain symmetry; a quantification requires the specification of a relevant physical property exhibiting the chirality in question. The most obvious way is to look at the chirality of the spatial topology of a molecule, and there are successful reports in the literature which consider the 'surface' of molecules [5]. This procedure works especially well for bridged aryl compounds which are effective dopants in thermotropic host phases. An extensive description of the possibilities of quantification of chirality is given in the review article of Mislow, Auf der Heyde and Buda [6].

In our approach, we represent a given molecule by the spatial coordinates of its atoms. The chirality of a group of points can then be defined via the geometrical differences between the object and its mirror image. The minimized and normalized lack of overlap, achieved by translations and rotations, is our measure for the chirality of the object; it can be quantified by the so-called minimal Hausdorff distance H_{min} as proposed by Mislow *et al.* [6]. Mathematically, the Hausdorff distance between two groups of points in space is defined as follows. Let the set of coordinates of the atoms of a chiral molecule be Q, and the corresponding set of the mirror image be Q'. The shortest distance between a point $q' \in Q'$ and Q is given by $\delta(Q, q')$. Then the Hausdorff distance $H(Q)$

is

$$H(Q) = \max[\sup \delta(Q, q'); \sup \delta(Q', q)].$$

$H(Q)$ depends on the relative position and orientation of Q with respect to its mirror image Q'. It can be minimized by translations and rotations; the resulting $H_{min}(Q)$ corresponds to the maximum overlap of object and mirror image. After normalization to the absolute size of the object, it represents the desired chirality measure; it can take values between zero and one.

In order to apply the formalism to real molecules, their atomic coordinates are determined by means of molecular modelling (software: MSI, workstation: SGI Indy). The set of coordinates of both enantiomers is then used as the input data for a further computer package (Match3d) which searches for the best spatial overlap between the sets of coordinates. A 'branch and bound'-procedure [7] was chosen as the search algorithm; this calculates global minima of the Hausdorff distance within a preset error interval. The reliability and performance of our procedure was checked by comparison with literature data for a chiral tetrahedron [6]. The method is suited to calculations for arbitrary molecules, and details will be described elsewhere [8].

In applying this method, one has to be aware of the fact that even simple molecules can adopt a large number of different conformations, each of which will exhibit a distinct Hausdorff distance. In most cases it is impossible to determine all the relevant conformational states of a chiral guest molecule in a host solution and to estimate or measure their population. Moreover, the calculation of a chirality parameter averaged over all conformations would lead to a further problem: the Hausdorff distance does not contain a sign.

On the other hand, the HTP of any chiral molecule can be positive or negative (right or left handed helix, depending also on the host phase). Radley *et al.* [9] reported that different conformers of a chiral dopant can contribute opposite amounts to the HTP in the same host phase. Thus the proposal of some correlation between the Hausdorff chirality parameter and the HTP must take signs into account. Therefore we restrict our discussion to a few single conformations (without averaging) which are probably the most essential ones in a micellar phase and discard discussion of the handedness.

3. Correlation between the Hausdorff chirality measure and the helical twisting power

Figure 3 shows the chiral molecules investigated. These kinds of dopant were chosen because (i) they possess only one chiral centre, (ii) their structure can be varied systematically by changing one substituent, (iii) they are amphiphilic and will solubilize within our host micelles with a non-zero orientational and positional order, (iv) the total numbers of possible conformations lie within a manageable range.

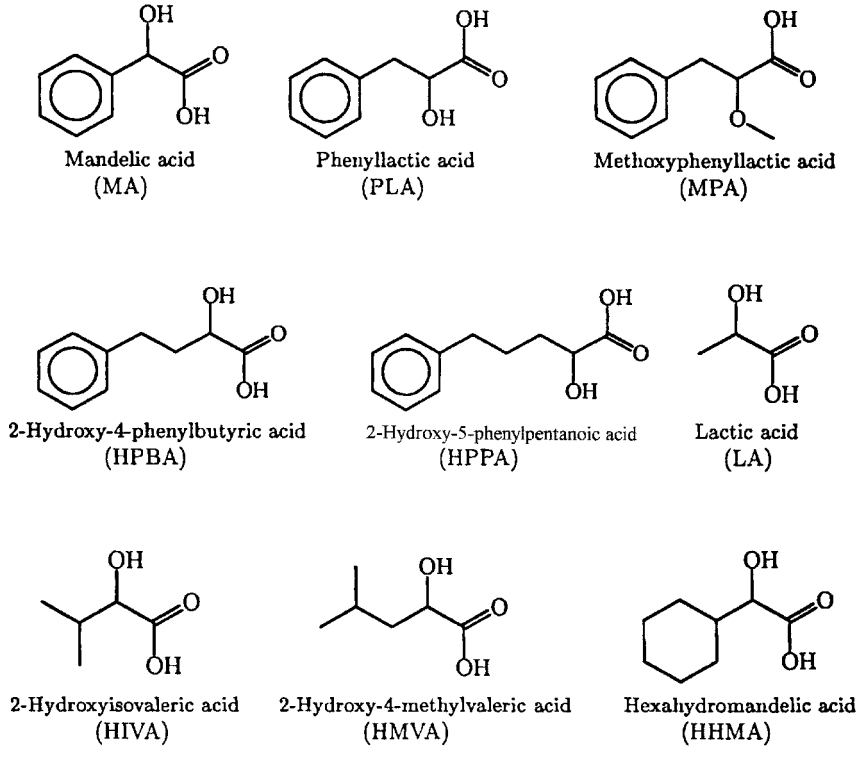

Figure 3. Chiral dopants investigated.

