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A Molecular Theory of the Cholesteric Phase and of the Twisting Power of Optically Active Molecules in a Nematic Liquid Crystal†

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Abstract—The molecular properties of optically active molecules are used to extend the molecular statistical theory of the nematic phase in order to explain the helical structure of the cholesteric phase. In order to account for these properties the dispersion energy between two molecules is calculated taking into account not only the dipole–dipole interaction but also the dipole–quadrupole interaction. The calculated twist has the right order of magnitude. The theory moreover explains the twisting power of optically active solute molecules in a nematic solvent and also the concentration dependence of the induced twist angle.

A consequence of this theory is that the helical structure only exists, if the distribution of orientations around the long molecular axes is not rotationally symmetric; one may expect this to be the case for e.g. planar molecules.

The cholesteric phase can be considered as a special case of the nematic phase.(1,2) The long axes of the anisotropic molecules are on the average aligned parallel to each other within planes; the direction of this alignment rotates smoothly as one proceeds in a direction perpendicular to the parallel planes. The pitch of this helical structure is of the order of 10^{3}(4) Å, corresponding to a twist angle between the planes of the order of minutes of an arc. The cholesteric phase occurs only with optically active molecules. It seems therefore reasonable to conclude that those molecular properties that are responsible for the optical activity also give rise to the helical structure. In order to account for these molecular properties we make an extension of the molecular statistical theory of

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Maier and Saupe⁽³⁾ for the nematic ordering. We calculate the dispersion interaction energy between two anisotropic optically active molecules i and j taking into account not only the dipole–dipole interaction but also the spatial variation of the mutually induced dipole fields, which is in fact also considering the dipole–quadrupole interaction.

The dispersion interaction energy V_{ij} between two molecules i and j is the second order perturbation energy of the electrostatic interaction H_{ij} between these molecules, i.e.,

$$V_{ij} = \sum_{\mu} \frac{\langle 0/H_{ij}/\mu\rangle\langle\mu/H_{ij}/0\rangle}{E_{0,\mu}} \tag{1}$$

Considering the molecules as an assembly of point charges e^{ki} distributed in space at various points $\mathbf{r}^{ki}$, this electrostatic interaction is given by

$$H_{ij} = \sum_{ki} \frac{e^{ki}\, e^{lj}}{|\mathbf{r}^{ki} - \mathbf{r}^{lj}|} \tag{2}$$

It is convenient to define the position of the point charges with respect to the position $\mathbf{r}^{i}$ of the origin of a coordinate system ξ, η, ζ fixed to the molecule, i.e., $\mathbf{r}^{ki} = \mathbf{r}^{i} + \boldsymbol{\rho}^{ki}(\phi_i, \theta_i, \psi_i)$, where ϕ, θ and ψ are the Eulerian angles⁽⁴⁾ that define the orientation of the molecular ξ, η, ζ coordinate system with respect to the fixed macroscopic x, y, z coordinate system.

By expanding $H_{ij}(\{\mathbf{r} + \{\boldsymbol{\rho}\}\})$ in a double Taylor series with respect to the $\boldsymbol{\rho}^{ki}$ and $\boldsymbol{\rho}^{lj}$, the electrostatic interaction can be written as an infinite sum of interactions between electric molecular multipoles, i.e.,

$$\begin{aligned} H_{ij} = (p^{i}_{\alpha} p^{j}_{\beta}) \frac{\partial}{\partial r^{i}_{\alpha}} \frac{\partial}{\partial r^{j}_{\beta}} \left(\frac{1}{r^{ij}}\right) + (p^{i}_{\alpha} q^{j}_{\beta\gamma}) \frac{\partial}{\partial r^{i}_{\alpha}} \frac{\partial}{\partial r^{j}_{\beta}} \frac{\partial}{\partial r^{j}_{\gamma}} \left(\frac{1}{r^{ij}}\right) \\ + (q^{i}_{\alpha\beta} p^{j}_{\gamma}) \frac{\partial}{\partial r^{i}_{\alpha}} \frac{\partial}{\partial r^{i}_{\beta}} \frac{\partial}{\partial r^{j}_{\gamma}} \left(\frac{1}{r^{ij}}\right) + \dots \end{aligned} \tag{3}$$

where the $p^{i}_{\alpha} = \sum_k e^{ki} \rho^{ki}_{\alpha}$, $q^{i}_{\alpha\beta} = \sum_k e^{ki} \rho^{ki}_{\alpha} \rho^{ki}_{\beta}$ are the components of the electric dipole, respectively electric quadrupole moment and $r^{ij} = |\mathbf{r}^{i} - \mathbf{r}^{j}|$ is the distance between the molecules; it is assumed that the molecules are neutral, $\sum_k e^{ki} = 0$. Repeated indices α, β, etc. which refer to the x, y, z components, have to be summed.

