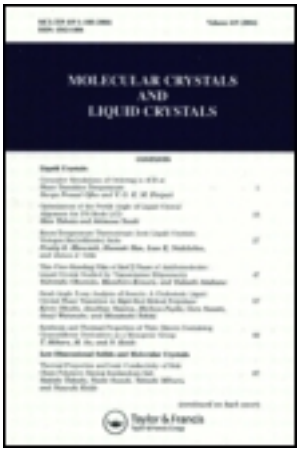

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Prediction of Pitch in Twisted Nematics: Puzzling Cases

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Prediction of Pitch in Twisted Nematics: Puzzling Cases

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The correlation between structure of chiral molecules and macroscopic properties of cholesteric phases is not obvious, but often the experimental behaviour can be rationalised by resorting to simple rules. However, there are cases in which solvent / temperature changes or introduction of substituents in the chiral molecules can produce dramatic and unexpected effects, including helix inversion. Some significant examples will be presented and discussed on the basis of theoretical predictions derived by the 'surface tensor' mean field model for molecular structures optimised with quantum-mechanical methods.

Keywords: chirality; cholesterics; mean field

INTRODUCTION

Handedness and pitch of pure and induced cholesteric phases depend on the coupling between chirality and orientational behaviour of the chiral mesogens or dopants. Therefore, there is no simple and general relation between the absolute configuration of the molecules and properties of the chiral mesophases. However, some empirical rules have been derived from experimental observations. For instance, it is well known that series of derivatives with a given absolute configuration produce twisted phases with the same handedness. This can be understood in view of the similar orientational behaviour expected for compounds belonging to a homologous

series. The above-mentioned empirical rule is no longer followed when bulky substituents are introduced, but again this is not surprising because large substituents can change completely the tendency to alignment of a substrate, besides bringing their own possible contribution to the molecular chirality. Less obviously, in some cases small susbtituents, which do not seem to perturb significantly the molecular structure, as well as solvent or temperature changes can produce dramatic and unexpected effects, including helix inversion, in the properties of the chiral mesophase.

A few years ago some of us presented a model relating the twisting power of chiral probes dissolved in nematics to the structure of the chiral dopants [1,2]. The model is based on the idea that the orienting potential experienced by a molecule depends on the morphological properties, such as anisotropy and helicity, of its surface. The twisting power of various series of chiral molecules, rigid and flexible, was successfully predicted by this model [2-4].

It is then challenging to use the model to investigate some examples of behaviour in contrast with simple expectations. In particular, we shall discuss in the following : (i) the ability of biphenyl derivatives, with very similar structure and the same absolute configuration, to induce cholesteric phases of opposite helicity; (ii) the dependence on medium and/or C(3) substituent of the helix pitch produced by cholesteryl derivatives.

MODEL AND CALCULATIONS

The model has been presented elsewhere, therefore only some relevant definitions will be reported in the following for the help of the reader.

The orienting potential experienced by a molecule in a cholesteric phase with helix pitch p or corresponding wave vector $q=2\pi/p$, at the origin of a laboratory frame (XYZ) having the Y axis parallel to the helical axis and the Z axis parallel to the director, is approximated in the limit $q\to 0$ by the following expression:

$$U(\Omega)/k_BT = -\varepsilon\sum_m (T^{2,m*} - qQ^{2,m*})D^2_{0m}(\Omega) \qquad (1)$$

where $D^2_{0m}(\Omega)$ are Wigner matrix components having as argument the Euler angles from the laboratory to a molecular (x,y,z) frame, ε is temperature dependent parameter giving the strength of the orienting interaction and $T^{2,m*}$, $Q^{2,m*}$ are irreducible spherical components of the surface and helicity tensors, respectively.

The second-rank traceless tensor **T** is defined as:

$$\mathrm{T} = -\sqrt{1/6}\int_S (3\vec{s}\otimes\vec{s} - 1)\, dS \ , \tag{2}$$

where the integral is over the molecular surface and $\vec{s}$ is a unit vector normal to the surface element dS. It follows from eq. (1) that, since $q \to 0$, the tensor **T**, which measures the anisometry of the molecular surface, essentially determines the orientational behaviour of the molecule, which can be quantified by the Saupe ordering matrix **S** [5].

