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Helical Twisting Power in Mixtures of Nematic and Cholesteric Liquid Crystals*

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The helical twisting power in nematic (methoxybenzylidene *p*-aminophenyl acetate)-cholesteric (cholesteryl propionate) mixtures as a function of cholesteric material concentration is studied by measuring the circular dichroism, the wavelength of selective reflection, and the Grandjean fringes. It is found that as the cholesteric material concentration increases, the twisting power of the mixtures increases linearly up to a certain concentration, beyond which, however, it increases more slowly, taking a maximum value at some specific concentration which normally falls in the high-concentration region.

The cholesteric phase may be regarded as a special case of the nematic phase since it forms a molecular structure having twisted nematic layers; each layer forms a two-dimensional nematic ordering, subsequent layers being twisted by a small angle.[1] If a small amount of optically active substance is added to the normally nematic substance, the mesophase is easily transformed into cholesteric mesophase.[2] The helical twist angle of such mixtures has been shown to be a linear function of the cholesteric material concentration in some limited range of low concentration.[3,4]

It is the purpose of this Letter to report results of investigation on twisting power as a function of the concentration of active cholesteric material over the whole range of concentration $(0.02 \leq C_2 \leq 1.0)$ in nematic-cholesteric mixtures. The samples investigated were nematic-cholesteric mixtures consisting of the nematic *p*-methoxybenzylidenyl acetate (MBA) and the cholesteric cholesteryl propionate (CP). The CP, which is a levorotatory and enantiotropic cholesteric liquid crystal, has no smectic phase at low temperature in its mesophase.[5] All mixtures were assured to be levorotatory.

Many properties of the cholesteric phase can be derived from the mean refractive index n of the birefrigent layers, the pitch p, and the sense of helix. In thermotropic liquid crystals, the knowledge of a change in the twist angle θ is equivalent to that in the pitch. The distance between subsequent layers may scarcely change with concentration in the MBA-CP mixtures, as the lengths of these molecules along their short axes are slightly different. Therefore we measured the pitch instead of the twist angle by using the usual methods: the circular dichroism and the wavelength of selective reflection were measured in the high-concentration region, and the Grandjean fringes were observed in the low-concentration region.

The cholesteric helicoidal structure can be easily recognized by observing regular fringes—Grandjean fringes—with a polarizing microscope. The spacing between alternating bright and dark retardation lines is equal to $p/2$.[1] In the selective reflection method,[6] the optical transmittance of circularly polarized light, either right-handed or left-handed, is measured near λ_0 ($=np$), the wavelength of maximum reflection. Upon irradiation of light parallel to the helical axis, a levorotatory substance scatters the left-handed component of the incident light and transmits the right-handed component.[1,6] Optical transmittance was measured by a Cary type 14 spectrophotometer whose sample and reference compartments were so devised as to facilitate the temperature control and rotation of both polarizer and $\lambda/4$ plates. A JASCO type J-10 apparatus was also used in the circular-dichroism measurement.

All the measurements were performed with the planar texture within the temperature range where the cholesteric mesophase was stable. Thin layers of mixtures were sandwiched between glass with Mylar spacers of two different thicknesses, i.e., approximately 25 and 50 μm. Planar texture films, when sheared between the glass plates, showed characteristic visible reflection colors of cholesterics when the CP concentration was within the range $0.35 \lesssim C_2 \leqslant 1.0$, or $0.25 \lesssim C_1 \leqslant 1.0$, where C_1 and C_2 designate the molar and weight concentration of the CP content, respectively. Roughly speaking, colors vary from red to blue as the concentration of cholesteric molecule increases, but its detailed behavior has been yet unknown.[7]

The CP concentration dependence of the helical twisting power obtained is shown in Fig. 1. The mean refraction index of all the mixtures is within the range $1.5 \lesssim n \lesssim 1.6$. Then the mean refractive index in the present case does not contribute much to the shape of the curve of helical twisting power versus concentration. Therefore only the product np is considered in this paper. In Fig. 1 temperatures at which measurements were carried out are all lower by 8°C than the cholesteric-isotropic transition points. It is easily noticed that, in the low-concentration region, θ is proportional to C_1 (or C_2), and that with increasing CP concentration θ deviates from the linear dependence and attains a maximum value at a certain concentration beyond which it decreases a little. In particular, it is interesting that MBA-CP mixtures with a small amount of MBA exhibit a helical twisting power which is larger than that of a simple CP.