Figure 4 shows a plot of the HTP of the molecules of figure 3 versus their Hausdorff distances. Although there is a large scatter of the data, a trend can be clearly recognized for some of the smallest α-hydroxy carboxylic acids: their HTP decreases with increasing chirality. From a naive point of view the opposite had been expected! In order to reveal the background to this surprising result, we applied the Hausdorff formalism to literature data of a thermotropic system. Figure 5 shows the evaluation for different phenyl- and methyl-substituted oxiranes and thiiranes in the thermotropic host phase MBBA [10]. Obviously a similar inverse relationship between HTP and the chirality measure also occurs for this thermotropic induced cholesteric system. Gottarelli *et al.* [10] interpreted their HTP data in terms of molecular similarity between the stereochemistry of the guest and host molecules. A detailed discussion of this behaviour is now given.

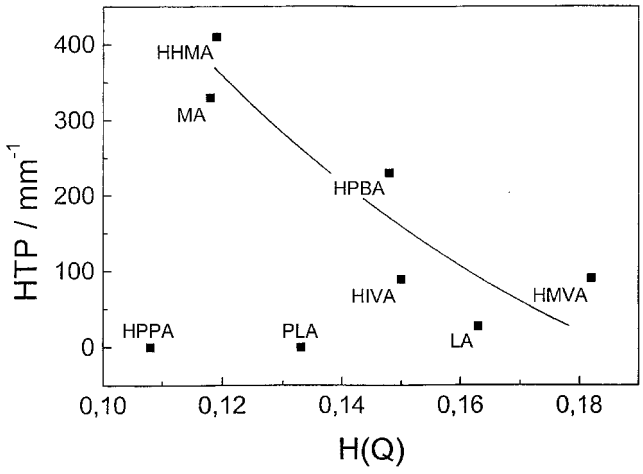

Figure 4. Helical twisting power (HTP) of the dopants investigated in the lyotropic host phase CDEA (≡ 28.3 wt % cetyldimethylethylammonium bromide/4.3 wt % decanol/67.4 wt % water) versus the Hausdorff chirality parameter, $H(Q)$.

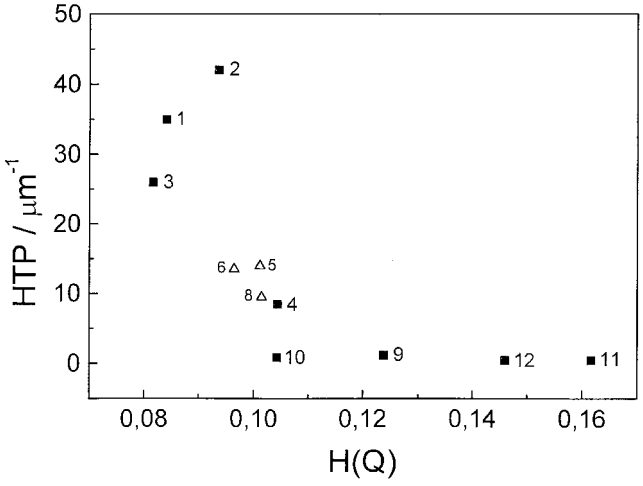

Figure 5. Helical twisting power (HTP) of some substituted oxiranes and thiiranes in the thermotropic host phase MBBA (≡ *p*-methoxybenzylidene *p*-*n*-butylaniline) versus the Hausdorff chirality parameter, $H(Q)$. HTP data and corresponding dopants: see Gottarelli *et al.* [10].

4. Molecular similarity

In 1984, Solladié and Zimmermann published a review on thermotropic induced cholesteric liquid crystals [11]. On the basis of experimental results they stressed the importance of the similarity of the molecular shape of chiral dopant and achiral host phase. The argument was based on a stronger molecular interaction corresponding to a 'better packing' and a 'better chirality transfer'.