The second-rank traceless pseudo-tensor **Q** is defined by:

$$\mathrm{Q} = \sqrt{3/8}\int_S \left[\vec{s}\otimes(\vec{s}\times\vec{r}) + (\vec{s}\times\vec{r})\otimes\vec{s}\right] dS \ , \tag{3}$$

where $\vec{r}$ is the position vector of the surface element dS in the molecular frame. This tensor measures the helicity of the molecular surface; in particular, its diagonal elements give the helicities along the coordinate axes. The average value of the helicity tensor in the liquid crystal phase is proportional to the chirality order parameter $\mathcal{Z}$, defined as

$$\mathcal{Z} = -\sqrt{2/3}\,\mathbf{Q}\cdot\mathbf{S}, \tag{4}$$

which is the key property of the chiral molecule entering the expression for the helical twisting power β:

$$\beta = \frac{RT\varepsilon\mathcal{Z}}{2\pi K_{22} v_m} \ , \tag{5}$$

where R is the gas constant, while K_{22} and v_m are elastic constant and molar volume of the solvent.

Analogous expressions can be written for the inverse pitch in pure cholesteric phases, in which case K_{22} and v_m are elastic constant and molar volume of the cholesteric nematics. In more generality, for cholesteric mixtures we can write

$$\frac{1}{p} = \frac{RT\varepsilon\sum_i x_i \mathcal{Z}_i}{2\pi K_{22}\sum_i x_i v_i} \tag{6}$$

where x_i is the mole fraction of the i-th component, v_i its molar volume and $\mathcal{Z}_i$ its chirality order parameter.

The quality of the predictions depends on the availability of reliable equilibrium structure and internal potentials for the chiral molecules. In the present case structures were obtained by a semi-empirical quantum-mechanical method (AM1), implemented in the package Gaussian 94 [6].

Once the molecular geometry is known, the molecular surface can be defined in the simplest way as the outer envelope of an array of overlapping van der Waals spheres centred at the nuclear positions [2,3]. Alternatively, the surface described by a sphere rolling over the van der Waals envelope [7] or that enclosing practically all the molecular charge density [8] have been considered. In the calculations presented here the rolling sphere method has been adopted, with a sphere radius R=3Å.

As appears from eqs. (5) and (6), a quantitative comparison with experimental data would require information about bulk properties, such as the twist elastic constants and the orienting strength at the temperature of measurement, which in many cases are not available. However, reminding that the factor between helical twisting power (or inverse pitch) and chirality order parameter is of the order of the unity [1-4], it makes sense, especially when different chiral molecules in the same solvent are considered, to compare experimental data directly with chirality order parameters $\boldsymbol{2}$, calculated at ε values providing reasonable values of the orientational order parameters. The data presented in the following refer to ε=0.04Å^{-3}.

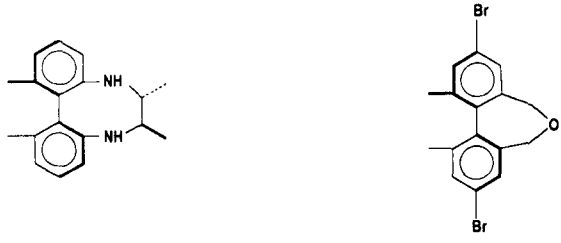
RESULTS AND DISCUSSION

A) Biphenyl derivatives

It has been observed that biphenyl derivatives and, in more generality, biaryl compounds, generally induce cholesteric phases with the same handedness as the helicity along the bond connecting the aryl moieties [9,10]. Thus, bridged derivatives, in which the twist angle between the aromatic units is constrained to a *cisoid* conformation, are expected to give left-handed or right-handed cholesterics according to their the M or P helicity. Predictions based on the surface chirality model for biphenyl, binaphtyl and a number of their derivatives are in agreement with such experimental findings [2-4].