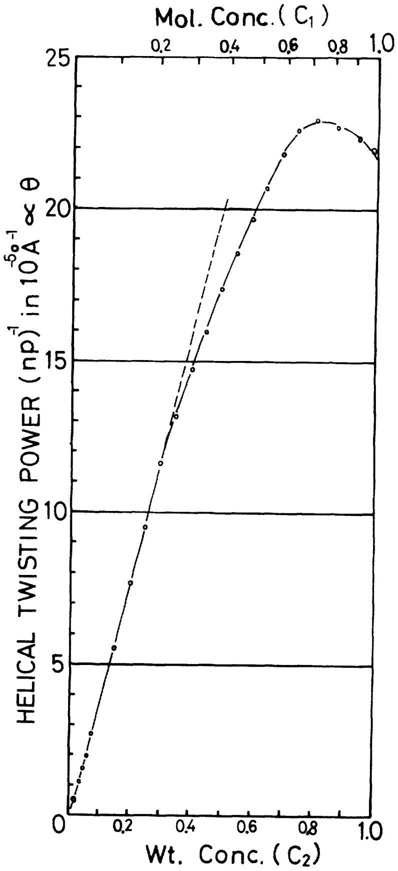

FIG. 1. The helical twisting power versus CP concentration in mixtures of nematic MBA and cholesteric CP. The temperature at which measurements were carried out are all 8°C below the cholesteric-isotropic transition points.

The helical twisting power versus temperature around the CP concentration where θ takes a maximum value is shown in Fig. 2. The temperature range of the measurement does not include the vicinities of the upper and lower transition points. Figures 1 and 2 indicate that

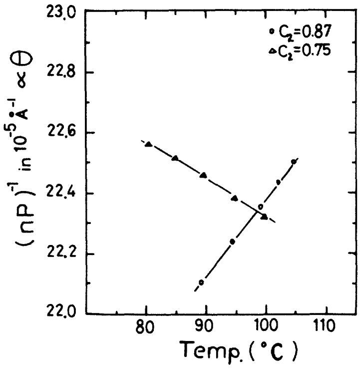

FIG. 2. The helical twisting power versus temperature around the CP concentration where θ takes a maximum value. The temperature range does not include the vicinities of upper and lower transition points.

the shape of the curve of twisting power versus concentration depends on temperature, that the value of C_1 (or C_2) at which θ takes the maximum value shifts a little with temperature, and that $\theta(C_2 = 0.8)$ is always larger than $\theta(C_2 = 1.0)$ regardless of temperature. It was also observed that $\partial\theta/\partial T < 0$ for $C_2 < 0.8$ and that $\partial\theta/\partial T > 0$ for $C_2 > 0.8$. The slopes are smaller than those of simple cholesterics. It is to be noted that a similar effect has been observed in mixtures of certain two-cholesteric liquid crystals.[8] However, at the present stage it is quite difficult to give a detailed discussion of this effect as no reliable theory exists yet.

The experimental formula for the concentration dependence of the induced twisting power is expressed by

$$\theta \propto \frac{n/N}{1 + A(n/N)^2} = \frac{C_1}{1 + AC_1^{\,2}}, \tag{1}$$

where N is the total number density, n is the number density of the optically active molecule (CP), and A is a constant related to properties of simple cholesterics and nematics. The experimental results are fitted well with the numerical calculation of the relation (1) with $A = 1.81$ over the whole CP concentration region. In the low-concentration region the relation (1) reduces to the simple relation

$$\theta \propto n/N = C_1. \tag{2}$$

Recently, an interesting molecular theory for cholesteric phase was proposed by Goossens.[9] The molecular interaction in the liquid crystals is given by the second-order perturbation energy of the electrostatic interaction,

$$\mathcal{H}_{ij} = p_\alpha{}^i p_\beta{}^j \frac{\partial}{\partial x_\alpha{}^i} \frac{\partial}{\partial x_\beta{}^i} \left(\frac{1}{r_{ij}}\right) + p_\alpha{}^i q_{\beta\gamma}{}^j) \frac{\partial}{\partial x_\alpha{}^i} \frac{\partial}{\partial x_\beta{}^j} \frac{\partial}{\partial x_\gamma{}^j} \left(\frac{1}{r_{ij}}\right) q_{\alpha\beta}{}^i p_\gamma{}^j \frac{\partial}{\partial x_\alpha{}^i} \frac{\partial}{\partial x_\beta{}^i} \frac{\partial}{\partial x_\gamma{}^j} \left(\frac{1}{r_{ij}}\right)$$
$$+ q_{\alpha\beta}{}^i q_{\gamma\delta}{}^j \frac{\partial}{\partial x_\alpha{}^i} \frac{\partial}{\partial x_\beta{}^i} \frac{\partial}{\partial x_\gamma{}^j} \frac{\partial}{\partial x_\delta{}^j} \left(\frac{1}{r_{ij}}\right) + \cdots, \tag{3}$$