Substitution of this equation into Eq. (1) gives the dispersion energy as a sum of terms,

$$V_{ij} = V^{pp}_{ij} + V^{pq}_{ij} + V^{qp}_{ij} \tag{4}$$

where V^{pp}_{ij} is the second order perturbation energy of the dipole–dipole interaction, i.e. the London–Van der Waals energy, and V^{pq}_{ij} the second order perturbation energy due to the combination of the dipole–dipole and dipole–quadrupole interaction. For these different terms we find:

$$V^{pp}_{ij} = \sum_{\nu\nu'} \frac{(p^i_\alpha/p^i_{\alpha'})_\nu\,(p^j_\beta/p^j_{\beta'})_{\nu'}}{E_{\nu\nu',00}}\,\frac{C^{ij}_{\alpha\beta}\,C^{ij}_{\alpha'\beta'}}{(r^{ij})^6} \tag{5}$$

$$\begin{aligned} V^{pq}_{ij} &= \sum_{\nu\nu'} \frac{(p^i_\alpha/p^i_{\beta'})_\nu\,(p^i_\beta/q^j_{\alpha'\gamma'})_{\nu'}}{E_{\nu\nu',00}}\,\frac{C^{ij}_{\alpha\beta}\,D^{ij}_{\alpha'\beta'\gamma'}}{(r^{ij})^7} \\ &\quad + \sum_{\nu\nu'} \frac{(p^i_\alpha/p^i_{\alpha'})_\nu\,(p^j_\beta/q^j_{\gamma\gamma})_{\nu'}}{E_{\nu\nu',00}}\,\frac{C^{ij}_{\alpha\beta}(r^{ij}_{\alpha'}/r^{ij})}{(r^{ij})^7} + \text{c.c.} \end{aligned} \tag{6}$$

where $(p^i_\alpha/p^i_\beta)_\nu = \langle 0 | p^i_\alpha | \nu \rangle \langle \nu | p^j_\beta | 0 \rangle$ etc., $C^{ij}_{\alpha\beta} = \delta_{\alpha\beta} - 3r^{ij}_\alpha r^{ij}_\beta/(r^{ij})^2$ and $D^{ij}_{\alpha\beta\gamma} = (3r^{ij}_\alpha/2r^{ij})(2\delta_{\beta\gamma} - 5r^{ij}_\beta r^{ij}_\gamma/(r^{ij})^2)$.

In order to show that the terms V^{pq}_{ij} can give rise to the twist we use the above pairpotential for an internal field approximation in which the precise interaction $V_i = \sum_j V_{ij}$ of one molecule with all the others will be approximated by a suitable averaged interaction V, i.e.

$$V = \sum_j \overline{V^{pp}_{ij}} + \sum_j \overline{(V^{pq}_{ij} + V^{qp}_{ij})} \tag{7}$$

For the calculation of this averaged interaction energy one has to make some assumptions on the distribution of the molecular orientations, consistent with the symmetry of the cholesteric phase. A simple model compatible with this symmetry is one in which for a given nematic ordering in parallel planes, which we consider to be parallel with the x–z plane, the molecules can have, independently of their position, only four distinct orientations with equal probability of occurrence, described by the possible combinations out of the set of Eulerian angles, $\phi_i = 0$, $\theta_i = \theta$, $\theta \pm \pi$, $\psi_i = 0$, $\pm\pi$; θ is the angle between the long (ζ) axes, which all lie in planes parallel with the x–z plane, and the z-axis. The calculation of V is now in principle reduced to the calculation of the dispersion energy V_{ab} between a molecule in a plane (a) and a molecule in a plane (b) averaged over all orientations and positions of these in the planes as described above; the quite formal summation, necessary to obtain V from V_{ab}