Exceptions to this general rule were recently found for some biphenyl derivatives [11]. Given the close similarity to other derivatives presenting the regular behaviour, no simple explanation for such an experimental result could be found [12]. In order to get some understanding and to test the ability of our model to catch the relevant features of the molecular interactions detrmining the cholesteric pitch, we performed calculations for the P enantiomers of the biphenyl derivatives shown in Fig.1 for which, in spite of

the similar structure, twisting powers fairly equal in magnitude, but opposite in sign were measured.



(a) (b)

FIGURE 1. Biphenyl derivatives under investigation

Results of the calculations are summarized in Table I. Good agreement between theoretical and experimental data appears from the Table; in particular, the handedness of the cholesteric phases induced by the compounds (**a**) and (**b**) is correctly predicted and the reason for the different sign can be understood by analysing in more detail the results. We can see in the Table that the surface helicities along the principal axes of the ordering matrix S are not very different for the two molecules, which on the other hand have a quite different orientational behaviour, as shown by the order parameters S_{ii}. The compound (**b**) has a strong tendency to align the *para* axis with the mesophase director, and no significant preference for the orientation of the other molecular axes. On the contrary, the (**a**) molecule shows a disc-like behaviour: the normal to the approximate molecular plane, which tends to orient perpendicular to the director, is now the main ordering axis, and alignment with the director of the C_2 axis is strongly preferred to that of the *para* axis. The main cause of the different behaviour of (**a**) and (**b**) is the presence of the 4,4′ substituents, which confer to the latter an elongate shape in the direction of the *para* axis.

As a further test, we considered two additional systems, labeled as (**a′**) and (**b′**), the former corresponding to (**a**) with two additional Br atoms in the 4,4′ positions, and the latter to (**b**) without the Br atoms. The results obtained for these systems, also reported in Table I, confirm the interpretation of the behaviour of (**a**) and (**b**). The addition of Br atoms to (**a**) has the effect of favouring the alignment of the *para* axis, so that the molecule, analogously to the (**b**) derivative, is predicted to induce left-handed cholesterics. On the contrary, the elimination of the Br atoms in (**b**) reduces the tendency to

alignment of the *para* axis; it turns out that **(b')** is characterized by a very low chirality order parameter, whose sign is strongly affected by the degree of ordering of the mesophase. The theoretical predictions are again in good agreement with experimental data, available for **(b')**.

TABLE I Components of the **Q** tensor and of the ordering matrix **S** in the principal axis frame of the chirality order parameters. The axes are labeled in such a way that z and x are close to the the *para* axis and parallel to the C_2 axis, respectively. Twisting power values refer to measurements in E7 for **(a)** [10] and in K15 for **(b)** and **(b')** [11].

	(a)	**(a')**	**(b)**	**(b')**
Twist angle	66°	66°	52°	52°
P/M	P	P	P	P
Q_{xx} /Å^3	-60	-72	-70	-58
Q_{yy} /Å^3	13	26	41	29
Q_{zz} /Å^3	47	46	29	29
S_{xx}	0.21	0.01	-0.17	0.01
S_{yy}	-0.23	-0.28	-0.31	-0.26
S_{zz}	0.02	0.27	0.48	0.25
$\mathcal{Z}$ /Å^3	11.6	-3.7	-10.1	0.2
β /μm^{-1}	20	-	-19.3	-0.3

B) Cholesteryl derivatives

Cholesteryl derivatives are the the compounds for which the existence of mesophases was first discovered, more than a century ago, and since then these compounds have been widely investigated. It has been found that, in spite of the presence of the same chiral centres with the same absolute configuration, located in the steroid skeleton, the handedness of the pure phases depends on the substituent attached at the C(3) positions. Thus, for mixtures of derivatives with different handedness helix inversion with temperature and concentration can be observed. Moreover it has been found that the handedness of the twisted phase cannot be univocally associated with

a given derivatives, since sign changes can occur when the medium is changed. Some experimental results are summarized in Table II.