where

$$p_\alpha{}^i = \textstyle\sum_k e^{ki} x_\alpha{}^{ki}, \quad q_{\alpha\beta}{}^i = \frac{1}{2} \textstyle\sum_k e^{ki} x_\alpha{}^{ki} x_\beta{}^{ki}$$

are the components of the electric dipole and quadrupole moments, respectively, and $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between two molecules i and j. Goossens showed that, in the second-order perturbation calculation, not only the dipole-dipole interaction but also the combination of the dipole-dipole and dipole-quadrupole interaction must be taken into account in order to explain the helical structure of the cholesteric phase, and that the induced twisting power in cholesteric-nematic mixtures is proportional to n/N [i.e., the relation (2)]. In the high-concentration region, however, the relation (2) is not justified.

We shall calculate the second-order perturbation energy ($V_{ij}{}^{qq}$) due to the higher-order terms in $\mathcal{H}_{ij}$; the terms calculated are the combination of the first and fourth terms, and that of the second and third terms.

The precise interaction $V_i{}^{qq} = \sum_j V_{ij}{}^{qq}$ is calculated by a molecular field approximation. The θ-dependent part of $V_i{}^{qq}$ is given by

$$V_{ab}{}^{qq} = \langle \textstyle\sum_j V_{ij}{}^{qq} \rangle = \frac{-3\pi\gamma}{8(r_{ab})^6} \cos 2\theta,$$

where r_{ab} is the distance between the successive planes a and b. Here we have adopted only the cyclic form $(\xi | \eta\zeta)$; ξ, η, and ζ are coordinate axes fixed to the molecule.[9]

Now, the θ-dependent part in the molecular interaction of the cholesteric phase is expressed by

$$V_{ab} = \langle \textstyle\sum_j V_{ij}{}^{pp} + \langle \textstyle\sum_j (V_{ij}{}^{pq} + V_{ij}{}^{qp})\rangle\rangle + V_{ab}{}^{qq} \tag{4}$$

$$= -\left(\alpha \cos 2\theta + \frac{2\beta}{r_{ab}} \sin 2\theta + \frac{\gamma}{r_{ab}{}^2} \cos 2\theta\right) \frac{3\pi}{8(r_{ab})^4}, \tag{5}$$

where α is related to the anisotropy of the molecular polarizability and β, γ are related to anisotropy of the molecule. By minimizing V with respect to θ, the stable twist angle θ is given by

$$2\theta \simeq \tan 2\theta = \frac{2\beta}{\alpha r_{ab} + \gamma / r_{ab}}. \tag{6}$$

In nematic-cholesteric mixtures, the first, second, and third terms on the right-hand side of Eq. (4) are proportional to N, n, and n^2/N, respectively. Then, the substitution of n/N by C_1 in the formula (6) leads to the expression

$$\theta = BC_1 / (1 + AC_1{}^2),$$

where

$$A = \gamma / \alpha r_{ab}{}^2, \quad B = \beta / \alpha r_{ab}.$$

The experimental result is well explained with just the terms mentioned above.

The cholesteric helical structure will probably depend on the weak dispersion forces given by the second-order perturbation of not only the dipole-dipole and the dipole-quadrupole interactions but also the quadrupole-quadrupole interaction.

Finally, it should be emphasized that the curve of helical twisting power versus concentration has a maximum value in nematic (MBA)-cholesteric (CP) mixtures and that it is quite useful for understanding the helical ordering of cholesterics.

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Energy Bands and the Soft-X-Ray Absorption in Si[†]

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The soft–x-ray absorption spectrum from the Si $L_{\mathrm{II,III}}$ shell is used to study several energy-band models for Si. The calculations are based on the empirical pseudopotential method. The results support the recent Si band model obtained by Stukel, Euwema, and Chaney, Lin, and Lafon. We suggest that the $\Gamma_{2'}$ level lies below Γ_{15} in the Si conduction band.

Silicon has a unique place in solid state physics. It forms a basis for much of our advanced solid-state electronics industry and is probably one of the most studied materials in existence. Silicon has been the subject of numerous band-structure calculations by orthogonalized plane-wave,[1] $\vec{K}\cdot\vec{P}$,[2] pseudopotential,[3] and tight-binding[4] methods. Nonetheless, the agreement between theory and