will be discussed only in connection with the concentration dependence of the twist induced in a nematic solvent by optically active solute molecules. To calculate V_{ab} from Eqs. (5) and (6), we express the components of **p** and **q** into components defined in the molecular ξ, η, ζ coordinate system by means of the standard transformation$^{(4)}$ $p_\alpha = T_{\alpha\xi}(\phi, \theta, \psi)\, p_\xi$ etc., and use for the description of the relative position of the molecules cylindrical coordinates with the normal to the planes as polar axis. The averaging is now straightforward; the expression obtained contains terms even in θ_{ab} and odd in θ_{ab} where $\theta_{ab} = -\theta_{ba}$ is the angle between the directions of alignment of the long axes in the respective planes. It is clear that the odd term will give rise to the twist. For this θ-dependent part we find:

$$-V_{ab} = \left(\alpha \cos 2\theta_{ab} + \frac{2\beta}{r_y^{ab}} \sin 2\theta_{ab}\right) \frac{3}{16(r_y^{ab})^4} \tag{8}$$

where $r_y^{ab} = r_y^a - r_y^b = -r_y^{ba}$ is the distance between the planes and where the molecular quantities α and β involve matrix elements expressed in the molecular ξ, η, ζ coordinate system:

$$\alpha = \sum_{\nu,\nu'} \frac{[(p_\zeta/p_\zeta)_\nu - (p_\xi/p_\xi)_\nu][(p_\zeta/p_\zeta)_{\nu'} - (p_\xi/p_\xi)_{\nu'}]}{4E_{\nu\nu',00}} \tag{9}$$

$$\beta = \sum_{\nu,\nu'} \frac{[(p_\zeta/p_\zeta)_\nu - (p_\xi/p_\xi)_\nu][(p_\zeta/q_{\xi\eta})_{\nu'} + (p_\xi/q_{\eta\zeta})_{\nu'} - (p_\eta/q_{\zeta\xi})_{\nu'} + c.c.]}{2E_{\nu\nu',00}} \tag{10}$$

α is related to the anisotropy of the molecular polarizability. A non vanishing β requires anisotropy of the molecule as well as non vanishing matrix elements of the form $(\xi/\eta\zeta)_{\text{cycl}}$. These matrix elements are non zero only if the molecules have no center or plane of symmetry. Whereas the optical activity of such molecules in random orientation is determined by electric dipole–magnetic dipole transitions, the present " asymmetric part " of the dispersion energy is determined by electric dipole–electric quadrupole transitions. Since the leavo and dextro modifications are the mirror image of each other, β and therefore the twist have opposite sign for these modifications; a racemic mixture will be nematic. Moreover, there is no direct correlation between the sign and magnitude of the optical activity and the sign and magnitude of the twist. By minimalizing V with respect to θ it follows that the magnitude of the twist is determined by the ratio of the coefficients of the odd and even terms in θ, i.e.,

$$2\theta_{ab} \cong tg\, 2\theta_{ab} = \frac{2\beta}{\alpha r_y^{ab}} \tag{11}$$

To estimate the order of magnitude of β/α we may state that β/α will be of the order of the fourth power of an atomic length divided by the molecular volume; we then find that β/α is of the order of 10^{-2}(3) Å. Another possibility is to state that β/α will be of the order of γ_0/Δ where γ_0 is the "optical rotary parameter" of the polarizability theory of Kirkwood(5,6)† and Δ the anisotropy of the molecular polarizability. Since typical values of γ_0 are of the order of 10^{-2} Å^4, this estimate gives the same order of magnitude for β/α. So we may conclude that the calculated twist angle has the right order of magnitude. One could hope to find also the correct temperature dependence of the twist by applying Boltzmann statistics within this molecular field approximation. Doing so one finds that the twist-angle is proportional to the two dimensional ordering parameter $S = \overline{\cos 2(\theta - \theta_0)}$, $\theta_0 = \bar{\theta}$, which is determined self consistently as a function of temperature by an equation quite analogous to that for the three dimensional ordering parameter.(3) Since S is a weakly decaying function of temperature, the twist should show the same behaviour. In general this is not the case; it is known that especially near the transition to the solid or smectic phase the twist angle falls off very steeply to zero with decreasing temperature. To calculate this temperature dependence one should go beyond the molecular field approximation; this has formally been done by Keating.(7) As to our model with only four orientations we like to remark that a more general assumption on the ordered distribution of orientations leads to essentially the same conclusions as to the necessary conditions for the occurrence of the "asymmetric part" of the dispersion energy and the order of magnitude of the twist.

It is known that a nematic liquid crystal can be converted into the cholesteric phase by an admixture of optically active solute molecules.

