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Preliminary Communication

A shape model for the twisting power of chiral solutes in nematics

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The twisting power of chiral probes in nematics is interpreted in terms of a shape model, in which the surface elements of the solute molecules tend to align with the local director. The theoretical treatment is based on a previous approach, suitable for relating order parameters in nematics to molecular shape, and leads to the definition of a molecular pseudo-tensor whose orientational average determines the pitch and handedness of the helical macrostructures. Results of numerical calculations performed for distorted biphenyl and binaphthyl molecules are in agreement with the experimental results.

It is well-known that small amounts of chiral probes dissolved in nematics are able to induce the transformation to a cholesteric mesophase [1, 2]. In such a phase, more properly referred to as a *twisted* or *chiral nematic*, the local director **d** rotates upon translation along the perpendicular direction identified by the unit vector $\mathbf{u}_Y$, giving rise to a helical structure of characteristic pitch p.

At low molar fractions, a helical twisting power β can be defined for the chiral solute in terms of the p-value, as

$$1/p = \beta x. \tag{1}$$

The twisting power of the guest molecule cannot be simply related to its optical rotation, and it depends upon the nature of the nematic host. Prediction of the helical sense of the induced cholesteric is a difficult problem, whose solution may require detailed knowledge of the solute–solvent interactions. However, the relevance of the probe's geometrical structure can be easily inferred from the available data. First of all, enantiomers generate cholesteric phases with opposite helical senses. Second, in series of similar solvents, the twist sense of the chiral solute determines unequivocally the right- or left-handedness of the cholesteric pitch.

In the following text, we shall propose a model for relating the twisting power of a molecule to its shape, by extension of a previous approach in which orientational properties in nematics were also related to the molecular shape [3, 4].

The solute is assumed to orient in such a way that each surface element dS of the molecule tends to be aligned with the local director **d**. The orienting potential is then written as the integral over the solute surface

$$U/k_{\mathrm{B}}T = \varepsilon \int \mathrm{d}S\, P_2(\mathbf{d}\cdot\mathbf{s}), \tag{2}$$

where P_2 is the second-order Legendre polynomial, ε is a constant related to the orienting strength of the medium, and **s** is a unit vector perpendicular to the surface element dS. In a nematic monodomain, **d** has a unique orientation through the sample, while in cholesteric phases it varies along the Y-axis according to

$$\mathbf{d}(Y) = \mathbf{u}_Z \cos(qY) + \mathbf{u}_X \sin(qY) \tag{3}$$

with $q = 2\pi/p$. Since the molecular dimensions are much smaller than the helical pitch, the orienting potential can be expanded up to linear terms in q. Then, for a molecule fixed at the origin of the laboratory frame we can write

$$U/k_{\mathrm{B}}T \approx \varepsilon \int \mathrm{d}S\, P_2(\mathbf{u}_Z\cdot\mathbf{s}) + 3\varepsilon q \int \mathrm{d}S (\mathbf{u}_X\cdot\mathbf{s})(\mathbf{u}_Y\cdot\mathbf{r}(\mathrm{s}))(\mathbf{u}_Z\cdot\mathbf{s}), \tag{4}$$

where $\mathbf{r}(\mathrm{s})$ is the vector position of the surface element. This expression can conveniently rewritten as

$$U/k_{\mathrm{B}}T = \varepsilon \sum_{i,j} Z_i Z_j \langle \tfrac{3}{2} S_i S_j - \tfrac{1}{2}\delta_{i,j}\rangle + 3\varepsilon q \sum_{i,j,k} X_i Y_j Z_k \langle r(\mathrm{s}) S_i R_j S_k\rangle \tag{5}$$

where (X_i, Y_i, Z_i) and (S_i, R_i) represent direction cosines of $(\mathbf{u}_X, \mathbf{u}_Y, \mathbf{u}_Z)$ and $(\mathbf{s}, \mathbf{r})$ in a molecular frame, and $r(\mathrm{s})$ is the length of the vector $\mathbf{r}(\mathrm{s})$. Angular brackets denote integration over the molecular surface. The second-rank Cartesian tensor of components $T_{ij} \equiv \langle \frac{3}{2} S_i S_j - \frac{1}{2}\delta_{i,j}\rangle$, and the third-rank tensor of components $Q_{ijk} \equiv 3\langle r(\mathrm{s}) S_i R_j S_k\rangle$ can be referred to as the ordering shape tensor and the

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chirality shape tensor, respectively. The definition of the shape tensor **T** differs by a numerical factor from that given elsewhere [4]. The chirality shape tensor can be related to the pitch of the induced cholesteric phase by interpreting, at the molecular level, the results of continuum theories [5, 6].