For thermotropics, it is reasonable that the similarity of shape implies a similarity of molecular size. In lyotropics there can be some doubt about this argument because the building block of the phase is not a single molecule but a micelle of about 200 monomers. As mentioned in the introduction, it was not clear if the transfer of chiral information within the lyotropic phase occurs directly between chiral molecules in adjacent micelles or if an intramicellar transfer is essential, occurring via a chiral interaction between chiral dopant and achiral surfactant molecules. In the first case, similarity of *molecular* size and shape should play only a minor role, whilst in the latter it should be as essential as in thermotropics. Our attempt to deal with this question was to modify the Hausdorff distance algorithm and to calculate a molecular similarity measure $H_x(Q)$. The new algorithm compares the sets of atomic coordinates of arbitrary molecules (i.e. the chiral dopant and the host phase molecule) instead of enantiomers. The index x specifies the host phase. Increasing $H_x(Q)$ means decreasing similarity [$H_x(Q)$ is essentially a 'dissimilarity measure']. For each dopant we calculated the H_x values for several conformations. Their relative energies were determined by means of molecular dynamics software (MSI) in order to average the H_x results according to Boltzmann statistics. For the host phase molecule, the lowest energy conformation was taken as the input of the $H(Q)$ algorithm.

As before, the data for the thermotropic mixtures of Gottarelli *et al.* [10] were used as a reference, see figure 6. The evaluation shows that obviously the oxirane dopants can be divided into two groups: the first correlates well with the expected course of decreasing HTP with decreasing similarity, whilst the second clearly deviates. A common feature of the first group is that all substituents are hydrocarbon in nature, while the members of the second group possess a carboxylic acid group connected to at least one chiral carbon. The deviation of the second

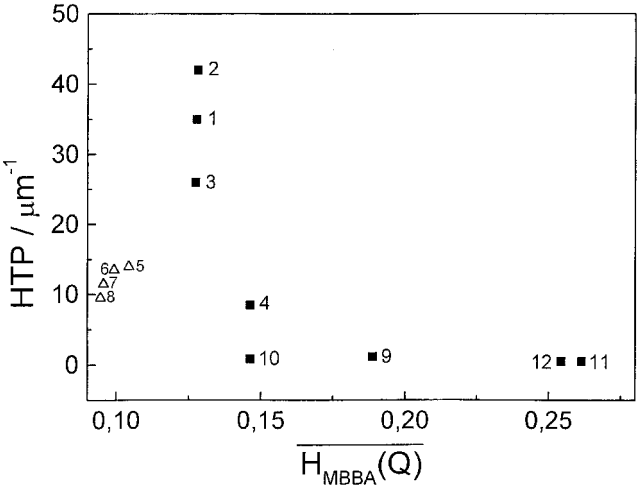

Figure 6. Helical twisting power (HTP) of the thermotropic systems of figure 5 versus the Hausdorff similarity parameter.

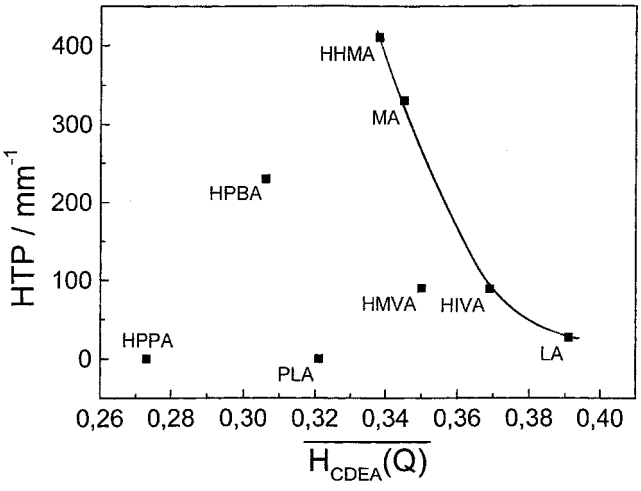

Figure 7. Helical twisting power (HTP) of the lyotropic systems of figure 4 versus the Hausdorff similarity parameter.

group indicates the importance of not only the similarity of geometry, but also of the similarity of chemical functionalities.

The analogous evaluation was then performed for our lyotropic systems and is shown in figure 7. The fit of the data to a curve is not as close as in figure 6, but a trend to the expected behaviour can be recognized. The HTPs approach zero with increasing dissimilarity. The smallest members of the series of homologues fit the curve best; their conformational variability is low and presumably matched well by our molecular modelling.

5. Conclusions

We have shown that in thermotropic as well as in lyotropic induced chiral-nematic phases there is no simple increase of helical twisting power with the quantified geometrical chirality of the dopant. Instead, a clearly dominating influence of similarity between host phase molecules and chiral dopant molecules is exhibited. Nevertheless we should expect that a suitable combination of Hausdorff chirality and Hausdorff similarity parameters will correlate well with experimentally observed HTPs; this has to be investigated in the future.

The strong influence of guest/host molecular similarity proves the essential role of a transfer of chirality information from the dopant to the surfactant molecule and confirms the evidence of an intramicellar chirality. In future extensions of this work, further physical properties of the molecules under consideration (e.g. mass density, electron density, ...) can be incorporated into a more sophisticated Hausdorff distance by increasing the dimensionality of the point groups representing the molecules.

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