TABLE II Inverse pitch and helical twisting power measured for cholesteryl derivatives. CH:cholest-5-ene; COH: cholesterol; CCl, CBr, CI: cholesteryl chloride, bromide and iodide; Cac, Cno, Cmy: cholesteryl acetate, nonanoate, myristate.

		CH	CCl	COH	CBr	CI	Cac	Cno	Cmy
$p^{-1}/\mu m^{-1}$	[13,14]	(+7)	+2	(+2)	+1.5	-0.2	-1.5	-2.5	-3
	Comp.mixt.[15]		+3	+2			-1.2		-7.5
$\beta/\mu m^{-1}$	5CB [16]		-3.5	-5.6		-1.5	-11.3	-9.6	-9.3
	MBAB [17]		-8.2	-5.7					-16,7
	MBBA [17]		-17.4	-1.1					-25.2

The analysis of these compounds is made arduous by their structural complexity. The steroid core is rather rigid but, due to the presence of eight chiral centres, its helicity is very sensitive even to small structural changes. In addition, the helicity is strongly influenced by the conformation of the flexible tail in C(17) and, in the case of fatty acid esters, also by that of the chain attached to C(3). Thus, without the pretence to perform an exhaustive investigation, but with the simple aim of shedding some light on the behaviour reflected by the experimental data, and in particular of analysing the effect of the C(3) substituent, we have calculated the chirality order parameter for selected structures of the derivatives listed in the Table.

(a) **(b)**

FIGURE 2 Structures considered for cholesteryl acetate.

One structure, hereafter denoted as **(a)**, was derived from crystal data of cholesteryl acetate [18], by replacing the acetate group with the various

groups present in the derivatives. In the case of nonanoate and myristate the fatty acid chain was taken in the *all-trans* conformation. Another structure, labeled as **(b)**, was obtained for each compound by optimizing the **(a)** geometry. In the case of fatty esters derivatives two conformers were considered, denoted as **(b)** and **(b')**, very close in energy and corresponding to opposite angles between the $C_{ring}OC_{carbonyl}$ and $OC_{ring}H$ planes. The **(a)** and **(b)** structures for cholesteryl acetate are shown in Fig. 2. The two structures differ in the geometry of the steroid core, which results to be slightly bent in the crystallographic geometry, and in the torsional angles of the C(17) alkyl chain, with differences however smaller than 15°.

The calculations indicate that all derivatives have a strong tendency to align the long molecular axis, as could be expected from their elongated shape, with minor differences between the two structures as far as the orientational behaviour is concerned. On the contrary, the helicity of the molecular shape comes out to be strongly affected by the relatively small changes in the geometry. This leads, for all but the long chain fatty acid esters, to opposite signs of the chirality order parameters for the two structures. Given the complexity of the systems, the results are not sufficient for an interpretation of the experimental behaviour, however they are rather illuminating. Firstly, left handed cholesterics with pitches decreasing with chain length are predicted for long chain esters, in keeping with experimental observations. There is more uncertainty about the sign of the helix produced by the other cholesteryl derivatives, which appear to be strongly affected by structural changes. This also agrees with the experimental findings: the different handedness observed when these derivatives are dissolved in cholesteryl and nematic solvents can be explained in terms of even small readjustments produced by interactions with the environment. Going into more detail, the theoretical results would suggest that a geometry close to that adopted in cholesteryl crystals is stabilized in cholesteryl media, but not in other nematic solvent.

TABLE III Chirality order parameters calculated for different structures of the cholesteryl derivatives listed in Table II.

χ /Å^3	CH	CCl	COH	CBr	CI	Cac	Cno	Cmy
(a)	4.8	3.5	3.7	3.9	3.0	4.7	-18.8	-30.9
(b) ; (b')	-7.6	-6.9	-7.3	-7.5	-7.1	-5.3; -9.0	-8.0; -8.2	-12.5;-4.8

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