This twisting power of optically active solute molecules in a nematic solvent and the concentration dependence of the induced twist follow directly from our theory. In Eq. (7) for the internal field,

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† In the notation of Ref. 6 γ_0 is $\beta^{(0)}$

$\overline{V_{ij}^{pq}}$ is, as shown above, non zero only if j refer to an anisotropic, optically active molecule, while i may refer to any anisotropic (nematic) molecule; in a mixture therefore only the optically active molecules contribute to the " asymmetric part " of the internal field V, obtained by summation of V_{ab}; this " asymmetric part " is now proportional to the number density n of the optically active solute molecules. If roughly spoken the structure of these solute molecules differs from that of the nematic solvent molecules only with respect to their optical activity then they contribute equally to the nematic ordering, determined by the first term on the right hand side of Eq. (7); this symmetric part of V is then proportional to the total number density N. The induced twist angle, determined by the ratio of the coefficients of the odd and even terms in θ, is in this case proportional to n/N, i.e., it is a linear function of the concentration, molar or by weight, of the optically active solute molecules. This conclusion agrees with the experimental results of Cano and Chatelain(8) and of Baessler and Labes,(9) who found that the pitch of such mixtures was proportional to the inverse concentration, at least in the investigated concentration range. In connection with these experiments Aleksandrov and Chystiakow(10) have investigated the optical activity of mixtures especially at low concentrations of the optically active solute molecules. They found a saturation of the optical rotary power as a function of the inverse concentration. They conclude that " evidently the proportionality between the pitch and rotary power holds true, hence it follows that the relation between pitch and the reciprocal of the titer should be analogous to the relation for the optical activity "; the simple theory of dilution therefore should not apply to mixtures with small concentrations. However, we doubt the validity of their conclusions. Examination of the theory of de Vries(11) shows that the proportionality between the pitch p and rotary power ceases to be valid if the pitch becomes to large, to be specific, one should not only have $p > \lambda$, which is generally known, but also $p < \lambda/\delta$; λ is the wavelength of the light and δ the relative anisotropy of the dielectric constant of the liquid crystal. Since $p = p_0/c$ and typical values of p_0, λ and δ are $5 \cdot 10^3$ Å, $5 \cdot 10^3$ Å and $5 \cdot 10^{-2}$ respectively, one finds that the assumed proportionality ceases to be valid at concentrations smaller than 5%. The tendency of the rotary power to saturate with increasing pitch can be demonstrated by explicit calculations; moreover, it is easily shown that for $p \gg \lambda/\delta$ the optical rotary power is proportional to p^{-1}. A region of saturation in between is therefore almost necessary.

If the molecular structure of the optically active solute molecules differ greatly from that of the nematic solvent molecules, such that they do not form a cholesteric phase by themselves, the concentration dependence of the induced twist will be more complex. To illustrate this point we consider the case that the optically active solute molecules do not contribute to the nematic ordering but only are aligned, which will be the case for small, anisotropic, optically active molecules. The " asymmetric part " of V is still proportional to the number density n of the optically active solute molecules, whereas the " symmetric part " is now proportional to the number density N–n of the nematic solvent molecules. The induced twist is for this case proportional to $(n/N\text{–}n)$; such solute molecules are more effective in producing a twist. One may expect that there is an optimum concentration of solute molecules with a maximum twist above which the nematic ordering and therefore the twist vanish.

As to the necessity of a planar structure of the optically active solute or cholesteric molecules it follows from our theory that if these molecules have a threefold or higher symmetry axis, which in general implies a rotational symmetric distribution of orientations around these axes, the " asymmetric part " of the potential and therefore the twist vanish. To show this one calculates the dispersion energy as a function of ψ which describes the rotation of the molecules around the long symmetry axis. The " asymmetric part " of the energy for these molecules is now proportional to $\cos 2\psi$; for a rotational symmetric distribution $\cos 2\psi$ has to be averaged giving zero. Baessler and Labes(9) have argued the necessity of a planar structure for steric reasons. They found experimentally that *l*- and *d*-mandelic acid did not have twisting power, which was attributed to the free rotation of the optically active groups. Buckingham and coworkers,(12) however, reported that *d*-tartaric acid converts the nematic phase of *p*-*n*-octyl-oxybenzoic acid into a cholesteric phase, which seems contradictory to the above results. The explanation, however, could be that free rotation is hindered by hydrogen bonds between the solvent and solute molecules. In connection with the above we like to remark that the ordered distribution of orientations of the optically active solute molecules need not necessarily be the same in different nematic solvents. In principle therefore it is possible that the magnitude and even the sign of the twist induced by the same optically active molecules in different nematic solvents are different.

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