The starting point is the definition of an overall free energy for the solution, constructed from additive contributions from a purely elastic term A_d^{solv} of the nematic solvent, and the surface-induced distortion energy calculated according to equation (2) for all solute molecules. Averaging over the solute configurations should then be performed in order to derive an explicit functional dependence of the distortion free energy $A_d(q)$ upon the wavenumber q. The detailed derivation will be presented elsewhere [7]; here it will suffice to say that the resulting effect is similar to the distortion of a nematic arrangement induced by the twisting of surfaces to which the director is anchored [5]. The distortion free energy per unit volume, in the case of diluted solutions of chiral probes in nematics, is obtained in the following form:

$$A_d(q) = A_d^{\text{solv}} + xA_d^{\text{probe}} + \tfrac{1}{2}K_2q^2 + x(RT/v_m)\varepsilon\mathcal{Q}q \tag{6}$$

where K_2 is the twist elastic constant, v_m is the solvent molar volume, and the chirality order parameter $\mathcal{Q}$ is defined as

$$\mathcal{Q} = \sum_{ijk} \overline{X_iY_jZ_k}Q_{ijk}, \tag{7}$$

where the bar denotes an average over the probe orientational distribution, determined by the local nematic environment. The equilibrium configuration of the induced cholesteric phase is recovered from the minimum of the distortion free energy $A_d(q)$ in relation to the wavenumber

$$q = -xRT\mathcal{Q}\varepsilon/K_2v_m, \tag{8}$$

and this expression allows the calculation of the helical twisting power $\beta = q/2\pi x$.

Calculations have been performed for the probes biphenyl and binaphthyl, with the aromatic moieties kept distorted at a fixed angle θ to mimic the structures of bridged biaryl compounds [8]. The molecular surfaces were defined by mimicking the probe structure as a collection of van der Waals spheres centred at the atomic positions.

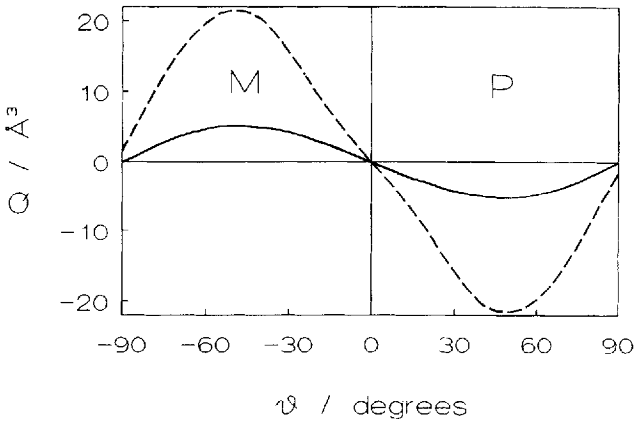
The values of the chirality parameter $\mathcal{Q}$ for the given probe depend upon the local nematic ordering, which is determined by the ε value entering the orientational potential. Because of the symmetry requirements for the nematic potential, the orientational average in equation (7) actually reduces to partial averaging of a second-rank pseudo-tensor, denoted by $\mathbf{Q}^{(2)}$, which results from the irreducible components of the third-rank tensor $\{Q_{ijk}\}$. It follows that

$$\mathcal{Q} = Tr\mathcal{S}\cdot\mathbf{Q}^{(2)}, \tag{9}$$

where $\mathcal{S}$ is the ordering matrix of elements $\mathcal{S}_{ij} = (3\overline{Z_iZ_j} - \delta_{ij})/2$.

In the figure, the dependence of the chirality parameter $\mathcal{Q}$ for rigid biphenyl and binaphthyl molecules upon the θ angle between aryl moieties is displayed. The results are obtained for $\varepsilon = 0{\cdot}05\,\text{Å}^{-2}$, corresponding to order parameters of about 0·3–0·4 for the solute alignment. Positive or negative values of the θ angle correspond to P or M biaryl helicity, respectively, and the range $[-90°, 90°]$ covers *cisoid* conformations of the binaphthyl molecule [8]. By taking $K_2 = 3 \times 10^{-12}\,\text{N}$, $v_m = 0{\cdot}3 \times 10^{-3}\,\text{m}^3$ and $T = 300\,\text{K}$, as appropriate for MBBA, one obtains $\beta = +45\,\mu\text{m}^{-1}$ for binaphthyl, corresponding to $\theta = 50°$, in good agreement in magnitude and sign with experimental results [8–10]. A much lower twisting power for biphenyl is predicted, as actually observed.

In conclusion, it is important to emphasize that the present treatment provides an interpretation of the structural properties of induced chiral phases, simply starting from a knowledge of the solute geometry and the nematic solvents' physical properties—elastic constants and order parameters. The numerical results show that the model is able to grasp the essential physics underlying the induction of helical macrostructures by chiral dopants. The model can also be easily extended to interpret temperature effects on the helical pitch due to the occurrence of conformational changes in the solute molecules.



Dependence of the chirality order parameter $\mathcal{Q}$ for rigid biphenyl (solid line) and binaphthyl (dotted line) molecules upon the θ angle between aryl moieties. The angle $\theta = 0$ corresponds to the planar configuration of biphenyl, and the planar *cis*-configuration of binaphthyl. Positive and negative θ values correspond to P and M biaryl helicity, respectively.

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